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Summary

This summary is written in July of 2022, and the most recent data point for the CO_2 concentration on Mauna Loa is 420.99 ppm. I was born in April 1994, at 361.36 ppm. Stopping the rapid rise of greenhouse gas concentration in our atmosphere to combat the climate crisis is the biggest challenge of this century and has to be set on track this decade. And we are lucky enough to have the capabilities to make the tools to get there. Changing our ways of generating energy from polluting fossil fuels towards sustainable and renewable energy sources like wind, water and sunlight will significantly contribute to mitigation of global warming. Electricity generation from sunlight, photovoltaics (PV), is on track to carry part of the burden, and can benefit from further innovations in power conversion efficiency, technological versatility (flexible, bendable, durable, ...), and cost reduction.

In this thesis, these aspects are addressed for a range of technologies. We design novel photovoltaic architectures for a range of established (Si, III-V materials) and novel (PbS quantum dots, Zn_3P_2, perovskites) absorber materials. Light management concepts are used to evaluate and improve the absorption of light for photovoltaic devices, solar cells. The improvements are based on nano- and micrometer sized structures at the front, centre, or rear of the solar cells and aim to enhance the absorption inside the absorber layer as a primary goal. Additionally, the spatial distribution of the absorbed light is also considered, to not just ensure successful generation of charge carriers from photons, but also successful extraction of the carriers. We demonstrate many of these designs experimentally, evaluate their electronic performance, and use commercially relevant scalable processes to maximize the application relevance of our designs.

The thesis starts by elaborating on the looming consequences of the rise of greenhouse gas concentration in our atmosphere (Chapter 1). Global warming is identified as a serious danger and the main challenge of the century. This, amongst other reasons, provides important motivation and justification for switching to energy generation from renewable sources. The basic principles of photovoltaic energy conversion are discussed, as well as the thermodynamic detailed-balance limit, as a physical limitation. Special attention is giving to the trends in increase of device efficiencies for different ab-

sorbers over the years, and their distinct advantages for PV applications are presented.

The first technology we look at are solution-processed thin-film PbS quantum dot solar cells (Chapter 2), for which we introduce an optically resonant bulk heterojunction solar cell design. The cell is designed to consist of a square lattice of PbS QD cylinders of 330 nm height, 320 nm diameter, and a pitch of 500 nm, embedded in ZnO. The QD cylinder dimension are chosen such that they support optical resonances, maximizing the absorption per unit volume by 20% compared to a planar reference. Electronic simulations predict a gain in short-circuit current density (J_{sc}) of 3.2 mA/cm^2, and an efficiency gain of 0.4%-absolute. In experiment, we first use substrate conformal imprint lithography (SCIL) to demonstrate patterning of ZnO solgel and find optical trends confirmed in the fabricated devices, along with an increased external quantum efficiency (EQE) that shows a J_{sc} gain of 0.74 mA/cm^2. Finally, this chapter highlights the importance of considering the charge carrier generation profile as the quantity that interfaces optical and electronic solar cell design. PbS quantum dot solar cells have a tunable bandgap, are thin, and solution processable, making them interesting prospects for ink-jet printed or slot-die coated solar cells, as well as potentially indoor light harvesting devices. Advances in PbS quantum dots solar cells often also have positive implications for the design of light emitting diode (LED) devices based on this absorber.

Concentrator photovoltaics (CPV) is a high-efficiency technology that relies on concentration of sunlight onto relatively small solar cells, and the concentration factor causes a logarithmic increase in the open-circuit voltage (V_{oc}), which allows for more efficient devices. Furthermore, the usage of much smaller cells (factor 100-1000) allows for consideration of expensive III-V technologies, such as GaAs-based solar cells. However, CPV requires large front metal contact coverage to collect the high generated currents, which causes significant reflection losses. In Chapter 3, we demonstrate contact cloaking by means of optical refraction from V-shaped grooves that are patterned into a glass-like polymer. We demonstrate high optical transparency (95.2%) and apply the layer to a Si solar cell. For a front metal coverage of 25%, the optical cloaking layer increases the J_{sc} from 29.95 mA/cm^2 to 39.12 mA/cm^2. Finally, a concentrator optics design is presented that allows for an effective shading of 1.8% at a concentration of 1000 suns, for which we predict an efficiency gain of 4.8%-absolute, according to the detailed-balance limit. Concentrator solar cells are the most efficient PV technology on record, with a maximum power conversion efficiency of 47.1%. Furthermore, they are well suited for combination with concentrated solar thermal setups in high irradiance regions on earth, making these architectures capable of sourcing electricity and heat from the sun simultaneously.

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Silicon PV is currently the commercially most relevant technology, owing to low end-user costs and high module efficiencies (above 20%). At the same time, thin-film PV applications are becoming increasingly important. The maturity of Si technology would make it an interesting contender for that market, but absorption in thin crystalline Si wafers is inhibited by poor absorption of light close to the bandgap (1000-1200 nm). Chapter 4 introduces a fabrication approach for two optical designs that can improve incoupling and light trapping in Si absorbers with flat surfaces to mitigate this issue. For incoupling, we demonstrate a square lattice of SiN_x nanocylinders (117 nm height, 190 nm diameter, 460 nm pitch) that acts as a broadband anti-reflection coating. The design currently yields a measured J_{sc} of 36.9 mA/cm^2, with the potential of achieving up to 39 mA/cm^2 on a 100 μm Si wafer. Such designs can also be used on thinner wafers to create high-efficiency flexible solar cells. Finally, we experimentally demonstrate a hyperuniform Si nanostructure on the surface of a Si solar cell, that can efficiently trap light in a thin Si cell, and investigate electronic passivation requirements for the strongly corrugated geometry. Thin crystalline Si wafers may find applications in vehicle-integrated PV, building-integrated PV, and in wearable and foldable electronics, and may enable a further cost reduction due to the use of a thinner absorber layer.

A highly promising path to enhance the power conversion efficiency of Si based PV is by the addition of a second absorber on top, creating a tandem solar cell device. The detailed-balance efficiency limit for such a cell is 45.1% for a perovskite top cell with a bandgap of 1.73 eV, which is significantly larger than the limit for a Si cell alone (33%). We adapt (Chapter 5) the detailed balance formalism to predict realistic efficiency limits, by tailoring the optical interface between Si and perovskite. We optimize the spectrally selective light reflection, so that the energy of the incoming photons can be harvested more efficiently. The calculations predict that a spectrally selective Lambertian light trapping layer can yield an efficiency gain of 2.7%-absolute for a 500-nm-thick perovskite layer with a bandgap that is close to the optimum (1.77 eV). With increasing bandgap, this effect becomes stronger, and can yield efficiency gains up to 6%-absolute. Perovskite/Si tandem devices have just achieved laboratory efficiencies of 31.3% and are already being commercialized. The high voltages that such tandem devices enable are also interesting for electrolysis applications such as solar-to-hydrogen conversion, where power from the solar cell facilitates water splitting.

Zn_3P_2 is an absorber material with long diffusion lengths and strong absorption but has received very limited attention in PV until just recently. New developments that allow for high-purity Zn_3P_2 crystals and removal of the absorber from the growth substrate now enable new design opportunities for the cell architecture. We propose (Chapter 6) a thin-film Zn_3P_2-TiO2 heterojunction solar cell design that consists of a cell stack of Au (back contact) – Zn_3P_2 (p-type absorber) – TiO_2 (n-type layer) – ITO (front contact). The design is derived from electronic drift-diffusion simulations and predicts a power conversion efficiency of 20% for 2-μm-thick Zn_3P_2. Improved light incoupling could increase the efficiency further. Zn_3P_2 consists of materials that are abundant in the earth's crust, and thus have the potential to become relevant for PV on a large scale due to lower material extraction costs, next to its good optoelectronic qualities.

For light management concepts to become interesting on an industrial scale, it is important that fitting nanofabrication processes are found. Substrate conformal imprint lithography (SCIL) is such a process and is used in many chapters of this thesis. In Chapter 7 we review further nanofabrication approaches for PV based on SCIL. Relying on the experience from the previous chapters, we identify three possible approaches. Next to indirect approaches that use SCIL to provide an etch mask for further lithography steps, we highlight direct imprinting as a simple one-step approach, that can be applied using dedicated solgels. SCIL has already been commercialized for a cassette-based wafer patterning approach and roll-to-roll soft-imprint patterning also exists commercially, so that these novel insights may find their way to large-scale applications.

Conceptually, this thesis integrates the optimization of light management with charge carrier management by carefully optimizing the three-dimensional charge carrier generation and collection profiles. We emphasize the importance of spatial control of absorption for the electronic solar cell performance. We investigate how absorption-enhancing nanostructures influence the electronic integrity of solar cells for a wide range of established as well as novel photovoltaic technologies. The insights derived in this thesis can lead to solar cells with thinner absorber layers, higher efficiencies, and may introduce the use of novel absorber materials and cell designs.