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Introduction

Wie viel Seiten hat ein unbeschriebenes Blatt?
Um wie viel Ecken muss man denken, damit das was man vorhat klappt?

Dort wo du wohnst – Clueso

1.1. Future goals for photovoltaics

As part of reaching the goals of the Paris agreement the European Union (EU) has guaranteed to reduce its greenhouse gas (GHG) emissions into the atmosphere by at least 40% by 2030 and 80% by 2050 compared to 1990 levels [1]. One important step in the planning towards this goal is the stepwise change to renewable energy sources for electricity production, with photovoltaics (PV) being one of the main technology options. To reach the goal of 100% carbon-free electricity production the installed PV capacity in the EU must grow from 117 GW_p in 2019 to at least 630 GW_p by 2025 and 1.94 TW_p by 2050 [2]. The future electricity demand is an important factor and uncertainty in these numbers. Figure 1.1 shows the actual and estimated installed PV power between 2010 and 2030 for different scenarios of the EUs long-term strategy on reducing GHG. If the growth in electricity demand is just 10% above the expectations in the EU scenarios the demand for installed PV power in 2030 would more than double to around 1.2 TW_p [3].

One challenge encountered in the expansion of PV capacity is the demand for area to install the solar panels on. It is important to develop strategies to increase PV capacity while balancing the need for land for nature and agriculture, for avoiding conflicts between the demand of area and societal acceptance of growth of PV capacity. Great effort is being made to find innovative ways of integrating PV into existing infrastructure as buildings, urban environments, roads, in agriculture or on vehicles [4]. For example in the Netherlands and Germany, 400 km^2 and 2.800 km^2 area of rooftops are potentially usable for photovoltaics. Those areas have a capacity of 66 GW_p and 500 GW_p respectively and can already provide for a big part of the required area for future PV installations [5, 6]. A key aspect of integrating PV into buildings, roads and vehicles is the design aspect of photovoltaics. Specifically, the color appearance of PV is an important parameter

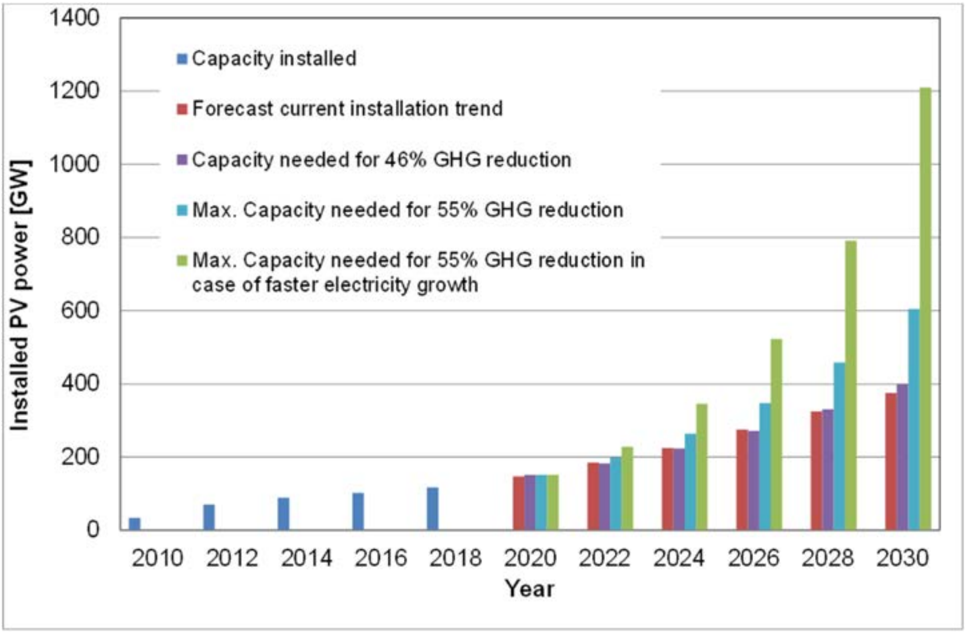

Figure 1.1: Installed and predicted installed PV power capacity in the EU from 2010 to 2030 for different scenarios of the EU's long-term strategies for 46% and 55% GHG reduction, as well as 55% GHG reduction with a faster electricity growth than expected (figure taken from [3]). (Installed PV power in GW_p; W_p is the power generated by a photovoltaic system under standardized illumination conditions.)

for designing building-integrated PV (BIPV). On the other hand a key goal in PV technology is increasing the efficiency of solar cells as that can reduce the cost per installed power. Also, higher-efficiency solar panels require less land area. To bring an example here, for the areas mentioned above for the Netherlands and Germany an increase in solar panel efficiency from 17% to 20% would save a land area of 60 km^2 in the Netherlands (size of Maastricht) and 300 km^2 in Germany (size of Munich). Therefore, increasing efficiency is one of the most followed research and development goals in PV. For Si solar cells the current efficiency record, while writing this thesis, of 26.7% [7] is already pretty close to the theoretical efficiency limit of 29.4% [8]. The technology of tandem solar cells that combine different absorber materials in one cell is a highly attractive approach to go well beyond the single-junction Si cell limit. In the past, tandem cell technologies were mostly based in III-V semiconductors that are quite expensive and were used in solar concentrator cells or for space applications [9]. In recent years perovskite solar cells have created major breakthroughs in PV research, with single-junction efficiencies now approaching those of Si solar cells. The most recent record at the time of writing this thesis for perovskite/ silicon tandem solar cells is 29.52% [10] and perovskite/silicon tandem cell efficiencies above 30% now appear well possible [11].

1.2. What nanophotonics can do for PV

The challenges mentioned in the last section require further advanced control over the management of light in the solar cells. Nanophotonic structures present an alternative technology beyond the conventional optical designs in PV, offering a strongly enhanced control over the harvesting of light [12, 13]. A key element in the application of nanophotonics in photovoltaics is the use of resonantly scattering metallic or dielectric nanoparticles with sizes in the order of the optical wavelength. Those particles can exhibit strong plasmonic or Mie resonances that are tunable by size and can therefore offer strong control over the scattering of light. Initially, the benefits of including such particles in solar cells were exploited by applying plasmonic particles for enhanced absorption in (thin film) cells [12]. Next, the benefit of dielectric particles which exhibit lower optical losses has been realized and was employed for light trapping and the creating of broadband anti-reflection coatings [14–16]. More recently, the nanophotovoltaics field evolved to the use of (periodic) arrangement of (non) resonant scatterers into metasurfaces. Those ultrathin photonic structures tailor the profile of the scattered light field so that it is optimally coupled, trapped and guided in the solar cell. Such metasurfaces are ultrathin, in the order of 100 nm, and light-weight, and can thus be easily integrated with existing solar cell designs.

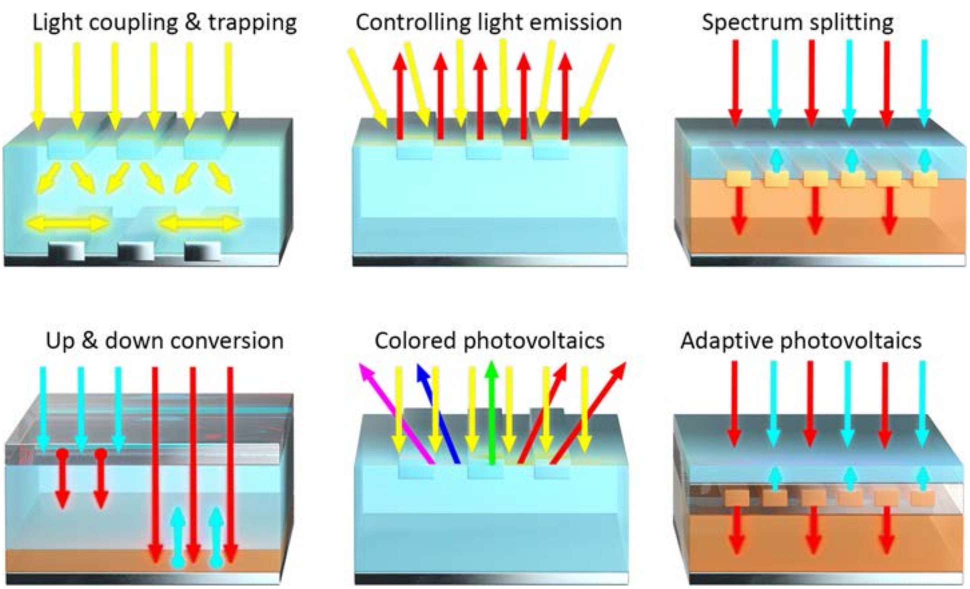

Figure 1.2: Schematics of possible functionalities of light scattering photonic structures and metasurfaces in solar cells. (Figure taken from [17])

Photonic structures have many different application possibilities in conventional single-junction cells, tandem cells, bifacial solar cells, luminescent solar concentrators and down and up conversion layers. As illustrated in Figure 1.2, they can enhance light trapping, control light emission, split the spectrum, support up and down conversion, can be used to color photovoltaics, and enable adaption of photovoltaics to e.g. the daylight spectrum [17]. In the next two paragraphs, we will explain in more detail how nanophotonic structures can be beneficial for two specific applications: colored photovoltaics, and high-efficiency tandem solar cells.

1.3. Dielectric nanoparticles for colored PV

As mentioned above BIPV can account for a big part of the required PV capacity, but their aesthetics is a crucial factor to blend PV into building materials and rooftops. Creating colorful PV will by definition introduce losses, as light has to be deliberately reflected or emitted for creating the colorful appearance. Many different methods have been used in the past to create colorful PV. We review some of them here and compare their advantages and disadvantages in table 1.1.

We compare multilayer interference coatings, distributed Bragg reflectors, resonant plasmonic structures as well as resonant dielectric nanoscatterers for the creation of colorful PV. Table 1.1 lists the most important factors that will be discussed in the following.

Method	Color range	Optical Losses	Angular behavior	Color quality	Comments on fabrication	Reference
Multilayer interference coatings	Pure colors, but not all mixed colors	low	Strongly angle dependent	Intermediate, strong dependence on number of layers	Expensive vacuum technologies	[18]–[21]
Distributed Bragg reflectors	Pure and mixed colors	low	Relatively independent	Good, intense colors in distinct wavelength range	Expensive vacuum technology	[22], [23]
Resonant dielectric nanoscatterers	Pure and mixed colors	low	Can be controlled, specular, Lambertian or specific angle range	Good, intense colors in distinct resonance	Soft imprint technology not demonstrated at large scale; potential for low-cost solution-based process	[24]–[26]
Resonant plasmonic structures	Pure (mixed colors possible but not demonstrated)	high	stable	Good, very intense colors in distinct resonance	Sputtering and annealing, potential for low-cost solution-based process	[27]

Table 1.1: Comparison of different technologies for coloration of solar cells. Positive features are marked in green, neutral features in yellow, and negative features in orange.

The first aspect is the freedom in the choice of coloration to be able to fill the entire color space, choosing between pure colors (single wavelength band, e.g. blue, green, yellow, red) as well as being able to mix the colors (combine different wavelength bands to create e.g. pink or white) is essential. This is possible for distributed Bragg reflectors by combining several layers on top of each other as they are optically independent. In the case of resonant dielectric particles the color mixing can by tailored in a single layer by mixing nanoparticles of different size.

Next, the optical losses which directly impact the efficiency of the solar cell are an important factor but are quite difficult to compare. All techniques can be tuned to lower reflectance which will always result in lower color intensity. It is important to avoid any unnecessary absorption, meaning that techniques based on dielectric materials are preferred over using metallic particles which suffer from parasitic absorption. Another option to avoid optical losses is to reduce the reflectance of colorful light to only the angular range that is of interest for an observer.

Another element to consider is the angular performance, describing if colors are stable under angled illumination and observation, and if the angular behavior can be designed at will. The Bragg reflectors as well as the particle-based techniques show angular stable coloration. None of the conventional techniques can control the angular behavior of the colored light that, as mentioned, would help to reduce the optical losses, and can add extra functionalities to the colored PV.

Furthermore, the quality of color depends mainly on how strong and clean a peak in reflectance can be tuned. Bragg reflectors are known for their sharp reflectance peaks. The color of multilayer coatings strongly depends on the number of layers and higher-order reflectance peaks can affect the quality of the color. The scattering spectrum of nanoparticles can be controlled to some extent to show distinct peaks.

Finally, to evaluate the fabrication procedure the cost and potential for large-scale fabrication should be discussed. The fabrication of interference coatings and Bragg reflectors is based on multiple-layer evaporation in high vacuum which is expensive, but is possible on a large-area industrial scale. For the dielectric particle based reflectors, so far lab-scale substrate conformal imprint lithography (SCIL) printing was done that may become industrially feasible for large-area fabrication for PV. Also, solution-based processes using spray coating of nanoparticles might lead to a route of inexpensive fabrication. It should be mentioned that the comparison of all technologies here is rather qualitatively because different papers use different figures of merit to describe the functionality of the respective technology. In future, a common ground to estimate the performance should be used in this field of research [28].

In summary, existing solutions to efficiently color PV still have some drawbacks . First, there is no control over the angular range, that the light is reflected to. The arrangement of dielectric nanoscatterers in metasurfaces can add this extra angle control to the colored PV. This has the advantage that the module can be applied in a very specific way, for example as rooftop PV with red light only scattering towards an observer on the street. Second, another challenge is the fabrication of structures with high-quality colors in an inexpensive, industry-compatible way. Coatings made of dielectric nanoparticles can be imprinted on the solar panel module glass, using soft conformal imprint lithography stamps in the lab, and have the potential to be fabricated with large-scale role-to-role imprint technology. In the first part of this thesis we exploit the light scattering from dielectric nanoparticles to create colorful photovoltaics and with tailored angular distribution beyond what has been realized so far.

1.4. Light management in tandem cells

Tandem solar cells have the potential to reach efficiencies well above 30%. In the two-terminal (2T) tandem geometry the two subcells are connected electrically and share the same current, while in the four-terminal (4T) case the tandem is composed of two independent cells with independent current collection circuits that are mechanically stacked on top of each other. Both configurations have their advantages and disadvantages. For

2T tandem cells the main advantage is the compact geometry that allows integration into existing module technology. The main disadvantage is that the fabrication of the cells can be quite challenging because the subcells have to be fabricated as a single stack, where subsequent fabrication steps can negatively affect the earlier-deposited layers by the use of high temperature, reactive solvents, or etching processes that introduce defects. Also, the current matching condition in 2T cells sets a restriction on the design and allows only combination of certain range of bandgaps for the top and bottom cells. In contrast, for 4T cells current matching is not required, which relaxes the flexibility and bandgap combination of top and bottom cells. In a 4T geometry the two subcells can be fabricated and optimized independently. However, the main disadvantage is that the two independent cells cannot be integrated in existing module technology and more complex wiring circuitry is needed to harvest the current in a module composed of 4T tandem cells.

In the following and overview is given of the different optical losses in 2T and 4T perovskite/silicon tandem cells and how nanophotonic concepts can be used to reduce them. Finally, we will give an outlook how such solutions are addressed in this thesis.

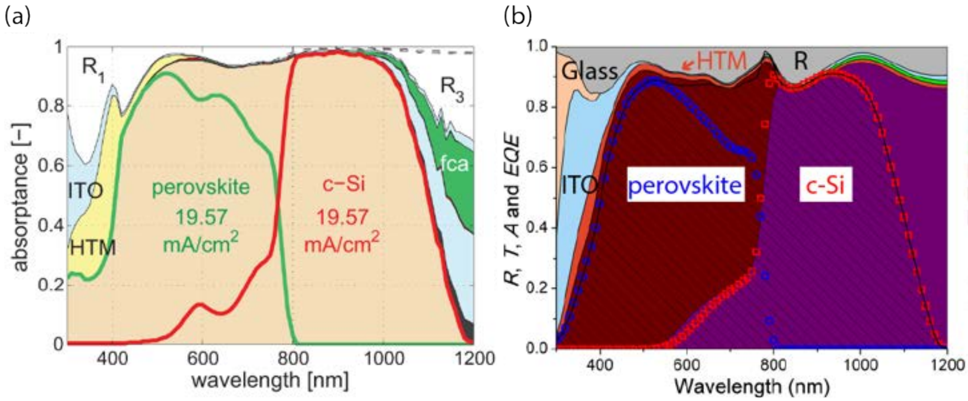

Figure 1.3: Loss analysis in 2T (left) and 4T (right) perovskite-silicon tandem solar cells, showing absorption in the sub cells with the perovskite and Si contributions indicated by the green and red curves (2T) and by the blue and red dotted curves (4T). Losses from reflectance and parasitic absorption in inactive layers of the cell are also indicated (ITO: indium-tin-oxide transparent contacts, HTM: hole/electron transport layers; FCA: free carrier absorption; R,$R_{1,3}$: reflection from perovskite and Si cell. From Refs. [29, 30]; additional labels added in (b).

For both 2T and 4T perovskite-silicon tandem cells proper light management is a critical factor to optimize the efficiency. The main optical losses are reflectance, parasitic absorption in inactive layers of the cell and non-ideal redistribution of spectral bands between the subcells [31, 32]. As an example, Figure 1.3 shows an analysis of the optical losses in a simulated 2T perovskite-silicon tandem cell [29] (J_{sc} = 39.1 mA/cm^2) and an experimental high-efficiency 4T tandem cell (η = 25.7%, J_{sc} = 36.5 mA/cm^2) [30]. In both cases, the perovskite top cells are flat and the silicon bottom cells have a textured front. Both images show the absorption in the tandem sub cells.

For both cells the same trends can be observed. First, reflectance induces losses of several mA/cm^2. Reflection of light occurs at the perovskite top surface, the interlayers and the silicon back surface. For the perovskite top cell, usually, a thin-film anti-reflection (AR) coating is applied. This could be replaced by a nanostructure layer that further reduces reflectance and couples light into the perovskite cell [15, 33, 34]. Texturing of the perovskite by applying perovskite directly on top of the textured silicon is still quite challenging (but has been recently demonstrated [35]). In the 2T example of Figure 1.3a, a barrier layer to planarize the silicon before applying the perovskite cell is modelled. In both 2T and 4T designs an interlayer in between the cells can be used to reduce reflectance from this part of the cell. In the 2T cell this requires integration with the intermediate carrier-selective contacts; in the 4T cell there is more room to design an optimized geometry between the two subcells. Applying nanostructures should optimize both optical impedance matching and carrier collection and conduction.

For the parasitic absorption in the other layers, mostly the transparent oxide (ITO in light blue in both figures) is responsible, next to the hole/electron transport layers and the glass top substrate. The perovskite material of the 2T geometry, shows free-carrier absorption (green area) which is not taken into account in the 4T structure. For the transparent intermediate and front contacts, metallic nanostructures as for example Ag nanowires could be an interesting consideration, as they can show lower absorption compared to ITO as shown in previous studies [36, 37].

Finally, in both cell geometries, a significant fraction of light with wavelengths closely below the bandgap of perovskite is transmitted to the underlying silicon cell instead of being absorbed in the perovskite cell. In the case of the 2T tandem cell current matching is required and for this the absorption of the top cell has to be tuned to an optimized value that depends on the bandgap. For 4T tandem cells, the top cell ideally fully absorbs all light above the bandgap, as a higher voltage can be gained there. Nanophotonic interlayers can therefore be beneficial to help reducing optical losses in 2T and 4T tandem cells, and are very flexible in application for the different cell geometries as well as different absorber materials.

In this thesis, we introduce spectral splitters for optimized redistribution of spectral bands between the subcells in 2T and 4T tandem solar cells. We take advantage of metasurface light scattering insights developed in the first part of the thesis to create colored PV. We provide a theoretical outlook for the potential of spectrum splitters in 2T perovskite/silicon tandem cells and present an experimental metasurface solution for 4T tandem cells that combines the functionality of spectral splitting, light trapping and reflectivity control in one metasurface structure.

1.5. From lab scale to large scale

This thesis demonstrates novel concepts to improve photovoltaics that are based on state-of-the-art cleanroom nanofabrication technologies, such as spincoating, electron-beam lithography, plasma etching and electron beam evaporation. All techniques used have the potential to be used to fabricate large-area structures at an industrial scale. Plasma-enhanced chemical vapor deposition (PECVD) is already widely used in PV industry to deposit thin-film anti-reflection and passivation layers. Substrate-conformal imprint lithography (SCIL) has already been developed into a large-scale fabrication technique using cassette-based multi-wafer handling [38]. The metasurfaces fabricated in this thesis, are partly based on patterns created by electron-beam lithography, but all of those could be transferred with SCIL.

To illustrate the potential of scaling up the structures proposed in this thesis, there are several companies already realizing tools for nanoimprint roll-to-roll processes. For example Morphotonics and Stensborg offer roll-to-roll nanoimprint methods. The plasma etchings step that is used in many fabrication routines of the thesis to transfer a nanopattern from the imprinting mask into the underlying material, could be replaced on large scales by wet etching processes. Alternatively, the metasurfaces could be imprinted directly, if a liquid sol-gel of the desired material is developed [16]. Recent advancements in the development of TiO_2 sol-gel are promising in this respect. Alternatively, the nanopatterns developed here inspire the use of spray coating of high index colloids, potentially in combination with self-assembly techniques, as it is already done widely for color coatings in the car industry. In summary, we think the designs and geometries presented in this thesis to improve PV have a realistic potential to be upscaled on industrial level and to be integrated into real-world devices.

1.6. Outline of this thesis

In this thesis we present the application of dielectric nanostructure for the improvement of photovoltaics. We design layers composed of scattering dielectric nanoparticles, arranged in metasurfaces and metagratings, that control the scattering of light in a tailored way. In the first part of the thesis we present the improvement of coloration of photovoltaics, from color creation through spectral control to more advanced directional control. In the second part of the thesis, we concentrate on improving the efficiency of perovskite/silicon tandem solar cells, applying spectral splitting metasurfaces.

Chapter 2 describes the coloration of silicon minimodules by an integrated scattering layer based on silicon Mie resonators. By tailoring the scattering particle size and shape we control the interference of electric and magnetic dipole modes of the nanoparticles to create resonant backscattering over a narrow spectral band. We show that a strong green coloration can be created that is only weakly dependent of the angle of incidence. The layer of Mie resonators is created by SCIL, describing a promising route for future large-scale fabrication. The structure shows low optical losses resulting in a drop of only 10% in the short-circut current of the silicon cell.

Chapter 3 further expands on the techniques introduce in Chapter 2. We show how the color space is increased and that multiple colors can be created. We extend the coloration to a technique in which we combine pixels of different colors, and experimentally demonstrate mixed colors and an example of a white coloration of a solar cell. Here the photocurrent losses are only ~19%, due to the fact that only a small desired spectral band of the light is reflected. The route of mixing colors by pixels shows a great flexibility in choosing colors by choice.

Chapter 4 is addressing the fact that the geometries in Chapter 2 and 3 are showing specular reflection behavior rather than scattering over a large angular band. This makes the coloration seem shiny and not matt as is preferred for some applications. To solve this issue, we create a reflecting Lambertian scattering metasurface, composed of individual metagratings that together result in reflectance at the resonant wavelength over a broad angular range, while at the same time cancelling the specular reflectance. We fabricate an array of amorphous silicon particles on top of a Ag mirror that is protected by a thin dielectric, using electron beam lithography. We characterize the angular reflectance profile and show a scattering efficiency of 90%. We also show that we can use a combination of differently designed metagratings to create resonant angular reflectance distributions at will.

In Chapter 5 we further expand on the technique introduced in Chapter 4 by designing a (semi-) transparent metasurface that reflects light on resonance in a determined angular range. With this, we enable coloration of rooftop photovoltaic only towards one half space to an observer on the street. This approach allows very efficient coloration with minimal losses as less light reflection is needed for a smaller angular range. By tailoring the interference between the light scattering modes of the nanoparticles we control the metasurface scattering spectrum on a transparent substrate and control the directivity by arranging the particles into gratings with different pitch. We use the combined metagratings approach of Chapter 4, adjusting the design to show very high diffraction efficiencies on a transparent substrate. We experimentally demonstrate a solar cell with angled colored distribution with a reduction of only 13% in short-circuit current.

Chapter 6 shows the theory, design and experimental realization of a broadband back reflector metasurface based on the Huygens-Fresnel principles. Using a phase gradient approach we design a theoretical metasurface with unity efficiency for back reflection. We then present an experimental realization in which the calculated phase gradient is discretized and TiO_2 nanowires of different height build up a unit cell on a Ag mirror. We show that the metagrating exhibits back reflection for a broad range of wavelengths from λ = 490-940 nm with an efficiency above 85%.

In Chapter 7 we theoretically study the benefits of a spectral splitter integrated into a perovskite/silicon 2T tandem solar cell. Based on detailed-balance calculations we first show that the absorption in the perovskite top cell is very sensitive to choosing the right thickness to match the currents of the sub-cells. We describe how a spectral splitter can enhance absorption in the perovskite top cell to achieve optimum voltage harvesting for the tandem. We calculate that a Lambertian spectral splitter in between the sub cells, in the thermodynamic limit, can lead to a 6% (absolute) efficiency enhancement for high-energy bandgap top cells.

Finally, Chapter 8 addresses spectral splitting in 4T tandem cells. We design a metasurface light trapping spectral splitter for a perovskite-silicon tandem cell. This metagrating has the property to efficiently reflect light with energies above the bandgap of perovskite back to the perovskite and introduce light trapping of the reflected light. At the same time, the spectral splitter reduces reflection in the infrared and therefore enhances current collection in the silicon sub cell. We build the metasurface using SCIL and integrate it in a tandem cell, showing a current increase in the top cell of at least 3%. We describe potential further enhancements for this novel spectrum splitter design and estimate that an efficiency enhancement of 0.40% (absolute) can be achieved in a realistic perovskite/silicon 4T geometry using a properly designed metasurface spectral splitter

In summary, this thesis provides key insights into the use of dielectric scattering particles and metagratings for the improvement of solar cells. We introduce the use of resonant metasurfaces and metagratings to control the color and angular scattering behavior of solar cells. Our work paves the way for potential large-scale application of these new concepts. We study the potential of spectral splitters in 2T tandem cells. Building on the metasurface and metagrating scattering concepts we introduce a new spectral splitter concept for 4T tandem solar cells that enhances current and voltage harvesting from the subcells. We present options for further improvements of the designs, and how they could potentially find applications in a wide range of tandem solar cell geometries.