

Light management for high efficiency silicon solar cells

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Light Management for High Efficiency Silicon Solar Cells

Yang Yang

A thesis submitted to University of New South Wales in fulfilment of the requirements for the degree of Doctor of Philosophy



School of Photovoltaic and Renewable Energy Engineering Faculty of Engineering The University of New South Wales

Sydney, Australia

August 2012

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Abstract

In this thesis, light trapping behaviour in silicon solar cells with textured front surfaces and rear reflectors has been characterised experimentally via two optical setups. Various types of novel rear reflectors involving the use and combinations of dielectric stacks (SiO₂; SiN_x), displaced and detached metal (Al; Ag) reflectors, scattering white paint and Ag nanoparticles have been applied on the rear of front-planar PERT (Passivated Emitter and Rear Totally-Diffused) cells with their optical and electrical properties extensively investigated.

Reflected light from textured front surfaces of a solar cell contains useful information about the surface geometry as well as the optical properties of the cell. The measured 2-D reflected light distributions from front surfaces of silicon cells textured in various ways are compared to those from conventional ray tracing models and are used to extract details of the surface morphologies. The impact of the encapsulant's refractive index on the amount of total internal reflection at the air-glass interface is also discussed.

The rear surface reflection of a solar cell is angularly dependent if a textured front surface is applied. The use of hemispherical silicon as a test substrate has been successfully implemented enabling the analysis of the angular reflection properties of the back surface reflector over all incident angles without the restriction caused by refraction at the Si-air interface. Results show that a dielectrically displaced rear reflector scheme using 200 to 300 nm of SiO₂ and an Ag mirror provides best angular reflection.

The novel planar rear structures with dielectric stacks have been experimentally demonstrated to increase the reflected light intensity by 2.5% absolute at 1200 nm and the internal quantum efficiency (IQE) by 30% relatively at 1150 nm with similar surface passivation quality, compared to a conventional reflector. The best performing scattering reflector using Ag nanoparticles to create localised surface plasmons on the rear of the solar cell enhances the measured external quantum efficiency (EQE) by more than 4-fold at 1160 nm, corresponding to a 16% photocurrent increase (calculated from

900 nm to 1200 nm), compared to a cell with a conventional Al reflector. Thicknesses of the rear surface passivation SiO_2 layer and the precursor evaporated Ag film are optimised to achieve maximum optical enhancement with minimum electrical losses. The optical and electrical properties of the rear light trapping designs are successfully separated and quantified. An optical enhancement of 6-fold is achieved at 1200 nm. Finally, an improved double-layer reflector using optimized Ag nanoparticles as the first layer and evaporated Ag as the second layer separated by MgF_2 is developed and optimised achieving a further current enhancement of 4.9 % compared to the single layer Ag nanoparticles scheme.

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Chapter 1. Introduction

This chapter reviews the fabrication processes and the properties of UNSW's world record silicon solar cells and the presently used light trapping schemes within the cells. The aim and the structure of the thesis have also been presented.

1.1 High efficiency solar cells structures

The passivated emitter, rear locally diffused (PERL) cell (Fig. 1.1) was developed at The University of New South Wales (UNSW), Australia [1] and has been proven to be the most efficient single crystalline silicon solar cell over the past 20 years [2] with a world record efficiency of 25.0% [3].

The PERL structure achieves high efficiency via three main features: (i) high quality and stable dielectric surface passivation; (ii) effective light trapping features and (iii) a method for surface carrier concentration control by either doping or electrostatic repulsion [4]. Other features also play a significant role in solar cell efficiency and will be discussed in detail.



Fig. 1.1: A cross-sectional drawing of the PERL cell structure. Image is taken from [1].

Other high efficiency structures such as passivated emitter, rear totally diffused (PERT) cells (Fig. 1.2a) and passivated emitter and rear (PERC) cells (Fig. 1.2b) also provide efficiency advantages. They were all devised by the UNSW.

The main features that distinguish the three cell types are the treatment of the rear and the substrate used. The PERL cell is commonly fabricated on a base with low to moderate resistivity (1–2 Ω cm) and with high minority carrier lifetime. In contrast, the PERT cell is normally fabricated on a high resistivity base (100 Ω cm) while the PERC cell is fabricated on a low resistivity base (0.1–0.2 Ω cm). The rear contact to the Si is made via Al for these high efficiency cells and is realised by opening small contact windows on the rear SiO₂ sufficiently spaced apart from each other so to keep the metal contact areas to the minimum (approximately 0.2% of the total rear) to reduce surface recombination.

Apart from the base resistivity, differences between the three types of cells are evident in the rear boron diffusion procedures. The locally heavily diffused boron areas near the contact areas in the PERL cell ensure good rear contact resistance and reduce contact recombination by keeping the minority carriers away from the region. A lightly diffused boron layer in the entire rear of the PERT cell forms a back surface field which provides a high-low field rear surface passivation. On the contrary, no boron diffusion is involved in the low resistivity PERC cell, but rather, a low resistivity substrate is used to maintain low contact resistance for the rear and can encounter high recombination problem at the metal contact areas.

In comparison to the PERL cell, the PERT cell has 15–20 mV lower V_{oc} and 0.8–1% lower efficiency. The PERC cell has 20–25 mV lower V_{oc} and 2–2.2% lower efficiency than the PERL cell [5].



Fig. 1.2: Cross-sectional drawings of the PERT cell structure (a) and the PERC cell structure (b). Image is taken from [5].

Similarities between the PERC, PERT and the PERT structures include the use of high quality floatzone thick *p*-type Si wafers with the front surface textured by inverted pyramids aimed at enhanced light trapping.

Heavy phosphorus diffusion is carried out at metal contact areas of the front of solar cell and the contact areas are kept very low to effectively suppress the surface minority carrier recombination in the contact region. It also assists in forming good ohmic contacts. A light phosphorus diffusion on the entire top surface contributes to an excellent blue light response [6]. Another contributor of such excellent spectral response is the use of Al-annealed thermally-grown SiO₂ to passivate the front surface [7, 8]. To further reduce the front surface reflection, Double-Layer Anti-Reflection coating (DLAR) which comprises of MgF₂ and ZnS [9] is used. The rear surface of a solar cell is also passivated by an Al-annealed thermal SiO_2 with a much thicker film (approximately 200 nm) than the front SiO_2 . This warrants good electrical property for light at near infrared spectrum. The thick dielectric together with a Al metal film (approximately 800 nm) produces an enhanced metallic rear reflector [4] which provides more than 95% reflection for the infrared light. The evaporated Al metal also acts as the rear electrode.

1.2 Presently used light trapping schemes of silicon solar cells

Light trapping in solar cells has played an important role in improving the efficiency of solar cells by allowing weakly absorbed light to go through multiple bounces in the cell increasing the probability of absorption. Light trapping can potentially increase the path length of light inside the solar cell by a factor of $4n^2$, where *n* is the refractive index of the medium [10]. This corresponds to a pathlength enhancement of around 50 for a high refractive index medium like Si. Given the merits of improved light trapping, it is necessary to explore methods for increasing the optical path length inside silicon solar cells.

Light trapping also enables a significant reduction in the active solar material thickness [11] and hence material cost as evident in thin film solar cells. It also greatly relaxes the silicon purity requirement because the current loss from reduced minority carrier diffusion length can be compensated for by the enhanced light absorption intensity.

A textured front surface and a highly reflective back surface are two general schemes involved in conventional silicon solar cell light trapping [4, 12] as shown in Fig. 1.3.



Fig. 1.3: A schematic of the conventional light trapping geometry formed by a textured front surface and a dielectrically displaced reflector used in silicon solar cells.

1.2.1 The textured front surface

Textured surfaces create three major optical benefits. First, they reduce the overall front surface reflection as they allow multiple impacts with the interface at the front surface, giving incident light more than one chance to penetrate into the cell [13]. Second, they allow light to enter the silicon at a more oblique angle, which increases the light collection probability due to a longer optical path length. Finally, a portion of the obliquely transmitted light with low energy impacts the cell's rear surface. This long wavelength light can be reflected efficiently back to the bulk region for further opportunities for electron-hole pair generation, having been effectively trapped in the cell by the surface texture.

Surface texturing can be realised by several techniques. Examples are chemical etching [14, 15], mechanical engraving [16] and plasma etching [17]. Chemical etching is the most popular method in solar cell manufacturing due to its low cost and effectiveness. In the chemical etching method, random arrays of upright pyramids with various sizes are usually formed on commercial single crystalline solar cells by an alkaline etch. To obtain regular arrays of inverted pyramids or grooves, a masking technique is needed prior to etching. Due to the high cost of the masking process, inverted pyramids are primarily seen on high-efficiency laboratory silicon solar cells [1, 12]. Campbell and Green [11] further optimised the inverted pyramid feature to be a "Tiler's pattern" by

shifting the pyramids by a small degree ($\sim 5^{\circ}$). This effectively reduces light escaping through the substrate.

Front texturing can also bring additional benefits for developing encapsulated commercial solar cells. Reflected light from the front cell surface has the potential to be completely internally reflected at the glass-air interface when the reflection angle is adequately large. A study by Gee et al. [18] has demonstrated that by carefully choosing the encapsulant's refractive index, total internal reflection can be optimised.

Different texturing techniques have been extensively investigated in the past. However, the optical performance from these textured surfaces has only been typically characterised by an optical spectrophotometer with and without integrating spheres. The total amount of light, either reflected by or escaping from front surface, is the most often measured quantity by the optical instruments without any information retrieved about the angular reflection. Only a small number of previous measurements of reflected light distributions from textured front surfaces have been published. The angular information of reflected light distribution contains useful information about the surface geometry as well as the optical properties of the cell. It is also helpful for further texturing design and optimization. The question arises as to how to extract details of surface morphologies and light collection process in silicon from the measured light distributions. This thesis investigates this issue. Results will extend Gee et al.'s [18] work on the optimisation of cell encapsulant refractive index and work by Baker-Finch and McIntosh [19], which will be discussed in Chapter 3.

1.2.2 The reflective rear surface

Most of the light coupled into silicon is absorbed before reaching to the rear surface. However, the weakly absorbed light at near infrared spectrum meets the rear reflector and splits into two separate intensities, one that propagates back into silicon as a reflected light ray (see R_b in Fig. 1.3) and another that's absorbed by the rear metal on each impact (see A_b in Fig. 1.3). Recent design studies of the highest performance silicon solar cells such as those conducted at UNSW have proposed that improvements in the rear optical properties are still warranted. Possible issues of existing silicon solar cells include light absorption by the rear reflectors which accounts for around 5% of the light impacting on the rear of the cell and light escaping from the front surface after the first double pass across the cell. In the latter case, approximately 40% of the long wavelength light reflected light from the back surface escapes after a double pass [20]. Therefore, it is possible to improve the efficiency by implementing a more efficient rear reflector.

The 5% light loss from rear parasitic absorption is angularly dependent on the reflection property of the rear scheme, as shown in Fig. 1.3. Previous studies largely focused on improving rear reflection for normally incident light, with nearly 100% reflection achieved at long wavelength in the past [21]. However, light propagating towards the rear surface follows an angular distribution due to the deflection from the front of the cell. For this light, it is necessary that the angularly broadband approaches are explored further. Moreover, rear surface reflection of solar cell is normally characterised together with the optical effect from front surface. There is hardly any method to measure the rear internal reflection directly. This leaves scope for the characterisation of angularly dependent rear internal reflection of solar cell. Once the angular dependence of the presently used rear reflector in high efficiency solar cells is measured and understood, efforts can be made to reduce such optical loss. This can be achieved by either optimising front texturing or by optimising the rear structure. The former method allows for the deflected light to impact rear surface with angles where reflection is at its maximum. The latter method involves making a good choice of the metal, dielectric material and dielectric layer thickness as part of the reflecting structure. In so doing, the reflection at the angles into which most of the deflected light falls can be maximised. Since surface texturing of inverted pyramids is a well developed technique, this thesis will focus on the design and fabrication of rear reflecting structures.

The 40% optical loss due to its escape from the front surface of the cell after reflection at the rear could be resolved by eliminating the symmetrical pattern of the inverted pyramids such as the use of the "tiler's pattern" as mentioned before. Another way to reduce light escaping is by using non-planar rear geometrical structures, such as reflection gratings and nanostructures. Rear geometrical structures can maximise scattering beyond the escape cone of the semiconductor. This enables total internal reflection and therefore increases the optical path length in the solar cell [11, 22]. These scattering approaches have been extensively investigated in thin film solar cells in the past. However, there is a knowledge gap associated with applying such geometrical structure to wafer based high efficiency devices. In this thesis, considerable effort is made to reduce the optical loss by replacing the conventional planar reflector with novel scattering reflectors.

1.3 Aims and structures of the thesis

There are two main aims of this thesis. Firstly, it aims to optically characterise textured front surface and reflective rear surface in conventional high efficiency silicon solar cells so to understand it light trapping properties (Chapters 3 and 4 of this thesis). Secondly, it seeks to design and apply novel rear reflectors (Chapters 5, 6 and 7), either specular or scattering, onto the rear of high efficiency solar cells so to improve the rear optical performance without any electrical quality degradation while maintaining compatibility to the existing high efficiency cell technology. There is a considerable effort in this thesis investigating the use of Ag nanoparticles for a rear structure which have been shown experimentally to be able to improve the rear optical properties. Unless otherwise specified, PERT cells are used for the application of rear optical schemes in this work.

Prior to the presentation of the original work in this thesis, a literature review is given in Chapter 2 to review various light trapping techniques and past work done on their characterisation.

Chapter 3 describes a novel optical measurement technique that has been developed in this work that measures the 2-D reflected light distributions from textured front surfaces of silicon cells. Measured reflected light distributions from various types of front surface textures are analysed and compared to those obtained by conventional ray tracing modelling. The reflected light distribution patterns are then used to extract details of the surface morphologies. Their impact on the encapsulant's refractive index for total internal reflection is also discussed. It is envisaged that the novel optical characterisation technique can be easily utilised in an industrial setting and be used as a tool to fine tune front texturing fabrication step.

Chapter 4 describes another original optical set up developed for this thesis to measure, for the very first time, the angularly broadband reflections from dielectrically displaced rear reflectors deposited on hemispherical silicon test substrates. Metal reflectors that use either Al or Ag displaced by SiO_2 of SiN_x have been successfully measured and analysed for their angular reflection properties over all incident angles. Recommendations on the preferred type of metal and dielectric thicknesses are made in this chapter.

Chapter 5 presents results of the newly designed and fabricated specular rear reflector with triple-layer dielectric stacks.

Chapter 6 discusses the development of a novel scattering rear surface-plasmonic structure using Ag nanoparticles which is further optimised in terms of dielectric thickness and metal mass thickness to maximise light trapping enhancement and minimise electrical degradation to their limits.

Chapter 7 presents results of applying the combination of dielectrically displaced; detached; specular; scattering; and plasmonic reflectors in single or multiple layer rear reflecting structures. A comparison is made between the proposed reflecting structures by examining their light trapping performance and electrical responses.

Chapter 8 summarises and identifies the contributions made by the present study. Recommendations for future research are also discussed.

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Chapter 2. Background

As discussed in Chapter 1, there is a lacking of optical characterisation to assess the angularly dependent reflection/deflection of a textured front surface and a rear reflector. This chapter examines the previously used characterisation methods for light trapping behaviour, and proposes possible rear schemes that can potentially improve the optical response of silicon solar cells.

2.1 Characterisation techniques to measure light trapping

2.1.1 Review of front side characterisation

Light absorption in the Si bulk, light reflection from the rear reflector and light reflection from the encapsulated air/glass interface are all correlated to the degree of light deflection from textured front surfaces, either inside (Fig. 2.1a) or outside (Fig. 2.1b,c) silicon solar cells.



Fig. 2.1: Schematic views of (a) deflected light within silicon (b) reflected light outside silicon (c) transmitted light outside silicon.

The deflected light distribution within silicon is hard to characterise due to the large refractive index step between air and silicon at the rear interface, see Fig. 2.1a. Most of

the previous studies have measured the reflected and transmitted light distributions outside silicon, see Fig. 2.1b,c, as a mirror image of light collection within silicon [1].

Parretta et al. [2, 3] have discussed several optical setups to study the angularly resolved back-reflected light from surfaces with different textures, but have not been experimentally investigated in any detail. The suggested optical setups can be simplified and improved to either visually inspect or record the back-reflected light distribution.

Other studies [4-6] have modelled reflections from randomly textured front surfaces by numerical ray tracing. Kuchler et al. [7] created a mathematical 3-D topography for random upright pyramids from experimental stereoscopic scanning electron microscopy (SEM) images on which future ray tracing work can be conducted.

Baker-Finch and McIntosh [8] have published a numerical ray tracing analysis for regular upright, regular inverted and random upright pyramids. The work presented the relevant reflection angles with their fractional intensities for perpendicular incident light. This work has been extended in a recent publication [9] showing the 1-D reflection distribution of square-based pyramids under various angles of incidence, characterised by a spectrophotometer with an angular reflectance accessory. Differences between ray-traced light paths and measured light paths indicate a non-ideal base angle for the texture, which is a valuable indicator for the surface texture behaviour. However, this method cannot fully record reflection distributions from anisotropically textured features. 2-D reflection measurements are required to obtain a complete pattern.

Foldyna et al. [10] have designed another characterisation technique by using a polarimetric imaging tool based on a microscope objective to measure angle-resolved emerging light distributions from dry plasma etched surfaces. As an improvement, this optical setup captures 2-D reflected images. However, the measurement has not been extended for the conventional surface textures such as random upright or inverted pyramids, and the results have not been fully analysed.

The transmitted angular intensity distribution from textured front surface also contains information about light trapping (Fig. 2.1c). Berner et al. [11] have built a new optical setup allowing laser radiation to enter a solar cell rear so that the front side transmission

distribution could be displayed on a screen and recorded by a CCD camera. The advantage of the system lies in the image capture and processing, which rectifies and performs a calibration on the image to correlate deflection angles and screen positions. The reduced specular transmission indicates enhanced light trapping.

Very few studies have measured light deflection distribution inside silicon as shown in Fig. 2.1a. This measurement, however, is not impossible if the setups built by Berner et al. [11] and others could be properly modified. Filling the rear side of silicon wafer with a material that has the appropriate refractive index and then attaching the flat side of a high index optical lens to this material can change the critical angle at the silicon rear interface. This enables light with larger angles to escape solar cell rear. This is beyond the scope of this thesis but nevertheless is appropriate for future work.

2.1.2 Review of rear side characterisation

Similar to the measurement limitation of the light deflection distribution within silicon (Fig. 2.1a), the characterisation of the rear angular reflection distribution is limited by the significant difference in the optical index between air and silicon when a flat wafer is used. This constrains incident light of any angle within a 17° cone after the light enters the silicon, as shown in Fig. 2.2a. Another measurement restriction comes from the reflected light detection process where the front surface of the wafer again introduces unwanted reflection. Therefore very few measurements of the angular reflection dependence of rear reflectors have been reported. Most studies are calculation based using various measured or estimated reflection parameters, see Fig. 2.2b.



Fig. 2.2: (a) A schematic showing the measurement limitations by using a flat wafer. The angle of incidence is restricted to within a 17° cone inside Si due to the difference in refractive index between air and silicon. (b) Optical model of reflection calculation for planar solar cells.

For a given front-planar solar cell, the rear internal reflectance R_b can be calculated from the following equation:

$$R_{b} = \frac{R_{t} - R_{fe}}{\left(\left(R_{t} - R_{fe}\right)R_{fi} + \left(1 - R_{fe}\right)\left(1 - R_{fi}\right)\right)\left(1 - A\right)^{2}}$$
(2.1)

where R_t is the measured total hemisphere reflectance, R_{fi} is the estimated front internal reflectance with a value of 91%–92% for front-planar cells, R_{fe} is the measured or approximated direct external reflectance from the front surface without any contribution from escaping light with its value at near-bandgap wavelengths (900 nm – 1200 nm) linearly extrapolated from the measured value of sub-bandgap wavelength. Parameter *A* is the light absorption by silicon each time it traverses the layer thickness, which can be expressed as:

$$A = 1 - e^{-\alpha w / \cos \theta_i} \tag{2.2}$$

where α is the absorption coefficient of silicon as a function of wavelength, *w* is the wafer thickness and θ_i is the angle of incidence inside silicon, as shown in Fig. 2.2a. Eqn.2.1 is also restricted to angles $\theta_i < 17^\circ$. An improved optical model with more optical parameters that considers textured front surfaces enables the optical calculation for larger θ_i [12]. This will be discussed in Section 6.3.3 in detail.

The angular rear reflection at different dielectric layer thicknesses has been calculated by Campbell [13, 14] based on a three-layer optical system resembling conventional solar cell rear, as shown in Fig. 2.3. A strong reflection dip at angles near the critical value for total internal reflection (TIR) at the Si/SiO₂ interface ($\theta_c + \delta \theta$) is the first observation of the study. The reason is attributed to the enhanced metal absorption when the refracted light travels almost parallel along the interface. This strong optical loss at angles near the critical value is a big limitation to the rear optical performance of solar cells. Therefore experimental characterisation is necessary to confirm this phenomenon.



Fig. 2.3: Calculated reflectance from a SiO_2 displaced Al reflector at the rear of silicon solar cell as a function of SiO_2 thickness, for various internal angles of incidence. Image is taken from [13, 15].

2.1.3 Innovative characterisation techniques

Having reviewed various suggested front optical measurement techniques, it is concluded that a much easier and faster method is required to solve the suggested issues both at the development and production stage. The use of photographic paper to record the image, first proposed by Parretta [2, 3], can be adopted to eliminate the distortion of the captured digital images and to simplify the optical setup. The calibration method

proposed by Berner [11] is also useful to analyse the captured digital images. Efforts also need to be put into image analysis to understand real surface morphologies and light collection process of solar cells textured with regular and random pyramids.

Having reviewed rear characterisation techniques, it is known that insufficient experimental data has been reported in the past. A novel optical setup allowing light illumination and detection from the rear surface reflector of a solar cell over a broad angular range is therefore needed. One approach is by using a silicon hemisphere as the substrate for reflector deposition. The incident light can pass through the air-silicon interface without refraction, see Fig. 2.4. This effectively solves the pre-suggested angular limitations involved in the flat wafer measurement (Fig. 2.2a).



Fig. 2.4: A schematic of the proposed measurement with a Si hemisphere allowing light illumination and detection at any angle between $0-90^{\circ}$.

Different rear structures can be fabricated on the flat side of the Si hemispheres. Laser light impacts the centre of the flat side with incident angles θ_i which can be varied from 0° to 90° . The detector senses the specularly reflected light. Note the rotation axis of the laser and the sensor should be both aligned at the centre of the flat side of the hemisphere in order to eliminate any distortion. This measurement idea will be implemented in Chapter 4.

2.2 Rear reflector designs

A superior rear reflector allows light to multiply pass through the silicon layer for low energy photons, i.e., near infrared (IR) light absorption within solar cells. Different types of rear reflectors, either planar or scattering, are reviewed in the section to justify the possibility of their application into high efficiency silicon solar cells.

2.2.1 Review of planar reflectors

Configurations of planar reflectors reviewed in this section are shown in Fig. 2.5.



Fig. 2.5: Schematic drawings of specular rear schemes (a) Si/alloyed Al (b) Si/dielectric/metal (c) Si/dielectric/detached metal (d) Si/Distributed Bragg Reflector (e) Si/Dielectric stack/metal. The slight rough surface in (a) is attributed to the alloying process. Structure (a) is commonly used in industrial cells and scheme (b) is most often applied in laboratory silicon solar cells. Schemes (c), (d) and (e) are regularly designed for thin films cells to improve light trapping.

2.2.1.1 Silicon/Aluminium alloying

Alloyed Al is usually applied to the entire rear of present industrial cells, acting as rear electrode and reflector [16, 17]. While the reflectance from a flat Si/Al interface is < 80% by optical calculation, in reality, the rear reflectance is much lower than this value due to roughened interface from alloying where parasitic metal absorption is significant, see Fig. 2.5a. The only optical advantage of this scheme might be the enhanced light diffusion and scattering from the roughened surface. In fact, optical performance is not the most important issue to be considered for cells with such rear configuration.

Potential current gain from an enhanced optical response can likely be counteracted by the unfavourable rear electrical quality of some schemes. The most substantial advantage of this approach lies in the ease of fabrication together with the back surface field (BSF) and the *p*-type contact formed by Si/Al alloying which is compatible to existing screen printing facility that are most favoured by solar cell manufacturers. However this rear scheme is not applied to high efficiency laboratory solar cells where cost is of much lower importance than optical and electrical performance.

2.2.1.2 Silicon/dielectric/metal

An added dielectric layer between the silicon and a metal film in combination with localised contacts ensures excellent rear surface passivation for high efficiency laboratory cells as discussed in Chapter 1 [18, 19]. Rear optical quality is also improved by the enhanced reflectance from the additional interfaces [20] (see Fig. 2.5b) and the attenuated light absorption on the metal surface (as will be discussed in Chapter 4) [21, 22]. For example, reflectance from the Si/SiO₂/Al system can be above 95% under normally incident light, much higher than that from the Si/Al system. The improved rear electrical quality also allows optical gain to contribute to the overall current generation.

Thermally grown SiO₂ [19] and plasma-enhanced chemical vapour deposition (PECVD) SiN_x [18] are two regularly used passivating dielectrics. According to Fresnel equations, thermal SiO₂ with a lower index of refraction provides higher specular reflection compared to SiN_x [23]. Together with its stable passivation, thermal SiO₂ is chosen to passivate most high performance silicon solar cells.

Al used in the Si/dielectric/metal rear scheme has an appropriate work function to make contact to *p*-type Si [20]. Its low material costs, good adhesion and corrosion resistance also make it a popular material in solar cell fabrication. However, previous studies have verified that the optical reflectance from Al is inferior to that of other noble metals, such as Ag. For Ag, the Fermi level does not fall within a bandgap. Therefore absorption is restricted to free carrier absorption rather than inter-band absorption at the photon energy range of interest [24]. Moreover, the angular reflection of Si/SiO₂/Al scheme is extremely low at angles close to the critical angle of Si/SiO₂ interface, as confirmed by Campbell [13]. The use of noble metals as rear reflectors can be attempted in order to

achieve high intensity, less angular-sensitive rear reflectance provided there is no compromise in the cell's rear electrical performance.

2.2.1.3 Silicon/dielectric/detached metal

Many metals performing well as reflectors in air will not provide the same optical properties when in contact with semiconductors. Detached reflectors, defined to be any reflectors without direct contact to solar devices (Fig. 2.5c), are ideal in many ways. Not only does detached reflector cause no surface degradation but the detached reflector can eliminate strong parasitic absorptions due to surface plasmon polaritons that would otherwise be present in direct metal reflectors [25]. Moreover, detached reflectors allow for more flexible topologies on the reflector surfaces which can potentially benefit light trapping [26]. Detached reflectors can either be a metal film or other material layers with light scattering properties. Some of the previous studies about thin film cells utilised this type of reflector because of its easy and flexible application method [26-28]. Detached reflectors. When incorporating such reflectors to silicon solar cells, the rear contact scheme needs to be modified accordingly.

2.2.1.4 Silicon/Distributed Bragg Reflector

High rear surface reflection can also be achieved by applying a Distributed Bragg Reflector (DBR) formed by multiple layers of dielectric with alternated refractive index, as shown in Fig. 2.5d. A DBR functions as an effective reflector for light over a broad angle and wavelength range, according to Bragg theory.

Carniglia and Apfel [29] have designed a highly reflective DBR by carefully choosing the thickness of each added layer so that the reflectance increase from each newly added pair is maximized. Optical constants of the dielectric material and the starting reflectance of the subsystem are considered to be two major factors determining the layer thickness. By modelling a rear scheme with just a few quarter-wave DBR pairs (Si/SiO₂ or Si/SiN_x), Yang [30] has optimised the reflection so that it approaches unity over a wavelength range of 800 nm – 1100 nm. As can be seen, the stop-band of the wavelength with high reflectance is expanded to several hundred nanometres. A relative *IQE* enhancement of 27% is obtained if 51 light paths were used, in comparison with *IQE* by light with singe path. Zeng [31] have reported a relative current enhancement of 6.4% and a relative efficiency enhancement of 9.2% by using the experimentally fabricated DBR on 5 μ m thick mono-crystalline Si thin film solar cells.

2.2.1.5 Silicon/Dielectric Stack/metal

An effective and low cost alternative to a DBR is a double or triple dielectric stack (DS) combined with a metal mirror (Fig. 2.5e). A high index difference between the neighbouring dielectrics is necessary to achieve reduced number of dielectric layers in the *DS* compared to that in the DBR. The entire dielectric stack can be used to passivate the rear surface of the solar cell compatible with existing device processes.

Surface passivation by dielectric stacks has been widely explored in the past. Some of the silicon compound based stacks such as SiO₂ and SiN_x have shown high quality and stable passivation. Schmidt et.al. [32] have showed that a stack of "thin thermal SiO₂ / PECVD SiN_x" yields much better thermal stability compared to a single layer of PECVD SiN_x, although both provide outstanding surface passivation on the 1 Ω cm *p*-type silicon base. McCann *et.al.* [33] have reported that the stack of "thin thermal SiO₂ / LPCVD SiN_x" also brings good thermal stability during high temperature treatment. Other DS combinations (e.g., PECVD SiO₂ / PECVD a-Si and PECVD a-Si / PECVD SiN_x stacks) have also shown electrical advantages [34-36]. However, the optical properties of a *DS* coupled to a metal layer have not been adequately studied, leaving scope for work in this thesis.

2.2.2 Review of scattering reflectors

As expected, the planar reflectors discussed above tend to be highly specular, limiting prospects for light trapping in solar cells. This section reviews possible rear structures which provide large angle scattering and hence have the potential to prevent light escaping from the top surface of the solar cell.



Fig. 2.6: Schematic drawings of proposed diffuse scattering rear reflectors (a) Rear geometrical structure (b) Commercial white paint (c) Metal nanoparticles (d) Diffraction gratings.

2.2.2.1 Rear geometrical structures

A diffuse reflector based on the rear geometrical structure of a solar cell (Fig. 2.6a) traps light within silicon similar to the way it is done by front texture. If light absorption is ignored in the geometrical structure, light trapping by a randomized surface resulting in a Lambertian light distribution is poorer than surfaces textured by random upright and periodically regular inverted pyramids. In fact, from ray tracing study, the best light trapping is achieved for solar cells textured by "perpendicular slats" on both sides, which potentially improves current generation by 4%, compared to solar cells textured by random pyramids on one surface only, see Fig. 2.7 [37].



Fig. 2.7 Calculated short circuit current as a function of solar cell thickness for various light-trapping schemes. Image is taken from [37].

However, texture on the rear surface increases the surface area of the devices and introduces undesirable rear recombination losses. Furthermore, the texture effect will be

transferred to the metal interfaces once a metal film is deposited. This greatly reduces light reflection because the multiple reflections at the textured metal's interface with the silicon provide more opportunities for absorption in the metal. The feasibility of using conventional rear point-contact techniques becomes another issue if rear geometrical structures were applied. This necessitates the study of alternative light trapping schemes.

2.2.2.2 Commercial white paint

Commercial white paint (Fig. 2.6b), such as that containing rutile titanium dioxide dispersed in a polymeric binder, is one possible candidate for a scattering reflector. Its low cost and easy fabrication provide additional benefits compared to other scattering structures. Previous studies have verified its practicability in thin film solar cells [27, 38], with a reported current boost as high as 41% [27]. Besides thin film devices, white paint also can be applied to silicon solar cells for light trapping, targeting the 900 nm – 1200 nm spectral range where light absorption in Si is weak. In this thesis, both the optical advantages and, the electrical impact of applying such material on the rear of wafer based silicon solar cells will be performed.

2.2.2.3 Metal nanoparticles

Another promising technique is the use of surface plasmonic particles as the rear surface reflector (Fig. 2.6c), which provides a tunable high scattering cross section to scatter light to larger angles, without increasing the silicon surface area and associated losses. It is possible to exceed the $4n^2$ limit of optical path length by using such plasmonic structure in thin and ultra-thin film photovoltaic cells due to optical field confinement in the active region [39-43]. Ag nanoparticles, owing to their high radiative efficiency and low parasitic absorption, are a good choice in this regard [44]. A detailed description of surface plasmons in Ag nanoparticles is given in section 6.1, Chapter 6.

2.2.2.4 Diffraction grating

A diffraction grating, commonly used in the fabrication of monochromators and spectrometers, is another candidate for large-angle reflection, see Fig. 2.6d. Light can be split and diffracted into beams propagating in certain directions if the periodical structure of grating (e.g. grating period, grating depth and grating duty cycle) is precisely controlled. This type of reflector has been used on some thin-film solar cells in the past [31, 45]. The patterned substrate can either be a dielectric [31], metal [46] or

semiconductor, such as a Si wafer [47]. A grating structure directly fabricated on the silicon wafer enlarges the surface area of the devices hence introduces more recombination losses. Therefore individually patterned gratings are greatly preferred.

Previous studies also show that an additional DBR deposited on the grating can further increase reflection resulting in a 18% current enhancement reported by using such a combination on a 675 μ m thick wafer based solar cell [47].

2.2.2.5 Other scattering reflectors

Other scattering schemes having the potential for improved photonic properties include low index spheres such as void spheres or SiO_2 spheres surrounded by higher index matrix [48]; binder-free coating of high index dielectric particles (such as rutile TiO_2) surrounded by air [49]; nanoimprinted patterns with precisely controlled size, shape and distribution of nano-features [50]; or a combination of light scattering schemes with angularly selective filters [51]. These structures are beyond the scope of this thesis.

2.2.3 Potential reflectors for high efficiency solar cells

This thesis applies and studies planar reflectors fabricated from Si/dielectric/metal, Si/dielectric/detached metal, Si/DS/metal layer stacks as well as diffuse scattering reflectors such as commercial white paint and Ag nanoparticles to the rear of high efficiency solar cells.

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Chapter 3. Front side characterisation of 2-D reflection patterns from textured surfaces

In this chapter, the two dimensional reflected light distribution patterns for various textured surfaces have been captured by an improved optical setup. The measured results are somewhat different from the ray-traced results reported by others. Reasons are found in non-ideal texture morphologies which are confirmed by SEM, atomic force microscopy (AFM) and focused ion beam (FIB) cross-sectional images. The reflected light distribution of the surfaces with regular inverted pyramids can be categorized into three groups, corresponding to major light paths A, B and C, following the nomenclature of Baker-Finch and McIntosh [1]. On the other hand, the reflection patterns for random upright pyramids are a function of size, shape and distribution of the pyramids. Instead of the expected distinct light reflection angles from the ray-traced predictions, the experimental results show angularly continuous light distributions with higher peak reflection weighting for larger sized pyramids. The impact of the encapsulant's refractive index on the amount of total internal reflection at the air-glass interface is also discussed for various types of textured surface.

3.1 Theoretical relationship between inverted pyramid geometry and reflection distribution

Incident light on surfaces with regular inverted pyramids can follow three general paths: (i) it bounces¹ once from the surface, while partially being coupled into the cell, (ii) it has a double bounce on the surfaces, while partially being coupled into the cell, or (iii) it has triple bounces on the surfaces, while partially being coupled into the cell. Even though multiple bounces offer more opportunities for the light to enter the Si, some is still reflected, as visualised by the ray-traced reflection analysis of paths A, B and C in Fig. 3.1a [1]. The right graph of Fig. 3.1a shows the impact-areas for the first bounces in a unit cell of one pyramid. Ray A corresponds to a path that undergoes double bounces

¹ Note: The words "reflections" and "bounces" are used as synonyms.

from the two opposite facets, while Ray B encounters 3 bounces, with the first two resembling bounces of ray A (but occurring near the pyramid bottom) and the third occurring near the pyramid top with light being eventually reflected off. The fraction of light split between path A and B is determined by the slope of the pyramid facets (Φ). A Φ of more than 60° enhances the triple bounce path B, while a Φ smaller than 54° results in the double bounces of path A only. For inverted pyramids with their ideal Φ of 54.74°, only a small fraction of light follows the triple bounces of path B. Path C also corresponds to a triple bounce reflection, but involves three neighbouring facets [2], instead of two.

Fig. 3.1b shows the expected reflected light distribution from the three rays A, B and C. Reflection angles of θ_{o_a} , θ_{o_b} and θ_{o_c} of the three rays relative to the vertical for (111) planes as well as their corresponding weightings R_{o_a} , R_{o_b} and R_{o_c} (which are normalised to be unity in sum) are shown in the inset of the figure. Geometrical equations used to calculate θ_o and R_o are listed in Table 3.1. Both θ_o and R_o depend only on the base angle Φ of the inverted pyramids [3].

The regions labelled A, B and C in Fig. 3.1b correspond to the reflection paths from Fig. 3.1a. The ray reflections A and B have four reflection regions, symmetrically distributed with respect to the x and y axes at two escape angles $\theta_{o_a}=38.9^{\circ}$ and $\theta_{o_b}=31.6^{\circ}$ respectively, see Fig. 3.1b. This assumes that all four facets of the pyramids have the same ideal slope $\Phi=54.74^{\circ}$. The 8 regions labelled C extend symmetrically from the four reference B regions and fall into the four quadrants. They correspond to the triple reflection by ray path C. Ray C ideally comes out at the same angle as ray B, but off-axis by 36.9° on either side due to the sidewall reflection, see Fig. 3.1b. This off-axis angle (δ_{o_c}) of ray C also depends on the pyramid base (slope) angle Φ and is calculated via Eq. 3.1.

$$\delta_{a,c} = \operatorname{arccot}[2\sin^2(\Phi)] \tag{3.1}$$



Fig. 3.1: (a) Schematic ray paths of reflection A, B and C for a regular inverted pyramid (left), as well as their corresponding areas of the first bounces in the top view of one unit cell of an inverted pyramid (right) [1]. (b) A idealised reflection pattern if the surface is hit by a relatively small beam of light. The inserted data indicate the ideal reflection angle θ_o and weightings R_o (right index), as well as the off-axis angle δ_o (left index) of the three ray paths.

Ray	Reflection angle θ_o	Weightings R _o		
Α	$\theta_{o_a} = 180^\circ - 4\Phi, 45^\circ < \Phi < 60^\circ$	$R_{o_a} = 1 - R_{o_b} - R_{o_c}$		
В	$\theta_{o_{-}b} = 6\Phi - 360^{\circ}, \Phi > 54^{\circ}$	$R_{o_{-}b} = \frac{\cos^2(5\Phi)}{\left \cos(\Phi) \cdot \cos(3\Phi)\right }$		
С	$\theta_{o_c} = \operatorname{Arccos}\left(\frac{\left[2 + 3\cos(2\Phi) - 2\cos(4\Phi) + \cos(6\Phi)\right]}{4}\right)$ where $45^\circ < \Phi < 60^\circ$	$R_{o_{-}c} = \frac{1 - \cos(\Phi)}{ \cos(3\Phi) }$		

Table 3.1: Geometrical equations used to calculate reflection angles θ_o and their reflection weightings R_o for the three rays A, B and C for regular inverted pyramids.

3.2 Experimental method

3.2.1 Samples

The two main surface textures studied in this work are regular inverted and random upright pyramids. The different features of the regular inverted pyramid texture are shown as SEM images in Fig. 3.2. The left side of the figure (a) shows a mono-modal pattern (one pyramid size) while Fig. 3.2b shows a bimodal pyramid pattern (two pyramid sizes), which shows interesting diffraction phenomenon (section 3.3.3). For the formation of regular inverted pyramids, the {100} Si surface is first covered by 100 nm thermally grown masking oxide. Square-arrays of window openings are then formed via photo-lithography. The wafers then are etched in a potassium hydroxide (KOH) solution at 70°C for 13-15 minutes. This is followed by a two-step acidic etch to ensure the pyramids are fully opened and nominally to reduce the surface-stress at the final passivating SiO₂/Si interface [4]. The effect of the alkaline and acidic etch processes on reflected light distribution will be discussed in detail in section 3.3.2. To allow easier physical and optical measurements and their comparison, the surface oxide is removed by a buffered HF solution. The base angles of the inverted pyramids are measured and compared to the ideal value of 54.74°. Inverted pyramids are either aligned in a regular square-like pattern to each other or in a 5° tilted "Tiler's Pattern" [5, 6]. Fig. 3.3 shows the SEM images of three variations of random upright pyramid textures. To obtain different surface morphologies as shown in Figs. 3.3a, b and c, the {100} oriented wafers were etched by a chemical mixture of NaOH, isopropanol and water with various mixing ratios, etching times and temperatures. Other types of surface textures together with their characterised reflection patterns are given in Appendix C.



Fig. 3.2: SEM images of (a) mono-modal inverted pyramid which will be further analysed in section 3.3.1 and (b) bi-modal inverted pyramid surface textures which will be further discussed in section 3.3.3.



Fig. 3.3: SEM images of three types of random upright pyramid surfaces: *Texture-a, Texture-b* and *Texture-c* as used by different manufactures. The properties of these surfaces are analysed in section 3.4.

Measured reflected light distributions and SEM pictures are used to estimate the size and shape of pyramids. The height and slope of random upright pyramids is measured via AFM, while the wall slope of inverted pyramids is measured via FIB.

3.2.2 Optical setup

The optical measurement setup in this work is shown in Fig. 3.4. A 532 nm (green) 5 mW laser was used to illuminate the textured front surfaces. The laser beam passes through a screen that is placed between the laser and the sample via a small opening. Green light was chosen as it is strongly absorbed by Si. This eliminated possible reflections from the cell back surface.



Fig. 3.4: A cross-sectional schematic of the experimental setup for the recording of front-reflected light distribution. The pierced screen is either semi-transparent to allow digital imaging from the back or consists of photosensitive photographic paper. The distance between the camera and screen is larger than suggested by the schematic to minimise distortion effects from its off-centre placement.

To image the direct specular reflection on the screen, the sample was tilted slightly away from perfect perpendicular illumination. As shown in Fig. 3.4, d_t is the distance from the textured surface to the screen (set to 15.3 cm), and d_s (θ_o) is the distance from the reflected light to the centre of the reflection pattern on the screen (point of specular reflection for planar surfaces). The reflected angle θ_o can then be calculated as:

$$\theta_o = \arctan(d_t / d_s) \tag{3.2}$$

The laser beam diameter of less than 5 mm, together with the chosen screen distance d_t of 15.3 cm, allows an angular resolution of $\pm 2^\circ$.

The screen is used to visualise the reflection pattern. As previously noted, either the pattern is recorded by a digital camera from the back by the use of a semi-transparent screen, or the screen consists of photographic paper (e.g., FOMA BOHEMIA with multigrade surface) and records the pattern directly. The exposed photographic paper can then be developed and scanned for digital analysis. For the chosen distance of $d_t = 15.3$ cm, a screen size of 30.5 cm x 40.6 cm was sufficient to capture the majority of the reflection patterns (0–63° in all directions). When using a digital camera to image the screen, the aperture and shutter speed was kept constant to allow direct comparisons of

different reflection patterns and intensities, as shown in Fig. 3.6a-c. The digitalised images, either from the digitalised photographic paper or direct from the camera, are then analysed via a MATLAB program to calculate the angular distributions of the reflection patterns.

3.3 Results and discussion for regular inverted pyramids

3.3.1 Measured reflection distribution

Fig. 3.5a shows the measured spatial reflection distribution on photographic paper placed $d_t = 15.3$ cm from the sample. The sample has mono-modal inverted pyramids without any antireflection coating. The same mono-modal inverted pyramids are shown in Fig. 3.5b, but with an oxidised surface of 110 nm SiO₂. The additional oxide coating clearly reduces the light intensity of the dominant large area reflection peaks.

The pattern of rays A, B and C in Fig. 3.5a are similar to those on Fig. 3.1b except they are located at different escaping angles $\theta_{o_a,b,c}$. Table 3.2 summarises the measured $\theta_{o_a,b,c}$ and the calculated number of bounces of each ray based on the measured pyramid wall slopes, see Table 3.3, in comparison to the case of ideal pyramid slopes of $\Phi = 54.74^{\circ}$. The measured $\theta_{o_a,b,c}$ are smaller than their theoretical values, attributed to the smaller than ideal average slope of the pyramid walls. Section 3.3.2.2 will discuss this in detail.

The reflection weighting $R_{o_a,b,c}$ of each of the rays A, B and C of the inverted pyramids is difficult to extract from our measurements due to numerous overlapping reflections. However, the images do provide a clear visual qualitative distribution of the three rays. Regions corresponding to ray A and C are more intense than the region corresponding to ray B, see Fig. 3.5a.

The observed approximately equally spaced dot-like reflections are due to diffraction effects with their spacing determined by the size of the inverted pyramids.



Fig. 3.5: Reflected light distribution from a mono-modal inverted pyramid texture on (a) uncoated silicon surface and (b) with a 110 nm thermally grown SiO₂ coating. Note: In order to not cover reflection peaks B in figure (a), the labels are off-centred.

	Calculated number of		Dofloatic	an angle A (deg)	Calculated off-axis angle		
Ray	bounces		Kenectio	In angle $\mathcal{O}_{o_a,b,c}$ (deg)	$\delta_{o_a,b,c}$ (deg)		
	Ideal (*)	Massurad (**)	Ideal Measured (+ 2°)		Ideal (*)	Measured	
	iucai ()			Measureu (<u>-</u> 2)	iucai ()	(**)	
A	2	2	38.9	24.6 to +x axis		0.0	
				29.0 to -x axis	0.0		
				27.3 to +y axis	0.0		
				27.0 to -y axis			
В	3	2~3	31.6	17.0 to +x axis		0.0	
				20.0 to -x axis	0.0		
				19.0 to +y axis	0.0		
				19.0 to -y axis			
С	3	3	31.6	22.7 in 1 st quadrant		38.8	
				22.9 in 2 nd quadrant	26.0		
				24.2 in 3 rd quadrant	30.9		
				21.9 in 4 th quadrant			

Table 3.2: Comparison between calculated and measured values for the number of bounces, reflection angles $\theta_{o_a,b,c}$, off-axis angles $\delta_{o_a,b,c}$ for all three types of reflected ray paths. The data are for regular inverted pyramids.

(*) = For an ideal pyramid wall slope of $\Phi = 54.74^{\circ}$.

(**) = For the measured pyramid wall slopes from Table 3.3.

3.3.2 Etching and the effect on the reflection pattern

To explain the non-ideal reflected ray angles in Fig. 3.5 and Table 3.2, the pyramid surface geometries were measured by SEM and FIB after each processing step. Fig. 3.6a-c shows the results for inverted pyramids in a mono-modal pattern (no Tiler's pattern). Note that Fig. 3.6c is identical to Fig. 3.5a. The corresponding top-view SEM images are shown in Fig. 6d-f. The cross-sectional FIB images after platinum deposition and milling are given in Fig. 6g-i. The platinum layer (lighter colour on top of the structures) in the FIB images is to be ignored; its only purpose is to provide a good contrast to visualise the silicon surface.

The measured average slopes Φ of the inverted pyramids after each processing along the *x* and *y* axes at the silicon surface via FIB are given in Table 3.3. The slope data are further correlated to reflection patterns shown in Figs. 3.6a-c and quantified in Table A.1. Since the actual reflected light from regular inverted pyramids is not a continuous function, and in addition to the discrete diffraction pattern, calculated $\theta_{o_a,b,c}$ and $R_{o_a,b,c}$ by using average numbers of the *y*-axis slopes from Table 3.3 are given in Table 3.4. *Y*-axis slopes are chosen to avoid/minimise the asymmetrical opposing slope that is evident for *x*-axis slopes. The parameters subsequently are used to calculate the data for the inverted pyramids in Fig. 3.11.



Fig. 3.6: Reflection patterns of silicon surface with inverted pyramids in a mono-modal arrangement after (a) alkaline etch; (b) 1st acidic etch; and (c) 2nd acidic etch. Figures (d)-(f) are the corresponding top view SEM images of the inverted pyramids. Figures (g)-(i) are the corresponding cross-sectional FIB images.

Table 3.3: Measured average wall slopes Φ for inverted pyramids along the *x*- and *y*axes after each processing step. The slope is given for both sides (or one side and opposing side) of the pyramids. The mean squared error is derived from repeated measurements (in some cells, repeated measurements gave identical values).

	<i>x</i> -	axis	y-axis			
	Wall slope	Opposite wall slope	Wall slope	Opposite wall slope		
Alkaline etch	$54.6^{\circ} \pm 0.05^{\circ}$	$55.8^{\circ} \pm 0.06^{\circ}$	$54.6^{\circ} \pm 0.09^{\circ}$	$55.3^{\circ} \pm 0.02^{\circ}$		
1 st acidic etch	$52.6^{\circ} \pm 0.09^{\circ}$	$54.1^{\circ} \pm 0.06^{\circ}$	$52.9^{\circ} \pm 0.01^{\circ}$	$53.6^{\circ} \pm 0.10^{\circ}$		
2 nd acidic etch	$51.5^{\circ} \pm 0.03^{\circ}$	$53.2^{\circ} \pm 0.20^{\circ}$	$52.0^{\circ} \pm 0.00^{\circ}$	$52.5^{\circ} \pm 0.00^{\circ}$		

Table 3.4: Angles of the pyramids walls Φ , calculated angle $\theta_{o_a,b,c}$ and weightings $R_{o_a,b,c}$ of each ray path of inverted pyramids after each etching step. The data are averaged *y*-axis values from Table.3.3. The parameters subsequently are used to calculate the data for the inverted pyramids in Fig. 3.11.

	Measured wall slope ${oldsymbol {\varPhi}}$	Ray A		Ray B		Ray C	
		θ_{o_a}	R _{o_a}	θ_{o_b}	R_{o_b}	θ_{o_c}	R_{o_c}
Alkaline etch	54.9°	39.6°	58.5%	30.6°	1.1%	32.2°	40.4%
1 st acidic etch	53.2°	32.8°	63.9%	N/A	N/A	26.1°	36.1%
2 nd acidic etch	52.3°	29.2°	66.5%	N/A	N/A	23.0°	33.5%

3.3.2.1 The effect of an alkaline etch on the reflection pattern

It can be concluded from the reflection pattern of Fig. 3.6a that reflection from an alkaline etched inverted pyramid surface is reasonably specular. The strong specular reflection at the reflection centre is caused by horizontal flat regions most clearly seen in Fig. 3.6d and 3.6g. In this case, they have a measured width of 2.6 μ m. This is significant, considering the overall pyramid width of only 10 μ m. The measured $\theta_{o_a,b,c}$ of the inverted pyramids after the alkaline etch, in particular the measured angles for ray C (see Table A.1), closely match the theoretical ones (Table 3.2). This is explained by the nearly ideal pyramid slopes of $\Phi = 54.74^{\circ}$ after an alkaline etch. The 6° degree of ray A blurring, as highlighted in Fig. 3.6a, is likely caused by non-planarity of the fabricated inverted pyramids.

As expected from theoretical calculations, sharp pyramid "tips" (see circular markers in Fig. 3.6g), would result in a ray B reflection with weighting $R_{o_b} = 0.8\%$. This ray is not

observed in Fig. 3.6a, presumably because it is below the detection limit of the used setup.

3.3.2.2 The effect of the 1st and 2nd acidic etches on the reflection pattern

The measured $\theta_{o_a,b,c}$ for rays A, B and C fall increasingly below their theoretically predicted angles with every acidic etch, see Tables 3.2, A.1 and A.2. This indicates a change in surface morphology, e.g., a reduction in wall slopes from 54.74° to 52°, see Table 3.3 and Figs. 3.6e, f,h and i.

The acidic etches are needed to enhance multiple reflections and to reduce specular reflection, Figs. 3.6b and c, that are caused by the horizontal flat regions, as seen in Figs. 3.6e,f,h, and i. These flat regions, or the spacing between pyramids, is reduced from 2.6 μ m to 0.4 μ m and then to 0.1 μ m. The etches furthermore round the pyramid "tips", see circled regions in Figs. 3.6h and i. This effectively increases the ray B reflection, as observed in reflection patterns Fig. 3.6c, to an extent that its reflection angle can now be measured, see Table A.1. In addition, with the flattened slope of the pyramid tips, the triple bounce of ray B disappears and converts to a second ray of type A. Due to the changed slope, its reflection angle θ_o a is smaller than the original ray A.

Another effect of the acidic etches is seen on the ray C reflections. Prior to the acidic etches, the eight ray C reflections were discrete as seen in Fig. 3.6a. However after the acidic etches, these reflections formed a continuum, see Figs. 3.6b and 3.6c. This blurring is likely caused by the roughened surface and edges which is most prevalent for ray C. This ray is most sensitive to surface roughness due to its second oblique reflection ideally at 78.9° in regards to the pyramid facet wall [3]. The roughened surface can be observed as slightly dark patches in the FIB image, see Figs. 3.6h and i. Compared to θ_{o_c} , the off-axis angle δ_{o_c} is less sensitive to changes of the pyramid wall slope, see Eq. 3.1 and Table 3.1. For example, a change in Φ from 55.2° to 52.3° (taken from Table 3.3) will change θ_{o_c} from 33.2° to 23.1° (30%). On the other hand, the off-axis angle δ_{o_c} changes only from 36.6° to 38.6° (5%), see ray C *x*-axis values in Table A.2. The rough surfaces from the acidic etch seem to have also an increased blurring effect on the reflection pattern of ray A. Blurring is increased from 6° to 9°, as seen Fig. 3.6a and 3.6c. Other possible reasons for a blurring effect could lie in slight variations of pyramid slopes which can create reflection patter the acidic etch seem to have discussed.

Another driver that changes the observed reflection pattern from the ideal case is nonideal wafer orientation. In Table 3.3 it is shown that the wall slopes difference from one to the opposing side of the inverted pyramids are 0.96% on the *x*-axis but 3.30% on the *y*-axis. This results in two asymmetrical ray A reflection angles θ_{o_a} that are 5° different from each other on the *x* axis. This is both seen in the calculated and measured values, see Tables A.1 and A.2. We assume that the original wafer was wafered 2.5° off its ideal {110} plane.

3.3.3 The diffraction phenomenon

Diffraction phenomenon appear for surfaces with periodic features and long coherence length (typical for lasers). Diffraction effects are apparent as evenly distributed features in the reflection pattern, see Fig. 3.5 and Figs. 3.6a-c. In our case these reflection features have a spacing d_{diff} of 3°. This agrees with Bragg's diffraction theory:

$$d_{diff} = \frac{\lambda}{s} \tag{3.3}$$

where λ is the wavelength of the illumination (532 nm) and *s* is the periodicity of the inverted pyramid (10 µm). Note d_{diff} is in radians. Reflection images with these periodic diffraction features can therefore be used to calculate the average spacing or size of regular inverted but also regular upright pyramids.

This phenomenon is most apparent for surfaces with bimodal inverted pyramid patterns, see Fig. 3.7. Typical for a bimodal surface is a diffraction pattern of alternating weak and strong reflections. Mono-modal surfaces on the other hand do not create these reflections of alternating intensity, see Fig. 3.5a. More on diffraction theory on pyramid tips can be found elsewhere [7, 8].

The diffraction effect allows light to be reflected from the cell's surface at larger angles than possible via geometrical optics. We measured the maximum diffraction angle as 74° (due to the limited screen size it is not visible in Fig. 3.7). Interestingly the intensity

does not attenuate for the diffracted light spots, especially if they are along the main xand y- axes. The diffracted light at large angles can be particularly beneficial for encapsulated cells as totally internal reflection between air and glass can be achieved. Such light will have an additional chance of absorption as it will strike the cell's surface again. However, this effect is limited by the relatively short coherence length of natural sun light.



Fig. 3.7: Distribution of reflected light from inverted pyramids with a bimodal pattern. The alternating weak and strong reflections are typical for this pyramid arrangement. The image was recorded on photographic paper.

3.4 Results and discussion for random upright pyramids

Fig. 3.8a,b,c show the reflection patterns for the random textured upright pyramids corresponding to Fig. 3.3a,b,c. Compared to the regular, periodically arranged pyramids, these patterns are relatively feature-less due to the randomness of the pyramid distributions.



Fig. 3.8: Reflected light distributions captured on photographic papers for the corresponding silicon surfaces with random upright pyramids from Fig. 3.3.

The reflection patterns were analysed via MATLAB after digitalising the developed photo paper. Data for $R_{ow}(\theta_o)$ are given as reflection weightings over an angular range (every half degree) instead of for discrete angles, due to the continuous reflected light distribution from random textures, see Eq. 3.4.

$$R_{ow}(\theta_o) = \frac{\int_{\theta_o}^{\theta_o + 0.5^\circ} \overline{r(\theta_o)} \cdot 2\pi \cdot d_t \cdot \tan(\theta_o) d\theta_o}{\int_0^{90^\circ} \overline{r(\theta_o)} \cdot 2\pi \cdot d_t \cdot \tan(\theta_o) d\theta_o}$$
(3.4)

Note $\overline{r(\theta_o)}$ are circular averaged intensity values, which are then weighted by the circumference of the escape cone $2\pi d_i \cdot \tan(\theta_o)$ to correct for errors from the plane-image measurement.

Fig. 3.9 shows the reflection weighting results (R_{ow}) for the three selected random textures: *Texture-a*, *Texture-b* and *Texture-c*, corresponding to Fig. 3.3a,b,c and Fig. 3.8a,b,c. The general trends of the curves from these are all alike; their R peaks occur at around 25° and fall off to near zero at about 50°. This trend is in good agreement with the recent 1-D measurements showing that reflection peaks occur in the 20° to 30° region for random pyramids [9]. The position of the R_{ow} peak allows the calculation of the average pyramid's slope Φ via the equations in Table 3.1. For example, for a texture with a doubly bounce reflection peak at 25°, the equation for ray path A in Table 3.1 will give an average wall slope of 51°. An AFM measurement confirmed this with a slope of 49° – 51° measured, as shown in Fig. 3.10.



Fig. 3.9: Distribution of reflected light weighting R_{ow} (over a half degree region) from the three selected surfaces with random textures *Texture-a*, *Texture-b* and *Texture-c* taken from Fig. 3.3. Data R_{ow} are circularly averaged intensity values that are weighted according to the circumference associated with the reflection angle θ_o and normalised to unity. Note the value of R_{ow} changes by selecting different angular regions in Eq. 3.4.



Fig. 3.10: An example of the AFM measurement for the slope of a random pyramid.

The differences between the three curves in Fig. 3.9 result from different pyramids sizes and surface morphologies of the random textures, see Fig. 3.3. *Texture-a* with its relatively large pyramids (~10 μ m) shows the highest peak *R*. The peak *R* decreases for *Texture-b* and *Texture-c* with smaller pyramids sizes (~5 μ m and ~3 μ m respectively).

This can be explained by the weakened effect of simple geometrical optics and the enhanced effects of scattering/diffraction when the pyramids sizes become smaller. For θ_o less than 14°, R_{ow} of *Texture-a* is lower than the other two, due to the reduced scattering impacts for the large sized pyramids.

As can be seen, the reflected light distribution provides insight into surface geometries of the texturing, which could be possible used as a tool to fine-tune and monitor fabrication processes for industrial solar cells.

The large-angle diffused/scattered light from random pyramids also can be beneficial for encapsulated solar cells. Hence the study of the reflected light distribution from different textured front surfaces gives the ground to optimise parameters of encapsulant materials, which shall be discussed in the next section.

3.5 Choice of encapsulant's refractive index

The fraction of total internal reflection f_{tir} indicates how much of light from the frontsurface of the cell is reflected back by the air-glass interface towards the cell again. A value of unity means none of the reflected photons from the cell's surface will escape the module, but are trapped in the encapsulant/glass structure (here the absorption by the encapsulant and glass shall be ignored).

The refractive index n_{enc} of the encapsulant is a dominating parameter determining f_{tir} . Baker-Finch and McIntosh [1] concluded from numerical ray-tracing that for cells with randomly textured front surfaces, the traditionally used $n_{enc} = 1.50$ gives a f_{tir} value of less than 3%. By increasing n_{enc} to 1.59, f_{tir} would increase to around 80%, and for n_{enc} = 1.91, f_{tir} would rise close to unity. However, based on the experimental measurement results, this study reaches different conclusions.

The total internal reflection ratio f_{tir} is defined as the intensity of the integrated reflected light outside the escape cone of the module ($\theta_{enc-cri}$ to 90°) over the intensity of the integrated reflected light from the cells surface (0° to 90°).

$$f_{tir} = \frac{\int_{\theta_{enc} cri}^{90^{\circ}} R(\theta_{enc}) d\theta_{enc}}{\int_{0}^{90^{\circ}} R(\theta_{enc}) d\theta_{enc}}$$
(3.5)

 $R(\theta_{enc})$ is here the angular total reflection weighting taken from Fig. 3.9 for the random textures and Table 3.4 for the inverted pyramids. The Lambertian case was calculated for its standard definition of constant, angularly independent R. The critical angle θ_{enc_cri} comes from Eq.B.3.c in the Appendix B and creates therefore a dependency to the encapsulant's refractive index n_{enc} . The relationship between f_{tir} and n_{enc} for surfaces with various different pyramids structures is summarised in Fig. 3.11.



Fig. 3.11: The fraction of front reflected light that is totally internal reflected as a function of the encapsulant's refractive index. Three vertical dashed lines for the encapsulant's index are given. A value of $n_{enc} = 1.5$ indicates a typical encapsulant, $n_{enc} = 1.6$ is an available encapsulant with relative high refractive index and $n_{enc} = 2.6$ indicates an ideal encapsulant for inverted pyramids.

Fig. 3.11 indicates that an encapsulant with a moderate refractive index n_{enc} of 1.5 [10] can cause a relative high fraction of total internal reflection f_{tir} of 54% if the surface is Lambertain. However this type of encapsulant would result in a f_{tir} of only 5% if the light is reflected off experimental randomly textured surfaces, due to the scarcity of large angle reflected light, see Fig. 3.9. By using an encapsulant with a slightly higher index n_{enc} of 1.6, f_{tir} is increased to 10%. A f_{tir} of nearly 60% is possible if the

encapsulant index exceeds 2.6. However such high index material is not a feasible option for solar cells encapsulant. This finding shows that previous publications [11] overestimated the reflection weighting R_{o_a} for ray A at large angles θ_{o_a} .

For inverted pyramids, f_{tir} (n_{enc}) is a step-wise function for the three curves corresponding to different etching processes. The first step of f_{tir} is caused by ray A at the largest reflection angle θ_{o_a} . The value of n_{enc} required for this increases is between 1.57 and 2.05. The slope reduction by acidic etches causes a smaller reflection angle θ_{o_a} and would requires therefore a higher n_{enc} for a good trapping effect.

From the results above, one can conclude that a higher index encapsulant is needed to promote total internal reflection for both random and regular textured surfaces. An alternative method to obtain a high total internal reflection ratio is by developing novel surface textures that reflect light primarily at oblique angles.

3.6 Conclusion

In this Chapter, the reflected distributions from various textured front surfaces are experimentally examined using an improved optical set-up and image processing. For surfaces with regular arrays, such as inverted pyramids, the measured reflected light distribution can be described by geometrical optics theory. Smaller angles than predicted by numerical ray tracing are measured, which are explained by decreased slopes of the pyramids from the acidic etching steps that were found necessary for implementing well-formed features experimentally. Surfaces with regular arrays of pyramids reflect a large portion of their light at relatively large angles, which is beneficial for light trapping. The impact of various encapsulant indices on light trapping for various textured surfaces is discussed. For random textures a conventional encapsulant with an index of $n_{enc} = 1.5$ will result in only a fraction of total internal reflection of $f_{tir} = 5\%$. An increase to $n_{enc} = 1.6$ will increase f_{tir} to 10% for random textures. Surfaces with random textures showed a smeared out reflection pattern with the peak occurring at around 25°, which agrees well with recent results via another measurement method. Differences in the reflection distribution were correlated with the pyramid size. The measured reflection pattern reveals furthermore the angular accuracy

of the wafer cut (crystal orientation) and allows estimation of the pyramid's wall slope. In the future, this work can be extended to take incoming light reflection and angles into account.

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Chapter 4. Rear side characterisation of angular reflection to reduce plasmonic losses in the back reflectors

In this chapter, angular rear reflection from various types of dielectrically displaced planar reflectors (SiO₂/Al or SiN_x/Al) has been investigated both experimentally and by simulation. A novel optical setup has been developed that allows the measurement of high resolution reflection characteristics over a broad angular range. The choice of dielectric type, dielectric thickness and metal type of the displaced reflector has been extensively discussed taking their angular reflection performance into consideration.

4.1 Surface plasmon polaritons losses

Surface plasmon polaritons (SPP) refer to longitudinal oscillations of electron charges at the metal dielectric interface on excitation. Such wave excitations propagate along metal surface, with the electromagnetic field strength decaying exponentially on either side with the maximum localised to the surface. Only *p*-polarized light effectively couples to the SPPs [1]. The SPP mechanism is regularly used to develop photonic devices, such as the miniaturized photonic circuits with much smaller length scales for waveguide application [2].

Coupling via a grating or by attenuated total reflection (ATR) are two general methods adopted to excite SPPs [1, 3, 4]. Coupling using a grating is most often achieved by incorporating a rough metal surface and is beyond the scope of the study which will look at smooth interfaces only. For a smooth metal surface, SPP cannot be excited at the air-metal interface by light due to the mismatching in the momentum with plasmons, $(k_x > \omega/c)$. The modes are forbidden when they cannot simultaneously satisfy the dispersion relation and the boundary conditions, as obtained from Maxwells equations. A prism coupler adjacent to the metal surface (known as Kretschmann configuration) or the prism and the metal surface separated by a small air (or dielectric) gap (known as Otto configuration) can however alter the wave vector to allow the momentum matching for coupling by attenuated total reflection.



Fig. 4.1: Schematic drawing of a dielectrically displaced rear reflecting system of solar cell, which also resembles an Otto configuration. SPP are excited by a laser beam at the resonance angle θ_r on the metal surface.

A commonly used Otto configuration is composed of a dielectric prism with refractive index larger than that of air and a thick metal slab with a small air gap in between. A solar cell rear structure involving a "Si / dielectric / metal" layer stack resembles such a configuration with the index of Si (representing the prism) larger than that of the dielectric (representing the air gap), as shown in Fig. 4.1. When the angle of incoming light (θ_i) approaches the resonance angle (θ_r) of the system [1], a propagating SPP would be created on the dielectric-metal boundary by the *p*-polarised light component. This causes light to be trapped at the metal interface. This is an optical loss mechanism for solar cells which will be experimentally confirmed in this chapter.

4.2 Experimental method

4.2.1 Samples

A silicon hemisphere is used to allow incident light to pass through the air-silicon interface without refraction, as proposed in Chapter 2. The use of Si hemisphere is superior to half silicon disk or silicon cylinders if the angular distribution of the scattered light from a scattered/textured rear reflector such as the plasmon resonances in Ag nanoparticles is to be measured.

Polished, 25 mm diameter, hemispherical silicon substrates used in this study are shown in Fig. 4.2. It has a refractive index of 3.48 at 1.5 μ m wavelength. Its surface quality is quantified as 60/40 in scratch/dig which is sufficiently smooth for this measurement. For the displaced metal reflector fabrication, SiO₂ with varying thicknesses ranging from 76 nm to 570 nm are thermally grown on the flat side of the hemispheres followed by Al (> 1 μ m) thermal evaporation onto the SiO₂ layer. After *R_b* measurement for the Si/SiO₂/Al structure, Al metal is chemically etched and replaced by a 300 nm Ag film to allow measurement for the Si/SiO₂/Ag structure. Finally, Ag film is chemically removed to allow for *R_b* characterisation of the Si/SiO₂ structure.



Fig. 4.2: Silicon hemispheres used as the substrates for the reflector deposition. Different colours on the flat sides indicate different thicknesses of the thermally-grown SiO₂.

4.2.2 Optical setup

The rear reflector of a solar cell (400 μ m thick or similar) is effective at wavelengths near the band-gap of silicon with the shorter wavelengths absorbed in the Si. For the purpose of measurement in the study, a slightly longer wavelength of 1310 nm is chosen as the light source so that light can reach the rear reflector without being attenuated by the 25 mm diameter silicon hemisphere.

Fig. 4.3 shows the custom made optical setup used in the study. Two high precision rotation stages are used to rotate the laser diode and the Si hemisphere to allow the reflected light to be detected by the sensor, (see the inset of Fig. 4.3). This set up minimises gear friction from the rotating stages, stepper motor, and avoid asynchronism

and inaccurate angle measurements if the sensor is otherwise rotated instead of the Si hemisphere. The pigtailed laser head is fixed on the radius-arm of the second rotation stage, as shown by the small triangle in Fig. 4.3. The laser beam first passes through the vertically arranged optical control box (composed by beam expander, optical linear polarizer, lenses, iris, and apertures etc.), and is then deflected by a mirror at 90°. The beam then travels on the horizontal detection plane and impacts on the centre of the flat side of the hemisphere. In this configuration, the mirror is the only item able to block the detection at shallow angles. The beam size is kept to less than 1 mm inside the silicon with a nearly ideal beam divergence of only 0.12°. Lenses and irises are also used on the detector side to focus the reflected beam to the IR detecting spot. The detailed schematics of the rear angular reflection setup are given in Appendix D. Fig. 4.4 shows the experimental setup on the optical bench.



Fig. 4.3: The schematic of the experimental setup for the angular rear reflection measurement. The inset indicates the rotating process during the measurement process.



Fig. 4.4: Pictures showing the optical setup mounted on the optical bench.

The measurement procedure begins with an initial alignment where the silicon hemisphere is rotated by 65° as the maximum incident angle and the laser is rotated by 130° to detect the reflected light at the maximum angle. The silicon hemisphere is then rotated back step by step with an angular interval 0.5° or 1° , while the laser is rotated back step by step with the double interval. The reflected light intensity is recorded by a Ge detector after each rotation step. This measurement process continues until the hemisphere is rotated to -65° as the maximum incident angle on the opposite side. This is required to check the symmetry of reflection on both sides which is an indication of the measurement accuracy. Finally, both the silicon hemisphere and the laser diode are rotated back to their initial positions. The stage rotations as well as optical measurement processes are automated and controlled by a Labview program. This together with the alignment enables sub-degree angular resolution ($\leq 0.5^{\circ}$) so that the reflection information near the critical angle can be finely recorded.

4.3 Results and discussion

4.3.1 Measured $R_b(\theta_i)$ from various rear reflectors

The measured absolute reflected light intensities R_b (θ_i) of the three rear reflector schemes described in section 4.2.1 are shown by a half-polar chart in Fig. 4.5. Measurements are carried out on both sides of the hemisphere. The three angular dead cones are caused by (1) Shading by the mirror placed in front of hemisphere as seen in Fig. 4.3, 4.4 at 0° to 2° incidence and (2) Shading by the hemisphere holder at 66° to 90° incidence. However, light reflection over these dead cones can be estimated from measured results at nearby regions. As can be seen, intensities on both sides are symmetric, although some small angular dependence beyond the dip region is observed in the negative quadrant but not present in the positive quadrant curves. This can be attributed to the non-ideal expansion of the laser beam inside a relatively small silicon hemisphere that introduces asymmetric reflection.





Fig. 4.5: Measured absolute reflected light intensities R_b (θ_i) as a function of incident angle (θ_i) for three fabricated rear schemes Si/SiO₂/Al; Si/SiO₂/Ag; and Si/SiO₂/air. The dielectric layer thickness is 366 nm for all structures. The measurements are taken in half degree steps.

As demonstrated by Fig. 4.5, R_b remains constant at angles below the critical angle of Si-SiO₂ interface (θ_c =24°) for rear schemes with displaced metal whereby most of the light is reflected back into silicon with a small portion being refracted into the dielectric and absorbed by the metal. R_b approaches unity at angles > 30° where TIR occurs. As light angle approaches θ_c , R_b decreases and is at its minimum at an angle of around 24.5°. This angle corresponds to the resonance angle θ_r of the propagating SPP. Fig. 4.5 shows that the value of θ_r is similar but not necessarily the same for the two metals. The slight difference between θ_r and θ_c is due to θ_r being related to the rear metal constants, as will be discussed in section 4.4.2.

Ag as a noble metal brings slightly higher reflection than Al at angles $< 18^{\circ}$, and clearly higher reflection at angles near the resonance angle θ_r where SPP is excited. This reflection difference comes from the different imaginary parts of the refractive index of the two metals which indicates the amount of associated light absorption. For angles above 30°, TIR occurs and the reflection from the two metals becomes comparable.

The use of metal redirects light that would otherwise be transmitted through the rear at angles below 17° if Si/SiO₂/air is used as the rear. Due to the lack of metal absorption, reflection by the Si/SiO₂/air structure is slightly higher than that by the Si/SiO₂/metal structure at the TIR angular region. R_b by the Si/SiO₂/air structure in the TIR region can therefore be used as a base measurement to verify the maximum possible R_b achieved from the fabricated samples. The near overlap of the three curves indicates that the optical alignment of the setup is reliable and repeatable. Appendix E presents more measured data for the Si/SiO₂/air structure under various SiO₂ thicknesses.

The reflection dip at the resonance $R_b(\theta_r)$ for the Si/dielectric/metal structure indicates a loss due to excitation of SPPs, which should be avoided in the solar cell. This can be done by optimising the front texture and/or appropriate choice of rear metal and rear dielectric with optimised thickness so that the refracted light into Si at the front interface is incident on the rear surface at an angle larger than or away from θ_r .

4.3.2 Measured $R_b(\theta_i)$ of Si/SiO₂/Al under various SiO₂ thicknesses

For the Si/SiO₂/Al scheme, the effect of SiO₂ thickness on the angularly dependent rear reflection is examined experimentally and using W-VASE simulation [5], as shown in Fig. 4.6. The experimental data are calibrated (whereby maximum light intensity is set to equal 100%) to enable comparison with simulated results.



Fig. 4.6: Rear Si reflectivity from structure Si/SiO₂/Al with various SiO₂ thicknesses over the angle range of 2° to 56° (a) measured or experimental (b) simulation.

As seen from Fig. 4.6, measured R_b is slightly lower than the simulated R_b possibly due to the existence of a thin Al_xO_y layer at the SiO₂/Al interface which is not simulated in the model. Nevertheless, the measured R_b and the predicted R_b show the same trends. For example, at near perpendicular angles (2°), both results indicate maximum reflection for dielectric with quarter wavelength optical thickness (¼ λ /n_{SiO2}, 214 nm) due to constructive interference, and minimum reflection for dielectric with double wavelength optical thickness ($\frac{1}{2}\lambda/n_{SiO2}$, 420 nm) due to destructive interference. R_b (2°) is also a sinusoidal function of dielectric thickness reaching the next maximum when the dielectric thickness equals $\frac{3}{4}\lambda$ optical thickness. As expected, R_b remains high at oblique angles where TIR occurs and is less sensitive to dielectric thickness.

Fig. 4.6 also indicates that front regularly-textured solar cells passivated by thin rear SiO_2 are inferior to cells with thicker rear SiO_2 due to i) increased parasitic absorption in the metal (especially when most of the normally incident incoming light is deflected to an angle of 42° by the textures of inverted pyramids where R_b is small) [6] and ii) poorer surface passivation quality. Hence we can conclude that rear SiO_2 with thickness < 200 nm should not be considered for high performance solar cells with dielectrically displaced metal back reflectors.

Both measurement and simulation results indicate the presence of a second reflection dip at smaller angles for the structure with 500 nm SiO₂. From optical simulation (see Fig. 4.7), multiple-dip reflections occur at angles below θ_r with increasing the SiO₂ thickness. In a solar cell structure with a back reflector, incompletely absorbed light can reflect off the metal and dielectric interfaces multiple times, making several passes through the semiconductor as in a Fabry–Perot cavity [7]. The incoherence in the results could be the effect of the interference effects that could see its onset close to thickness in the order of wavelength of light. This effect reduces rear reflection at small angles and hence should be avoided.



Fig. 4.7: Simulated results showing multiple-dips in the reflection from structure $Si/SiO_2/Al$ with increasing SiO_2 thickness (\geq 500 nm).

The dips in reflection caused by the excitation of SPP $R_b(\theta_r)$ are more dramatic but narrower (i.e., over a shorter wavelength range) for schemes with thicker dielectrics (e.g. oxide thicknesses > 300 nm). For the wavelength under study here, the thinner oxide layers (<quarter wavelength thickness) go undetected by the incident light. This means the light does not see an interface and hence the coupling of the evanescent field through the dielectric and hence excitation of SPPs is not an efficient process. However as the oxide thickness is gradually increased, the tunnelling effect becomes more prominent showing as sharp reflection dips which is a characteristic of SPP excitation.

4.4 Optical simulation

Besides SiO_2 , SiN_x is also used as the surface passivation film for high performance solar cells. The surface passivation properties by SiO_2 and SiN_x have been widely investigated in the past [8] but the angular dependence of reflection properties of the rear that involves these dielectrics have not been experimentally studied and compared previously.

4.4.1 $R_b(\theta_i)$ of Si/dielectric/Al with different dielectric indices

In this section, R_b (θ_i) of these four rear structures i) Si/SiO₂/Al; ii) Si/SiN_x/Al; iii) Si/SiO₂/Ag; iv) Si/SiN_x/Ag is simulated by varying the refractive index of SiN_x from 2.0 to 2.6. Thicknesses of SiO₂ and SiN_x films are kept as ¹/₄ λ optical thickness aimed at 1310 nm. This gives theoretically the maximum reflection for perpendicular incident light if the front surface of solar cell is planar. Fig. 4.8 shows reflectivity of rear schemes under non-polarised and *p*-polarised light illumination over 0° - 70° angular range. Note that *p*-polarised light is of interest to study its optical losses at the metal interface as only *p*-polarised light can excite SPPs.



Fig. 4.8: Simulated rear reflectivity of structure "Si/dielectric/Al" over 0° -70° angular range. Curves with solid dots correspond to non-polarised light illumination while curves with hollow dots are for *p*-polarised light. Thickness is calculated to be ¹/₄ λ .

The location of the dip is determined by the optical index of the dielectric. A denser layer tends to move the dip to larger angles due to the changed resonance angle for an Otto system, see Appendix F for the detailed explanation. For high efficiency cells textured by inverted pyramids, SiN_x (especially when n=2.2) is not an ideal candidate compared to SiO_2 . This is because the reflection is very low at angles around 40°, where most of the incoming light will be deflected.

The reflectivity of SiN_x curves only exceeds those from SiO_2 over the $22^{\circ}-26^{\circ}$ angular range. An increase in the SiN_x index further weakens its performance over these angles.

Hence for solar cells textured by random pyramids, unless a significant part of the deflected light falls into the $22^{\circ}-26^{\circ}$ angular region, SiO₂ is still considered to be optically superior to SiN_x.

In order to gain better understanding of the SPP phenomenon, the effect of dielectric refractive index and its thickness on the resonance angle, θ_r and reflectivity at SPP resonance, $R_b(\theta_r)$ is simulated.

4.4.2 Resonance angle θ_r

The wave-vector for SPP excitation is matched for the system shown in Fig. 4.1 when [1]:

$$\frac{\omega}{c}\sqrt{\varepsilon_0}\sin\Phi_r = \frac{\omega}{c}\sqrt{\frac{\varepsilon_1\varepsilon_2}{\varepsilon_1+\varepsilon_2}}$$
(4.1)

Here, " ω " is the radial frequency and "c" is the light velocity. ε_0 , ε_1 , and ε_2 are the relative permittivities of the three media Si, dielectric and metal respectively (see Fig. 4.1). The left side of Eqn.4.1 is the wave-vector k_0 for photons travelling in medium ε_0 , while the right side is the wave-vector for SPP excited at the dielectric/metal interface k_x . As ε_2 is a large real negative number and ε_1 is a smaller real positive number, k_x is largely imaginary. The imaginary component of k_x , k_{xi} , indicates the wave oscillation intensity decay along the dielectric/metal interface which enhances absorption in the metal [9].

The resonance angle θ_r corresponding to the SPP can then be derived from Eqn. 4.1. The equation shows that θ_r is related to the permittivity of each medium of the system. Therefore different dielectric materials or metal types can result in varying θ_r values.

The condition for TIR at the Si/dielectric interface is

$$\sin \theta_c = \frac{n_1}{n_0} \tag{4.2}$$
This explains $\theta_r \approx \theta_c$ observed in section 4.3.1.

SPP resonance calculation in Eqn. 4.1 can be rewritten as [1]:

$$\sin \theta_r = \sqrt{\frac{\varepsilon_1}{\varepsilon_0}} \sqrt{\frac{\varepsilon_2}{\varepsilon_1 + \varepsilon_2}}$$
(4.3)

Assuming the imaginary part of ε_0 and ε_1 can be neglected, the first part of the left of Eqn. 4.3 is simplified to be " n_1/n_0 ". When ε_1 is much smaller than ε_2 , the second part in Eqn. 4.3 will approach unity. Therefore the value of θ_r and θ_c can be quite close to each other when the permittivity difference between the dielectric and the metal is large enough.

Fig. 4.9 shows the resonance angle θ_r as a function of dielectric thickness for structure Si/dielectric/metal. The results show that θ_r is dependent on the material (dielectric and metal) permitivities. Note that θ_r is more sensitive to dielectric refractive index while it is slightly different if Ag is used instead of Al.

Note θ_r is very sensitive to the dielectric thickness for thicknesses less than 200 nm. θ_r becomes larger with decreasing dielectric thickness. This is because as the dielectric becomes thinner, the Si/dielectric becomes much more like a high index dielectric to the model and does not sense the interface. This thickness dependent effect is most apparent for low index dielectric (SiO₂) compared to high index dielectric (SiN_x, n=2.6), see Fig. 4.9.



Fig. 4.9: The resonance angle θ_r of rear structure Si/dielectric/metal as a function of the dielectric thickness. Curves with solid dots are for the structure with Al metal and curves with hollow dots are for the structure with Ag metal.

4.4.3 $R_b(\theta_r)$ under different dielectric thicknesses

Figs. 4.10a and 4.10b show $R_b(\theta_r)$ of the structure "Si/SiO₂/Al" and "Si/SiO₂/Ag" as a function of SiO₂ thickness respectively. The use of Ag results in less SPP related loss than the use of Al. However the use of Ag limits the thickness of SiO₂ for the $R_b(\theta_r)$ study to less than 2000 nm. This is because beyond this thickness, additional reflection fluctuations at small angles are resulted with reflection dips other than those caused by the SPP resonance [8]. Fig. 4.10 is very useful for the design of rear structure that involves the use of displaced metal by SiO₂ providing the range of SiO₂ thicknesses that minimises SPP related loss.



Fig. 4.10: Simulated reflection at the resonance $R_b(\theta_r)$ of rear structure (a) Si/SiO₂/Al and (b) Si/SiO₂/Ag as a function of the dielectric thickness, under non-polarised and *p*-polarised light illumination.

Fig. 4.11 shows R_b (θ_r) of structure "Si/SiN_x/metal" under various dielectric indices. The results provide a good reference for suitable SiN_x thicknesses that result in minimum SPP losses for each of these refractive indices (n=2.0; 2.2; 2.4; 2.6). Again the use of Ag limits thickness of the SiN_x. Interestingly, the use of SiN_x (n=2.0) results in the lowest SPP losses for the Si/SiN_x/Ag scheme. The observed curve tendencies can be explained by the Fresnel equations and Snell's law as given in Appendix F.



Fig. 4.11: Simulated reflection at resonance $R_b(\theta_r)$ as a function of the dielectric thickness and refractive index of structure (a) Si/SiN_x/Al and (b) Si/SiN_x/Ag. Curves with solid dots are for structures under non-polarised light illumination and curves with hollow dots are for structures under *p*-polarised light illumination.

4.4.4 Weighted rear reflectivity *R*_{wb}

While it is useful to understand the SPP losses associated with displaced metal reflectors for high efficiency cells, the most effective way of quantifying and comparing the optical performances of the various types of displaced metal reflectors is the calculation of the weighted rear reflectivity " R_{wb} " [10, 11] under the hypothesis that a front surface texture exists so the deflected light towards back reflector follows a Lambertian distribution (an isotropic luminance). This has a practical significance to optically optimise the rear design of silicon solar cells, especially when they were randomly textured. R_{wb} can be expressed as:

$$R_{wb} = \frac{-\int_{0}^{\pi/2} R_{b}(\theta_{i}) \exp(-\alpha w/\cos\theta_{i}) \cos\theta_{i} \sin\theta_{i} d\theta_{i}}{\int_{0}^{\pi/2} \exp(-\alpha w/\cos\theta_{i}) \cos\theta_{i} \sin\theta_{i} d\theta_{i}}$$
(4.4)

where "w" is the wafer thickness, " θ_i " is the incident angle on the rear side, and " α " refers to the absorption coefficient of Si for light at a particular wavelength. The light wavelength used in the simulation study is also 1310 nm and the absorption coefficient " α " is set to zero at 1310 nm and other absorption processes such as free carrier absorption and lattice absorption are considered negligible [6]. The integration is taken from 0° to 60° instead of 0° to 90° because light is rarely deflected into the extra-large angular region for the reflectors studied in this work.

Fig. 4.12 shows the calculated R_{wb} for rear reflectors Si/SiO₂/Al, Si/SiN_x/Al, Si/SiO₂/Ag and Si/SiN_x/Ag with varying dielectric thicknesses (from 0 nm to 2000 nm) and varying refractive index of SiN_x from 2.0 to 2.6. Fig. 4.13 shows the absolute R_{wb} increase by replacing Al with Ag.



Fig. 4.12: Calculated weighted reflectivity R_{wb} of scheme (a) Si/SiO₂/Al and Si/SiN_x/Al (b) Si/SiO₂/Ag and Si/SiN_x/Ag with varying refractive index of SiN_x from 2.0 to 2.6, as a function of dielectric thickness.



Fig. 4.13: Absolute R_{wb} increase calculated from $R_{wb Ag}$ - $R_{wb Al}$.

As seen from Fig. 4.12, a low refractive index dielectric results in higher R_{wb} over the entire thickness range because of the different Fresnel coefficients at the Si/dielectric

interface (r_I), and the different phase/attenuation factor (δ_I). Both of these affect the reflection amplitude for a single film system, see Appendix F [7].

 R_{wb} increases with dielectric thickness, especially at the first 1 µm. This trend is more apparent for the high index dielectric. For example, R_{wb} increases by nearly 4% for SiN_x (n=2.6) from thickness 280 nm (first wave trough) to 2000 nm but only by less than 1% for SiO₂ from thickness 500 nm (first wave trough) to 2000 nm. This indicates if a high index dielectric is used to displace metal reflector on the rear of solar cells, it is beneficial to keep its thickness reasonably thick, i.e., 1 µm or greater.

When a high index dielectric is used as the rear surface passivation film, Fig. 4.13 suggests that Ag is a much better mirror compared to Al.

When designing dielectric thicknesses for the displaced metal reflectors, two observations are worth noting. Firstly, fluctuations in R_{wb} as a function of dielectric thickness are higher for higher index film. Secondly, R_{wb} drops dramatically for very thin dielectrics. Fig. 4.12 serves as a reference for appropriate dielectric thickness for displaced metal reflectors so to capture R_{wb} 's maxima. If SiO₂ is used, one may choose a thickness close to 320 nm where a maximum in R_{wb} occurs or use thicker oxide, where R_{wb} fluctuations are smaller and less sensitive to thickness variations, depending on surface passivation quality provided by such film and compatibility in the entire solar cell processing sequence. If SiN_x is used, dielectric thickness corresponding to either of the first two R_{wb} maxima at ¹/₄ or ³/₄ λ can be considered.

4.5 Conclusion

In this chapter, a detailed study of angular dependence of the reflection from various planar rear reflectors is carried out both experimentally and through simulation. The novel optical setup allows for accurate, high resolution angular reflection measurements over -65° to $+65^{\circ}$. The use of hemispherical silicon as a test substrate has been successfully implemented enabling the analysis of the angular reflection properties of the back surface reflector over all incident angles without the restriction caused by

refraction at the Si-air interface. Four key findings emanate from this study of the displaced metal reflectors for silicon solar cells. Firstly, Ag yields higher reflection than Al metal over an angular range of $18^{\circ}-28^{\circ}$, where the excitation of surface plasmon polaritons at the Al interface causes strong light absorption losses. Secondly, the reflectivity of the reflector using SiN_x only exceeds those using SiO₂ over the $22^{\circ}-26^{\circ}$ angular range. An increase in the SiN_x index further weakens its performance over these angles. Hence for solar cells textured by random pyramids, unless a significant part of the deflected light falls into the $22^{\circ}-26^{\circ}$ angular region, SiO₂ is considered to be optically superior to SiN_x. Thirdly, if SiO₂ is to be used for displaced metal reflectors, thickness should not be less than 200 nm. Simulation shows a thickness close to 320 nm yields maximum weighted reflectivity (R_{wb}). Fourthly, if SiN_x is used, dielectric thickness corresponding to either of the first two R_{wb} maxima at ¹/₄ or ³/₄ λ can be considered.

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Chapter 5. Rear side study of planar reflectors on PERT cells

In the previous chapter, the angularly dependent rear reflection from various planar reflectors of solar cell was examined both experimentally and via simulation. The results demonstrate a clear reflection reduction at incident angles near the critical angle of the silicon-dielectric interface. Light losses in this angular region need to be prevented for enhanced optical response. This chapter describes studies of the effect of rear passivation layer thickness on both optical and electrical properties of present high efficiency cells rear. Also the design of novel planar rear reflectors formed by a three layer dielectric stacks and a metal mirror to minimize the absorption losses observed in the previous chapter are presented. Finally the corresponding optical and electrical effects on the solar cell rear by using the newly designed planar reflectors are assessed.

5.1 Reflection theory for a three-layer reflecting system

5.1.1 A three-layer reflecting system

The reflection consisting of two reflected beams with different phases for a three layer system is shown in Fig. 5.1, if the multi-reflection phenomenon is considered negligible. Layer 0 is the initial light travelling medium, layer 1 is the thin solid film, and layer 2 is the substrate. The rear of solar cell just resembles this type of system: layer 0 is the bulk silicon, layer 1 is the dielectric film, and layer 2 is the metal. The reflection of the system can be calculated by using the two methods developed by O.S. Heavens [1]: One method is the approximate method for transparent layers on transparent substrates, and the other is the general graphical method for all kinds of systems with no approximation.



Fig. 5.1: Schematic drawing of beam reflection from a three layer reflecting system. This neglects the multi-reflection phenomenon.

The Fresnel reflection coefficients of the two interfaces r_1 and r_2 can be written as:

$$r_{1} = \frac{(n_{0} - ik_{0})\cos\varphi_{0} - (n_{1} - ik_{1})\cos\varphi_{1}}{(n_{0} - ik_{0})\cos\varphi_{0} + (n_{1} - ik_{1})\cos\varphi_{1}} = -\sigma_{1}e^{-i\beta_{1}}$$
(5.1)

$$r_{2} = \frac{(n_{1} - ik_{1})\cos\varphi_{1} - (n_{2} - ik_{2})\cos\varphi_{2}}{(n_{1} - ik_{1})\cos\varphi_{1} + (n_{2} - ik_{2})\cos\varphi_{2}} = \sigma_{2}e^{-i\beta_{2}}$$
(5.2)

where *n* and *k* are the real and imaginary parts of the refractive index of the medium respectively. The angles φ_0 , φ_1 and φ_2 are those of the incident light inside each medium. The parameters σ_1 , σ_2 , β_1 , β_2 are the loci constants for the two reflection coefficients, with σ being the real amplitude and β being the phase change at the surface. The phase difference of the two beams from layer 0 / layer 1 and layer 1 / layer 2 interfaces is then expressed as the sum of phase difference due to the light wave traversing the layer σ_1 , σ_2 : $\sigma_{(1,2)}$ and the phase difference obtained from the reflection at the boundary β_1 , β_2 : $\beta_{(1,2)}$:

$$\sigma_{(1,2)} + \beta_{(1,2)} = 2\delta_1 + \beta_{(1,2)}$$
(5.3)

With δ_1 defined as the phase change of the beam propagating in layer 1:

$$\delta_1 = \frac{2\pi}{\lambda} n_1 d_1 \cos \varphi_1 \tag{5.4}$$

Here, λ is the wavelength of the incoming light in vacuum, d_1 is the thickness of layer 1. Note $\beta_{(1,2)}$ is the phase angle difference of the two interfaces determined by the material constants of the two mediums.

For a rear interface involving a dielectric in contact with a metal in a solar cell under perpendicular illumination, r_2 can be rewritten as Eqn. 5.5 ignoring the imaginary part of the dielectric index.

$$r_2 = \frac{(n_1 - n_2) + ik_2}{(n_1 + n_2) - ik_2} \tag{5.5}$$

The corresponding reflectance at the interface is then given by:

$$R_{2} = \frac{(n_{1} - n_{2})^{2} + k_{2}^{2}}{(n_{1} + n_{2})^{2} + k_{2}^{2}}$$
(5.6)

The light losses at the interface can ultimately be written as [2]:

$$1 - R_2 = \frac{4n_1n_2}{k_2^2} / \left(1 + \left((n_1 + n_2)/k_2\right)^2\right) \approx \frac{4n_1n_2}{k_2^2}$$
(5.7)

From Eqn. 5.7, light losses can be reduced by having n_1 (index of the dielectric) small. This indicates the advantage of using SiO₂ as the rear dielectric, which has a smaller n compared to other passivating dielectrics, such as SiN_x. This agrees well with the results shown in Fig. 4.12, Chapter 4 where the scheme with SiO₂ has the highest R_{wb} . Eqn. 5.7 also shows that a smaller n_2 (metal) can lead to reduced light losses. Therefore noble metals such as Cu and Ag with n much smaller than the unity can be chosen for this purpose. The theoretical calculation is only taken for the Si/SiO₂/Al rear scheme in this section.

5.1.2 Approximate method

The approximate method is valid for systems with transparent films on transparent substrates. In this case the multi-reflection phenomenon can be neglected due to the small Fresnel coefficients of the films. The total reflectance (R) equals to:

$$R = \frac{r_1^2 + 2r_1r_2\cos(2\delta_1) + r_2^2}{1 + 2r_1r_2\cos(2\delta_1) + r_1^2r_2^2}$$
(5.8)

Eqn. 5.8 is only accurate when both r_1 and r_2 are $\ll 1$ (e.g., system of solar cell front air/SiO₂/Si). Under this condition $\beta_{(1,2)}$ in Eqn. 5.3 approaches to zero and the phase change (*pc*) for quarter wavelength thick film under normal incident light can be expressed as:

$$\sigma_{(1,2)} = \frac{4\pi}{\lambda} n_1 d_1 \cos \varphi_1 = \frac{4\pi}{\lambda} n_1 \frac{\lambda}{4n_1} = \pi$$
(5.9)

As can be seen, the two beams have the opposite phase which can result in the minimum reflection (destructive interference). This is the reason why a $\frac{1}{4} \lambda$ thick dielectric is normally chosen as the antireflection coating for solar cells. However, for rear reflecting system Si/SiO₂/Al, the phase angle difference $\beta_{(1,2)}$ in Eqn. 5.3 can not be neglected because the Al metal is not a transparent substrate and has a large k value. In fact for the Si/SiO₂/Al system, the total phase change is around 2π (constructive interference) because $\beta_{(1,2)}$ is close to π for this layer stack. This is why an approximately $\frac{1}{4} \lambda$ thick dielectric is used as rear passivation film for dielectrically displaced reflectors. In the next section, a general method is introduced to calculate the reflection of rear schemes with both transparent and absorbing films.

5.1.3 General graphical method

The phase change of the two beams can be calculated by Eqn. 5.10:

$$\sigma_{(1,2)} + \beta_{(1,2)} = \angle NED - \beta_1 \tag{5.10}$$

The position of points *N*, *D*, and *E* located in the Argand diagram is calculated by Eqns. 5.11 & 5.12 & 5.13:

$$N = \frac{r_1}{r_2} \tag{5.11}$$

$$D = \frac{1}{r_1 r_2}$$
(5.12)

$$E = -\exp(-2i\delta_{1})$$

$$= -\exp(-2i\frac{2\pi}{\lambda}(n_{1} - ik_{1})d_{1}\cos\varphi_{1})$$

$$= -\exp(-\frac{4\pi}{\lambda}k_{1}d_{1}\cos\varphi_{1})\exp(-i\frac{4\pi}{\lambda}n_{1}d_{1}\cos\varphi_{1})$$
(5.13)

As can be seen, point N and D are only related to the Fresnel reflection coefficients of the two interfaces (r_1 and r_2), whereas point E also depends on the film thickness. By plotting these values on an Argand diagram, angle $\angle NED$ could be easily found as shown in Fig. 5.2. The pink square is point D, the blue square is point N. The circle formed by yellow triangles corresponds to point E with different SiO₂ thicknesses. If β_1 has a very small value it can be ignored and the phase change can be observed by angle $\angle NED$ in the diagram: $pc=0^{\circ}$ (constructive interference) for 190 nm SiO₂, and $pc=180^{\circ}$ (destructive interference) for 400 nm SiO₂. This is in good agreement with the conclusion made in section 5.1.2.



Fig. 5.2: An Argand diagram for rear scheme $Si/SiO_2/Al$. Different SiO_2 thicknesses result in the yellow circles corresponding to the *E* points.

The total reflectance of the system can be calculated by:

$$R = \frac{P^2}{\sigma_1^2} \tag{5.14}$$

with *P* given by:

$$P = \frac{EN}{ED}$$
(5.15)

5.1.4 Analytically calculated and simulated R of Si/SiO₂/Al

The magnitude of the reflection, R, for the rear scheme of an Si/SiO₂/Al layer stack is calculated analytically by the two methods presented in the section above and simulated using the W-VASE software package for normally incident light. The results are given in Fig. 5.3. The secondary *y*-axis indicates the corresponding phase change (*pc*) of the two reflected beams from the two interfaces. As clearly shown, *R* depends on the SiO₂ thickness periodically, with R_{max} (constructive interference) located at around 200 nm SiO₂ and R_{min} (destructive interference) located at 400 nm SiO₂ in the first period. The calculated results here greatly match the measured results in Fig. 4.6, Chapter 4. The position of R_{max} corresponds to pc_{min} (about 0°) while the position of R_{min} corresponds to pc_{max} (about 180°). The good matching of R curves from general method and W-VASE simulation verifies the accuracy of the general method for R calculation, see section 5.1.3. The approximate method results in much lower R because of the estimation made from transparent substrate.



Fig. 5.3: Calculated (by general method and approximate method) and simulated (by W-VASE) R of rear scheme Si/SiO₂/Al under normal incident light. The phase change of the two beams is shown by the pink curve with hollow circles.

5.2 Effect of rear SiO₂ thickness

The reflection theory given in the last section reviews how the rear internal reflectance is affected by the SiO_2 thickness in the rear scheme $Si/SiO_2/Al$. In this section, the effect of SiO_2 thickness on the cells optical response and electrical quality are experimentally investigated.

5.2.1 Sample description

Seven front-planar PERT cells were fabricated on the 1.5 Ω 400 µm thick *p*-type FZ Si wafers. Rear thermally-grown SiO₂ films with an initial thickness of 134 nm were thinned to be 8 nm – 134 nm respectively. Al grids with surface coverage less than 15% were evaporated to the back of the cell as rear electrodes which are necessary for preliminary electrical measurements. After initial characterisation, 1.3 µm thick Al layers were evaporated onto the rear of the cell to act as reflecting mirrors, see Fig. 5.4. Both optical and electrical measurements were carried out subsequently. The details of the characterisation methods can be found in section 6.2.2, Chapter 6.



Fig. 5.4: Schematic drawing of the fabricated PERT cell rear with a conventional reflector. SiO_2 layer thicknesses are varied from 8 to 134 nm.

5.2.1 Results and discussion

The measured EQE enhancement, defined as the ratio of the EQE measured with rear reflectors to the EQE without rear reflectors, by planar reflectors under different passivation layer thicknesses is shown in Fig. 5.5, over a wavelength range of 900 nm to 1200 nm. Fig. 5.5 indicates that a thicker passivating layer results in a greater EQE enhancement. The enhancement brought about by the optical effect of the rear reflector starts at around 1000 nm, becomes maximal at about 1120 nm, and diminishes back to the baseline at 1200 nm. The fluctuations between 900 nm – 1000 nm are the effects from rear electrical properties (or surface passivation) by the deposited rear reflectors.



Fig. 5.5: Measured *EQE* enhancement for solar cells with conventional rear scheme $Si/SiO_2/Al$ at different SiO₂ thicknesses compared to cells with only the rear grid.

For the cell with 8 nm SiO₂ film, *EQE* is increased over the wavelength range of 1030 nm – 1200 nm (positive optical response), and is decreased over 950 nm – 1030 nm (negative electrical response). The clearly degraded electrical response can be attributed to the very thin SiO₂ film which contains only a small amount of hydrogen that is needed for passivating dangling bonds at the Si/SiO₂ interface [3]. The enlarged Si/Al contacting areas through pinholes in the extremely thin SiO₂ layer may further degrade the electrical quality as the surface recombination velocity is significantly higher in the areas. This is an artefact from the etching back process. The overall impact, both optical and electrical, of the SiO₂ thickness on the solar cell performance can be indicated by the current enhancement, see Fig. 5.8. *EQE* enhancements for SiO₂ > 8 nm are all above the baseline (black solid curve) over the entire interested wavelength range, indicating improved short circuit currents for all.

Optical absorption of cells with different rear SiO_2 thicknesses in Fig. 5.6 indicates that thinner SiO_2 leads to slightly higher absorption. However, this measured absorption contains parasitic metal absorption which is related to the dielectric layer thicknesses as characterized in Chapter 4. Therefore the measured absorption can not be used to indicate and explain the different optical properties. An optical factor that only represents base region absorption (effective absorption) is needed for quantifying rear optical properties of solar cells.



Fig. 5.6: Measured optical absorption for solar cells with conventional rear scheme $Si/SiO_2/Al$ at different SiO₂ thicknesses.

Basore's approach [4] is adopted to distinguish rear optical and electrical properties by analysing measured internal quantum efficiency (IQE), refer to Chapter 6, section 6.3.3 for the detailed analytical methods. The optical properties are quantified by an effective

optical path length Z and the electrical properties are quantified by a minority carrier diffusion length L. Fig. 5.7 shows the calculated Z and L for cells with rear scheme $Si/SiO_2/Al$ at different SiO₂ thicknesses.

The optical factor Z is increased by 23% by increasing SiO₂ thickness from 8 nm to 134 nm. This trend is consistent with the trend in the *EQE* enhancement in Fig. 5.5, but is reverse to the trend of the measured optical absorption in Fig. 5.6. Solar cells with a thick passivating film tend to have reduced rear parasitic metal absorption and hence a better optical response. The interference effect from different SiO₂ thicknesses discussed in section 5.1 can also enlarge this optical performing difference. Note the *Z* trend agrees well with the calculated *R* trend in Fig. 5.3 for the SiO₂ thicknesses studied.

The minority carrier diffusion length L increases along with the SiO₂ thickness by and large due to the different surface passivation provided as a function of dielectric thickness, as discussed above.



Fig. 5.7: Calculated effective optical path length Z and base region minority carrier diffusion length L of the high efficiency PERT cells with planar rear reflector $Si/SiO_2/Al$ under various rear passivation layer thicknesses.

The calculated current enhancement by applying a planar rear reflector as a Si/SiO₂/Al layer stack with different SiO₂ thicknesses is shown in Fig. 5.8. Current is calculated from the EQE measurements at short-circuit and the AM1.5G spectrum. Thicker SiO₂ has higher current enhancement due to both improved optical and electrical responses. The short circuit current is actually reduced for a reflector with 8 nm of SiO₂ because of its strongly degraded electrical quality.



Fig. 5.8: Current enhancement of solar cells with the $Si/SiO_2/Al$ rear structure at different SiO_2 passivation layer thicknesses.

5.3 A novel planar reflector design

To further enhance the rear optical properties of c-Si cells, designed planar rear structures consisting of high-low refractive index dielectric stacks (*DS*) and a back metal layer (e.g., $SiO_2 / SiN_x / SiO_2 / back metal)$, with precisely control of the thickness and refractive index of each dielectric have been fabricated. The angular dependence of reflections from these new structures is also explored. Apart from their optical merit, some of the *DS* have the potential of providing high quality and stable surface passivation as suggested in previous researches [5-7]. Therefore the new *DS* designs have been developed with attention paid to both optical and electronic properties.

5.3.1 Sample fabrication

Four newly designed planar reflectors with *DSs* were fabricated on the rear of 400 μ m thick *p*-type FZ Si wafers, as shown in Fig. 5.9. The first dielectric layer adjacent to the bulk silicon is a high quality thermal oxide grown in oxygen gas with 2% trichloroethane (TCA) at 1050 ° C. Subsequent layers were prepared by plasma-enhanced chemical vapour deposition (PECVD) at different conditions. The SiN_x layers were deposited at 400°C or 200°C, with the Si-content in the films controlled by the SiH₄/NH₃ gas ratio during deposition. In contrast, the third PECVD SiO₂ layers were

deposited at 400°C with a fixed SiH₄/N₂O gas ratio. The dielectric layer thickness was precisely controlled by the deposition duration. Here the thermal grown oxide instead of PECVD deposited oxide was used as the first dielectric to ensure excellent rear surface passivation [8]. It is important to at least maintain the rear electronic quality while addressing optical improvements in the cell. The details of the recipes used for PECVD SiN_x and SiO₂ depositions are attached in Appendix G.

400	um	FΖ	Si
-----	----	----	----

Thermal SiO ₂	
PECVD SIN _x	
PECVD SIO ₂	
Metal	

Fig. 5.9: Fabricated sample structure for rear optical property improvement. Triple dielectric stacks are deposited on the FZ silicon substrate.

The four reflectors with *DS* have the structure "Si / 210 nm SiO₂ / SiN_x / 200 nm SiO₂ / Metal", with the *n* of the SiN_x film increasing gradually from 2.0 to 3.2. An optimized ¹/₄ λ optical thickness (λ =1200 nm) for each dielectric layer is used to achieve maximum *R* under normally incident light. The choice of ¹/₄ λ optical thickness for each layer of the triple *DS* is determined from W-VASE simulation results. A reference structure consisting of a "Si / 210nm SiO₂ / Al" layer stack applied in current high efficiency solar cells is used to evaluate the performance enhancement of the newly designed reflectors.

Table 5.1 shows the thickness and the refractive index of the middle dielectric layer, characterised by W-VASE software through analysing the measured reflectance and transmittance data of single SiN_x films deposited on glass slices [9]. Thickness and index of SiN_x deposited on silicon is difficult to be directly characterised by ellipsometry due to its high refractive index which is quite close to that of silicon. The thickness and refractive index of the SiO_2 film deposited on the silicon wafers were directly measured by ellipsometry. Once the deposition conditions (e.g. gas ratio, time, temperature) of each individual film have been obtained separately according to the

measured/analysed data, the *DS* were then fabricated on the silicon wafer to form the novel planar reflectors.

Table 5.1: Measured/simulated thicknesses and refractive indices of the middle dielectric layers of the fabricated rear reflectors. The 210 nm SiO_2 is the middle dielectric layer for the reference as only one film is available.

Rear reflector	Refractive index (<i>n</i>)	Thickness
Reference	1.5	210 nm
DS1	2.0	150 nm
DS2	2.6	115 nm
DS3	3.0	100 nm
DS4	3.2	94 nm

The fabricated reflectors are measured optically using a PerkinElmer spectrophotometer, and electronically by a Photoconductive Decay (PCD) method to obtain the minority charge carrier lifetime. *IQE* is determined by the ratio of photon absorption in the Si bulk region and the total photon absorption in the cell.

5.3.2 Resulting optical reflectance

According to simulation, the index of refraction, n, of films contacting Si and back metal has to be small, while the n of the middle dielectric film has to be large in order to achieve maximum R. The large index step at material interfaces can result in higher R, as shown in section 5.1. Besides the often mentioned electrical advantage, this is another reason why SiO₂ with a small index is chosen as the first and third dielectric of the *DS* system.

Fig. 5.10 shows the experimentally measured total $R(R_t)$ for the fabricated structures at long wavelength light. The data plotted in Fig. 5.10 is an average R_t taken from measurements made between 1200 nm and 1300 nm on the structures. As can be seen, R_t is improved incrementally by increasing n of the middle dielectric. Replacing the conventional Al layer by a noble Ag metal layer yields a higher R_t due to the superior optical properties of Ag. This agrees well with the measured internal reflection results in Fig. 4.5, Chapter 4. The R_t of the sample with Al metal after forming gas annealing increases slightly because of the densification of the film and the reduction of interface defects after the heat treatment.



Fig. 5.10: Measured R_t , the value of which is an average taken from measurement data between 1200 nm – 1300 nm wavelength, for samples with rear schemes of *DSs* and metal film fabricated on Si substrates. The *n* of the middle dielectric is varied from 1.5 to 3.2. The three curves correspond to the different metal films used.

5.3.3 Resulting internal quantum efficiency

5.3.3.1 IQE from PC1D simulation

PC1D was used to estimate how much *IQE* gain can be obtained by increasing the rear internal reflectance (R_b). Solar cell parameters were kept the same during modelling, except for R_b , as shown in Table 5.2. The *IQE* is improved most over wavelengths between 1000 nm – 1200 nm when R_b reaches very high values, from 90% to 100% as shown in Fig. 5.11. This indicates the importance of the further rear internal reflectance enhancement.

Device area	10 cm^2	Bulk recombination	900 µs
Front external reflection	2%	Front recombination	10 cm/s
Front internal reflection	91%	Rear recombination	50 cm/s
Rear internal reflection (R_b)	90% - 100%	Excitation mode	Transient
Emitter contact internal series	1E-6 ohms	Base circuit	-0.8 - 0.8V
Base contact internal series	1E-6 ohms	Light intensity	0.1 W cm^{-2}
Cell thickness	400 µm	Spectrum	AM 1.5
P-type background doping	1E16 cm ⁻³	Surface texturing	No
1 st front diff: N type	5E19 cm ⁻³	Internal shunt elements	No

Table 5.2: Solar cell parameters used in PC1D for IQE calculation



Fig. 5.11: PC1D simulated internal quantum efficiency (*IQE*) as a function of rear internal reflectance R_b . Solar cell parameters are given in Table 5.2.

5.3.3.2 IQE from estimated calculation

Assuming all photon-generated carriers are collected by the solar cell, which is roughly the case in a PERT cell, the *IQE* can be defined as shown in Eqn. 5.16.

$$IQE = \frac{A_s}{A_T} = 1 - \frac{(1 - R_b)T^+}{1 - R_b T^+ T^-}$$
(5.16)

$$T^{+}T^{-} \approx e^{-2\alpha w/\cos\theta_{i}} \tag{5.17}$$

Here, A_S is the absorption in the bulk silicon region of the cell, and A_T refers to the total absorption of solar cell, ignoring front surface, $A_T=A_S+A_B$, with A_B defined as back reflector absorption. The *IQE* equals to the ratio of A_S and A_T as indicated in Eqn. 5.16. Formulae for A_S and A_T are given in [10].

 R_b is the rear internal reflectance from the solar cell reflector. T^+ is the fraction of light transmitted to rear surface and T^- is the fraction of light reflected from the rear side to the front surface. An approximation of T^+T^- is used to simplify the calculation as shown in Eqn.5.17 [10]. Note the coefficient on "*aw*" in Eqn. 5.17 depends on the incident light angle towards rear reflector. For a solar cell with a planar front surface, $\theta_i = 0^\circ$, α =-2; for a solar cell with ideal inverted pyramids, $\theta_i = 42^\circ$, α =-2.8; for solar cell with a random textured front surface resulting in a Lambertian light distribution within silicon, α can be taken as -4, since the effective light path angle θ_i can be regarded as 60° approximately [4].

The simulated R_b and calculated *IQE* for solar cells with the fabricated rear structures (see Table 5.2) under perpendicular incident light at near/sub bandgap wavelength are shown in Fig. 5.12. An obvious improvement of both R_b and *IQE* by increasing the middle layer refractive index is indicated, which is consistent with the measured optical results in Fig. 5.10. The calculated *IQE* is a little higher than that in reality at 1190 nm - 1250 nm because other absorption processes not producing electron hole pairs (e.g., free carrier absorption, lattice absorption) are not involved in the calculation [11].



Fig. 5.12: R_b and IQE for solar cells with the fabricated rear reflectors under perpendicular incident light over wavelength range of 900 nm – 1250 nm. Indices of the middle dielectric vary from 1.5 to 3.2.

5.3.3.3 Improved DS design

The weighted rear internal reflectance (R_{wb}) under Lambertian light distribution is calculated by Eqn. 4.4. The enhancement of R_{wb} by the fabricated triple *DS* reflector is much smaller compared to the enhancement under perpendicular incident light. The resulted *IQE* is very marginally improved as well. Table 5.3 lists the calculated short circuit current over 900 – 1200 nm for solar cells with the fabricated rear reflectors under three different incoming light distributions within the silicon layer. As indicated, the enhancement from the fabricated *DS* is most obvious under normal incident light, with a maximum enhancement of 7.3%. However, as just mentioned, the enhancement from *DS* reflector for incident light at 42° and following a Lambertian distribution is less obvious due to the changed angles for the light. For incident light at 42°, R_b approaches unity so the current is maximal between the three light distributions in the case. Table 5.3: Calculated short circuit current over 900 nm - 1200 nm for solar cells using the fabricated rear reflectors, for three different light distributions within silicon. Values in brackets indicate the corresponding current enhancement over the reference structure (n=1.5).

	n=1.5	n=2.0	n=2.6	n=3.0	n=3.2
0°	11.35	11.70 (3.0%)	11.97 (5.4%)	12.14 (6.9%)	12.19 (7.3%)
42°	12.77	13.13 (2.8%)	13.12 (2.8%)	13.11 (2.6%)	13.10 (2.6%)
Lambertian	11.93	11.92 (-0.03%)	11.95 (0.15%)	11.97 (0.35%)	11.98 (0.39%)

A new triple *DS* "100nm SiO₂ / 100nm a-Si / 250nm SiO₂" is designed to improve the rear optical response of a solar cell for light with a broad angular distribution. In order to analyse the angularly distributed R_b with the light absorbed by the first pass through the silicon layer excluded, the back metal absorption after the first light pass, A_b , is expressed as:

$$A_{b} = (1 - R_{b}(\theta_{i}))e^{-\alpha w/\cos\theta_{i}}$$
(5.18)

As shown in Fig. 5.13a, rear absorptions of the newly designed structures at small incident angles ($<20^{\circ}$) are nearly halved compared to that of the conventional reflectors, and the peak absorption near the critical angle is also lowered. Both indicate the improved angular response of the newly designed structure. For incident light at more oblique angles ($>35^{\circ}$), there is hardly any absorption for all of the reflectors studied. In practice, it would be most important to reduce absorption for light at small and near critical angles as these are the angle regions into which a large portion of the front-deflected light will fall.

Different metal mirrors can also make clear differences in A_b , see Fig. 5.13b,c. Noble metals such as Ag and Cu substantially improve the optical properties of the back reflector over a broad angular range (0°–35°) compared to the conventional Al, which agrees well with the conclusion from Eqn. 5.7. Fig. 5.13b,c also indicate that reflectance becomes less sensitive to the angle of incidence when noble metals such as Ag and Cu are used.



Fig. 5.13: (a) Comparison of light absorption by conventional and newly designed reflectors at 1120 nm after first light path inside Si. (b) Effect of different metal types on the light absorption by conventional rear reflectors. (c) Effect of different metal types on the light absorption by newly designed reflectors.

Fig. 5.14 shows the calculated *IQE* enhancement from the fabricated (bottom pink curve) and newly designed (top blue curve) rear reflectors for light with a Lambertian distribution, both over the reference reflector. The newly designed reflector brings about an enhancement of about 25% at 1200 nm, much higher than that from the fabricated reflector with $\frac{1}{4} \lambda$ thickness of each dielectric. A corresponding J_{sc} absolute improvement of 0.56 mA / cm² is achieved over the reference reflector.



Fig. 5.14: Calculated *IQE* enhancement of the *DS*/Al rear reflector (with different dielectric layer thicknesses) over the SiO_2/Al reference reflector under Lambertian distributed light incidence. The top dark blue curve is the enhancement by the newly designed reflector. The bottom pink curve is the enhancement by a fabricated reflector listed in Table 5.1.

5.3.4 Resulting minority carrier lifetime

The surface passivation technique involving an "Al-anneal" process is used for solar cells with conventional Si/SiO₂/Al rear scheme. The "Al-anneal" step is critical for good surface passivation. It is achieved by thermally evaporating aluminium to overcoat the SiO₂ passivating layer, followed by a 400°C sinter in forming gas for 30 mins. The heat treatment together with Al effectively causes residual water molecules (H₂O) contained in SiO₂ layer to release a large amount of atomic hydrogen to passivate silicon dangling bonds at the Si/SiO₂ interface. This is the well known hydrogen passivation effect. The work function difference in the Si-Al system also improves passivation since its appearance is similar to the effect brought on by additional positive oxide charges at that interface. This can result in a surface recombination velocity (SRV) below 11.8 cm/s (usually 20-50 cm/s) for low resistivity *p*-type FZ wafers [8].

Another widely used passivation layer is PECVD SiN_x , which contains a large amount of atomic hydrogen to passivate dangling bonds at the Si/SiN_x interface. However, this PECVD SiN_x layer is not usually applied to the rear side of high efficiency solar cells (e.g., PERL, PERT cell) because of the inversion layer effect on rear side of the *p*-type wafer. Therefore, one appropriate way to utilize the benefit of an SiN_x film is to insert an SiO_2 layer in between the Si and the SiN_x [12]. The thermal grown SiO_2 provides high quality Si/SiO_2 interfaces, while a large reservoir of hydrogen in the SiN_x layer provides hydrogen passivation after annealing in the case where the SiO_2 is permeable to the hydrogen [3]. Therefore, the newly designed triple *DS* "SiO₂/SiN_x/SiO₂" is well suited to take advantage of this potentially good surface passivation.

5.3.4.1 Sample structure

The sample structures used for the lifetime study are shown in Fig. 5.15. The wafer's front sides are all Al-annealed to ensure a good front side passivation so the difference of electrical quality only comes from the rear side which is passivated by the *DSs*. The structures of the *DSs* are the same as those listed in Table 5.1. Sample preparation and lifetime measurement processes are briefly listed in Table 5.4.

Thermal SiO ₂ (Al-annealed)	Thermal SiO ₂ (Al-annealed)
P-type FZ Si wafer	P-type FZ Si wafer
Thermal SiO ₂ (Al-annealed)	Thermal SiO ₂ (heat treatment)
PECVD SiN _x (heat treatment)	PECVD SiN _x (heat treatment)
PECVD SiO ₂ (heat treatment)	PECVD SiO ₂ (heat treatment)
(a)	(b)

Fig. 5.15: Fabricated sample structures for the study of rear surface passivation by the three-layer DSs. (a) First SiO₂ layer of rear DS is subjected to the Al-anneal step. (b) First SiO₂ layer of rear DS experiences heat treatment only. The front sides of both structures have been Al-annealed.

Step	Processing		
1	Thermally grow SiO ₂ onto both sides of <i>p</i> -type FZ silicon wafers		
2	Evaporate Al to either both sides or one side of the wafers		
3	Forming gas annealing at 390°C for 30 mins		
4	Remove Al metal from wafers, to prepare for subsequent lifetime measurements and PECVD dielectric depositions		
5	Lifetime measurement by PCD		
6	PECVD SiN _x deposition, with refractive index n changing from 2.0 to 3.0		
7	Heat treatment - forming gas annealing at 390°C, in various durations		
8	Lifetime measurement by PCD		
9	PECVD SiO ₂ deposition		
10	Heat treatment - forming gas annealing at 390°C, in various durations		
11	Lifetime measurement by PCD		

Table 5.4: Processing sequences for sample structures used for lifetime study.

In step 3, the side of the wafer with Al resembles the conventional rear passivation procedure for the $Si/SiO_2/Al$ system. The front side of each wafer experiences this Al-annealing process. Samples are sorted into two types: "both sides Al-annealed" as in Fig. 5.15a and "one side Al-annealed" as in Fig. 5.15b, according to the presence of Al during the heat treatment.

5.3.4.2 Measured lifetime

The measured lifetimes of the four selected samples after each processing step are shown in Fig. 5.16. As can be seen, the lifetime of all samples is reduced after PECVD SiN_x deposition, very possibly owing to the breaking of as-formed Si-H bonds on the Si/SiO₂ interface from previous thermal oxidation. The following heat treatment increases the lifetime for all samples because the hydrogen is transported from SiN_x film to the Si/SiO₂ interface. The lifetime values can reach or even exceed the original, depending on the hydrogen content in the deposited SiN_x film. Surface passivation tends to be stable after a heat treatment of 10–15 mins. Further heat treatment can very possibly degrade surface passivation, as new silicon dangling bonds will be created at the Si/SiO₂ interface [7]. Subsequent PECVD SiO₂ depositions again lower the lifetime due to the hydrogen loss. The next heat treatment restores lifetime to varying extents.



Fig. 5.16: Measured minority carrier lifetime of the four selected samples after each processing step. The sample structure is shown in Fig. 5.15. The durations of the heat treatments are measured in minutes.

By comparing the two blue curves (one with hollow triangles and the other with solid triangles), one can find that the additional Al-anneal step for the first SiO₂ layer (step 2 and 3) is not required. The difference of the two curves with and without the anneal step becomes much more apparent after heat-treatment. For the Al-annealed Si/SiO₂ interface (Fig. 5.15a), the heat treatment first breaks previously formed Si-H bonds, then helps hydrogen in SiN_x to be transported to passivate Si/SiO₂ interface again. For the non-annealed Si/SiO₂ interface (Fig. 5.15b), the heat treatment directly helps the hydrogen transport without the breaking of Si-H bonds, which is much more efficient than the case for the Al-annealed Si/SiO₂ interface.

Lifetime results vary a lot after the first heat treatment for samples with one side Alannealed and with different indices and thicknesses of the middle dielectric. The curve with n=2.5 has the maximum lifetime while the curve with n=2.0 has the minimum lifetime. This can be explained by the different hydrogen content within the SiN_x layers after PECVD deposition as the surface passivation quality relates directly to the hydrogen content. Hydrogen content in the *DS* is measured via Fourier Transform Infrared Spectroscopy (FT-IR), showing that the structure with n=2.5 has the maximum hydrogen in the film, and the structure with n=2.0 has the minimum hydrogen. Note the hydrogen content is determined by both SiN₄ gas ratio and SiN_x deposition time. Table 5.5 shows a lifetime comparison for silicon wafers passivated in different ways. Paying attention to the rear side only, the rear of the first wafer is covered by the best performing *DS* (top curve in Fig. 5.16), and the second one is covered by SiO₂ only without being Al-annealed, while the third one resembles the convention rear structure for high efficiency cells (blue curve with hollow triangles in Fig. 5.16). As can be seen, the lifetime of the best performing rear (with *DS*) is 1100 μ m, quite close to the 1300 μ m lifetime from the standard rear. Therefore the electrical response of the *DS* structure does not significantly degrade, verifying that this kind of rear structure could be applied to high efficiency solar cells. Further lifetime improvement is possible by optimizing PECVD SiN_x deposition recipe.

Table 5.5: Measured lifetime of three selected structures at the injection level 1E16 cm⁻³.

Sample structure	Measured litetime (µs)
1) Al-annealed $SiO_2 / Si / SiO_2 / SiN_x$ (n=2.5) / SiO_2	1100
2) Al-annealed SiO ₂ / Si / SiO ₂	971
3) Al-annealed $SiO_2 / Si / Al$ -annealed SiO_2	1300

Another finding is that SiN_x and SiO_2 PECVD layers should be deposited separately rather than in immediate succession, as the long preheating of the subsequent PECVD SiO_2 deposition may cause hydrogen to escape from the Si/SiO_2 interface rather than passivating it. It is beneficial to leave samples in air for a few days before the deposition of the second PECVD SiO_2 . Fig. 5.17 shows the lifetime difference between samples with the two PECVD layers (SiN_x and SiO_2) deposited separately and samples with two PECVD layers deposited one immediately after the other. The lifetime of four sample groups was measured at the injection level of 5E15 cm⁻³. Samples with two layers deposited separately show about 100 µs lifetime improvement (a mean difference) compared to samples with two layers deposited in an immediate succession.



Fig. 5.17: The lifetime difference of samples with PEVCD SiN_x and SiO_2 layers deposited separately and in an immediate succession. The lifetime was measured after *DS* deposition plus 30 mins heat treatment at 5E15 cm⁻³. The mean value of the lifetime difference and its standard deviation based on the statistics of the eight samples are 108 μ m and 66 μ m, respectively.

The effect of the first thermal SiO₂ thickness on the lifetime has also been investigated as shown in Fig. 5.18. The best lifetime given by the very thin 50 nm SiO₂ is in good agreement with the conclusion made by Larionova [3], demonstrating that thin SiO₂ allows for a much easier hydrogen transport from the SiN_x layer to passivate the silicon interface during heat treatment, as the consumption of hydrogen by dangling bonds in SiO₂ layer is small. In this case the amount of hydrogen contained in the SiN_x layer rather than that contained in thermal SiO₂ layer determines the surface passivation quality. When the thermal SiO₂ becomes thicker (e.g., 130 nm in the study), a large fraction of hydrogen is consumed by the SiO₂ layer before it can reach to the Si/SiO₂ interface during heat treatment. When this thermal SiO₂ becomes even thicker (e.g., 200 nm in the study), SiN_x layer improves passivation by supplying hydrogen atoms from residual water contained in the SiO₂ layer to passivate silicon surface. In this case, the role of SiN_x is similar to that of the conventional Al, though its performance is slightly inferior. Fig. 5.18 again shows the lifetime dependence on hydrogen content in SiN_x film as discussed previously.



Fig. 5.18: Effect of the first thermal SiO₂ thickness on surface passivation. The refractive index of SiN_x film is varied from 2.0 to 3.0. Thicknesses of the second SiN_x and the third SiO₂ layers are still kept as $\frac{1}{4} \lambda$ of the optical thickness at 1200 nm.

The relatively short lifetime for samples shown in Fig. 5.18 is due to the non-Alannealed front surface. A further optimization study taking both optical property and electrical quality into consideration is needed for the planar reflector design with a *DS*.

5.4 Conclusion

In this chapter, both conventional and newly designed planar rear reflectors have been fabricated and studied from optical and electrical perspectives for high efficiency silicon solar cells.

First, the reflection theory for a three-layer reflecting system is extensively examined via two calculation methods. For solar cell rear scheme involving a Si/SiO₂/Al layer stack, reflection results from a general graphical method exactly match results from software simulation. Both show that a rear scheme with a $\frac{1}{4} \lambda$ thick dielectric brings the highest rear internal reflection under perpendicular incident light.

Second, for PERT cells with a conventional rear scheme of $Si/SiO_2/Al$ layers, the effect of the rear SiO_2 thickness on both the optical property and electrical quality have been experimentally investigated via quantified optical and electrical parameters. The overall current enhancement is directly proportional to the dielectric thickness for the 8 nm to 134 nm dielectric thicknesses studied in the thesis. The rear optical properties will possibly dominate the overall current if the SiO₂ thickness is further increased, because of the saturated rear surface passivation which is independent of the dielectric thickness.

Third, planar rear reflectors with triple dielectric stacks have been fabricated to improve a cells rear internal reflection. Under illumination at normal incidence, a maximum absolute reflection increase of 2.5% is observed at 1200 nm via optical measurement, and a relative *IQE* improvement of 30% is obtained at 1150 nm via a quantitative estimate, with both compared to the conventional rear reflector with ¹/₄ λ thick singlelayer dielectric. The triple *DSs* are then re-optimised considering the broad angular distributions of the incident light due to textured front surfaces. A further *IQE* enhancement of near 20% is calculated at 1190 nm by using the re-optimised *DSs* for light with a Lambertian distribution. Moreover, these *DSs* structures show high-quality and surface passivation similar to that from conventional Al-anneal technique.
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Chapter 6. Rear side study of surface plasmonic particles on PERT cells

This chapter investigates the possibility of using scattering back reflectors by means of Ag nanoparticles on the rear of front-planar PERT cells to improve optical path length of light targeting the weakly absorbed spectrum range from 1000 nm to 1200 nm. Such rear reflector provides a tuneable high scattering cross section to scatter light at larger angles. Variations of this rear structure that combine Ag nanoparticles, dielectric layers and back metal reflectors have been compared and analysed. The electrical and optical properties of the novel rear light trapping designs have been successfully separated and quantitatively analysed, from the measured spectral response and optical absorption data. In the end, rear schemes with Ag nanoparticles were further optimised in terms of Ag mass thicknesses as well as various dielectric thicknesses. An interesting trade-off between maximising both the optical cross section and coupling fraction of the nanoparticles (thin SiO₂ needed), and maintaining high quality passivation (thick SiO₂ needed) by the variation of rear passivation SiO₂ thickness was extensively investigated.

6.1 Background

The idea of surface plasmons has been studied and extensively used for thin-film solar cells. The attractiveness lies in the effective light trapping mechanism, simple fabricating process when compared to traditional surface texturing techniques and also the fact that they are only optically coupled to the device, allowing independent optimisation irrespective of the electrical properties of the test device. Not many experimental results have been reported on the effect of surface plasmons for the wafer based devices. Schaadt et. al reported a photocurrent increase in the visible region from spherical gold nanoparticles using colloidal deposition from a Si diode [1]. They used spherical nanoparticles [2]. Furthermore, the coupling of scattered light into the substrate is reduced due to the relatively larger average spacing between nanoparticles

and substrate for this geometry [3]. In Supriya's earlier study, self-assembled silver nanoparticles were deposited onto the front surface of the finished planar wafer based PERL (Passivated Emitter Rear Locally diffused) cell with a prominent photocurrent enhancement at near band gap wavelengths [4]. However, photocurrent in the visible spectrum increased only marginally, with a reduction at wavelengths below the plasmon resonance, which is attributed to the interference effects of surface plasmon scattered light and the incident light when placed at the front of a device [5]. To overcome this issue, along with any potential parasitic losses in the metal at shorter wavelengths, it was demonstrated that having the particles on the rear side could be more beneficial [6, 7]. Performance enhancement of nanoparticle arrays fabricated at the rear of a 100 μ m bifacial crystalline Si solar cells has been reported earlier with a 2.1-fold increase at 1100 nm using a TiO₂ undercoating layer [8]. However, this study focuses on further improvements of the light trapping of the 400 μ m thick high efficiency Si solar cells that already have a good back reflector design based on evaporated displaced Al film. The potential for enhancement is close to the bandgap of Si.

Plasmonic structures provide the opportunity to tune the resonance and hence scattering closer to the bandgap of silicon where absorption in the cell is weak. Unlike other studies that compare the performance of plasmons with bare structures, this work compares the light trapping effectiveness of different configurations of plasmons on PERT cell rear to that of a conventional metal back reflector PERT cell. The motivation is to eventually use plasmonic structures together with front surface textures as 'hybrid' light trapping structures to enhance broadband absorption over the entire spectral range of interest.

6.2 Integration of Ag nanoparticles to the rear side of PERT cells

6.2.1 PERT cell modifications

Planar PERT cells were fabricated on the 1.5 Ω cm 400 µm thick *p*-type FZ Si wafers without front texturing. Information about PERT cell fabrication details can be found in Chapter 1. Since these cells are un-textured and without anti-reflection coating layers, cell performance is somewhat lower than the 25% devices reported elsewhere [4]. The typical performance of a plasmonic device used in this work was circa 18% with V_{oc} = 654 mV, J_{sc} = 35.5 mA/cm² and with a fill factor of 78.8%. The best light trapping schemes investigated during this work increased J_{sc} by 1.1 mA/cm², corresponding to a 2% relative increase in overall performance.

In this work, Ag nanoparticles were formed by the self-assembly technique of thermal evaporation of thin Ag films followed by a one hour N_2 atmosphere anneal process at 200°C [4]. Note a recent study by Hairen Tan [9] shows that if the anneal temperature is increased to 400°C, a more efficient scattering can be obtained due to the reduced surface coverage and the eliminated formation of small and irregular nanoparticles. The Ag film thicknesses were estimated using a quartz crystal monitor at the time of deposition. The particles have a flat base and a large surface area in contact with the substrate making the geometry ideal for near-field coupling [3]. The different modification steps for PERT cell rear schemes are shortly listed in Table 6.1.

Step	Processing
1	Thin the back passivating SiO ₂ layer to the desired thickness
2	Evaporate Al film with thickness around 800 nm
3	Remove the evaporated Al film
4	Thermally evaporate Al metal grids with less than 15% coverage of the rear
	active area
5	Fabricate newly designed rear structures with Ag nanoparticles as shown in
	Fig. 6.1b

Table 6.1: Modification steps for PERT cell rear schemes.

In step 1, a thin surface passivation SiO_2 layer is kept before rear reflectors fabrication, to maintain reasonable rear electronic property for high efficiency solar cells. In step 2, as mentioned earlier, Al film acts as both metal contact and optical reflector, representing a conventional rear scheme (reference) in the study. For solar cell with back reflector by surface plasmons, Al metal grids deposition in step 4 with a surface coverage less than 15% is used to aid the *EQE* measurement by allowing rear metal contact and to aid the subsequent nanoparticles deposition (as only nanoparticles deposited outside Al grids area can provide scattering effect). Optical (reflectance & transmission) and *EQE* measurements are carried out after each modification step.

6.2.2 General characterisation procedures

For the optical characterisation, reflection and transmission spectra were measured using a PerkinElmer spectrophotometer with an integrating sphere. Light absorption was then calculated by subtracting measured reflection and transmission from unity. For electrical measurements, *EQE* measurement was carried out for each of the rear structures. *EQE* is the photo generated carriers that are collect by the p-n junction at short circuit. It is calculated as the ratio of the photo generated carriers (obtained from the measured current) to the incident photons as a function of wavelength. *I-V* measurements were used to track the overall performance of the cells. Short circuit current was calculated by integrating the product of measured *EQE* and photon flux under the standard AM1.5G Spectrum. Scanning electron microscope (SEM) images were used to characterise the size and distribution of nanoparticles deposited on the solar cell. The dielectric layer thicknesses were measured using an ellipsometer. Note the characterisation methods in this chapter are also available for samples fabricated in Chapter 5 and Chapter 7.

Throughout the studies in Chapter 5, 6 and 7, we focus on the 900 - 1200 nm wavelength regime. Response at wavelengths below 900 nm reflects the performance of the front/base of the cell, which is not the focus of the present study. Response at the near infrared wavelength (i.e. 900 nm - 1000 nm) provides insight into the electrical performance of the rear i.e., surface passivation. Optical response might also show

impacts over this wavelength range. Response at the near and below band-gap wavelength (i.e. 1080 nm - 1200 nm) is mostly influenced by the optical effects, as light is absorbed spatially uniformly over this wavelength range [10, 11].

6.3 Rear scheme variations with Ag nanoparticles

6.3.1 Sample description

7 types of rear structure were fabricated on the rear of the planar PERT cell. The first one resembles that of a standard PERT cell, with a 800 nm evaporated Al film on the rear SiO₂ as shown in Fig. 6.1a. Six variations of modified rear reflectors based on the same solar cell incorporating Ag surface plasmons rear reflectors were fabricated as shown in Fig. 6.1b. A list of the different structures along with their represented names used in figures is as shown in Table 6.2. The Ag film used for the cell has a thickness of 23 nm. The SiO₂ passivating layer was thinned to be 40 nm, as a compromise between the coupling and scattering behaviour of the Ag surface plasmons and the surface passivation provided by the SiO₂ layer. The plasmon resonance is sensitive to the surrounding medium and is red-shifted to longer wavelengths with increased effective refractive index due to depolarisation effects [12]. Hence a 10 nm ZnS which has a refractive index of 2.2 was used to overcoat the nanoparticles by inducing a change in refractive index of the surrounding medium. Note: the "back reflector", as illustrated in Fig. 6.1b, is absent in variation 1, 2 & 5, but is present in variation 3 & 4 as a detached Al reflector layer and in variation 6 as an evaporated Al layer. Detached Al uses air as the overcoating layer whereas evaporated Al uses a dielectric (MgF₂ in this case) as the overcoating layer.



Fig. 6.1: (a) Rear structure corresponding to a standard PERT cell. (b) Modified rear structures with various possible combinations of Ag nanoparticles, dielectric films and back reflector. The drawings are not to scale.

Table 6.2: List of six variations of the rear structures along with their represented names
used in the figures for the cells discussed in the chapter. Nano Ag stands for Ag metal
nanoparticles.

Var. No.	Rear Structures	Represented Names
Var. 1	Ag nanoparticles	Nano Ag
Var. 2	Ag nanoparticles / 10 nm ZnS film	Nano Ag / ZnS
Var. 3	Ag nanoparticles / Detached Al mirror	Nano Ag / D Al
Var. 4	Ag nanoparticles / 10 nm ZnS film / Detached Al mirror	Nano Ag / ZnS / D Al
Var. 5	Ag nanoparticles / 10 nm ZnS film / 170 nm MgF ₂ capping layer	Nano Ag / ZnS / MgF ₂
Var. 6	Ag nanoparticles / 10 nm ZnS film / 170 nm MgF ₂ capping layer / 800nm evaporated Al	Nano Ag / ZnS / MgF ₂ / E Al

6.3.2 Results and discussion

For the solar cell with rear structure in Fig. 6.1a, it is worth noting that no noticeable EQE degradation (not shown) was measured after modification steps (1), (2) and (3). This suggests the surface passivation quality of the thinned SiO_2 has been maintained. Fig. 6.2a shows the measured EQE data of the cell with seven rear structures, six of which are variations using Ag surface plasmons. The small box on the upper right of the figure shows the short circuit current of various schemes over the wavelength of 900 nm - 1200 nm. The sequences of the current values correspond to the names of rear schemes listed in the same figure's legend. Fig. 6.2b shows the corresponding EQE enhancement factor which is the ratio of the EQE with the metal nanoparticles to the case with conventional Al ($EQE_{plasmons}/EQE_{reference}$). It is interesting to note that all six rear Ag surface plasmons structures have shown EQE improvement over the reference structure in the wavelength range 1060 nm to 1200 nm. As expected, light below 980 nm is fully absorbed by the Si wafer during the first pass, hence no enhancement by surface plasmons is observed. Ag nanoparticles alone bring a 1.7-fold enhancement at 1160 nm while Ag nanoparticles combined with a detached Al reflector, leads to more than 2.4-fold enhancement. A combination of Ag nanoparticles, ZnS and detached Al brings a further EQE enhancement of 2.6-fold.



Fig. 6.2: (a) Measured *EQE* of the planar PERT cell with rear planar reflector as the reference (blue solid line, snowflakes) and six variations of rear Ag surface plasmons light trapping schemes. Fig. 6.2a contains short circuit current as well as current enhancement (in the bracket) of various reflectors calculated from 900 nm to 1200 nm. The sequences of current values correspond to names of reflectors listed on the left. (b) Calculated *EQE* enhancement of the six rear Ag surface plasmons light trapping schemes over reference rear structure. For both figures, solid lines indicate light tight rear structures while dashed lines represent non-light tight rear structures.

The 40 nm SiO_2 used as the rear surface passivation layer is not the optimised thickness for highest photocurrent enhancement, although light trapping has been improved by Ag nanoparticles deposited on it. Reducing this SiO_2 layer thickness might enhance the light trapping but degrade the electrical quality. There is a limitation to the rear SiO_2 thickness below which surface passivation quality will be noticeably degraded, cancelling out any benefits of optical enhancement from surface plasmon coupling and scattering. This minimum tolerable thickness might be different to that needed for front surface passivation for PERT or PERL cells, due to different optical and electrical requirements for front and rear [13]. The results of the optimised thickness of the SiO₂ thermal oxide layer was investigated independently and is discussed in section 6.4.2 to achieve the maximum optical gain without or with minimum rear electronic quality degradation.

The effect brought about by incorporating a 10 nm thick ZnS layer is due to the redshifting of the Ag surface plasmons resonance by this relatively high refractive index over coating film which has been observed in earlier study as well [6, 14]. The thickness of the ZnS was chosen to induce a change in the dielectric medium around the metal nanoparticles to provide the relevant shift of the resonance to longer wavelength and not to compromise on the preferential scattering into the higher index Si substrate. It is found that the ZnS thickness has to be around 10 nm - 15 nm to increase the scattering; thinner ZnS shows little effect while thicker ZnS decreases the optical property compared to the reflector "Nano Ag". Refer to section 6.4.3 for the optical effect by using various ZnS thicknesses. A lower index MgF₂ (n = 1.4) was chosen as an overcoating layer medium. 170 nm MgF₂ capping layer inserted between Ag particles and evaporated Al is used to avoid Al caulking (into gaps between Ag particles) which might affect scattering behaviour of Ag nanoparticles and avoid shunting. The choice of the overcoating layer is a critical factor to be taken into account due to outcoupling losses. The thickness effect of the MgF₂ capping layer will be discussed in Chapter 7.

The *EQE* enhancement is slightly reduced by the MgF₂ capping layer. The modified dielectric environment leads to a decreased scattering cross section of the rear localised Ag particles into Si. Following the deposition of the Al film as a back reflector to the MgF₂ capping layer, *EQE* enhancement is improved in comparison to rear design "Nano Ag", but remains inferior when compared to rear structure "Nano Ag / Detached Al". This is attributed to the rough interface of the evaporated Al owing to conformal deposition of MgF₂ on Ag nanoparticles, leading to excitation of propagating plasmons that are lossy [15, 16]. It is also reported that metal surface in the proximity of a dipole can affect its scattering property by interference of light reflected from the mirror and at the interface of two different dielectrics with different refractive indices, causing the

molecules to either radiate strongly in that direction or not radiate at all. This has been extensively studied by Drexhage [17] in the context of fluorescing dipoles adjacent to a metal but applies to any scattering medium influenced by the driving field. This results in reduced reflectance properties from the back reflector and necessitates the optimisation of the thickness of the capping layer. The result has been further confirmed by the measured optical absorption spectra as given in Fig. 6.3. Throughout the wavelength range 1000 nm to 1060 nm, *EQE* data of all surface plasmons based rear schemes decrease slightly compared to the original. This is either due to optical losses or to electrical degradation. A detailed analysis of the electrical degradation will be shown in section 6.3.3. The detached metal reflector further enhanced light trapping by reflecting the otherwise transmitted light.



Fig. 6.3: Calculated absorptance of the cell with no light trapping (blue, hollow diamonds); with reference rear structure (pink, hollow triangles); and with a selection of rear structures' using Ag surface plasmons.

Fig. 6.3 shows the absorptance of the cell with no back reflector (blue, hollow diamonds); with reference rear structure (pink, hollow triangles); and with a selection of rear structures using Ag surface plasmons. A clear absorption enhancement is observed when Ag particles are applied to the rear compared to the reference curve. Further absorption enhancements are achieved by incorporating dielectrics and metal reflectors, see curves with (red) crosses and (purple) circles. Although the measured absorption includes metal parasitic absorption that is lossy, the trend of absorption data of various

structures in Fig 6.3 are all in good agreement with that of the *EQE* enhancement in Fig 6.2b, except for the rear structure "Nano Ag / ZnS / MgF₂ / E Al", for which highest absorptance does not result in highest *EQE*. Calculation and measurement of the absorption loss at rough metals can be found in [18-20].



Fig. 6.4: Photoluminescence (PL) image of the wafer containing six 2 cm x 2 cm cells in the middle with reflector "Nano Ag" and six 1 cm x 1 cm cells with reflector "Evaporated Al".

Photoluminescence (PL) can also be used to characterise the optical enhancement brought by Ag particles via the emitted PL signal, which is indicated by the brightness of the active area and is scale marked on the right light-bar of the image, see Fig. 6.4. An 815 nm single wavelength laser was used to illuminate the entire silicon wafer to generate free electron and hole carriers. A silicon CCD camera was used to detect the PL signal (emitted light at near band-gap wavelength). Fig. 6.4 shows the PL image for a wafer containing six 2 cm x 2 cm cells located in the middle with scattering reflector "Nano Ag" and six 1 cm x 1 cm peripheral cells with conventional reflector "Evaporated Al". As can be seen, cells with nano Ag as rear reflectors emit much stronger PL signals compared to cells with Al reflectors, indicating significantly enhanced light absorption in the rear. The four criss-cross lines within each cell are the modified rear metal contacts (Al grids).

6.3.3 Further analysis of optical and electrical enhancements

6.3.3.1 Analytical method

The electrical and optical effects by various rear schemes were separated using Basore's approach [10, 21] which is summarised below in a condensed form for planar front surfaces and perpendicular incident beams. As used, the method does not account for parasitic absorption or optical non-planar back reflector characteristics.

All needed measurement data are extracted from internal quantum efficiency (*IQE*) measurements. Inverse *IQE* is plotted against the inverse of the absorption coefficient of silicon α^{-1} instead of the commonly used photon wavelength λ , see Fig. 6.5. The plot has three characteristics relevant for further calculations. The linear slope m_1 , defined in the region $\alpha^{-1} = 0.01$ mm to 0.13 mm (corresponding to $\lambda = 800$ nm to 990 nm), the linear slope m_2 , defined in the region $\alpha^{-1} = 1.3$ mm to 5.0 mm (corresponding to $\lambda = 1070$ nm to 1120 nm) and the value *Intcpt* that is the linearly extrapolated *IQE*⁻¹ from region where m_2 is defined to a corresponding $\alpha^{-1} = 0$ (corresponding to $\lambda = \infty$ nm).



Fig 6.5: IQE^{-1} vs α^{-1} of the front-planar cell studied in section 6.3.2, with back reflector "Nano Ag / ZnS / MgF₂ / E Al". The plotted wavelength range is from 800 nm to 1100 nm (absorption length from 0.01mm to 3.00mm). The slope of the first linear region is m_1 , and the slope of the second linear region 2" is m_2 .

The effective diffusion length L_{eff} which defines the dark saturation current density of the bulk region and the optical collection efficiency η_c are defined as [25, 26]:

$$L_{\rm eff} = 1/m_1 \tag{61}$$

$$\eta_{\rm c} = C/Intcpt \tag{6.2}$$

The correction factor *C* is conveniently found from two graphs, see Fig. 6.6. They summarise the influence of various geometric optical effects on η_c . The *Intcpt* value, the cell thickness *W* and the slope m_2 are used to find a value for the back reflectance R_{back} (step (a) in Fig. 6.6), which acts as an intermediate value to find *C* (step (b) in Fig. 6.6).



Fig. 6.6: Correction factor *C* is looked up via the intermediate value back reflectance R_{back} (b) in the lower graph. R_{back} itself is linked to the *incept* value, the cell thickness *W* and the slope m_2 , see upper part of the graph (a). (Values for *incept* and m_2 are found in Fig. 6.5.) Values for planar front surfaces are taken from Basore [10].

No analytical expression can be given for the minority carrier diffusion length of the base region L. Instead Eqn. 6.3 with Eqn. 6.4 is solved for L. Subsequently the back surface recombination velocity S is found via Eqn. 6.4.

$$L_{\rm eff} = L \frac{D + LS \tanh\left(\frac{W}{L}\right)}{LS + D \tanh\left(\frac{W}{L}\right)}$$
(6.3)

$$S = \frac{D \cdot \left[L \tanh\left(\frac{W}{L}\right) - \eta_{c}W \right]}{L^{2} \cdot \left[\cosh^{-1}\left(\frac{W}{L}\right) - 1 \right] + L \eta_{c}W \tanh\left(\frac{W}{L}\right)}$$
(6.4)

D is the minority carrier diffusion coefficient, which is estimated to 25 cm²/s for the solar cell used in the study. *W* is the wafer thickness of 400 μ m. The wavelength dependent absorption coefficient of silicon at 300 *K* [22] is taken from Ref. 22, while the *EQE* was measured at 295±1 K. The optical absorption constant α was accordingly corrected for the 5 K difference by using Ref. 23 [23]. The free carrier absorption of Si and the metallic absorption of the Al grid, as well as for the Ag nanoparticles are considered to be negligible in this study.

The minority carrier bulk lifetime τ_{bulk} is found with L via Eqn. 6.5.

$$\tau_{\rm bulk} = L^2/D \tag{6.5}$$

The thickness normalised effective optical path length Z represents the light trapping properties of photons with sub-bandgap energy, see Eqn. 6.6.

$$Z = \frac{1 - \left(R_{\text{front,m}} + T\right)}{m_2 \eta_c W \cdot \left(1 - R_{\text{front,e}}\right)}\Big|_{\lambda > 1200 \text{nm}}$$
(6.6)

 $R_{front,m}$ and T are the measured reflectance and transmittance of photons with subbandgap energy. T is a needed extension of Basores original equation to accommodate samples without back-reflector structures. $R_{front,e}$ is the direct reflectance from the front surface, without any contribution from escaping light. For photons below 1000 nm, $R_{front,m}$ and $R_{front,e}$ are identical, since all photons entering the cell are absorbed due to the short absorption length. For photons with $\lambda > 1000$ nm, $R_{front,e}$ cannot be directly measured as non-absorbed photons start to exit through the front. However, if the direct reflectance $R_{front,e}$ is assumed to be linear in its characteristics for $\lambda > 700$ nm, $R_{front,e}$ can be linearly extrapolated from the measured value $R_{front,m}$, see Fig. 6.7. Modifications of the back structures have obviously no influence on the direct reflectance $R_{front,e}$.



Fig. 6.7: Measured total reflectance (red, hollow triangles) and the linear approximated front surface reflectance (blue, hollow squares) of the solar cell with rear structure "Ref: Evaporated Al". The cell has a 110 nm SiO_2 front surface passivation coating with rudimentary antireflection properties.

6.3.3.2 Calculated Z, S and L

Table 6.3 shows the optical and electrical parameters as well as their uncertainties as relative errors for the five selected rear schemes.

Table 6.3: Calculated optical parameter Z and electrical parameters L, S and τ_{bulk} for a selection of five rear structures. Needed values for the calculation of these key parameters are also shown. The relative uncertainties err_{rel} are calculated via Gaussian Error Propagation unless mentioned in the text.

			Ref.:				Var.2: Nano		Var. 4: Nano		Var. 6: Nano	
	Evaporated			ated Al	l Al		Ag/ZnS		Ag/ZnS/D Al		Ag/ZnS/	
		·				U		0		MgF ₂ /E Al		
Origin	Parameter	Unit	Value	$\operatorname{err}_{\operatorname{rel}}$	Value	err _{rel}	Value	err _{rel}	Value	$\operatorname{err}_{\operatorname{rel}}$	Value	$\operatorname{err}_{\operatorname{rel}}$
Fig. 6.5	<i>m</i> ₁	[mm ⁻¹]	0.349	4.4%	0.508	4.1%	0.535	4.0%	0.506	2.9%	0.614	2.1%
Eq. 6.1	L_{eff}	[µm]	2,865	4.4%	1,969	4.1%	1,870	4.0%	1,975	2.9%	1,628	2.1%
Fig. 6.5	Intcpt	[]	1.089	3.5%	1.162	3.5%	1.130	3.0%	1.088	3.6%	1.222	3.1%
	W	[µm]	400	1.3%	400	1.3%	400	1.3%	400	1.3%	400	1.3%
Fig. 6.5	<i>m</i> ₂	[mm ⁻¹]	0.106	3.9%	0.162	2.6%	0.131	2.0%	0.106	4.1%	0.139	2.2%
	Intcpt/(W*m ₂)	[]	25.73	5.4%	17.95	4.5%	21.56	3.8%	25.62	5.7%	21.97	4.0%
Fig. 6.6	R _{back}	[]	86.1%	0.7%	80.6%	0.7%	83.5%	0.7%	86.0%	0.7%	84.1%	0.7%
Fig. 6.6	С	[mm ⁻¹]	1.075	0.5%	1.099	0.5%	1.086	0.5%	1.076	0.5%	1.085	0.6%
Eq. 6.2	η_c	[]	98.7%	3.6%	94.6%	3.5%	96.1%	3.0%	98.9%	3.7%	88.8%	3.1%
(approx)	D	[cm ² /s]	25	8.0%	25	8.0%	25	8.0%	25	8.0%	25	8.0%
Eq. 6.3 ,6.4	L	[µm]	1,218	8.7%	1,061	5.7%	1,007	4.3%	1,001	5.1%	1,022	4.4%
Eq. 6.4	S	[cm/s]	20	64.2%	43	30.0%	38	28.7%	27	49.4%	71	16.6%
Eq. 6.5	T bulk	[µs]	593	19.2%	450	14.0%	406	11.7%	401	13.0%	418	11.9%
(approx)	$R_{front,m}+T$	[]	89.7%	0.2%	67.9%	0.3%	71.6%	0.3%	62.1%	0.3%	61.0%	0.3%
Fig. 6.7	R _{front,e}	[]	21.4%	0.9%	21.4%	0.9%	21.4%	0.9%	21.4%	0.9%	21.4%	0.9%
Eq. 6.6	Ζ	[]	3.14	5.6%	6.67	4.4%	7.17	3.7%	11.48	5.6%	10.05	3.9%

For the effective optical path length Z, the reference rear structure "Ref: Evaporated. Al" has a normalised optical path length factor Z of only 3.1 at 1200 nm. The addition of Ag particles increases the path length factor Z beyond the reference. The combination of Ag particles, ZnS and a detached Al reflector performs best with a Z of 11.5. The trend of increasing Z is in good agreement with that of the *EQE* enhancement over the wavelength range of 1100 nm to 1200 nm. This indicates *EQE* values at near bandgap wavelength are closely related to the light trapping property of the cell rather than the electrical quality of the back. On the other hand, the absorption value (1- ($R_{front,m}+T$)) itself is not a sufficient indicator for light trapping in a silicon solar cell, see Table 6.3. Absorption is influenced by non-light trapping related effects, such as free carrier absorption. The normalised effective optical path length factor Z is the most accurate indicator for light trapping properties.

Electrical properties were analysed for the cell with various rear reflectors, to explain the slight EQE decrease at wavelength 1000 nm - 1050 nm. Table 6.3 shows the calculated electrical parameters of a selection of rear structures. The PERT cell with the reference reflector shows good values of diffusion length L, surface recombination velocity S and carrier lifetime τ_{bulk} . After modifying the rear design by replacing the Al layer with Ag nanoparticles, the surface recombination velocity increases by 10-20 cm/s while τ_{bulk} decreases, due to the chemical processing involved, e.g. whole rear Al removal, Al grids deposition. This could explain the slightly decreased EQE values of the cell with modified rear structures over the wavelength range 1000 nm - 1060 nm as in Fig. 6.2b. The rear recombination losses seem to dominate, rather than optical losses as the light trapping is improved as indicated in Table 6.3. These electrical related photocurrent losses could be avoided / minimised by further optimizing the rear structure, especially by optimising rear SiO₂ passivating film thickness as it is of essential importance for maintaining good real electronic quality. Section 6.4 gives a detailed study about the optimization process for the thickness of the dielectric layer as well as the thickness of Ag mass of the rear scattering scheme integrated Ag nanoparticles.

6.3.3.3 Uncertainty analysis

The linear least square fit, as indicated in Fig. 6.5, provides the parameters *Intcpt*, m_1 and m_2 . The fit also provides their statistical Gaussian uncertainty for each parameter. The *Intcpt* uncertainty further increases by a common absolute 0.2% offset uncertainty of the reflectance and transmission measurement and a common relative 2% offset uncertainty from the quantum efficiency measurement. Values, such as $R_{front,m}$, T and $(R_{front,m} + T)$ are only subject to common absolute 0.2% offset uncertainty. The visible step at $\alpha^{-1} = 0.16$ mm ($\lambda = 1000$ nm) in Fig. 6.5 is an equipment related artifact and is compensated prior linear fitting.

Uncertainties for W and D are estimated. The uncertainty of C is dominated by the limits of the digitalisation process of Basore's graphs. An additional, but neglected,

uncertainty might arise from parasitic absorption or optical non-planar back reflector characteristics.

All uncertainties for L_{eff} , η_c , τ_{bulk} and Z, see Eqns. 6.1, 6.2, 6.5, 6.6, are calculated by including all errors via Gaussian error propagation. Uncertainties for L and S, Eqns. 6.3 and 6.4, were found numerically by varying the input parameter within their uncertainty boundaries. However, considering the low value of S, this is an acceptable accuracy.

6.4 Further optimization of rear schemes with Ag nanoparticles

6.4.1 Impact of the Ag mass thickness

The effect of the as-deposited Ag film thickness (before annealing) on optical enhancement has been investigated in this section.

6.4.1.1 Sample description

Ag films of 5 different thicknesses varying from 12 nm to 28 nm (with 4 nm steps) were evaporated to the back of five planar PERT cells, as well as to the microscope glasses which were used to study the resonance position and broadening of the scattering for different sized nanoparticles. The five cells with nano Ag were fabricated on the same wafer to ensure the similar initial performance. The rear SiO₂ passivating layer of the wafer for the Ag thickness study was thinned to be 20 nm. Two rear schemes of "Nano Ag" and "Nano Ag / D Ag" were applied to the cells.

6.4.1.2 Results and discussion

The as-deposited Ag film thickness (before annealing) was used as a variable parameter to achieve the maximum light trapping enhancement. A subsequent anneal of this layer at fixed temperatures yielded nanoparticles as has been mentioned before. Since this is a self assembly technique, there is not much control over the particle size/shape/distribution, hence Ag mass thickness is used as a reference for nanoparticle features. Interestingly, results in Fig. 6.8 show that approximately 28 nm Ag film brings highest *EQE* enhancement for the thick wafer based solar cells, which is in agreement to

the trend seen in Pillai's previous study [4]. The current enhancement integrated from 900 nm to 1200 nm in the brackets shows the same trend. With the 28 nm Ag mass, a very promising current improvement of 17% is achieved by "Nano Ag", and 25.7% by "Nano Ag / D Ag". If integrating the entire spectrum from 300 nm to 1200 nm, the enhancement is 3.1% and 4.7% respectively.



Fig. 6.8: (a) *EQE* enhancement by rear reflector "SiO₂ / Nano Ag" with different mass Ag thicknesses. Data in the bracket is the corresponding current enhancement calculated from 900 nm – 1200 nm. (b) *EQE* enhancement by rear reflector "SiO₂ / Nano Ag / D Ag" with different mass Ag thicknesses. The enhancements for both figures were compared to cells without any rear reflector.

The net absorption increase by the presence of Ag nanoparticles and a combination of Ag nanoparticles and detached Ag under different Ag mass thicknesses is shown in Fig. 6.9. As indicated, more than 35% and nearly 50% net increases are achieved by using Nano Ag and Nano Ag / D Ag at 1120 nm, respectively. The trends of net absorption

increase almost agree with the *EQE* trends in Fig. 6.8. The slight differences lie on the different metal grids coverage as well as the free carrier absorption which does not contribute to the electron-hole pair creation.



Fig. 6.9: Net optical absorption increases by rear reflector (a) Nano Ag (b) Nano Ag / D Ag, over the reference at different Ag mass thicknesses.

The calculated optical path length factor Z for cells with different mass silver thicknesses is given in Fig. 6.10. Z of the solar cell with 12 nm Ag mass is clearly lower than cells with other Ag mass thicknesses because of its poorest dipole scattering at such thin Ag film. The calculated Z trend matches EQE and optical trends very well, with the maximum Z value of 22.3 for reflector "Nano Ag / D Ag" with 28 nm Ag mass.

Note the Z values of cells in this section are not comparable to those in other sections due to the different types of anti-reflection coatings applied. Double layer antireflection coatings composed of MgF_2 and ZnS are used for cells in this section, while single layer

coatings of SiO_2 are used for cells in other sections. The optimization of Ag mass thickness can be viewed as a separate work of the whole rear scheme.



Fig. 6.10: Calculated effective optical path length Z for the five cells with different Ag mass thicknesses by using rear reflector Nano Ag and Nano Ag / D Ag.

From SEM measurement in Fig. 6.11, the single isolated small particles (with 12 nm mass thickness) tend to assemble and form multiparticle clusters of the same height when the mass Ag film thickness increases to 24 nm and 28 nm. The scattering resonance behaviour is therefore changed due to the size, shape and coverage variations of nanoparticles. Transmittance measurement in Fig. 6.12 indicates that the resonance position (dip of transmittance plotting) of Ag particles on glass moves towards longer wavelength and becomes broader by increasing mass thickness of the deposited Ag film. Larger particles have a larger scattering cross section and higher radiative efficiency and hence redshift the dipole resonance peak compared to small particles. The broader resonance for larger sized particles indicates the scattering efficiency becomes more uniform over the entire spectrum range. Light trapping difference from the larger sized particles becomes less apparent when the particle size keeps increasing, as shown in Fig. 6.8a. It is very likely that multipole oscillations set in for these shapes, however the contribution from dipole scattering still would be more significant in this case [2]. For mass silver with even thicker film, it is very possible that the optical enhancement will wane, due to the strong excitation of multipole oscillations that can significantly reduce the scattering effect. Since the particles are located on the rear, suppression of enhancement and reduced coupling of higher order modes will not affect the

performance of the cell. Hence in the study 28 nm mass thickness of silver is used for a marked and stable optical gain.



Fig. 6.11: SEM images of Ag nanoparticles with various mass Ag thicknesses (12nm, 20nm, 24nm, 28nm) deposited on the surface of bare silicon wafers.



Fig. 6.12: Transmittance measurements of different sized Ag particles on microscope glasses, samples are deposited and annealed together with corresponding solar cells.

6.4.2 Impact of the rear SiO₂ thickness

The thickness effect of rear SiO_2 passivating layer, targeting an optimised trade-off between optical gain and electrical loss will be looked into in detail in this section.

6.4.2.1 Sample description

The fabricated planar PERT cells for the study of SiO₂ passivating thickness have the same original SiO₂ thickness and similar initial performance. After initial characterisation, the rear SiO₂ layer of each cell was etched back to eight different thicknesses varying from 0 nm to 134 nm. For oxide thicknesses below 20 nm, estimations of the thickness were made by carefully controlling etching time assuming the etching rate is a constant. Ag nanoparticles with 28 nm Ag mass thickness (optimised in section 6.4.1) were then deposited on the rear SiO₂ of each cell. Two rear schemes of "Nano Ag" and "Nano Ag / D Ag" were applied to the eight cells.

6.4.2.2 Results and discussion

The choice of oxide thickness is critical to obtain improved light trapping, as well as maintain high quality surface passivation. For the high efficiency cells, a thicker SiO₂ layer is preferable considering rear electrical qualities. As a thicker SiO₂ layer contains more H₂O which releases more H atoms during the Al-anneal step to passivate dangling bonds at the Si/SiO₂ interface [24]. While it is desirable to have a thin spacer layer for Ag nanoparticles located at the front of a device to enhance photocurrent, for Ag nanoparticles located on the rear, it is better not to use any spacer layer due to different scattering behaviour compared to the front [6]. The wavelength of strongest scattering activity shifts to the longer photon wavelength (preferred in this work) with decreasing spacer layer thickness. This is evident when the spacer layer thickness is similar to or smaller than the near-field extension of the surface plasmon excitation (a few tens of nm). Beyond this thickness, the effect of the Si substrate on the nanoparticles becomes negligible and hence no additional shift in resonance is expected. Additionally the coupling effect between the plasmons to the Si substrate also depends on the distance between nanoparticles and this substrate. Short distance leads to high coupling efficiency. However surface passivation is critical for high efficiency solar cells, which heavily depends on the thickness of the oxide layer.

Fig. 6.13 shows the measured EQE of solar cells with rear nano Ag deposited on passivating SiO₂ layers with different thickness. The right inset shows the corresponding short circuit current integrated over 900 – 1200 nm. Though the EQE values and current values represented are not comparable with each other because of different solar cells used, the figure does give insights that how different passivation

layer thicknesses differ *EQE* response. Clearly, *EQE* of solar cell without surface passivation at near infrared wavelength is extremely lower than others, and the *EQE* values at near band-gap wavelength are heavily influenced by the oxide thicknesses.



Fig. 6.13: Measured *EQE* of solar cells with rear nano Ag deposited on passivating SiO₂ layers with different thickness. The right inset shows the corresponding short circuit current integrated over 900 nm – 1200 nm. The sequences of current values correspond to different SiO₂ thicknesses listed on the left.

Fig. 6.14 shows the corresponding effect of rear SiO₂ thickness on *EQE* enhancement, by using rear reflector "Nano Ag" and "Nano Ag / D Ag" when compared to the reference reflector (134 nm SiO₂ / Evaporated Al). A maximum 4-fold *EQE* enhancement at 1160 nm was achieved as shown in Fig. 6.14b by using the 19 nm rear SiO₂. Note here the *EQE* enhancement is much higher than that of the cell discussed in section 6.3 (2.6-fold) because of the optimised rear SiO₂ thickness as well as the optimised Ag mass thickness, see section 6.4.1. Thin SiO₂ layer brings more *EQE* enhancement at wavelength above 1050 nm, due to the strong surface plasmon coupling and scattering effect.



Fig. 6.14: (a) *EQE* enhancement by rear reflector "SiO₂ / Nano Ag" with different SiO₂ thicknesses at back. (b) *EQE* enhancement by rear reflector "SiO₂ / Nano Ag / D Ag" with different SiO₂ thicknesses at back. The enhancements for both figures were compared to cells with conventional rear reflectors "134 nm SiO₂ / Evaporated Al".

The cell with thinnest SiO₂ at the rear (0 nm SiO₂) does not show the highest *EQE* increase although this case showed the best optical enhancement by absorption measurement in Fig. 6.16 as will be discussed. This is attributed to the cell's poor rear surface passivation quality which can be observed from the slightly decreased *EQE* at 950 nm – 1050 nm, and also from the lowest *L* value shown in Fig. 6.15. The degraded electrical property limits the *EQE* gain when compared to the optical enhancement. When no surface passivation layer or very thin surface passivation layer is applied, the cell's surface recombination velocity increases significantly.

Fig. 6.15 shows the calculated Z and L for cells with the two scattering schemes under different SiO₂ thicknesses. As indicated, the Z trend is inversely proportional to SiO₂ thickness and the L trend is directly proportional to SiO₂ thickness.



Fig. 6.15: Calculated effective optical path length Z and base region minority carrier diffusion length L of the high efficiency PERT cells with scattering reflectors (a) Nano Ag and (b) Nano Ag / D Ag, under various rear passivation layer thicknesses.

The optical absorption measurements represented in Fig. 6.16 are in good agreement with the calculated Z values, except for the cell with 0 nm and 8 nm SiO₂. The cell with 0 nm and 8 nm SiO₂ gets the highest optical absorption, but their Z factors are slightly lower than the cell with 19 nm SiO₂. This is because of the poor surface passivation by the 0 nm and 8 nm SiO₂ resulting in more light absorption by the back reflector, and hence reducing light trapping. It also shows that the detached mirror increases the

absorption for all eight SiO_2 thicknesses compared to the case with just the nanoparticles.



Fig. 6.16: Measured optical absorption of solar cells with (a) SiO_2 / Nano Ag. (b) SiO_2 / Nano Ag / D Ag.

Besides calculated *L*, the electrical properties of solar cells can also be indicated by the V_{oc} value from light *I-V* measurements. Fig. 6.17 indicates how the cell's V_{oc} changes using the rear structure "Nano Ag" compared to the reference, using different rear SiO₂ thicknesses. V_{oc} decrease is maximum for the cell with no SiO₂ on the rear, and moderate for cells with thin SiO₂. For the cell with thickest rear SiO₂, V_{oc} increases slightly due to the enhanced current caused by the metal nanoparticles (as V_{oc} depends on the short circuit current).



Fig. 6.17: Measured V_{oc} increase/decrease from cells with back reflector "SiO₂ / Nano Ag" to cells with conventional back reflector "134 nm SiO₂ / Evaporated Al". Eight different SiO₂ thicknesses (0 nm –134 nm) were used for reflectors "SiO₂ / Nano Ag".

Current enhancement integrated from 900 nm to 1200 nm over the reference reflector "134 nm SiO₂ / Evaporated Al" is calculated in Fig. 6.18, to find the trade-off between optical and electronic properties due to variation of the SiO₂ thickness. The current increases for all eight cells, with the maximum increase of 16% for the cell with 19 nm SiO₂, and minimum increase of 2% for cells with 0 nm, 96 nm, and 134 nm SiO₂ using the reflector "Nano Ag / D Ag" scheme on the rear. The small current increase for thick SiO₂ comes from the marginally enhanced optical properties due to Ag nanoparticles deposition; and the small increase for 0 nm SiO₂ is because of its degraded electrical quality cancelling out a large part of its excellent optical enhancement. Note that 34 nm is the thickness below which cell's rear surface passivation begins to apparently degrade. Hence an optimized SiO₂ thickness around 20–30 nm was found by slightly compromising the electrical quality but compensating for this by the large optical enhancement. By adding a detached Ag layer, photocurrents of cells with 8–34 nm SiO₂ were nearly doubled compared to without detached Ag layer and enhanced by 4 to 5 fold for cells with thick SiO₂ as seen in Fig.6.18.



Fig. 6.18: Current enhancement by rear reflector "SiO₂ / Nano Ag" (square) and "SiO₂ / Nano Ag / D Ag" (triangle) with different SiO₂ thicknesses at back. The enhancements for both curves were compared to cells with conventional rear reflectors "134 nm SiO₂ / Evaporated Al".

It is interesting to note that the current enhancement due to metal nanoparticles tend to decrease as the oxide layer thickness increases. This is consistent with theory that the coupling into Si reduces as the distance of the scattering plasmons increase from the substrate. The enhancements observed with the detached reflector are due to the effect of the metal reflector reducing transmission losses. The small dip at 55 nm SiO_2 on the top curve is either due to measurement error because the detached reflector does not provide a completely repeatable measurement situation, or possibly to the different air gap thicknesses in between of nano Ag and the detached reflector, which might cause variable interference effects.

Fig. 6.19 shows calculated Z factors for the cell with optimised rear SiO₂ thickness (19 nm) as well as the optimised Ag mass thickness (28 nm). As can be seen, when no back reflector was applied, the planar cell has a normalized optical path length of 2, because of the reflection for the first light path from the back surface "Si/SiO₂/Air". By adding an evaporated Al film, the Z factor was increased to around 3 as a result of the enhanced rear surface reflection. Ag nanoparticles acting as a scattering back reflector drives Z factor up to more than 14, and a further value of 18 by combining a detached Ag. This is the best Z value that has been obtained for planar cells at present. The enhancement factor from "Nano Ag / D Ag" to "Al" is around 6-fold.



Fig. 6.19: Calculated effective optical path length Z under four different rear structures, for the cell with optimised rear SiO_2 thickness (19 nm).

In this chapter, considerable efforts are made to optimise SiO_2 thickness and Ag mass thickness. The rear SiO_2 thickness discussed in this section is the most critical parameter for high efficiency solar cells incorporated scattering reflector of nano Ag, as both optical scattering effect and electrical surface passivation are heavily determined by this parameter. Ag mass thickness is also important as it is closely related to the scattering resonance behaviour of nano Ag.

Rear schemes "SiO₂ / Nano Ag" and "SiO₂ / Nano Ag / D Ag" optimised in the last two sections are already very efficient reflecting systems. To further improve solar cells rear optical response, the thickness effect of dielectric film ZnS is discussed in the next section.

6.4.3 Impact of the ZnS thickness

The thickness effect of ZnS layer coating the pre-deposited Ag nanoparticles, aimed for the maximum optical enhancement is studied optically in the section.

6.4.3.1 Sample description

ZnS layers with thicknesses varied from 0 nm to 50 nm were thermally evaporated to cover the pre-deposited Ag nanoparticles on the back of solar cells as well as microscope glasses, which were used to study the resonance position and broadening of the scattering for Ag particles covered by different ZnS thicknesses. The PERT cells

used in this section are with 28 nm Ag mass thicknesses and 34 nm rear SiO_2 thicknesses.

6.4.3.2 Results and Discussion

Fig. 6.20 shows the measured absorption of the solar cells with different ZnS thicknesses as a coating film on Ag particles. ZnS with a thickness of 30 nm results in highest absorption as shown by the top green curve. Cells with 50 nm and 16 nm ZnS perform moderate, while solar cells with 0 nm and 8 nm ZnS do not show an obvious optical improvement. However, as mentioned before, the absorption measurement is not sufficient to indicate cells optical response, since ZnS layer itself can absorb light as well. Further investigations on *EQE* and photocurrent enhancement will be helpful.



Fig. 6.20: Absorption of solar cells with the "SiO₂ / Nano Ag / ZnS" rear scheme at wavelength of 1000 nm to 1200 nm. The ZnS layer thickness is varied from 0 nm to 50 nm.

Transmission measurements of Ag particles covered by different ZnS thicknesses on microscope glasses are shown in Fig. 6.21. It is indicated that the resonance position of nano Ag covered by ZnS on glass moves towards long wavelength by increasing the ZnS layer thickness. The 50 nm thick ZnS layer results in the greatest red-shift. However this thickness doesn't lead to the highest optical absorption as shown in Fig. 6.20. This is very likely due to the reduced amount of scattering light into Si when the high refractive index ZnS layer exceeds its thickness limitation.



Fig. 6.21: Transmission measurements of Ag particles covered by different ZnS thicknesses on microscope glasses (substrates). Samples were deposited and annealed together with corresponding solar cells.

6.5 Conclusion

In this chapter, the proposed novel light trapping schemes using Ag nanoparticles have been incorporated into the rear of planar high efficiency PERT cells and compared with a conventional back Al reflector. A maximum 4.0-fold *EQE* enhancement at 1160 nm and 16% current improvement calculated from 900 nm to 1200 nm were achieved by the optimised rear reflector "19 nm SiO₂ / Nano Ag / Detached Ag" in comparison with the cell with standard rear reflector. An interesting trade-off for the rear surface passivation SiO₂ thickness of around 20-30 nm is found in this study, maximising both the optical cross section and coupling fraction of the nanoparticles, and maintaining high quality passivation. The optimum thickness of Ag island film is approximately 28 nm, much higher than used in previous studies.

Further analysis of the experimental electrical and optical data has been carried out to characterise the optical and electrical properties of the various rear light trapping schemes. The latter provides insights and pointers for further fabrication improvements. Optical quality is expressed by a quantitative optical path length factor *Z*, and electrical performance is expressed by *L*, *S* and τ_{bulk} for the novel rear light trapping schemes reported in this chapter. A 6-fold *Z* factor enhancement of the best performing Ag surface plasmons light trapping scheme is reported over the standard front-planar PERT rear. The effect of ZnS thickness is optically studied.

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Chapter 7. Rear side study of various light trapping schemes on PERT cells

As discussed in the previous chapter, rear scattering reflector by means of Ag nanoparticles brings about enhanced light trapping, which significantly exceeds the performance by the conventional "Si/SiO₂/Al" rear. To investigate the possibility for further optical improvement, a thorough experimental study of single and double layer rear reflectors, either planar or scattering; direct or detached, are reported in this chapter. The samples used in the chapter are untextured.

7.1 Sample description

The modifications of the rear of PERT cells prior to the application of various rear reflectors are similar to that outlined in section 6.2.1, where the rear passivating oxide has been thinned down, and aluminium contacting grids are deposited prior to the application of a reflector.

In this work, a reflector is defined as the rear material which effectively reflects (specularly or diffusely or both) the non-absorbed light back into the bulk Si. A single layer reflector comprises of one reflective medium while a double reflector comprises of two reflective media. Various types of reflectors investigated in the chapter are shown in Fig. 7.1 (single layer reflectors) and Fig. 7.2 (double layer reflectors).


Fig. 7.1: Schematic drawings of the studied single reflecting structures: (a) Evaporated Al (E Al) or Evaporated Ag (E Ag); (b) Ag nanoparticles (nano Ag); (c) White Paint (WP); (d) Detached Al mirror (D Al) or Detached Ag mirror (D Ag) or Detached White Paint (D WP)



Fig. 7.2: Schematic drawings of the studied double reflecting structures: (a) Nano Ag/Air/D Al or Nano Ag/Air/D Ag; (b) Nano Ag/Air/D WP; (c) Nano Ag/MgF₂/E Al or Nano Ag/MgF₂/E Ag; (d) Nano Ag/MgF₂/WP

7.1.1 Single reflecting schemes

The single layer reflectors as shown in Fig. 7.1 and listed in Table 7.1 are categorised into three general types (a): (1) Specular reflectors are the conventional evaporated metal reflectors using an Al or Ag layer as a mirror (specular reflection) whereby the light is reflected at the same angle as incident light; (2) Scattering or diffuse reflectors can consist of Ag nanoparticles or commercial white paint. In the case of nano Ag, a mass thickness of 28 nm is used as the precursor layer for the Ag nanoparticles. This mass thickness has been found to give the best results as reported in Chapter 6. In the case of a white paint reflector, rutile titanium dioxide pigments are directly brushed onto the rear of solar cells [1]. The third type of single reflector uses a detached

reflecting device that does not make physical contact to the silicon cell. Two different thicknesses for the passivating SiO_2 are used: 55 nm and 96 nm.

Single Rear Reflectors					
Planar	Evaporated Al (E Al)				
	Evaporated Ag (E Ag)				
Scattering	Ag nanoparticles (nano Ag)				
	White Paint (WP)				
	Detached Al mirror (D Al)				
Detached	Detached Ag mirror (D Ag)				
	Detached White Paint (D WP)				

Table 7.1: Variations of single-layer rear reflectors.

7.1.2 Double reflecting schemes

To capitalize on the benefits brought about by the nano Ag reflector, improved double layer reflectors are investigated as shown in Fig. 7.2 and listed in Table 7.2. This additional reflector is introduced to eliminate the plasmon-induced light scattering away from the Si layer and light escaping through gaps between the silver nanoparticles, such that light can be redirected back into Si. The second reflector is either detached by an air gap or separated by a 500 nm MgF₂ film (its thickness is optimised in section 7.2.3). The rear passivating SiO₂ thickness in this part of the study is 19 nm as optimised in Chapter 6.

Table 7.2: Variations	of double-layer	rear reflectors.
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Double Rear Reflectors					
Ag nanoparticles / Detached Al mirror (Nano Ag / Air / D Al)					
Ag nanoparticles / Detached Ag mirror (Nano Ag / Air / D Ag)					
Ag nanoparticles / Detached White Paint (Nano Ag / Air / D WP)					
Ag nanoparticles / MgF_2 / Evaporated Al (Nano Ag / MgF_2 / E Al)					
Ag nanoparticles / MgF_2 / Evaporated Ag (Nano Ag / MgF_2 / E Ag)					
Ag nanoparticles / MgF_2 / White Paint (Nano Ag / MgF_2 / WP)					

The characterisation methods are the same as those listed in section 6.2.2, Chapter 6. Apart from those, the optical setup utilised in Chapter 4 was used to measure the angularly distributed reflection intensity for the rear scheme Si/SiO₂/metal and W-VASE was used to simulate rear reflection properties [2] of double-layer rear reflector "Nano Ag / MgF₂ / E Ag".

7.2 Results and discussion

7.2.1 Single reflector schemes

The measured *EQE* enhancement for solar cells with various single reflectors is shown in Fig. 7.3. It is calculated as:

 $EQE_{enhancement single} = \frac{EQE_{single reflector} - EQE_{without reflector}}{EQE_{without reflector}}$ (7.1)

Here "without reflector" indicates the case with only the rear Al grids.



Fig. 7.3: *EQE* enhancement by different single-layer rear reflectors over wavelength 950 nm to 1200 nm (a) Solar cell with 55 nm rear passivation film (b) Solar cell with 96 nm rear passivation film.

As indicated by both *EQE* figures in Fig. 7.3, at near band-gap wavelengths, scattering reflectors have an enormous optical advantage over the detached and planar reflectors due to their ability to enhance light trapping. Ag nanoparticles perform better than commercially available white paint, whereas the particles without a back reflector transmit light. This is remarkable which indicates the excellent broad-angle scattering by metal nanoparticles though transmission losses are associated. The poorer optical performance by white paint is possibly due to the low scattering efficiency from the pigments (compared with Ag nanoparticles) and/or the high absorption in the pigments, as seen from absorption results in Fig. 7.4. However, a white paint single layer reflector when directly applied on the rear without the use of an air gap can be a more

economical option as a scattering reflector for high efficiency commercial silicon solar cells.

There are also red-shifts in EQE enhancement peaks for the scattering reflectors, as is most prominent for the nano Ag. Scattering reflectors with relatively large scattering cross section and high radiative efficiency can potentially redshift the dipole resonance peak evident from previous studies in Chapter 6 [3]. The red-shift from about 1120 nm to around 1150 nm in Fig. 7.3 is indicative of the response of the Ag nanoparticles corresponding to 28 nm Ag mass. Further increase in particle size compromises the scattering with decrease in the EQE. There are also red-shifts in EQE enhancements by application of white paint, which is dependent on the size of its rutile titania dielectric particles [4]. Since angular scattering does not occur in planar rear reflectors, there is an absence of red-shift and a much flatter and lower EQE enhancement for these reflectors.

The evaporated metal reflectors result in lowest EQE gain at near band-gap wavelength due to the parasitic absorption in the evaporated metal (in particular for Evaporated Al, as shown in Fig. 7.4). Another reason for better performance by the detached reflectors is the additional light reflection at the air/metal and the SiO₂/air, see illustration in Fig. 7.1d. Evaporated Al and Evaporated Ag show similar optical response. This is due to the near perpendicular angle of the light striking the rear of the solar cells. The rear angularly dependent reflection measurement in Fig. 7.8 shows that, as a back reflecting mirror, the two metals have similar reflectivity for near perpendicular incident light at 1310 nm. See Chapter 4 for the details of the optical setup for the angular reflection measurement.



Fig. 7.4: Optical absorption by selected single-layer rear reflectors over the 900 nm to 1200 nm wavelength range for cells with (a) 55 nm and (b) 96 nm passivating oxide.

The optical absorption data shown in Fig. 7.4 indicates that scattering reflectors clearly show higher absorption than planar reflectors after 1000 nm wavelength due to the significantly enhanced light trapping, agreeing well with the *EQE* enhancement in Fig. 3. However, for planar reflectors, Evaporated Al brings slightly higher absorption than Evaporated Ag, opposite to the *EQE* trend, which is due to the increased parasitic absorption in the Al metal than Ag metal. The higher absorption brought by WP compared to nano Ag can also be explained by the enhanced material absorption. *EQE* value near-bandgap wavelength is hence a more accurate pointer for indicating optical property of different reflectors.

EQE enhancements after the inclusion of reflectors at 980 nm are shown in Fig. 7.5. The existence of an air gap in detached metal reflectors reduces surface recombination

and results in positive EQE enhancements. Nano Ag reflectors also result in positive EQE enhancements due to low surface coverage of nano Ag (<60%) resulting in low surface recombinations. Amongst all reflectors, nano Ag performs best due to its excellent optical response as shown by its current enhancement in Fig. 7.6.



Fig. 7.5: *EQE* enhancement for different single reflectors at 980 nm when combined with two different passivating oxide thicknesses: 55 nm and 96 nm.

The direct application of reflectors whether in the form of evaporated metal or white paints introduce surface recombination at the contacts and hence EQE degradation. Amongst these reflectors, E Ag is the worst due to (1) a more ideal metal work function of the Al [5]; (2) no strong optical advantage over Evaporated Al as discussed before and (3) absence of scattering mechanism when compared to white paint.

For cells with scattering rear reflectors responding to wavelengths > 1000 nm, thinner passivating SiO₂ results in higher *EQE* gain, see Fig. 7.3a, due to better scattering properties and coupling efficiency of nanoparticles (in the case of nano Ag reflector) or dielectric particles (in the case of WP) as they are closer to the absorbing Si layer when SiO₂ is thinner. This result agrees with the findings from an earlier study on thin-film c-Si solar cell on glass using rear nano Ag [6].

For cells with direct and detached Al and Ag reflectors responding at wavelength 1130 nm, thicker SiO_2 results in better *EQE* enhancement: 19.1% for direct reflector and 9.0% for detached reflector respectively. This is due to optical effects, in particular interference effects, rather than surface passivation by different SiO_2 thicknesses, as 96

nm is closer to the quarter wave dielectric thickness than 55 nm SiO_2 (200 nm SiO_2 is optimum for constructive interference at wavelength 1200 nm) [7].

At λ =980 nm where electrical performance of the rear becomes the determining factor for the *EQE* response, cells with nano Ag perform better using the thicker oxide of 96 nm SiO₂ attributed to better surface passivation. The short circuit current enhancements over the 900 nm – 1200 nm range by various reflectors are shown in Fig. 7.6 to evaluate the overall *EQE* effects on solar cell performance. Note that detached and scattering reflectors perform better when combined with thinner passivating SiO₂ suggesting optical enhancements brought about by these reflector-oxide combinations outweigh the reduced surface passivations from thinner oxides. On the other hand, surface recombination dominates the electrical performances of the evaporated metal reflectors without the use of air gap. Hence the use of thicker passivating oxide is desirable for the evaporated metal reflectors.



Fig. 7.6: Current enhancement calculated from 900 nm to 1200 nm for solar cell with various single layer reflectors and two different passivating oxide thicknesses: 55 nm and 96 nm.

In light of the benefits brought about by the nano Ag reflector (17% current enhancement, see Fig. 7.6), improved double layer reflectors are developed and studied with the aim of reflecting back light forward scattered or escaping through gaps between the silver nanoparticles. This type of double-layer reflectors has shown current advantage on thin film solar cells [8] in the past, by using a combination of Ag

nanoparticles and a binder-free titania coating. In this study, a different 2^{nd} reflector is used to be more compatible with wafer based solar cell fabrication.

7.2.2 Double reflector schemes

In this part of the work, *EQE* enhancements by various double layer reflectors (shown in Fig. 7.2 and listed in Table 7.2) over the single nano Ag reflector are calculated:

$$EQE_{enhancement double} = \frac{EQE_{double layer reflector} - EQE_{single nano Ag reflector}}{EQE_{single nano Ag reflector}}$$
(7.2)

The two layer reflectors either have an air gap or MgF₂ sandwiched in between. The benefits of using a dielectric layer include 1) better adhesion and better protection of the metal nanoparticles that would otherwise be easily removed during handling and in between processes; and 2) isolating the first layer nano Ag reflector from the second scattering or reflecting layers that could potentially interfere with the scattering properties of the first layer. The choice of MgF₂ follows from its relatively low refractive index (n_{MgF2} =1.37 as opposed to n_{SiO2} =1.53 and $n_{SiNx} \approx 2.0$ at 1200 nm) minimising the undesirable forward scattering (whereby some light is scattered into the dielectric layer rather than into the silicon cell when an above unity refractive index material is used as an over-coating for the nanoparticles [9]). Other practical considerations involved in selecting MgF₂ include ease of deposition and its established use as an anti-reflection layer in high efficiency solar devices [10].

Note that in this part of the work, for cells with the second reflector detached via an air gap, only 0.02% of the cell's rear is contacted via the structure Si/Al. The rest of the rear is not contacted though some areas resemble the structure Si/nano Ag (0.14%) and some is in the form of Si / SiO₂ (99.84%).

For cells with the second reflector separated via an MgF₂ layer, evaporated Al or evaporated Ag or brushed white paint is directly applied and therefore make physical contact to the MgF₂ layer. Again 0.02% of the rear is contacted via Si/Al. In addition, 0.14% of the rear is contacted via the structure Si/nano Ag/MgF₂/E Al or Si/nano

Ag/MgF₂/E Ag. It is likely that there exists some leakage in the MgF₂, enough to result in recombination losses via these contacts as observed by the poorer infrared responses, see solid lines Fig. 7.7. To avoid such losses in future devices to maximise benefits brought about by these reflectors, an improved rear contact design will be required.

Fig. 7.7 shows the *EQE* enhancement brought about by double layer reflectors compared to single layer nano Ag reflectors. Double layer reflectors detached by an air gap generally perform better than those separated by MgF_2 at near band-gap wavelengths. This is due to the reduced forward scattering by the Ag nanoparticles into the air gap. As discussed before, when MgF_2 is used as an over-coating film for the nanoparticles, a larger fraction of light is scattered into the dielectric layer rather than into the silicon cell [9]. The high light absorption by the rough surfaces of the second reflectors separated by MgF_2 also reduces the cell optical response.



Fig. 7.7: *EQE* enhancements for solar cells with various double reflectors compared to cells with single nano Ag reflector.

Amongst the MgF₂ separated double reflectors, WP as the second reflector results in the least *EQE* enhancement. This is because the key role of the second reflector is to provide high reflectivity rather than high scattering which has already been effectively fulfilled by the first reflector using nano Ag (both from Si and from the second reflector) back into silicon. Other shortcomings of using physically deposited WP compared to metals are its high material absorption (see Fig. 7.4) and its method of application which can cause mechanical damage to the underlying MgF₂ and nanoparticles. This not only reduces the cell optical response, but also degrades the electrical response due to the introduced Si/WP contact, see Fig. 7.5.

Interestingly, for both types of double reflectors, Ag is the best material for use as the second reflector. This can be explained by the better angular dependent reflectivity of Ag compared to Al as confirmed by the measured reflection as a function of incident angle for the two reflectors as shown in Fig. 7.8. This has the important implication that the incident light on the second reflector is no longer perpendicular but follows an angular distribution due to scattering from the nanoparticles. Previous simulation studies of the angular spectrum of the scattered light on a Si/air interface show that a large fraction of the forward-scattered light by metal nanoparticles falls into the angular region of 0° -30° [9]. Our measured results show an obvious drop in Al's reflectivity (by up to 14% compared to Ag) at 20°-30° incident angle. The angular reflectivity difference of the two metals can be used to explain the poorer performance by nano Ag/MgF₂/E Al compared to nano Ag/MgF₂/E Ag (see Fig. 7.7). Note the surface roughness of the evaporated metals owing to conformal deposited Ag nanoparticles may also exacerbate this difference [11, 12]. Moreover, a thinner oxide layer between the rear metal and Si as is the case in this study, could also increase the losses further to make the difference between the two metals noticeable. The higher light absorption enhancement by evaporated Al and WP than evaporated Ag as the second reflector in Fig. 7.9 is mainly caused by the material absorption rather than active Si absorption.



Fig. 7.8: Measured absolute reflection intensity of rear "Si/SiO₂/Al" and "Si/SiO₂/Ag" reflector. The incident angle inside Si material is varied from 0° to 65° . The SiO₂ thickness is 366 nm (the drop in reflection at angles below 3° is a measurement artefact).



Fig. 7.9: Optical light absorption enhancement by solar cells with various double reflectors over cells with single nano Ag reflector.

Short circuit current enhancement by various double reflectors over single nano Ag reflector is calculated over the wavelength region of 900 nm – 1200 nm as shown in Fig. 7.10. It is concluded that suitable double reflector structures are those that utilize Ag as the second reflector. Even though the results suggest the use of an air-gap gives excellent performance both optically and electrically, this may not be practical, as there maybe not sufficient protection for the Ag nanoparticles from oxidation and damage without the use of a dielectric over-coating film. This motivates an optimisation of the nano Ag/MgF₂/E Ag double reflector in the next section.



Fig. 7.10: Short circuit current enhancement over 900 nm to 1200 nm by the double layer reflectors compared to the single layer nano Ag reflecting scheme.

7.2.3 Optimum MgF₂ thickness

In this part of the work, five different thicknesses of MgF₂ layer were trialled for the nano Ag/MgF₂/E Ag double reflector. The precursor Ag film thickness is kept at 28 nm. The passivation oxide is either 8 nm or 19 nm thick. *EQE* enhancements at 1150 nm wavelength by the nano Ag/MgF₂/E Ag reflectors over the nano Ag single reflector are calculated and are shown in Fig. 7.11. Both the *EQE* enhancement and the absorption data (see Fig. 7.12) at a given wavelength are a function of MgF₂ thickness and are at their minimum when MgF₂ is around 300 nm thick.



Fig. 7.11: *EQE* enhancements at 1150 nm by the double layer reflector nano $Ag/MgF_2/E$ Ag over the single nano Ag reflector using various MgF_2 and SiO₂ thicknesses.



Fig. 7.12: Optical absorption by devices with double layer nano $Ag/MgF_2/E$ Ag reflector using various MgF_2 layer thicknesses and (a) 19 nm SiO₂; (b) 8 nm SiO₂.

W-VASE simulation is carried out to investigate the interference effect by the MgF₂ with varying thicknesses using the model shown in Fig. 7.13. Note the model does not account for Nano Ag. Fig. 7.14 shows the rear reflection (into Si) data over the wavelength range of 900 nm – 1200 nm. The use of 100 nm MgF₂ results in good reflection over the wavelength range of interest. When the MgF₂ thickness exceeds 200 nm, rear reflection decreases especially for the wavelength range 900 nm – 1050 nm. A minimum reflection occurs at 950 nm when MgF₂ thickness increases to 300 nm, after which the reflection dip is slightly red-shifted to longer wavelength. When the thickness increase and approaches a near maximum again when MgF₂ is 500 nm thick. From the simulation results, we can conclude that *EQE* enhancement is at its minimum when MgF₂ is 300 nm in Fig. 7.11 because of the destructive interference between the scattered light and back metal reflected light. Moreover, with the presence of surface plasmons at the interface, the low reflection at the Si rear surface results in decreased electric field,

which further reduces the scattering by the metal nanoparticles as the scattering is proportional to the driving field [6]. This results in less than ideal light trapping and ultimately a reduction in photocurrent.



Fig. 7.13: W-VASE simulation model used to study MgF₂ thickness effect for a double layer reflector.



Fig. 7.14: W-VASE simulated rear reflection with various MgF_2 layer thicknesses, over the wavelength range of 900 nm – 1200 nm.

This sinusoidal dependence on MgF_2 thickness indicates either thin MgF_2 (100 nm) or thick MgF_2 (500 nm) can be used for the double reflector structure. Nevertheless thickness between 400 and 500 nm will be more desirable due to its ability to provide good isolation between the two reflectors.

7.3 Conclusion

In this chapter, various types of rear reflecting schemes are successfully fabricated on the front-planar PERT solar cells and their optical and electrical effects on cell performance have been studied. As a single layer reflecting scheme, nano Ag as a scattering reflector outperforms all other single layer reflectors, giving the highest optical improvement and the least electrical degradations. A maximum current enhancement of 17% (calculated from 900 nm to 1200 nm) is achieved compared to solar cell without a reflector. Commercially available white paint can be considered due to its cost effectiveness. Detached planar reflectors are found to be both optically and electrically superior to the undetached metal reflectors.

For the study of double reflecting layer schemes using the optimized nano Ag as the first reflecting layer, the second reflecting layer of Ag separated via MgF_2 is shown to be the most promising candidate due to the excellent angular broadband reflectivity provided by the second Ag layer. The MgF_2 serves well as over-coating layer to the nanoparticles and performs best with minimum undesirable interference effects when its thickness is in the range of 400 nm – 500 nm.

The optimized Ag nanoparticles/MgF₂/E Ag double layer reflector achieves a total current enhancement of 24.1% over the 900 nm – 1200 nm wavelength range, compared to solar cell without a reflector. This is a promising technology that further improves light trapping for high performance cells and for cells using thin substrates.

References

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Chapter 8. Conclusion

This chapter concludes the critical findings and original contributions of the present study, and also gives recommendations for future research.

8.1 Discussion

8.1.1 Successful characterisation of light trapping behaviour

The light trapping behaviour enabled by various types of front surface textures has been characterised by an appropriate two dimensional reflected light distribution measurement set up. For textured surfaces with regular arrays, such as inverted pyramids, the measured reflected light distribution can be described by geometrical optics theory categorised into three groups corresponding to major optical paths A, B and C, using the nomenclature proposed by Baker-Finch and McIntosh [1]. The measured reflection angles are somewhat smaller than those predicted by numerical ray tracing, explained by decreased slopes of the pyramids from the acidic etching steps that were found necessary for implementing well-formed features experimentally. The physical characterisations of these features were confirmed by the FIB cross-sectional imaging. The reflection patterns for random upright pyramids are found to be a function of the size, shape and distribution of the pyramids. Their measured angular distributions are very different from the ray-traced predictions. Instead of the expected distinct light reflection angles, the experimental results in this study showed angularly continuous light distributions with higher peak reflection weighting for larger sized pyramids. The impact of various encapsulant indices applied on various textured surfaces on light trapping was discussed. For random textures, a conventional encapsulant with a refractive index, n_{enc} , of 1.5 resulted in only a fraction of total internal reflection, f_{tir} , of 5%. An increase in the value of n_{enc} to 1.6 increased the f_{tir} to 10% for random textures.

Furthermore, the measured reflection pattern revealed the angular accuracy of the wafer cut (crystal orientation) and allowed estimation of the pyramid's wall slope.

The light trapping behaviour of dielectrically displaced planar reflectors has been characterised by another novel angularly dependent rear reflection measurement technique which enabled the accurate measurement of high resolution angular reflection characteristics over a broad angular range. The measured results clearly showed that Ag yields higher reflection than Al over an angular range of $18^{\circ}-28^{\circ}$. Results also show the excitation of surface plasmons at the metal-insulator interface caused strong light absorption losses. Simulation indicates that the reflectivity of the reflector using SiN_x only exceeds those using SiO₂ over the $22^{\circ}-26^{\circ}$ angular range. An increase in the SiN_x index further weakens its performance. Hence for solar cells textured by random pyramids, unless a significant part of the deflected light falls into the $22^{\circ}-26^{\circ}$ angular region, SiO₂ is still considered to be optically superior to SiN_x. Finally, a weighted factor R_{wb} was introduced to quantify the angular broad band reflection for Lambertian-distributed incoming light. If SiO₂ is to be used for displaced metal reflectors, a thickness close to 320 nm yields maximum R_{wb} . If SiN_x is used, dielectric thickness corresponding to either of the first two R_{wb} maxima at ¹/₄ or ³/₄ λ can be considered.

8.1.2 Successful application of various types of rear reflectors

Novel planar rear reflectors formed by triple dielectric stacks with high to low refractive index modulations and a metal mirror have been fabricated to improve rear internal reflection of solar cells. For light of normal incidence, optical measurements showed a maximum absolute reflection increase of 2.5% at 1200 nm and a relative *IQE* improvement of 30% was estimated at 1150 nm over those of the conventional rear reflector with $\frac{1}{4} \lambda$ thick single-layer dielectric. The triple dielectric stacks were subsequently re-optimised considering the angularly broad band light distributions. *IQE* enhancement of near 20% was achieved at 1190 nm from calculation for light under a Lambertian distribution. The minority carrier lifetime of samples passivated by the triple-layer dielectric stacks provided comparable surface passivation as obtained from conventional Al-annealing technique.

Novel scattering rear reflectors using Ag nanoparticles have been applied to the rear of the PERT front-planar cells for the very first time. A maximum 4.0–fold *EQE* enhancement at 1160 nm and 16% current improvement calculated from 900 nm to 1200 nm was obtained by the optimised rear reflector in comparison to a cell with a standard dielectrically displaced reflector. The rear surface passivation SiO₂ thickness was found to be optimal at approximately 20–30 nm. There appeared to be a trade-off between maximising both the optical cross section and coupling fraction of the nanoparticles and maintaining high quality passivation. The thickness of the Ag film that was evaporated as a precursor was optimized at approximately 28 nm. A further analysis of the optical and electrical properties of the various rear light trapping schemes and further fabrication improvements of this rear structure in Chapter 6 produced a 6-fold optical path length factor enhancement of the best performing Ag surface plasmons light trapping scheme on a standard front-planar PERT cell.

An iteration of applying, measuring and analysing (optically and electrically) various types and combinations of rear reflectors, using either planar or scattering; direct or detached; single layer or double layer on the rear of the PERT front-planar solar cells produced some major findings. Firstly, the scattering Ag nanoparticles as a single layer reflecting scheme outperform all other single layer reflectors, giving the highest optical improvement and the least electrical degradations. Secondly, commercially available white paint though does not perform as well optically, can be considered due to its cost effectiveness. Thirdly, detached planar reflectors have been found to be both optically and electrically superior to the undetached metal reflectors. Finally double layer reflecting scheme using SiO₂ / Ag nanoparticles / MgF₂ / Evaporated Ag yielded the most promising result. This was due to the excellent angularly broad band reflectivity boosted by the second Ag layer and the practicality of using MgF₂ over air. An MgF₂ thickness of 400 nm to 500 nm was found to provide minimum undesirable interference effects resulting in a final current enhancement of 24.1% over the 900 nm to 1200 nm wavelength range.

8.2 Original contributions of the thesis

The present study has offered a number of original contributions. These include:

- Characterisation of 2-D reflected light distributions from various front textures using an appropriate optical setup.
- Correlation of the measured reflection patterns to the surface morphologies of both regular inverted and random upright pyramids.
- Investigation of the impact of the encapsulant's index on the amount of total internal reflection for various types of front textures.
- Investigation and characterisation of the angularly broad band reflection of dielectrically displaced reflectors in silicon solar cells via a novel self-developed optical setup including the development of hemispherical silicon as the test substrate for reflector deposition to enable illumination and detection of back reflector properties without refraction at the Si-air interface.
- Fabrication and reflection measurements of novel planar reflectors consisting of triple high-low refractive index dielectric stacks and a back metal layer, with their optical and electrical impacts being extensively examined.
- Application of Ag nanoparticles as scattering rear structures on the rear of PERT front-planar silicon solar cells to create surface plasmons for light trapping enhancement and optimisation of Ag precursor thickness and rear SiO₂ thickness for solar cells with Ag nanoparticles as the rear reflector.
- Separation and quantification of the electrical and optical properties of novel rear light trapping designs by analysing the measured spectral response and optical absorption data.
- Fabrication and comparison of various types and combinations of rear reflectors, either planar or scattering, direct or detached, single-layer or double-layer on PERT front-planar silicon solar cells by examining their optical and electrical effects including the optimisation of the MgF₂ spacing layer thickness inserted between of the two reflecting layers for a double-layer reflector.

8.3 Recommendations for future research

Further research on light trapping characterisation within silicon solar cells would be beneficial in the following areas:

- Although the impact of various encapsulant indices on the amount of total internal reflection at the air-glass interface for various textured surfaces has been discussed in Chapter 3, their effects on the reflection of front incoming light have not been taken into consideration. Future studies should be conducted in order to determine the most appropriate encapsulant index that accounts for both effects for each texture.
- 2. The optical setup measuring reflected light distribution in Fig. 3.4 can be simplified to allow fast, perhaps in-line, measurements for the fine tuning of the industrial surface texturing etching processes, see Fig. 8.1.



Fig. 8.1 Suggested improvement to the optical setup used for front side characterisation.

3. The characterisation study of angularly dependent rear internal reflection should be extended from conventional planar reflectors (formed by one dielectric layer and a metal mirror) to (i) double or triple dielectric stacks in combination with a metal film and (ii) scattering reflectors such as Ag nanoparticles and white paint using silicon hemispheres as test substrates. 4. A characterisation study of the propagation path for light inside silicon after being deflected by various textured front surfaces should be carried out. Attaching the textured wafer to the flat side of hemispherical silicon is recommended. A material with the proper refractive index will be needed to fill the air gap between silicon hemisphere and silicon wafer.

In addition, it is recommended that future work on the application of light trapping schemes for silicon solar cells be conducted in the following areas:

- 1. Investigate further possible optical path length enhancement by Ag nanoparticles on the rear of very thin wafer based solar cells.
- Develop method of reducing the surface roughness of the island film or planarizating dielectric spacing layer in double layer reflecting scheme so to reduce surface roughness and parasitic light absorption of the 2nd Ag reflecting layer.
- 3. The application of the optimised rear scattering reflectors on front textured solar cells (only front planar cells used in this thesis). Such application should capitalise on the broadband light trapping advantages brought about by the use of surface plasmons. This may provide work to optimise the front and rear light trapping schemes independently.
- 4. The optimisation of the PECVD depositions for the layers in the dielectric stacks to achieve optical gain without compromising surface recombination losses.

References

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APPENDIX A. Measured and calculated reflection angles θ_o for inverted pyramids

Table A.1 shows the measured $\theta_{o_a,b,c}$ for ray A, B and C from Fig. 3.6a-c. Please note that the measured reflection angles after the final process step (2nd acidic etch) match the measured values from Table 3.2. Table A.2 lists the calculated $\theta_{o_a,b,c}$ by using the measured slopes Φ from Table 3.3 and the equations from Table 3.1. The values are calculated for each of the four characterized facets along the +*x*, -*x*, +*y*, and -*y* axes. The calculated angles $\theta_{o_a,b,c}$ after the alkaline etch are closer to the theoretical values in Table 3.2 than the measured ones in Table A.1. The measured results are likely affected by the geometrical diversities of the real pyramids.

Table A.1: Measured reflection angle $\theta_{o_a,b,c}$ of ray A, B and C, and off-axis angles δ_{o_c} of ray C, after each processing step. Averages of the two reflection angles and two off-axis angles for ray C in each quadrant are taken.

		Me	Measured δ_{o_c} (deg)			
		Ray A	Ray B	Ray C		Ray C
Alkaline etch	+x axis	30.6	N/A	1 st quadrant	29.2	28.9
	- <i>x</i> axis	35.4	N/A	2 nd quadrant	31.7	31.6
	+y axis	33.0	N/A	3 rd quadrant	31.4	34.0
	-y axis	33.0	N/A	4 th quadrant	30.2	26.6
1 st acidic etch	+x axis	27.0	N/A	1 st quadrant	24.1	N/A
	<i>-x</i> axis	31.5	N/A	2 nd quadrant	26.3	N/A
	+y axis	30.0	N/A	3 rd quadrant	25.4	N/A
	-y axis	30.0	N/A	4 th quadrant	25.5	N/A
2 nd acidic etch	+x axis	24.6	17.0	1 st quadrant	22.7	N/A
	- <i>x</i> axis	29.0	20.0	2 nd quadrant	22.9	N/A
	+y axis	27.3	19.0	3 rd quadrant	24.2	N/A
	-y axis	27.0	19.0	4 th quadrant	21.9	N/A

		Cal	Calculated δ_{o_c} (deg)			
		Ray A	Ray B	Ray C		Ray C
Alkaline etch	+x axis	38.2	32.7	1 st quadrant	30.9	37.0
	- <i>x</i> axis	43.2	25.1	2 nd quadrant	35.5	36.2
	+y axis	38.3	32.6	3 rd quadrant	30.1	37.0
	-y axis	41.1	28.3	4 th quadrant	33.6	36.5
1 st acidic etch	+x axis	30.3	N/A	1 st quadrant	23.9	38.4
	- <i>x</i> axis	36.5	35.2	2 nd quadrant	29.4	37.3
	+y axis	31.4	N/A	3 rd quadrant	24.9	38.2
	-y axis	34.3	N/A	4 th quadrant	27.4	37.7
2 nd acidic etch	+x axis	25.8	N/A	1 st quadrant	20.1	39.3
	- <i>x</i> axis	32.8	N/A	2 nd quadrant	26.1	37.9
	+y axis	28.0	N/A	3 rd quadrant	22.0	38.8
	-y axis	30.0	N/A	4 th quadrant	23.7	38.5

Table A.2: Calculated reflection angle $\theta_{o_a,b,c}$ of ray A, B and C, and off-axis angles δ_{o_c} of ray C, based on the measured wall slopes Φ in Table 3.3.

APPENDIX B. Total internal reflection at air-glass interface of encapsulated solar cells

Snell's law is used to define the relationship of angles θ_o at the encapsulant-glass and the glass-air interface, visualised in Fig. B.1.



Fig. B.1: Light travelling-path at module's front following Snell's law.

$$n_{enc}\sin(\theta_{enc}) = n_{glass}\sin(\theta_{glass})$$
(B.1.a)

$$n_{glass}\sin(\theta_{glass}) = n_{air}\sin(\theta_{air})$$
(B.1.b)

Each interface has its critical angles θ_{glass_cri} and θ_{enc_cri} at which total internal reflection will occur. The first critical angle in the encapsulant $\theta_{enc_cri_1}$ is for the encapsulant-glass interface, while the second one is in glass θ_{glass_cri} for the glass-air interface:

$$(\text{Eq.B.1.a}) \xrightarrow{\theta_{glass}=90^{\circ}} \theta_{enc_cri_1} = \arcsin\left(\frac{n_{glass}}{n_{enc}}\right)$$
(B.2)
$$(\text{Eq.B.1.b}) \xrightarrow{\theta_{air}=90^{\circ}} \theta_{glass_cri} = \arcsin\left(\frac{n_{air}}{n_{glass}}\right)$$
(B.3.a)

Eq.B.3.a can be rewritten with Eq.B.1.a as a second critical angle in the encapsulant $\theta_{enc_cri_2}$:

$$n_{enc} \sin(\theta_{enc_cri_2}) = n_{glass} \sin(\theta_{glass_cri})$$

$$\rightarrow \sin(\theta_{enc_cri_2}) = \frac{n_{glass}}{n_{enc}} \sin\left(\arcsin\left(\frac{n_{air}}{n_{glass}}\right)\right) = \frac{n_{glass}}{n_{enc}} \frac{n_{air}}{n_{glass}} = \frac{n_{air}}{n_{enc}} (B.3.b)$$

$$\rightarrow \boxed{\theta_{enc_cri_2} = \arcsin\left(\frac{n_{air}}{n_{enc}}\right)}$$
(B.3.c)

By considering the refractive index for air $n_{air} = 1.0$ and glass $n_{glass} = 1.5$ it turns out that the critical angle $\theta_{enc_cri_2}$ (Eq.B.3.c) is always smaller than the first one $\theta_{enc_cri_1}$ (Eq.B.2). $\theta_{enc_cri_2}$ is therefore the exclusive dominant angle. Therefore in section 3.5, $\theta_{enc_cri_2}$ is referred as the critical angle θ_{enc_cri} , the index "2" is neglected.

$$n_{air} < n_{glass} \xrightarrow{Eq.B2, Eq.B3.c} \theta_{enc_cri_2} < \theta_{enc_cri_1} \rightarrow \theta_{enc_cri_2} \quad (B.4)$$

APPENDIX C. Characterised reflection patterns from other surface textures



Fig. C.1: (a) SEM image of a grooved silicon surface. (b) The corresponding reflected light distribution.



(a)

(b)

Fig. C.2: (a) SEM image of a randomly textured silicon surface (b) The corresponding reflected light distribution.



Fig. C.3: (a) SEM image of a randomly textured silicon surface (b) The corresponding reflected light distribution.

APPENDIX D. Detailed schematics of the rear angular reflection setup

The detailed schematic drawings of the experimental setup used for rear angular reflection measurement in Chapter 3 are shown in Fig. D.1 and D.2 from vertical and horizontal view respectively.



Fig. D.1: Vertical view of the experimental setup [1]. (a) laser source, (b) beam expander, (d) iris, (e) lens to compensate the hemispheres focus, (g) hemisphere, (i) lens to compensate the hemispheres focus, (j) iris and (k) detector. Rotation stages are in purple. In green colours are various micrometer alignment stages for tilt and linear translations.



Fig. D.2: Horizontal view of the experimental setup [1]. (a) laser source, (b) beam expander, (c) optional linear polarizer, (d) iris, (e) lens to compensate the hemispheres focus, (g) hemisphere, (h) measurement point and common rotation axis, (i) lens to compensate the hemispheres focus, (j) iris and (k) detector.

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APPENDIX E. Characterised $R_b(\theta_i)$ of the Si/SiO₂/air rear scheme



Fig. E.1: Experimentally measured angularly dependent reflection of the Si/SiO₂/air scheme at different SiO₂ thicknesses by using the optical setup as shown in Fig. 4.3. The flat curves after 17° indicate the condition of total internal reflection.

APPENDIX F. Conditions for zero reflection from solar cell rear

This part discusses the effect of the dielectric and metal type on the minimum reflection intensity for a single film system resembling the solar cell rear with dielectrically displaced reflector. This system also resembles an Otto configuration which can excite a SPP as shown in Fig. 4.1.

The reflection amplitude from a single film system is given by [1]:

$$R = \frac{r_1 + r_2 e^{-2i\delta_1}}{1 + r_1 r_2 e^{-2i\delta_1}}$$
(F.1)

Where r_1 and r_2 are the Fresnel coefficients under s and p polarisations given by:

$$r_{1s} = \frac{n_0 \cos \varphi_0 - n_1 \cos \varphi_1}{n_0 \cos \varphi_0 + n_1 \cos \varphi_1}$$
(F.2)

$$r_{1p} = \frac{n_0 \cos \varphi_1 - n_1 \cos \varphi_0}{n_0 \cos \varphi_1 + n_1 \cos \varphi_0}$$
(F.3)

with similar expressions for r_{2s} and r_{2p} . φ_0 is the angle of incidence in the initial medium (Si in this study), and φ_1 is the angle of light in the film (dielectric in the study), given by Snell's law. n_0 and n_1 are the refractive index of the Si and the dielectric respectively.

 δ_l is a generally complex phase/attenuation factor given by:

$$\delta_1 = \frac{2\pi d}{\lambda} n_1 \cos \varphi_1 \tag{F.4}$$

Where *d* is the film thickness and λ is the wavelength.

For zero reflection condition under *p*-polarised light [2]:

$$r_{1p} = -r_{2p}e^{-2i\delta_1}$$
(F.5)

$$\frac{n_0 \cos \varphi_1 - n_1 \cos \varphi_0}{n_0 \cos \varphi_1 + n_1 \cos \varphi_0} = -\frac{n_1 \cos \varphi_2 - n_2 \cos \varphi_1}{n_1 \cos \varphi_2 + n_2 \cos \varphi_1} e^{-2i\delta_1}$$
(F.6)

With permittivities $\varepsilon_i = n_i^2$ and $k_0 = 2\pi / \lambda$, Eqn. F.6 can be rearranged to be [2]:

$$\left(\frac{\varepsilon_1\gamma_0}{\varepsilon_0\gamma_1} - 1\right)\left(\frac{\varepsilon_1\gamma_2}{\varepsilon_2\gamma_1} + 1\right) = \left(\frac{\varepsilon_1\gamma_0}{\varepsilon_0\gamma_1} + 1\right)\left(\frac{\varepsilon_1\gamma_2}{\varepsilon_2\gamma_1} - 1\right)e^{-2ik_0\gamma_1 d}$$
(F.7)

Where
$$\gamma_i = n_i \cos \varphi_i = \sqrt{n_i^2 - n_0^2 \sin^2 \varphi_0} = \sqrt{\varepsilon_i - \varepsilon_0 \sin^2 \varphi_0}$$
 (F.8)

If a solution exists for Eqn. F.7, the film thickness *d* would relate to the permittivities of both the dielectric and the metal. This explains the shifting of the minimum $R_b(\theta_r)$ in Fig. 4.11 when the dielectric index or the metal type is changed. However, the condition for this solution limits the range of the permittivities, therefore zero (or near zero) reflection does not exist for each dielectric index or each metal type, see *p*-polarised curve with SiN_x (n=2.0) in Fig. 4.11b.

References

[1] O.S. Heaven, Optical Properties of Thin Solid Films, Butterworths Scientific Publications, London, 1954, pp. 57.

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APPENDIX G. Deposition recipes of the rear dielectric layers

Table G.1: Deposition recipes of PECVD SiN_x films and the resulting film thickness & refractive index. W-VASE software was used to fit the film parameters based on the measured reflectance/transmittance data. The highlighted rows are those of the desirable recipes used in the final dielectric stack depositions in Chapter 5. A 24 hours annealing at 600°C was carried out for sample G1-14 to achieve a shrunk dense film with an index of 3.2.

	PECVD recipe								Deposited dielectric				
Sample ID	Power	Temp. (°C)	Duration (s)	Pressure	SiH ₄ GF	NH ₃ GF	Ar	N ₂ O GF	RF Vol.	RF power	Fitted t (nm)	Fitted n	Film property
_							GF						
G1-1	650	400	155	0.3	26	34	40	1	150	300	151	2.06	Good
G1-2	650	400	310	0.3	26	34	40	1	150	300	282	2.02	Good
G1-3	650	400	111	0.3	42	27	40	1	150	300	105	2.59	Good
G1-4	650	400	222	0.3	42	27	40	1	150	300	220	2.62	Moderate
G1-5	650	400	86	0.3	62	6	40	1	150	300	80	2.99	Moderate
G1-6	650	400	172	0.3	62	6	40	1	150	300	NA	NA	Powdery
G1-7	650	400	86	0.3	70	0	40	1	150	300	113	2.57	Good
G1-8	650	400	172	0.3	70	0	40	1	150	300	211	2.89	Good
G1-9	650	200	90	0.2	30	0	30	0	150	300	60	2.94	Good
G1-10	650	400	90	0.2	30	0	30	0	150	300	105	3.01	Non-uniform
G1-11	650	200	90	0.4	30	0	30	0	150	300	NA	NA	Powdery
G1-12	650	200	90	0.2	30	0	30	0	150	400	NA	~2.72	Powdery
G1-13	650	200	83	0.1	30	0	30	0	150	300	103	2.95	Good
G1-14 (Anl.)	650	200	83	0.1	30	0	30	0	150	300	95	3.20	Good
G1-18	650	400	111	0.3	38	30	40	1	150	300	120	2.35	Powdery
G1-19	650	400	111	0.2	38	30	40	1	150	300	123	2.53	Good
G1-20	650	200	150	0.2	30	0	30	0	150	300	127	2.53	Good
G1-21	650	300	85	0.1	30	0	30	0	150	300	100	3.00	Good

Note: Ar gas is used to stabilize plasma during deposition. It has been found that both high RF power and high gas pressure result a powdery film. This is because when more gases enter the chamber, the gas reaction occurs overheard the sample surface instead on its surface. This unstable reaction results in powdery grains falling onto the film surface.

	PECVD recipe										Deposited dielectric		
Sample ID	Power	Temp. (°C)	Duration (s)	Pressure	SiH ₄ GF	NH ₃ GF	Ar	N ₂ O GF	RF Vol.	RF power	Meas. t (nm)	Meas. n	Film property
							GF						
Y-1	650	400	220	0.3	20	0	40	40	150	300	NA	NA	Non-uniform
Y-2	650	400	250	0.3	20	0	50	50	150	300	113	1.51	Uniform
Y-3	650	400	240	0.1	30	0	90	90	150	300	NA	NA	Non-uniform
Y-4	650	400	500	0.3	20	0	55	55	150	300	NA	NA	Non-uniform
Y-5	650	400	400	0.3	20	0	50	50	150	300	175-327	1.3-1.5	Non-uniform
Y-6	650	400	250	0.1	20	0	50	50	150	300	145	1.47	Uniform
D-1	650	400	320	0.1	20	0	50	50	150	300	203	1.44	Uniform
D-2	650	400	500	0.1	20	0	50	50	150	300	300	1.52	Non-uniform
D-3	650	400	250	0.1	20	0	50	50	150	300	149	1.46	Uniform
D-4	650	400	500	0.1	20	0	50	50	150	300	300	1.50	Non-uniform
D-5	650	400	750	0.1	20	0	50	50	150	300	450	1.45	Non-uniform

Table G.2: Deposition recipes of PECVD SiO_2 films and the resulting film thickness & refractive index characterised by an ellipsometer. The highlighted row corresponds to the satisfactory film recipe that was used in the final dielectric stack deposition in Chapter 5.

The uniformity of PECVD SiO_2 thickness is affected by the gas pressure and the deposition duration. It has been found that low gas pressure was benefit for the film uniformity. Fig.G.1 demonstrates the relationship between the deposition duration and the a) middle area thickness; b) middle area refractive index n; c) thickness difference between middle and edge area of one sample.



Fig. G.1: Relationship between SiO_2 deposition time and the resulting (a) Middle area thickness; (b) Middle area index; (c) Thickness difference between the middle and edge area of one sample.

Sample ID	Temp. (°C)	Duration (mins)	Final thickness (nm)		
T-1	1050	108	130		
T-2	1000	50	50		
	1050	180	210		
	1050	81	106		
T-3	1050	105	180		
	1050	45	202		
	1000	50	50		
T-4	1050	90	133		
	1050	95	200		

Table G.3: Deposition recipes of thermal grown SiO₂. The highlighted rows correspond to the desirable recipes used in Chapter 5.

APPENDIX H. List of abbreviations for optical parameters

Angles:

 θ_o : Angle of reflected light (outside silicon) from textured front surfaces

- θ_i : Angle of deflected light (inside silicon) from textured front surfaces
- δ_o : Light off-axis angle (outside silicon) from textured front surfaces

 θ_{enc} : Angle of light propagating in the encapsulant

- φ : Angle of light propagating in any medium of a three layer system
- θ_r : Resonance angle of the propagating SPP at the rear metal interface of a solar cell
- θ_c : Critical angle of the rear Si/SiO₂ interface of a solar cell
- Φ : The slope of the pyramid facets

Reflections:

 R_o : Reflection weightings of the reflected light from textured front surfaces

 R_{ow} : Reflection weightings over an angular range for randomly textured front surfaces

 R_b : Reflected light intensities from the back surface of a solar cell

 R_{wb} : Weighted reflected light intensities from the back surface of a solar cell for light under Lambertian distribution

 R_t : Measured total reflected light intensities from a solar cell

 f_{tir} : The fraction of total internal reflection at air-glass interface of an incapsulanted solar cell

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