Light trapping in solar cells using resonant nanostructures
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Citation for published version (APA):
Spinelli, P. (2013). Light trapping in solar cells using resonant nanostructures
We present an entirely new concept that allows suppressing the reflection of light from a silicon surface over a broad spectral range. A two-dimensional periodic array of sub-wavelength silicon nanocylinders designed to possess strongly substrate-coupled Mie resonances yields almost zero total reflectance over the entire spectral range from the ultraviolet to the near-infrared. This new antireflection concept relies on the strong forward scattering that occurs when a scattering structure is placed in close proximity to a high-index substrate with a high optical density of states.

6.1 Introduction

Reflection is a natural phenomenon that occurs when light passes the interface between materials with different refractive index. In many applications, such as solar cells or photodetectors, reflection is an unwanted loss process. Many different ideas have been developed over the years in order to reduce reflection in optical and optoelectronic devices [111, 112]. A single transparent dielectric layer is commonly used as an anti-reflection (AR) coating. Based on destructive interference between the incident and reflected light, perfect optical impedance matching can
be achieved for one specific wavelength. Micron-sized pyramidal surface texturing is also widely used in e.g. crystalline silicon solar cells. The angular randomization of the scattered light at the surface can increase light absorption in an optical medium up to a factor of 4n^2. Surface structures composed of periodic or random arrays of semiconductor nanowires and nano-pyramids have also proven to reduce reflection over a broad range of wavelengths and angles of incidence. The reduced reflection is due to multiple scattering of light as well as adiabatic coupling due to a gradually increasing refractive index towards the substrate surface. Recently, we have shown that optimized arrays of metal nanoparticles reduce reflection of Si in the range of wavelengths relevant for solar applications. The preferential forward scattering by the plasmonic point scatterers strongly reduces the reflection, thus allowing almost perfect impedance matching of sunlight into a Si wafer.

Here, we present an entirely new concept to eliminate reflection from a silicon wafer that makes use of much simpler nanostructures than the ones reported before, does not involve metals, and can be applied to any high-index material. It is based on the fact that dielectric nanoscaters possess geometrical Mie resonances with scattering cross sections larger than the geometrical ones. A recent paper by Cao et al. has shown that Mie resonances provide a very efficient mechanism for light absorption in Si nanowire based solar cells. In that work, however, Si nanowires were on a glass substrate and only absorption in the nanowires was considered. In this Chapter, we demonstrate that light that is stored in Mie resonances can be also very efficiently coupled to a Si substrate. From a fundamental point of view this light coupling mechanism based on weak (lossy) Mie resonances is entirely different than all other methods commonly known in the field of anti-reflection coatings. We demonstrate experimentally that an array of low aspect-ratio Si nanocylinders etched into a Si wafer shows an average reflectivity as low as 1.3% in the 450-900 nm spectral range. The strongly reduced reflectivity is observed for angles of incidence up to 60 degrees. The monolithic nature of the nanostructures makes this novel anti-reflection concept to be easily applicable to a wide range of devices, including (ultra-thin) solar cells based on any high-index semiconductor.

### 6.2 Mie scattering on a Si substrate

Figure 6.1(a) shows the calculated scattering cross section spectra, normalized to the geometrical cross section, for a Si sphere in air (blue) and a Si sphere (green) and cylinder (red) on top of a Si substrate. The scattering spectrum for the sphere in air shows two distinct resonances corresponding to the first- and second-order Mie modes. These geometrical resonances reflect the fact that the particle acts as a nano-cavity for light. The scattering cross section at resonance is more than 8 times larger than the geometrical cross section, and the cavity quality factor (Q = 10) is mostly determined by radiation losses from the cavity mode. The two
scattering resonances are clearly visible when a Si substrate is introduced below the spherical particle (green line), indicating only weak coupling of the well-confined Mie modes to the substrate. However, when a cylindrical nanoparticle is placed on the Si substrate, the resonances broaden and merge into a broadband feature (red line). This behaviour is due to the introduction of a leaky channel into the substrate for the light that is resonantly confined in the particle.

Figure 6.1: Mie scattering on a Si wafer. (a) Scattering cross sections, normalized to the geometrical cross section, for a Si sphere in air (blue), a Si sphere on a Si substrate (green) and a Si cylinder on a Si substrate (red). The spheres have diameter $d = 150$ nm, the cylinder an in-plane diameter of 150 nm and height of 100 nm. Mie resonances of first ($n = 1$) and second ($n = 2$) order are indicated in the figure. (b-g) Electric field intensity (color scale) in a cross section of the particle for a sphere in air (b, e), a sphere on substrate (c, f) and a cylinder on substrate (d, g), for Mie modes of first (b-d) and second (e-g) order. The wavelengths considered for these calculations are indicated in each panel. The field distribution for the cylinder at resonance overlaps with the substrate, thus introducing a loss channel for the light confined in the particle that broadens the resonances. Plots for a sphere in air are calculated with Mie theory; plots for particles on a substrate are simulated. The scale bar in (e) represents 50 nm, and refers to (b) and (e). The scale bar in (f) represents 150 nm and refers to (c), (d), (f) and (g).

To understand this mechanism, Figs. 6.1(b)-(g) show the calculated distribution of light (electric field intensity, color scale) inside a Si sphere in air (b, e), a Si sphere on a Si substrate (c, f) and a Si cylinder on a Si substrate (d, g), for Mie modes of
first (b-d) and second (e-g) order. Comparison of the field distributions shows that the geometrical modes inside a spherical Si particle are nearly unaffected by the presence of the substrate and light is in both cases well confined inside the particle. However, for a cylindrical particle the field distribution of the Mie resonances has a clear overlap with the Si substrate. Both direct near-field absorption in the substrate and radiative emission into the substrate introduce a loss channel for the light confined in the particle, thus yielding broadening of the resonances in the scattering cross section spectrum (Q ~ 5, see also supplementary Fig. 6.6). The field distributions in Figs. 6.1(b)-(g) suggest that a cylindrical Si nanoparticle can effectively couple light into a Si substrate.

To study this further we perform simulations of the reflectance spectra of cylindrical nanopillar (NP) arrays with different NP dimensions. Figure 6.2(a) shows the simulated total reflectance spectra from a square array of Si NPs spaced by 500 nm, for cylinder diameters of 75, 100 and 125 nm. The reflectance from a bare flat Si surface (35-60%) is also shown for comparison (black line).

The data in Fig. 6.2(a) show that the dielectric particle array reduces the reflectance of a Si surface over the entire spectral range shown. The key role of the Mie resonances in the reduced reflection is clear from the fact that broad reflection dips are observed on resonance, at wavelengths (700, 830, 1000 nm) that increase with nanopillar diameter (150, 200, 250 nm). This redshift for increasing diameter is similar to that observed for Mie resonances for isolated particles with increasing diameter (see supplementary Fig. 6.6). The sharp decrease in reflectivity at the wavelength of 500 nm, i.e. equal to the array pitch, is explained by a Rayleigh anomaly [132] from the grating formed by the regular array of nanoparticles (see supplementary Fig. 6.7). The strong coupling of light on resonance is explained by the strong forward scattering of light into the substrate from the resonant Mie scatterers, due to the high optical mode density of the high-index Si substrate [99]. The resonant nature of this effect leads to a large cross section, so that even an array of scatterers covering only 30% of the surface area leads to nearly complete interaction with the incoming plane wave.

Figure 6.2(b) shows the simulated reflectivity spectra for a bare flat Si substrate (black), a flat Si substrate coated with a standard 80 nm Si$_3$N$_4$ anti-reflection coating (blue), a Si surface with bare Si NP on top (green), and a Si surface with Si NP on top coated with a 50 nm Si$_3$N$_4$ layer (red). Given its index (n = 2.0), Si$_3$N$_4$ is the optimum antireflection coating for a Si wafer (n = 3.5-4.0 in the visible-to-near-infrared spectral range). As can be seen in the figure, it only leads to vanishing reflectivity for a specific wavelength (650 nm in Fig. 6.2(b)), determined by the Si$_3$N$_4$ layer thickness. The bare array of Si NPs shows a broadband reduced reflectivity spectrum that is lower than that for the standard AR coating above 850 nm and below 550 nm, and higher in the range 550-850 nm. Both spectra show a large increase in reflectivity for wavelengths below 500 nm. A Si$_3$N$_4$ layer with properly chosen thickness can be used as a coating, conformal to the nanostructures, in order to compensate for the losses in this spectral region. The reflectance spectrum from a coated array of NPs (Fig. 6.2(b), red) shows that reflectivity can be
6.2 Mie scattering on a Si substrate

Figure 6.2: Ultra-low reflectivities. (a) Simulated reflection spectra from a regular square array of Si NPs spaced by 500 nm, for cylinder diameters of 150 (blue), 200 (red) and 250 nm (green) with a height of 150 nm. Reflectance from a flat Si surface is also shown for comparison (black). The Si NP arrays reduce the reflectivity over the entire spectrum. The broad dip in reflectivity that redshifts for increasing particle diameter is due to enhanced forward scattering from the Mie resonances in the particle. (b) Simulated reflection spectra for a bare flat Si substrate (black), a flat Si substrate coated with a standard Si$_3$N$_4$ anti-reflection coating (blue, thickness $t=80$ nm), a Si surface with bare Si nanostructures on top (green), and a Si surface with Si nanostructures on top coated with an optimized Si$_3$N$_4$ layer (red, $t=50$ nm). For each configuration the average reflectivity, weighted with the AM1.5 solar spectrum in the 300-1100 nm spectral range, is indicated (R). (c) Measured total reflectivity of a bare Si wafer (black), an uncoated Si NP array (red) and four Si NP array coated with Si$_3$N$_4$ layers of different thicknesses $t$ (colors). The Si NPs have a diameter of 125 nm, height of 150 nm and are spaced by 450 nm. For each configuration the average reflectivity, weighted with the AM1.5 solar spectrum in the 450-900 nm spectral range, is indicated (R). Reflectance is reduced over the entire spectral range, due to coupling of the Mie resonant scattering to the Si substrate. (d) Same reflectivity data plotted in logarithmic scale. Individual curves are described by legend of Fig. 6.3c. The effect of the Mie resonance is visible in the broad dip in reflectivity observed in the 700-800 nm range.
reduced down to less than 2% over the entire spectral range from 400-1100 nm, with the exception of a small peak around 650 nm. The low reflectivity stems from the combined effect of the strongly coupled Mie resonances in the red and near-IR part of the spectrum and the interference anti-reflection effect from the Si$_3$N$_4$ layer, tuned for the blue part of the spectrum. Figure 6.2(b) also shows the average reflectivities for each configuration, obtained by weighting over the AM1.5 solar spectrum in the 300-1100 nm spectral range. As can be seen, both coated (1.8%) and uncoated nanopillar arrays (8.1%) show lower reflectivity than the standard 80 nm Si$_3$N$_4$ coating (10.3%).

6.3 Black silicon

The antireflection properties of Si NP arrays have been studied experimentally using Si(100) wafers on which square arrays of Si nanocylinders (250 nm diameter, 150 nm height, 450 nm pitch) were fabricated using substrate conformal soft-imprint lithography in combination with reactive ion etching. The total hemispherical reflectivity was measured using an integrating sphere, with an angle of incidence (AOI) of 8° off the surface normal. Figure 6.2(c) shows the measured total reflectivity spectrum of a bare Si wafer (black), of a bare Si NP array (red) and four Si NP arrays coated with different Si$_3$N$_4$ layer thicknesses (green to purple color lines). All geometries show reduced reflectivity with respect to the bare Si wafer, over the entire spectral range. The array coated with a 60 nm thick Si$_3$N$_4$ layer (purple line) shows a reflectivity of less than 3% over the entire spectral range 450-900 nm. The AM1.5-averaged reflectance from a bare Si substrate (32.2%, black) is reduced to 7.5% by patterning the Si surface with an optimized Si nanopillar array (red). Combining Si NPs and a Si$_3$N$_4$ coating leads to an average reflectivity as low as 1.3% (blue). This value is in excellent agreement with the calculated data in Fig. 6.2(b), taking into account the different spectral range over which the average reflectivity is calculated (see supplementary Fig. 6.10). An average reflectivity of 1.3% is lower than that of standard antireflection schemes used for commercial crystalline Si solar cells (see supplementary Fig. 6.9). Figure 6.2(d) shows the same reflectivity spectra plotted on a logarithmic scale. The broad dip in the reflectivity spectra at wavelengths between 650-850 nm, is attributed to the first-order coupled Mie resonances. The sharp dips at a wavelength of about 510 nm are consistent with a Rayleigh anomaly for light incident with an AOI of 8° (see supplementary Fig. 6.11).

With the reflection of light effectively vanished, light is then either transmitted into the Si substrate or absorbed in the NPs. For example, for silicon in the 800-1000 nm spectral range the linear absorption over the thickness of the nanocylinders is less than 1%; it is enhanced in the cavity by the quality factor Q≈3. Indeed, simulations (see supplementary Fig. 6.8) show that in this spectral range absorption in the NPs is negligible and the NPs behave as almost pure scatterers (i.e. the albedo is almost 1). For the UV/blue spectral range, Si is strongly absorbing and light is absorbed inside the Si nanocylinders. Indeed, an optimized solar cell design based
6.4 Angle resolved reflectivity

on substrate coupled Mie resonators will have the p-n junction integrated inside the nanoparticles, which can easily be done using gas-phase doping.

Figure 6.3: Black silicon. (a) Photograph of a bare flat 4-inch Si wafer (left) and a 4-inch Si wafer fully imprinted with an optimized (250 nm diameter, 150 nm height, 450 nm pitch) Si NP array and over-coated with a 60 nm thick Si$_3$N$_4$ layer (right). Scale bar represents 1 inch. (b) SEM image taken under an angle of 40° of a bare Si NP array (scale bar represents 500 nm) and (c) a Si NP array coated with a 60 nm thick Si$_3$N$_4$ layer (scale bar represents 1 µm).

Figure 6.3(a) shows a photograph of a bare flat 4-inch Si wafer (left) compared to a 4-inch Si wafer that has been patterned over the entire wafer area with an optimized Si NP array and over-coated with a 60 nm thick Si$_3$N$_4$ layer (right). The photograph shows a clear visual effect of the reduced reflectivity due to the patterning of the Si wafer surface with resonant Mie scatterers. Figure 6.3 also shows a SEM image of a bare (b) and a 60 nm Si$_3$N$_4$ coated (c) NP array. The sample shown in Fig. 6.3 was fabricated using interference lithography and soft-imprint lithography, demonstrating this new AR coating design can be applied at large-area using standard inexpensive processes.

6.4 Angle resolved reflectivity

In order to be relevant for e.g. photovoltaic applications, an AR coating must show low reflectivity over a wide range of angles of incidence and for both polarizations of light. Figure 6.4 shows the specular reflectivity measured as a function of AOI, for
wavelengths of 514 nm (a, d), 632 nm (b, e) and 405 nm (c, f). Figures 6.4(a)-(c) show reflectance for s- (solid symbols) and p-polarized (open symbols) incident beams, whereas Figs. 6.4(d)-(f) show the average reflectivity for s- and p- polarizations, plotted on a logarithmic scale. In each graph, reflectivities from a bare Si wafer (black lines), a flat Si wafer with a 60 nm standard Si$_3$N$_4$ coating (red) and a 60 nm thick Si$_3$N$_4$ coated NP array (blue) are shown.

Figure 6.4: Angle resolved reflectivity. Specular reflectivity measured as a function of AOI, for wavelengths of 514 nm (a, d), 632 nm (b, e) and 405 nm (c, f). Panels in the top row show results for s- (solid symbols) and p-polarized (open symbols) incident beam, whereas the bottom row show an average of s- and p- polarizations, plotted on a logarithmic scale. In each graph, reflectivities from a bare Si wafer (black lines), a 60 nm standard Si$_3$N$_4$ coating (red) and a coated NP array (blue) are shown. The excellent AR properties of Si NP arrays are maintained over the entire range of AOI from -60 to +60 degrees.

At a wavelength of 514 nm, the 60 nm standard coating and the coated NP array show a total reflectivity for near-normal incidence of 0.1% and 0.05% respectively (Fig. 6.9(a)). Figure 6.4(a) shows that for both samples and polarizations the reflectivity remains below 1% in a wide range of AOI. While no difference between the standard coating and the Si NP array is seen for the s-polarization, the Si NP array shows lower reflection of p-polarized light at large angles. Averaging the two polarizations (Fig. 6.4(d)) yields similar results for the standard and the Si NP coatings, with better AR properties from the latter for angles above 14°. At wavelengths of 632 nm and 405 nm (Figs. 6.4(b) and (c), respectively), the Si NP array shows lower reflectivity than the standard Si$_3$N$_4$ coating, for both polarizations and over the entire range of AOI. As Figs. 6.4(e) and 6.4(f) show, the low reflectivity from the coated Si NP array is maintained over the entire angular range up to 60 degrees.
6.5 Random and periodic arrays of Si Mie scatterers

The configuration of Si Mie scatterers studied so far is periodic square array. However, this configuration yields extra grating effects that affect the reflectivity, as already shown in Fig. 6.2 and in the supplementary Fig. 6.7. In order to decouple the collective scattering by the grating from the scattering of single Mie resonators, we study the case of a random array of Si NPs, by means of numerical simulations. The random array is generated by defining a random position for each Si NP in a $10 \times 10 \, \mu \text{m}^2$ box, with the boundary condition that the NPs cannot overlap. Figure 6.5(a) shows an example of random configuration of nanoparticles in a $10 \times 10 \, \mu \text{m}^2$ simulation box.

Figure 6.5(b) shows the simulated reflectivity spectra for a periodic square array (red) and a random array (blue) of Si NPs with diameter 250 nm and height 150 nm. The total NP surface coverage is the same for the periodic and random geometries. The reflectivity spectrum of the periodic array is the same shown in Fig. 6.2(b). As can be seen in Fig. 6.5(b), the two reflectivity spectra overlap for large part of the spectral range 300-1100 nm. Both reflectivity spectra show the broad dips at wavelengths of 530 nm and 800 nm due to scattering of light through Mie resonances in the Si NPs. Overall, the reflectivity of a random array is slightly lower than that of the periodic array. This result suggests that the collective scattering from the grating formed by the Si NPs plays a very minor role in reducing the reflectivity of a bare Si substrate. The single particle Mie scattering mechanism dominates the scattering of light by the array of Si NPs.
6.6 Conclusion

Sub-wavelength resonant Mie scatterers at the surface of a Si wafer cause the reflection of light from the wafer to vanish. The resonant Mie modes have large scattering cross section, leading to strong interaction with the incident light. Coupling of these modes to the substrate leads to strong preferential forward scattering due to the high mode density in the high-index substrate. Full-wafer Si nanocylinder arrays were fabricated using a soft-imprint technique capable of large scale, high-fidelity surface patterning. Total reflectance spectroscopy shows an average reflectivity of only 1.3% over the 450-900 nm spectral range. The strongly reduced reflectivity is observed for a broad range of angles of incidence up to ±60°. Due to the monolithic nature of the Mie scatterers this novel anti-reflection concept is easily applicable to any high-index material. It can readily find application in solar cells, including thin-film designs on which the standard texturing cannot be applied.

Methods

Numerical calculations

The scattering cross section spectra and field distributions shown in Fig. 6.1 were calculated using Mie theory [83] (blue line in Fig. 6.1(a) and Figs. 6.1(b) and (e)) and finite-difference time-domain (FDTD) calculations (green and red lines in Fig. 6.1(a), and Figs. 6.1(c), (d), (f) and (g)). For a definition of scattering cross section please refer to Ref. [48], chapter 2. A commercial software package was used to perform FDTD calculations [90]. A simulation box size of 1×1×0.8 µm with perfectly matched layer (PML) conditions on every boundary was used. The light source was a broadband (300-1100 nm) plane wave, with normal incidence to the substrate. The mesh grid was set to 5 nm over the entire simulation volume, with a refinement (1 nm) over the volume occupied by the particle. A total-field scattered-field (TFSF) method was used to directly calculate the scattered power by means of frequency-domain transmission monitors positioned in the scattered field region. A two-dimensional frequency domain field monitor cross-cutting the particle in its center was used to calculate the electric field intensity distribution (as shown in Fig. 6.1(b)). FDTD simulations were also used to study the antireflection properties of Si NP arrays on a Si substrate (Fig. 6.2(a) and (b)). In this case, the box size was equal to p×p×0.6 µm, where p is the array pitch, and periodic boundary conditions (PBC) were used in the in-plane directions. The reflectivity spectra were directly calculated with a frequency-domain transmission monitor placed above the plane-wave source. Optical constants of Si and Si₃N₄ were taken from the literature [92].
Fabrication of Si nanopillar arrays

Substrate Conformal Imprint Lithography (SCIL) was used to fabricate large area Si NP arrays. This soft-imprint fabrication technique is capable of large scale, high-fidelity surface patterning and is fully compatible with standard techniques used in e.g. solar cell manufacturing. It uses a rubber (PDMS) stamp in which a pattern is molded from a master Si wafer that is patterned using optical interference lithography or electron beam lithography. The rubber stamp is used to replicate the patterns in a sol-gel layer spin-coated on the Si wafer. The patterned sol-gel layer is then used as a mask for a reactive ion etching process that results in the formation of Si nanocylinders in the Si wafer. For this work master template containing a $4 \times 4 \text{ mm}^2$ array of 250 nm wide, 150 nm high Si nanopillars with array pitch of 450 nm was fabricated on a 4-inch Si(100) wafer using electron beam lithography and etching. The pattern in the sol-gel was transferred to the Si wafer with two-step reactive ion etching (RIE): a N$_2$ and CF$_4$ gas mixture was used to etch through the sol-gel layer and N$_2$ and Cl$_2$ gases were used to etch the Si wafer. The sol-gel etch mask was removed with diluted HF after which the samples were coated with Si$_3$N$_4$ layers of different thicknesses using low-pressure chemical vapor deposition (LPCVD) at 850°C. The 4-inch wafer shown in the photograph of Fig. 6.3 was fabricated with a similar process, where the master pillar pattern was made using optical interference lithography with a 266 nm wavelength laser.

Optical measurements

The total reflectivity spectra in Fig. 6.2(c,d) were measured in a Labsphere 4-inch integrating sphere, using a supercontinuum broadband light source (Fianium SC450-A, spectral range 0.45-2 µm). The beam spot on the sample was 1 mm in diameter. Light from the integrating spheres was collected with a multimode optical fiber and sent to a spectrometer, comprising a spectrograph (Acton, SpectraPro 300i) and a Si CCD array (Princeton Instruments). The data were confirmed by measurements in a PerkinElmer Lambda950 spectrophotometer, using a tungsten-halogen lamp and deuterium lamp as sources, a PM R6872 detector for the UV-VIS spectral range and a Peltier-cooled PbS detector for NIR range. Specular reflectivity for varying AOI (Fig. 6.4 and supplementary Fig. 6.11) was measured in a double rotation stage (Huber), where the sample was mounted in the inner stage and a power meter (Thorlabs, PM300) on the outer one. For the measurements at the 632 nm wavelength, a Helium-Neon laser source and a Thorlabs LPVIS 100 broadband linear polarizer were used (incident power on the sample: 4mW); an Argon-Kripton laser source and a ColorPol VIS500 linear polarizer (10mW on the sample) were used for the 514 nm wavelength; a diode laser source and a Thorlabs LPUV 050 polarizer (3mW on the sample) for the 405 nm wavelength. In all cases, the beam spot size on the sample was 1 mm in diameter.
Supplementary figures

Figure 6.6: (a) Normalized scattering cross section (grey scale) as a function of wavelength (horizontal axis) and particle diameter (vertical axis) for a spherical particle in air. A redshift of all the Mie modes is observed as the particle size increases, as expected for a geometrical resonance in a cavity. (b, c) Normalized scattering cross section (gray scale) of a single Si nano-sphere (b) and nano-cylinder (c) on a substrate, as a function of wavelength (horizontal axis) and substrate refractive index (vertical axis). The Mie modes of a sphere do not shift or broaden as the substrate index is increased, due to the fact that light at resonance is confined inside the nano-sphere. For a cylindrical particle on a substrate a broadening of the resonance is observed as the substrate index is increased. This happens because the substrate introduces a loss channel for the light resonantly stored in the nanoparticle, both by radiative losses and near-field absorption. For the case of Si (n=3.5), the resonance is broadened over the entire range 500-800 nm.

Figure 6.7: (a) Simulated reflectance spectra of a bare Si wafer (black), and Si NP arrays with 500 nm pitch, for cylinder heights of 100, 150 and 200 nm. Broad reflection dips are observed for wavelengths at which Mie resonances occur. The lowest reflectivity is found for a height of 150 nm. (b) Reflectance spectra of 250 nm wide, 150 nm high Si NP arrays for different array pitch. All reflectivity spectra show a sharp decrease in reflectivity at a wavelength equal to the array pitch, due to a Rayleigh anomaly from the grating formed by the regular array of nanoparticles. (c) Absorption spectra of Si NP arrays for different array pitch. Here, absorption is monitored that takes place in the Si NPs only. Clear peaks are observed at wavelengths equal to the pitch, due to the fact that the scattered light travels with an in-plane momentum (Rayleigh anomaly) and is thus more strongly absorbed in the Si NPs.
6.6 Conclusion

Figure 6.8: Transmission (blue), absorption in the NPs (green) and reflection (red) spectra for the optimized Si NP array (250 nm diameter, 150 nm height, 450 nm pitch). The first order Mie resonance of the NPs is at 850 nm. Interestingly, in the spectral range 700-1000 nm almost 100% transmission is observed and absorption is very low. This is due to the fact that NPs of such size have high albedo, i.e. they behave as pure scatterers.

Figure 6.9: Comparison with standard antireflection coatings. (a) Top panel: reflectivity spectrum of a Si wafer with surface texture optimized for a solar cell (red) and that of an un-coated Si NP array (blue). The reflectivity from a bare Si wafer is also shown for reference (black). Patterning the surface of a Si wafer with Mie resonators yields a better AR effect than that of a standard surface texturing, over the entire 450-900 nm spectral range. The Mie scattering scheme can be applied to any (even thin film) substrates, whereas textures can only be applied in limited cases. Bottom panel: measured reflectivity spectra of a bare Si wafer (black), a Si wafer coated with a 60 nm thick standard Si$_3$N$_4$ AR coating (red), an optimized textured and Si$_3$N$_4$-coated solar cell (green) and an optimized coated Si NP array (blue). The coated Si NP array AR coating outperforms both the 60 nm Si$_3$N$_4$ AR coating and the solar cell. (b) Average reflectivity, weighted with the AM1.5 solar spectrum in the 450-900 nm range, for a bare Si substrate (black, 32%), a standard Si$_3$N$_4$ coating (red, 6.25%), a textured and AR-coated solar cell (green, 3.38%) and a Si NP array coated with a Si$_3$N$_4$ layer with variable thickness (blue). The average reflectivity of the optimal configuration is 1.3%.
Figure 6.10: Measured reflectivity for the optimized Si$_3$N$_4$ coated Si NP array (red), extending well into the UV, compared with the simulated reflectivity (blue). Excellent agreement between the measurement and the simulation is observed.

Figure 6.11: Diffraction effects. (a) Measured reflectance as a function of collection angle for for angles of incidence of 5°, 15°, 25°, 40°, 50° and 60° and wavelength of 632 nm. As can be seen, for AOI below 25° only the m = 0 order (specular reflectivity) appears in the collection plane. For incident angles larger than 25° a contribution from m = +1 order is also present with intensity comparable of the m = 0 order. For all AOI, the collection angles at which the m = +1 order appears fulfill the grating relation: sin(θ$_i$) + sin(θ$_c$) = mλ/p, where θ$_i$ is the AOI, θ$_c$ is the collection angle, m the grating order, λ the wavelength and p the grating pitch. The reflectivity of the diffraction peaks varies between 1 and 5%. (b) Reflectivity as a function of collection angle for wavelengths of 405 nm (blue) and 514 nm (green), for a fixed AOI of 20°. Here, the m=0 and m = +1 diffraction peaks have intensities in the range 0.01-0.3%. The reflectance due to diffraction from the grating formed by the SiNPs is small and it thus not significantly affect the AR properties of the SiNP arrays. Diffraction losses can be avoided by using a random configuration of Si NPs.