Light trapping in solar cells using resonant nanostructures
Spinelli, P.

Citation for published version (APA):
Spinelli, P. (2013). Light trapping in solar cells using resonant nanostructures

General rights
It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations
If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: http://uba.uva.nl/en/contact, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.
Introduction

1.1 Photovoltaics

Photovoltaics (PV) is the physical process of conversion of solar energy into electricity, by using semiconductor materials. The term photovoltaics is derived from the combination of the Greek word φῶς (phōs) meaning “light” and the unit for electrical voltage, volt, named after the Italian physicist Alessandro Volta (1745-1827). Photovoltaic power generation typically uses solar modules, which are made of a number of interconnected solar cells. The physics and basic operation of a solar cell device is described in many academic textbooks [1] [3], and we will not repeat this here. However, the importance of PV as a source of renewable energy, and its future perspectives are described first.

The average world power consumption in 2010 was 17 TW, and according to the International Energy Agency (IEA) this number is expected to double by 2050 [4]. In order to meet the increasing energy demand, we cannot rely on conventional fossil fuel sources (oil, carbon and gas) as their resources are limited and energy generation from these sources creates environmental pollution. Ideally, renewable and clean (i.e. CO₂-free) sources of energy must be used. Among these, PV has a great potential due to the virtually unlimited resources. The average amount of energy the Earth receives from the Sun is over 1000 times the total world consumption today. Even taking into account limited photovoltaic conversion efficiency of solar cells and the fact that only a small fraction of the surface of the Earth can be covered with solar panels, PV has the potential to become a major source of energy for our society.

An important reason that photovoltaics has not yet become a major source of energy so far is costs: in the past the cost of generating one kilowatt-hour of electric-
ity with solar panels was much higher than the cost of generating the same amount from fossil fuel sources or using nuclear energy. In the past few years however the cost of solar power has strongly decreased. At the same time, in the past decade the cost of “conventional” energy (while fluctuating in time) has strongly increased. In January 2013, the sales price of a crystalline Si solar module had dropped to only 0.69 $/Wp [5].

Today, about 0.1% of the total energy produced in the world is generated by photovoltaic systems [6]. While this is still a small number, the growth over the last ten years has been exponential and the share of solar energy in the total energy market is bound to increase rapidly. Figure 1.1 taken from the PV Status Report published by the Joint Research Center (JRC) [7], shows the cumulative installation of PV systems for the period 2000-2013. As can be seen, the installation of solar modules has soared over the last ten years, despite the world financial crisis that started in 2009. The total cumulative power installed up to 2012 was 100 GWp, with more than 70 GWp installed in Europe, with Germany and Italy the leaders.

The spectacular growth shown in Fig. 1.1 is due to many factors such as the reduced costs of solar modules, technological improvements that have lead to higher solar cell efficiencies and in some cases the introduction of government subsidies. Despite the impressive growth of PV installations worldwide, further advances in technology are required for PV to breakthrough as one of the major energy sources for our society.

Figure 1.1: Cumulative solar module installation (MWp) for the period 2000-2013 (source: JRC PV Status Report 2013) [7].
1.2 Silicon solar cells

Silicon is the most widely used material for solar cells. Around 85% of the installed solar modules are based on Si [7]. Typical efficiencies of crystalline Si solar cell modules that are on the market today are between 15% and 21%. The world record efficiency for a crystalline Si solar cell is 25.0%, realized by the group of Green at the University of New South Wales (UNSW) in 1999, on a 4 cm$^2$ area cell [8]. This record still holds today.

A major factor limiting the efficiency of Si solar cells is carrier thermalization [1]. When a photon with energy higher than the bandgap energy is absorbed, at most an amount equal to the bandgap energy can be converted into electrical energy; the rest of the photon’s original energy is lost by the creation of phonons [9]. This “quantum defect” effect is schematically shown in Fig. 1.2(a).

Figure 1.2: (a) Spectral intensity of the AM1.5 global solar spectrum (blue) and maximum spectral intensity that can be effectively converted to electricity, after taking into account quantum defect losses (red). (b) Spectral intensity of the AM1.5 global solar spectrum (blue) and spectrum that can be effectively absorbed by a 2 µm thick Si slab, in a single pass (red) and in the 4$n^2$ limit (green). In both panels, the vertical dashed line indicates the Si bandgap wavelength (~1110 nm).

Figure 1.2(a) shows the spectral intensity of the AM1.5 global solar spectrum (blue), in the spectral range 300-1400 nm. The red line represents the spectral intensity that can be effectively converted to electricity assuming that every incident photon with an energy above the bandgap creates an electron-hole pair at an energy equal to the bandgap. As the wavelength is reduced below the bandgap, a progressively larger fraction of the incident photon energy is lost due to the quantum defect. The graph in Fig. 1.2(a) also shows a second important loss mechanism in the spectral range above the Si bandgap wavelength: photons with an energy smaller than the Si bandgap are not absorbed by the cell. The losses due to the quantum defect and above-bandgap losses can be tackled by using multi-junction cells [10, 11], which can be optically connected either in series (in a multi-layer stack) [12–14] or in parallel (with a spectrum-splitting element) [15–18]. The first concept has lead to devices with efficiencies up to 44.4% under
concentrated sunlight, but relies on expensive III-V semiconductors; the second concept is still in an early stage of development. In addition to this, so called third-generation photovoltaic concepts \cite{19,21}, such as quantum-cutting \cite{22-25}, quantum-pasting \cite{24,26}, multiple-exciton generation \cite{27,29}, hot-carrier collection \cite{30,31}, and intermediate-band photovoltaics \cite{32-34} are currently being investigated. Despite a large research effort, these third-generation concepts still await practical demonstration.

The theoretical efficiency limit for a single-junction solar cell, taking into account the quantum defect and above-bandgap photon losses, was first calculated by Shockley and Queisser in 1961 \cite{35}. In this model for a p-n junction solar cell current is collected at a voltage determined by the quasi-Fermi level splitting in the semiconductor, which in turn is determined by the carrier collection and radiative recombination rates determined by detailed-balance thermodynamic arguments. Figure 1.3 shows the Shockley-Queisser (SQ) limit as a function of the bandgap energy of the solar cell material (black line). As can be seen, efficiencies up to 33.7% can be achieved for a semiconductor with a bandgap energy of 1.34 eV. The graph also shows the world record efficiencies, as of June 2013 \cite{36}, for crystalline Si (c-Si, red dot, 25.0%), GaAs (blue, 28.8%), InP (purple, 22.1%), copper-indium-gallium-selenide (CIGS, green, 20.4%), CdTe (light blue, 19.6%) and amorphous Si (a-Si, orange, 10.1%) solar cells. All world record efficiencies are well below the SQ limit. GaAs solar cells with a record efficiency of 28.8% come closest to the SQ limit (33.0% for a bandgap of 1.43 eV).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.3.png}
\caption{Shockley-Queisser efficiency limit as a function of the bandgap energy of the solar cell material (black line). The colored dots represent the current world record efficiencies for c-Si (red), GaAs (blue), InP (purple), CuInGaSe (CIGS, green), CdTe (light blue) and a-Si (orange) solar cells \cite{36}.}
\end{figure}

For a c-Si solar cell with a bandgap of 1.12 eV the SQ limit is 33.4%. This calculation however assumes a semiconductor in the radiative recombination limit, i.e. the
1.2 Silicon solar cells

dark current of the p-n junction is not affected by non-radiative processes. In Si this limit cannot be achieved as Auger recombination, in which multiple carriers interact, is a loss mechanism that cannot be neglected. Moreover, due to the indirect bandgap, the radiative emission rate of Si is small, and competing non-radiative processes at impurities, point defects, grain boundaries and surfaces cannot be neglected.

Table 1.1 reports the short-circuit current ($J_{SC}$), open-circuit voltage ($V_{OC}$), fill factor (FF) and efficiency ($\eta$) of the best and second-best efficiency c-Si solar cells reported in the literature so far (first two rows). The short-circuit current, or the photocurrent at zero voltage, is directly related to the solar intensity spectrum, and is taken for 1-sun illumination; for Si, it is 43.8 mA/cm$^2$ assuming full absorption of the AM1.5 global solar spectrum (ASTM G173)\cite{37} up to the bandgap and 100% photon-to-electron conversion efficiency. The open-circuit voltage, i.e. the voltage without current load, is much lower than the Si bandgap and is determined by the quasi-Fermi level splitting in the solar cell, which is in turn determined by the carrier densities across the p-n junction. Non-radiative recombination thus strongly affects $V_{OC}$. The theoretical maximum of $V_{OC}$ depends on the cell thickness as thicker cells suffer from larger bulk recombination. For a 160 $\mu$m thick cell, and including Auger recombination, $V_{OC}$ for a c-Si solar cell is calculated to be 770 mV\cite{38}. The fill factor, defined as the maximum achievable power per unit area JV relative to the product $J_{SC}V_{OC}$, reflects the contribution of non-radiative recombination as well as that of series resistance in the Si wafer and the contacts and shunt resistance across the junction.

<table>
<thead>
<tr>
<th>c-Si solar cell</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>$V_{OC}$ (mV)</th>
<th>FF</th>
<th>$\eta$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>UNSW (PERL, &gt;400 $\mu$m)</td>
<td>42.7 (43.8)</td>
<td>706 (760*)</td>
<td>82.8%</td>
<td>25.0%</td>
<td>[8]</td>
</tr>
<tr>
<td>Panasonic-Sanyo (HIT, 98 $\mu$m)</td>
<td>39.5 (43.8)</td>
<td>750 (780*)</td>
<td>83.2%</td>
<td>24.7%</td>
<td>[39]</td>
</tr>
<tr>
<td>Ideal cell (160 $\mu$m)</td>
<td>43.8</td>
<td>770*</td>
<td>83.2%</td>
<td>28.1%</td>
<td></td>
</tr>
<tr>
<td>Ideal cell (10 $\mu$m)</td>
<td>43.8</td>
<td>810*</td>
<td>83.2%</td>
<td>29.5%</td>
<td>*[38]</td>
</tr>
</tbody>
</table>

Table 1.1: Short-circuit current ($J_{SC}$), open-circuit voltage ($V_{OC}$), fill factor (FF) and efficiency ($\eta$) measured for the best and second best c-Si solar cells (first and second row, respectively), and for two ideal cells with thickness 160 $\mu$m and 10 $\mu$m (third and fourth row, respectively). The calculated “ideal” $J_{SC}$ for full light absorption and “ideal” $V_{OC}$ (from Ref.\cite{38}) for each thickness are indicated between brackets.

The world record efficiency Si solar cell is a passivated-emitter-rear-locally-diffused (PERL) p-n homo-junction cell realized at UNSW\cite{8}. As can be seen, the $J_{SC}$ is close to the maximum limit, indicating that the cell shows almost perfect absorption of the solar spectrum above the bandgap. This was achieved by using an effective inverted pyramid light-trapping scheme in combination with a Si$_3$N$_4$ antireflection coating and a relatively large cell thickness (>400 $\mu$m). However, the large cell thickness resulted in enhanced bulk carrier recombination that, together...
with the highly recombination-active doped diffused emitter, limited the $V_{OC}$ to 706 mV. This yields an efficiency of 25.0%.

The second-best efficiency c-Si solar cell is a hetero-junction-with-intrinsic-thin-layer (HIT) cell, made by Panasonic-Sanyo in 2013 [39]. This hetero-junction cell is based on a much thinner c-Si wafer (98 µm), on which a few-nanometer-thick hydrogenated amorphous Si (a-Si:H) layer is deposited to form a crystalline-amorphous Si hetero-junction. The advantage of the hetero-junction design is that no highly doped regions are required, thus reducing bulk carrier recombination. The relatively small thickness of the cell, the absence of a highly-doped emitter layer and the excellent surface passivation properties of a-Si yield $V_{OC}$ as large as 750 mV. However, in these cells $J_{SC}$ is limited by parasitic losses in the transparent conductive oxide (TCO) top contact layer and the a-Si:H layer. The reported efficiency of the best hetero-junction cell is 24.7%. If the light absorption in the active layer of the hetero-junction solar cell could be enhanced the efficiency could be increased further.

The third and fourth rows of Table 1.1 show the electrical characteristics of two ideal homo-junction cells with thicknesses of 160 µm and 10 µm, respectively. For both cell thicknesses, we assume maximum $J_{SC}$ of 43.8 mA/cm$^2$. For $V_{OC}$ we take optimum values calculated for thick (770 mV) and thin (810 mV) cells. We take the FF equal to that of the Panasonic-Sanyo HIT cell. The resulting efficiencies are 28.1% and 29.5% for the thick and thin cells, respectively. The higher efficiency of the thinner cell is due to the lower bulk recombination.

Table 1.1 defines the road to achieve c-Si solar cells with efficiency approaching the Shockley-Queisser limit. First, reducing the solar cell thickness is crucial to obtain high $V_{OC}$. Simultaneously, the use of thinner Si wafers allows a reduction in fabrication costs, as the Si wafer accounts for a significant fraction of the cost of a crystalline Si solar module [5]. Furthermore, perfect absorption of the solar spectrum is needed to achieve optimum $J_{SC}$. Finally, for thinner cells excellent surface passivation is crucial to achieve large $V_{OC}$.

Achieving all these goals at the same time is a major challenge. The first challenge is to absorb the full solar spectrum in a thin Si layer. Figure 1.2(b) shows the spectral intensity of the AM1.5 global solar spectrum (blue), and the spectral intensity absorbed in a single pass through a 2-µm-thick Si slab (red). As can be seen, a significant fraction of the solar spectrum in the spectral range 600-1100 nm is not absorbed by the thin layer. In particular, photons in the near-bandgap spectral range are very poorly absorbed. In order to enhance absorption, a light-trapping scheme is essential. Light-trapping can be achieved by using scattering structures that increase the optical path length in the cell and/or trap light by total internal reflection [40].

The green line in Fig. 1.2(b) shows the maximum spectral intensity that can be absorbed in a 2-µm-thick Si cell using light trapping schemes in the classical ray-optics limit [41]. This is usually referred to as “$4n^2$ limit” as it has been shown that the maximum optical path length enhancement that can be achieved in a Si slab with Lambertian scattering surfaces is equal to $4n^2 \approx 50$, where $n$ is the refractive
index of Si \[42\]. As can be seen, even in the \(4n^2\) limit, light in the spectral range near the bandgap of Si is not fully absorbed in a 2-\(\mu\)m-thick layer.

Conventional c-Si solar cells use micron-sized pyramidal surface texture as a light-trapping scheme \[43\] [44]. This geometry however cannot easily be applied to devices thinner than 20 \(\mu\)m, as the typical feature size is several microns. Furthermore, surface texture increases the surface area of the cell, and thus leads to enhanced surface recombination. Therefore, it is of great interest to investigate novel light scattering architectures that can serve to efficiently couple and trap light into thin Si layers. In the past few years, it is being realized that nanostructures integrated with the solar cell can serve to couple and trap light in the solar cell \[40\]. Nanostructures also offer the possibility to be integrated with passivated flat Si layers, without harming the surface passivation properties of the cell \[45\] [46].

In this thesis, we study the integration of metallic and dielectric resonant nanostructures with c-Si wafers and films, and study enhanced light absorption and light trapping. The implications for enhanced solar cell performance are discussed.

### 1.3 Resonant nanostructures for light management

The research field of Nanophotonics studies the behavior of light at the scale of nanometer, i.e. at a scale comparable to or smaller than the wavelength of light. The “elementary particles” of this field are metallic and dielectric nanoparticles (NPs) that can show resonant interaction with light.

![Normalized scattering cross section](image)

**Figure 1.4:** (a) Normalized scattering cross section spectra for a 120-nm-diameter Ag (red) and Si (blue) nanoparticle in air. (b) Electric field distribution for a localized surface plasmon resonance for Ag and (c) Mie resonance for Si. Scale bars represent 100 nm.

Figure 1.4(a) shows the normalized scattering cross section of a 120-nm-
diameter Ag (red) and Si (blue) sphere in air. The normalized scattering cross section is defined as the particle scattering cross section divided by its geometrical cross section (i.e. the NP projected area). The spectrum for a Ag NP shows a clear resonance at a wavelength of 430 nm, whereas for the Si NP two resonances are observed, at wavelengths of 440 nm and 520 nm. The nature of these optical resonances in a Ag and Si nanoparticle is very different, due to the intrinsic difference in the optical constants of metals and dielectrics. Metal NPs are characterized by localized surface plasmon resonances (LSPRs), which originate from the collective excitation of the free electrons in the metal by the electric field of the incident light [47]. At resonance, the field is confined at the NP surface (Fig. 1.4(b)). Dielectric nanoparticles, on the other hand, possess geometrical resonances where light is confined in a well-defined geometrical mode inside the NP [48]. Figure 1.4(c) shows the electric field distribution inside the Si NP, for the resonance at 520 nm. The geometrical resonances are also called Mie resonances, after the German physicist Gustav Mie (1869-1957) who first solved the Maxwell’s equation for a plane wave incident on a spherical particle in a homogeneous medium. Note that Mie theory holds for particles made of any material, i.e. both dielectrics and metals. However, the different dielectric permittivity of metals and dielectrics results in the distinctly different resonance spectra and field distributions shown in Fig. 1.4(a) and Figs. 1.4(b,c). For both metallic and dielectric NPs, the scattering cross section at resonance can be as large as 5-10 times the NP geometrical cross section. This means that when a material is covered with an array of NPs with surface coverage of only 10-20% nearly full interaction with incident light with the scattering nanostructures can be achieved.

The strong resonant scattering of light by metallic or dielectric nanoparticles can be used to couple and guide light in thin solar cells. To do so, the relatively narrowband resonances shown in Fig. 1.4(a) need to be made broadband. As we will show in this thesis, this can be done by changing the NP size, shape or distribution, as well as the degree of coupling to the substrate. Furthermore, as it turns out, light scattering from the NPs occurs preferentially in the forward direction, into the solar cell, due to the high density of optical states in the substrate, in particular for high-index materials.

In the past few years, several designs for “light management” in solar cells using resonant nanostructures have been proposed [40]. They include designs in which NPs are placed at the front [49–55], at the back [56–65] or inside the solar cell active layer [66–73]. Despite this earlier work, fundamental understanding of the light scattering and trapping phenomena in solar cells with metallic and dielectric nanoparticles is lacking.

In this thesis we investigate the fundamental aspects of resonant scattering of light by metallic and dielectric nanoparticles placed on top of a high-index Si substrate. The novel insights gained by these fundamental studies enable future studies of light trapping architectures for solar cells with higher efficiency. We discuss several practical implementations of nanostructures in solar cell devices.
1.4 Thesis outline

In this thesis, each of the Chapter 3 - 9 presents an advance in understanding the scattering properties of metallic (Chapters 3 - 5) and dielectric (6 - 9) NPs for application to light trapping in solar cells.

Chapter 2 introduces the nanofabrication techniques used in some of the following chapters to fabricate the nanoparticles. Substrate conformal imprint lithography (SCIL) is presented as a large area, non-expensive, high-fidelity technique to fabricate NP arrays on full wafers. Furthermore, a reactive ion etching (RIE) recipe based on fluorine compound gases is used to fabricate Si nano-pillar arrays on large-area Si wafers.

In Chapter 3, we study the scattering of light by plasmonic (Ag) NPs placed on a substrate. In particular, the key role of Fano resonances is identified and used to define guidelines for designing a plasmonic antireflection coating (ARC) for Si solar cells.

Based on these results, a plasmonic ARC with better performance than a standard flat Si$_3$N$_4$ ARC is presented in Chapter 4. This is a result of a full parameter space optimization carried out with numerical simulations. We use electron beam lithography (EBL) to fabricate Ag NP arrays on crystalline Si solar cells. Reflection spectroscopy is used to quantify the light coupling into the Si solar cells.

Chapter 5 explores the possibility to use the near-field enhancement of plasmonic (Ag) NPs embedded in a solar cell, to enhance the optical absorption in the active layer. We find that this approach is strongly limited by the Ohmic losses in the metal NP, and cannot be used for crystalline or amorphous Si solar cells. However, it can be used to enhance the absorption of light in ultrathin organic/polymer based solar cells.

In Chapter 6, a new way of suppressing the reflection of light from a Si surface is presented. The reflectivity of a full-size Si wafer is reduced from over 35% to 1.3% (averaged over the solar spectrum) by covering the wafer with an optimized array of Si Mie resonators. The wafer patterned with a Si NP array appears thus completely black. The fundamental physics of light scattering by Mie resonances in the Si NPs is studied.

The same Si Mie coating is used in Chapter 7 to study light trapping in thin (20-100 µm) and ultrathin (1-20 µm) crystalline Si solar cells. Numerical simulations are used to calculate the absorption in the thin Si slab covered with the Si Mie coating. An electrical model including bulk and surface recombination is then used to estimate the solar cell efficiency. We find that for realistic values of surface recombination velocity and carrier bulk lifetime, a 20-µm-thick cell with 21.5% efficiency can be made.

Chapter 8 presents an experimental demonstration of light trapping in thin film Si slabs on glass, patterned with arrays of Si Mie NPs. Total reflection and transmission spectroscopy is used to measure the absorption spectrum of the thin Si slab with the Si Mie coating, and compare it to that of a flat Si slab. In the infrared spectral range, optical path length enhancements up to a factor of 65 are measured.
well beyond the geometric Lambertian $4n^2$ limit for Si at this wavelength.

In Chapter 9, a TiO$_2$/Al$_2$O$_3$ Mie coating is presented. This coating combines very good antireflection properties with excellent surface passivation. The antireflection effect stems from the preferential forward scattering of light by Mie resonances in the TiO$_2$ NPs and yields a solar-spectrum averaged reflectivity as low as 1.6%. An ultrathin Al$_2$O$_3$ layer provides excellent passivation of the Si surface, with surface recombination velocity of only 3.3 cm/s after fabrication of the TiO$_2$ NPs.

Finally, Chapter 10 presents several new concepts and ideas for integrating plasmonic and Mie NPs on realistic solar cell designs. We show that resonant nanostructures can be beneficial not only for several crystalline Si solar cell designs, but also for GaAs and polymer cells. Practical aspects such as the effect of polymer and glass encapsulation of solar modules are also analyzed.

Altogether, this thesis provides fundamental insights in light scattering and trapping phenomena of resonant metallic and dielectric nanostructures integrated with thin and thick Si wafers. The results may be used to design novel Si solar cell architectures with higher efficiency that can be made at lower costs.