Bright Ways to Utilize the Sun

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Towards Solar to Fuel Devices

2018

Wouter Visselaar

BRIGHT WAYS TO UTILIZE THE SUN: TOWARDS SOLAR-TO-FUEL DEVICES

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Table of contents

Chapter 1 General Introduction	1
1.1 General introduction	1
1.2 Aim and scope of the thesis	4
1.3 References.....	6
Chapter 2 Silicon Micro- and Nanowire Arrays: From Efficient PV Cell to Photocathode ...	7
2.1 Introduction	7
2.2 PEC hydrogen generation	11
2.2.1 Why hydrogen?	11
2.2.2 Choice of semiconductor material	12
2.2.3 Device design concepts.....	15
2.2.4 Charge separation	19
2.2.5 Catalyst materials	20
2.2.6 Important parameters for a PEC cell	20
2.3 Micro- and nanowired silicon structures.....	22
2.3.1 Light management in Si based PEC and PV cells.....	22
2.3.2 p/n junctions in highly structured Si PV devices	25
2.3.3 Catalysts on micro- and nanowire arrays.....	28
2.4 Conclusions and outlook	36
2.5 References.....	37
Chapter 3 Effects of Pillar Height and Junction Depth on the Performance of Radially Doped Silicon Pillar Arrays for Solar Energy Applications.....	45
3.1 Introduction	46
3.2 Results and discussion	47

3.3	Conclusions	53
3.4	Acknowledgements	53
3.5	Materials and methods	53
3.5.1	Fabrication of radial p/n junctions in silicon micropillar arrays	53
3.5.2	Atomic layer deposition	54
3.5.3	JV measurements	54
3.6	References	55
 Chapter 4 Photo-Electrical Characterization of Silicon Micropillar Arrays with Radial p/n Junctions Containing Passivation and Anti-Reflection Coatings.....57		
4.1	Introduction	58
4.2	Results and discussion	59
4.2.1	FEM simulations of reflectivity	59
4.2.2	Anti-reflection coatings.....	62
4.2.3	JV measurements	64
4.2.4	Deconvolution of the contributions of passivation and anti-reflective properties.....	66
4.3	Conclusions	68
4.4	Acknowledgements	69
4.5	Materials and methods	69
4.5.1	Fabrication of radial p/n junctions in silicon micropillar arrays.....	69
4.5.2	Atomic layer deposition	71
4.5.3	Low pressure chemical vapor deposition	71
4.5.4	Sputtering	71
4.5.5	Ellipsometry	72
4.5.6	Focused ion beam structuring.....	72
4.5.7	JV measurements	72

4.5.8	Finite element modeling of the reflectivity of silicon micropillars	72
4.6	References.....	73
Chapter 5 Textured and Micropillar Silicon Heterojunction Solar Cells with Hot-Wire Deposited Passivation Layer.....		77
5.1	Introduction	78
5.2	Results and discussion	79
5.2.1	Randomly textured SHJ cells.....	79
5.2.2	Micropillar SHJ cells.....	79
5.2.3	a-Si:H/SHJ tandem cells.....	82
5.2.4	a-Si:H/a-SiGe:H/SHJ triple junction cell.....	84
5.3	Conclusions	85
5.4	Acknowledgments	86
5.5	Material and methods	86
5.5.1	SHJ fabrication	86
5.5.2	Texturing.....	87
5.5.3	SHJ micropillar fabrication	88
5.5.4	Tandem cell micropillar fabrication.....	89
5.5.5	Triple cell micropillar fabrication.....	89
5.5.6	Current density-voltage measurements	90
5.5.7	Imaging	90
5.6	References.....	90
Chapter 6 Spatial Decoupling of Light Absorption and Catalytic Activity of Nickel-Molybdenum on High-Aspect-Ratio Silicon Micropillar Arrays.....		93
6.1	Introduction	94
6.2	Results and discussion	95
6.2.1	Photoelectrical (<i>JV</i>) measurements	98

6.2.2	Dark electrochemical (<i>JE</i>) measurements	99
6.2.3	Photoelectrochemical (<i>JE</i>) measurements	100
6.3	Conclusions	104
6.4	Acknowledgements	104
6.5	Materials and methods	105
6.5.1	Fabrication of radial n+/p junctions in silicon micropillar arrays.....	105
6.5.2	Low pressure chemical vapor deposition of SiO ₂ passivation layer.....	106
6.5.3	Local removal of SiO ₂ from the tops of micropillar arrays	106
6.5.4	Catalyst deposition.....	107
6.5.5	<i>JV</i> measurements	107
6.5.6	<i>JE</i> measurements	108
6.5.7	Gas chromatography.....	108
6.6	References	108

Chapter 7 Optimization of Spatially Decoupling of Light Absorption and Catalytic Activity of Nickel-Molybdenum on Passivated High-Aspect-Ratio Silicon Microwire Arrays 111

7.1	Introduction	112
7.2	Results and discussion	113
7.2.1	Photovoltaic (<i>JV</i>) measurements (bare).....	115
7.2.2	Photovoltaic (<i>JV</i>) measurements (with catalyst)	117
7.2.3	Dark electrochemical (<i>JE</i>) measurements	118
7.2.4	Photoelectrochemical (<i>JE</i>) measurements	121
7.3	Conclusions	124
7.4	Acknowledgements	124
7.5	Materials and methods	124
7.5.1	Local removal of SiO ₂ over a defined length of Si microwire arrays	125
7.5.2	Electrical contacts	126

7.5.3	Catalyst deposition	126
7.5.4	<i>JV</i> measurements	127
7.5.5	<i>JE</i> measurements	127
7.5.6	Light source and calibration	128
7.6	References.....	129
Chapter 8 Nickel Silicide Interlayers Render Si Microwire Photocathodes Stable in Strong Alkaline Electrolyte		131
8.1	Introduction	132
8.2	Results and discussion	133
8.2.1	Development of a NiSi interlayer	133
8.2.2	Photocathodes with a NiSi interlayer	139
8.3	Conclusions	142
8.4	Materials and methods.....	143
8.4.1	Fabrication of radial n ⁺ /p junctions in silicon microwire arrays	143
8.4.2	Local removal of SiN _x from the tops of microwire arrays	143
8.4.3	Protective Ni and NiSi deposition	144
8.4.4	Catalyst deposition	145
8.4.5	NiSi formation on n-type Si with different dopant levels.....	145
8.4.6	<i>JE</i> measurements	146
8.5	References.....	147
Chapter 9 A Stand-Alone Membrane-Embedded Microporous PEC Cell.....		149
9.1	Introduction	150
9.2	Results and discussion	152
9.2.1	Operational PEC cell	154
9.2.2	pH gradient formation in microporous PEC devices	156
9.2.3	pH gradient simulation.....	159

9.3	Conclusions	162
9.4	Materials and methods	163
9.4.1	Triple PV cell	163
9.4.2	Sputtering	163
9.4.3	Deep reactive ion etching	164
9.4.4	Membrane dropcasting	164
9.4.5	Gas chromatography.....	164
9.4.6	COMSOL modelling	164
9.5	References	166
Summary.....		169
Samenvatting		175
Dankwoord.....		181

Chapter 1

General Introduction

1

1.1 General introduction

Humanity does not only desire energy to survive, but also to sustain and increase prosperity of a rapidly expanding population. The increase of the energy demand is especially true for Developing Countries, which contain the majority of the, increasing, population these days. A vast fraction of the current energy supply comes from the burning of fossil fuels. However, the worldwide dependence on fossil fuels can only be temporary, since the fuel resources are finite. Figure 1.1A shows schematically the worldwide primary energy consumption on a yearly basis (green), with respect to the worldwide reserves of oil, gas, and coal. These carbon reserves may provide enough energy for the coming decades, but will be depleted eventually.¹ At the same time, the combustion of fossil fuels is a major source of greenhouse gas emissions, mostly carbon dioxide (CO₂), and thus is responsible for global warming.²

For these reasons, one of the world's key challenges is to switch from a fossil fuel-based economy to a more sustainable alternative energy economy. At present, more than 80% of our primary energy is provided by fossil fuels, due to their high energy density, ease of handling, storage, and transportation.^{3,4} A possible solution to this challenge is the use of renewable energy sources, since these energy sources are not depleted like fossil fuels, but are available in a continuous fashion. Figure 1.1B shows the yearly energy potential of different renewable energy sources, with respect to our yearly consumption.¹ From all these energy sources, solar energy is believed to be the only one able to scale with our increasing energy requirements. With a ~120.000 TW average yearly irradiation at the earth's surface (see Figure 1.1B), solar energy is about 4 orders of magnitude larger than the current rate of worldwide technological energy use by humans.⁵

Figure 1.1 (A) Fossil fuels expressed with regard to their total worldwide estimated reserves. (B) Renewable energy sources to their yearly potential. Reproduced with permission.¹ Copyright 2012, Wiley-VCH.

Nowadays it is cost effective to place photovoltaic (PV) panels in residential areas owing to the fact that the relentless decline in PV module prices has continued at a rate of $\sim 5\%$ annually for the past decade.⁶ A bidding war in 2017 resulted in PV cells being produced for less than $0.242 \text{ \$/kWh}$.^{7,8} This impressive cost reduction is primarily caused by an increase in production rate.

Unfortunately, solar energy is inherently more variable and uncertain than the traditional dispatchable oil and coal-based energy generators that have historically provided a majority of grid-supplied electricity. The output of solar-generated current is variable over time, driven by weather, and dependent on the Earth's rotation and orbit around the sun. These fluctuations in energy production lead to an unsteady power output on a daily basis, and on a yearly basis as well due to seasonal changes, and thus cause a mismatch between energy production and consumption. To cope with this intermittency issue, the production of solar fuels using sunlight has great potential in order to provide a high-density storage medium of solar energy in the form of fuel. In this manner solar energy can be stored, transported and regained when required. Solar fuels include hydrogen after water splitting, or carbon-based fuels from reduced CO_2 . This concept is also known as solar-to-fuel (S2F), and has already been proven to be functional on lab-scale.

A S2F device requires the coupling of multiple processes, *i.e.* light harvesting, charge separation, charge transport, catalysts to perform the required fuel formation, and produced fuel separation and collection. One of the most popular and investigated fuels is hydrogen, and it is believed to aid in a sustainable hydrogen economy. To produce hydrogen in a S2F device, a photovoltage of 1.23 V is required in theory. Practically an extra 0.6 V is required, due to imperfect materials characteristics, complexity of the O₂ formation process, etc.⁹ To overcome this overall potential, a single semiconductor with a bandgap of >2 eV is required to drive the reaction. Semiconductors with such a large bandgap use only a fraction of the incoming photon flux, as is depicted in Figure 1.2. This results in a very low overall efficiency, estimated at about ~10% theoretically, whereas only ~1% has been proven practically.¹⁰

Figure 1.2 Plot of the solar flux as function of wavelength, as incoming black body (black line), extraterrestrial (blue line), and AM1.5g (orange). The amount of possible absorbed photons with respect to a specific bandgap is shaded, for materials with a bandgap of 1, 2 and 3 eV.

A bandgap of >2 eV can also be obtained by combining a set of semiconductors with a smaller bandgap, *i.e.* a tandem device. This concept results in a larger photon absorption (see Figure 1.2) and may therefore be more efficient. Theoretically, a set of a smaller (0.92 eV) and a larger (1.59 eV) bandgap would result in an overall efficiency of 28%.¹⁰

In order to choose the correct and required materials two key aspects are of main importance: earth-abundance and high performance. Both are required when S2F devices should become relevant for the world production scale (terawatt). To date, these two requirements are most of the time conflicting, necessitating further research. Silicon, however, with a bandgap of 1.1 eV, makes a very interesting candidate for the lower bandgap material in a tandem device. This is mainly due the low production cost, earth abundance, non-toxicity, and widely gained knowledge in the nano/micro-fabrication

world.¹¹ Moreover, the knowledge gained in Si PV cells can directly be implemented in a S2F device, with Si as one of the absorbers. Although Si is very good photon absorber, it has very sluggish reaction kinetics towards the hydrogen production and is sensitive to oxidation. Therefore, Si needs to be combined with a catalyst in order to produce hydrogen efficiently.

The best known heterogeneous catalysts for hydrogen production are all based on platinum,¹² but this happens to be also one of the most scarce elements on earth.¹³ Tremendous research effort has been performed in the search for earth-abundant catalysts that are as active as platinum.¹⁴ Far less research is available on how to implement these new materials with a photon absorber, like silicon. Here, the main problem is that most earth-abundant catalysts are optically opaque, but require high mass loadings ($\geq 1 \text{ mg/cm}^2$) to achieve the required catalytic activity. Few systems have been realized that use earth-abundant semiconductor and catalyst materials for the half-reactions involved in solar-driven water-splitting, while also achieving high energy conversion efficiencies.

1.2 Aim and scope of the thesis

The main aim of the work described in this thesis is to improve the insights in and fabrication methods of silicon-based solar-to-fuel devices. Here, we first optimize a new type of micro-structured PV cell, *i.e.* a microwire array, in terms of doping, aspect ratio, and passivation. These substrates are used as a platform for a highly efficient lower bandgap absorber in a tandem S2F configuration, to be combined with earth-abundant catalysts to create a hydrogen-producing photocathode.

Chapter 2 provides a literature overview of the state-of-the-art on high-aspect-ratio structured PV cells. It is discussed how similar structures can be employed as efficient hydrogen photocathodes, by applying catalyst material on these structures.

Previous studies showed the possibilities that Si microwires could potentially be effective PV cells. Chapter 3 describes the optimization of the efficiency of radially doped microwire arrays, in terms of wire height and junction depth. First, the height of the microwires was varied between 0 and 60 μm . Secondly, by adjusting the doping time and temperature, the junction depth was varied between shallow (140 nm) and deep (1640 nm). The effects of both wire height and junction depth were analyzed subsequently by photoelectrical measurements, in order to find the optimum between the two parameters.

Chapter 4 continues with the optimization of silicon microwire arrays, by the addition of a passivation and anti-reflection coating (Al_2O_3 , SiO_2 , and SiN_x). The optimal thickness for light trapping was simulated for each of these materials. Subsequently, these layers were

grown on microwires by different techniques. High-resolution scanning electron microscopy (HR-SEM) was used to investigate the 3D deposition characteristics of the chosen techniques. Finally, the electrical properties were measured, to quantify and deconvolute the improvements of the performance achieved by passivation and anti-reflection properties effectuated by the layers.

In Chapter 5, possibilities are described to increase the photovoltage of a Si-based microwire PV cell. Here, hot-wire chemical vapor deposition is employed to deposit a passivation layer, and a second or a third absorber over the microwire structures. The maximum height of microstructures is investigated for functional single, tandem, and triple microwire PV cells. The constructed PV cells are characterized by *JV* measurements, and the deposition is investigated by HR-SEM.

In Chapter 6, Si microwires arrays are converted to highly efficient hydrogen half-cells with an earth abundant catalyst. NiMo, as earth abundant catalyst, is spatioselectively deposited on Si microwire arrays, and its performance is compared to platinum, which is one of the best performing hydrogen catalysts to date. Both the photoelectrical and photoelectrochemical performances are assessed and compared to microwire arrays onto which the catalyst is deposited over the entire microwire surface.

In Chapter 7, a deeper understanding is developed for the parameters influencing the efficiency of Si microwire photocathodes, as described in Chapter 6. Here, a parametric sweep is performed, to investigate limiting factors of spatioselectively functionalized Si microwire photocathodes. The microwire pitch is varied between 8 and 24 μm , and the catalyst coverage over the microwires is varied between 2 and 36 μm . The limiting efficiency factors are assessed via both photoelectrical and electrochemical characterization of every cross combination within the parameter variation.

In Chapter 8, an interlayer is described to improve the chemical resistivity and applicability of Si microwire arrays in alkaline electrolyte. Electrodeposited catalysts are granular, through which the underlying Si microwires are etched, leading to rapid degradation of the performance of Si photocathodes in alkaline electrolytes. We develop NiSi as an effective interlayer to protect the Si microwire arrays, and assess its performance by photoelectrochemical characterization of NiSi-protected, NiMo-covered photocathodes.

In Chapter 9, a full wireless solar-to-fuel device was fabricated by taking various concepts and elements from literature. We employ microporosity to introduce shortcuts for ionic transport, with the aim to avoid the buildup of a pH gradient that would limit the S2F performance. Micrometer-sized islands of catalysts are created on the illuminated side of the device to avoid parasitic light absorption. A nanometer-scale, thin membrane is used to reduce proton transfer resistance across the membrane. The influence of

microporosity on the device performance is studied by experimental (photo)electrochemistry as well as by analytical and finite-element models.

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Chapter 2

Silicon Micro- and Nanowire Arrays: From Efficient PV cell to Photocathode

2.1 Introduction

The world's major challenge is to switch from an oil-based economy to a more sustainable alternative energy economy. At present, more than 80% of our primary energy is provided by fossil fuels, due to their high energy density, ease of handling, storage, and transportation.^{1,2} To get a sense of the magnitude of this challenge, in 2016, only the U.S. had already over 266 million registered vehicles, (*i.e.* light duty vehicles, buses, trucks and motorcycles), which consumed 11.3 million barrels of oil to travel 3.0 billion miles on a daily basis. This represents a staggering 10% of the total worldwide fossil fuel consumption.³ At the same time, the combustion of fossil fuels is a major source of greenhouse gas emissions, mostly carbon dioxide (CO₂), and thus contributes strongly to global warming.⁴

A possible solution to this challenge is the use of solar energy, which provides a ~120.000 TW average yearly irradiation at the earth's surface, which is about 4 orders of magnitude larger than the current worldwide energy consumption by humans.⁵ Nowadays it is cost effective to place photovoltaic (PV) panels in residential areas due to the fact that the relentless decline in PV module prices has continued at a rate of ~5% annually for the past decade.⁶ Recently, the 20% efficiency line for PV modules has been crossed for commercial PV cells, and PV cells can be produced for less than 0.242 \$/kWh.^{7,8} However, employing solar energy on a large scale has a couple of major drawbacks, firstly the intermittency of the day-night cycle, secondly the seasonal change in power density, thirdly PV cells only generate electricity for direct use, and lastly solar energy density around the poles is less than around the equator (*i.e.* lower overall efficiency). The intermittency leads to a surplus of energy during the day, whereas during the night there is a shortage (Figure 2.1A).⁹ This needs a short-term storage solution, *i.e.* storing the surplus of electricity during the day and use of this stored energy during the night (Figure 2.1B). The seasonal change in energy output of PV cells requires energy to be stored for longer periods (*i.e.* months) of time without degradation of the stored energy. Furthermore, it is more cost effective to produce electricity in more sunlit countries, *e.g.* in the proximity of the equator.¹⁰ The produced energy has to be distributed in some

manner to all of the other parts of the world. A new energy grid over such distance involves enormous investments. Thus, while PV cell technology has been largely directed to electricity generation,¹⁰ we note, as stated above, that a major part of the energy is needed in a storable and transportable form. All of these problems can be solved by storing solar energy in a fuel.¹¹ Many individual options are available to store solar energy into a fuel, which all have their advantages, e.g. photothermal, PV-electrolysis, or photoelectrochemical. A list of advantages and disadvantages, specifically focused on the relationship with the transient behavior of the sun, is given below.

Figure 2.1 The red curve represents the PV production, while the black line is an average day consumption. (A) A surplus in energy production is visible, while a shortage occurs during the night. (B) The red arrows indicate the surplus that should be stored during the day and used during the night periods.⁹

Photothermal systems make use of two-step thermochemical cycles of metal oxide redox pairs (e.g. $\text{Ce}_2\text{O}_3/\text{CeO}_2$,¹² Zn/ZnO ,¹² $\text{FeO}/\text{Fe}_3\text{O}_4$,¹³ and SnO/SnO_2 ,¹⁴). These cycles are driven by the heat obtained from concentrated solar radiation. All of these materials can be thermally reduced at high temperatures, releasing oxygen. The reduced compound can then be used to split H_2O or CO_2 , to produce H_2 or CO , respectively. Together, these products form syngas, which can be converted into denser diesel-type fuel using the Fischer-Tropsch process. Significant research and technology developments are needed to overcome the key technological challenges for the more advanced solar thermochemical fuel production technologies: (i) development of stable reactor designs, which can handle the high operating temperatures (up to $\sim 2000^\circ\text{C}$), (ii) increase of the overall efficiency to $>10\%$ (state-of-the-art is $\sim 2\%$), (iii) scaling of reactor technologies to an industrial level, and (iv) development of dynamic models and control systems that deal with the inherently intermittent nature of solar radiation.^{12,15,16}

PV-electrolysis makes combined use of a conventional water electrolyzer and the electrical output of PV devices. Given that typical conversion efficiencies are 20% for commercial PV systems and 80% for electrolyzers, overall conversion efficiencies of approximately 16% are expected and have been reported for optimized, combined PV-electrolyzer systems. The most obvious advantage of this approach is that both PV and electrolysis systems are commercially available, although large-scale electrolysis systems are not nearly as extensively available as PV systems.^{17,18} While impressive advancements

have been made in the last decade on electrolysis system materials, cost reduction and efficiency, still one of the major hurdles for electrolyzers is the degradation and failures induced by intermittency.¹⁹ There are only a few literature studies quantifying the performance degradation due to intermittency.¹⁹ Petipas *et al.* realized a test with an electrolyzer under steady-state and on-off cycle operation and showed a degradation of 3 $\mu\text{V/h}$ and 10 $\mu\text{V/h}$, respectively. This result leads to an expected lifetime of 2.5 years, assuming a maximum cell voltage of 2 V, and is thus less favorable in an intermittent setup.²⁰ Especially when the expected life time of a PV cell is 25 years, an electrolyzer has to be replaced 10 times.

A photoelectrochemical (PEC) cell combines the functions of light collection, charge separation, and electrolysis in a single device. This is achieved by replacing one or both of the metallic electrodes in a conventional electrolysis cell by a semiconductor. The advantage of this approach is that it offers opportunities to minimize cost by eliminating redundant support structures and energy losses associated with cell interconnections.^{1,21} Furthermore, PEC cells are specifically developed to cope with the transient behavior of the sun. Lastly, the current density of a PEC cells is much lower as for an electrolyzer. (*i.e.* $\sim 20 \text{ mA/cm}^2$ vs. $\sim 1 \text{ A/cm}^2$). Therefore the material requirements are much less stringent, as for an electrolyzer.

Of these three systems, the use of a PEC cell seems the most favorable. Photothermal systems require a constant energy input, because of the high temperatures and the rapid degradation upon cooling and heating cycles of the reactors. PV-electrolyzers still suffer from degradation induced by the transient behavior of the sun. Furthermore, Pinaud *et al.* made a cost analysis for industrial scale solar fuel plants.²¹ Herein it was suggested that integrated PEC devices could possibly produce solar fuels at a lower cost than a PV-electrolyzer system. Lastly, the purpose of solar fuel research is to provide a sustainable alternative to fossil fuels, and thus the environmental impact of PEC cell production and operation, or its alternatives, is an essential factor when evaluating different approaches.²² Zhai *et al.* concluded that the solar-to-hydrogen (STH) efficiency and longevity of the PEC device are key parameters in a net energy analysis. Therefore they analyzed three cases, low, medium and high, and found that compared with multi-crystalline Si PV the PEC device requires less energy to manufacture in a low and medium case analysis, but more energy in the higher case analysis.²²

One recurring theme is: earth abundance. Developing low-cost and earth-abundant materials for PEC cells that could demonstrate a performance comparable to that of high-end materials although at a lower cost is highly required, in order to up-scale the production to the terawatt scale. The design and fabrication of PEC cells is still at its infancy, but does constitute a widely researched topic, whereby the publications still increase every year (*i.e.* hits in Scopus in 2016 on "PV electrolysis": 36 vs.

“photoelectrochemical water splitting”: 648).²³ The wealth of information is rapidly expanding on the choice of materials for photoanodes, photocathodes, and catalysts. Therefore we focus in this review on the selection of the work done on silicon micro- and nanowire Si photocathodes with earth-abundant catalysts to produce hydrogen (H₂) as fuel.

As light absorber, we focus on silicon (Si), due to low production cost, earth abundance, non-toxicity, and the widely gained knowledge in the nano/micro-fabrication world (see Section 2.2.2).²⁴ However, Si has two major disadvantages, it reflects ~35% of the incoming solar light over a broad spectrum, and has very sluggish kinetics to produce H₂. These two drawbacks lower its possible maximum efficiency. As a consequence, Lewis and coworkers have proposed a micro- or nanowired Si photocathode with a catalyst to overcome both drawbacks. The implications of nano- and microwire arrays on reflection of Si is discussed in-depth in Section 2.3.1. The efficiency of a Si photocathode is tremendously enhanced, by incorporating a *p/n* junction (see Section 2.2.4). Moreover, a Si photocathode with a *p/n* junction is similar to a Si PV cell with a buried *p/n* junction underneath a catalyst. Knowledge and improvements gained in the field of highly structured silicon PV devices can therefore directly be implemented in nano- and microwire Si photocathodes to improve their efficiency. Therefore, an overview is given in the advances of *p/n* junctions in highly structured Si PV devices in Section 2.3.2. To maximize the efficiency of Si photocathodes, electrocatalysts are commonly used to facilitate the chemical reactions at the electrode surface, by lowering the overpotentials and thus accelerating the production rates. Platinum (Pt) and other noble metals are still the best electrocatalysts for the hydrogen evolution reaction (HER). In Section 2.3.3 an overview is given of the implementation of Pt as catalyst in Si micro- and nanowired photocathodes. However, the high cost and scarcity of Pt greatly limit the large-scale deployment. Therefore, the use of low-cost and earth-abundant catalysts, which could demonstrate performance comparable to that of Pt-group metals, is highly desirable. Section 2.3.3 describes the impact of earth-abundant catalysts in combination with highly structured Si.

Because of the rapid developments in this emerging field, we do not attempt to cover the full body of work related to Si photocathodes; instead, we highlight the key discoveries that have advanced fundamental understanding and have influenced the research directions in the field of micro- and nanowired Si photocathodes.

2.2 PEC hydrogen generation

2.2.1 Why hydrogen?

In order to produce a chemical fuel, two half-reactions need to be combined, *i.e.* an oxidation and a reduction reaction. The most investigated oxidation reaction for PEC cells is water oxidation:²⁵

The produced protons and photogenerated electrons can be used in many different ways to form different chemical fuels. At the moment two main precursors are used at the cathode, either the protons can be used directly to form molecular hydrogen (H₂), or carbon dioxide (CO₂) is added to form carbon-based chemical fuels, see the following equations:²⁵

The production of H₂ occurs at a theoretical potential of 1.23 V (Equation 2.1 and 2.2). H₂, the most elemental fuel, has many attractive attributes. An advantage of solar-generated H₂ is that it has zero CO₂ emissions, when used in combustion engines of fuel cells, and has solely H₂O as "waste". At this moment, the majority (>95%) of global H₂ is produced from fossil fuels, primarily via steam methane reforming and it would be a breakthrough if this could be done by solar-generated energy.²¹ However, a major drawback of H₂ is that it has a low volumetric energy density, cannot be stored easily, or distributed like hydrocarbon fuels, since it evolves as a gas under standard test conditions.²⁶ Its envisioned use as a clean energy carrier on a large scale is hindered by the need for a cost-competitive and renewable production route, efficient storage and furthermore, the new infrastructure needed to distribute the fuel.^{21,27} All of these drawbacks could be overcome if the efficiency of renewable H₂ is increased substantially.^{21,26}

Another precursor which is widely investigated is CO₂. Today, the atmospheric concentration of CO₂ is increasing at a rate of ~1.8 ppm/y, and this rate is expected to increase unless efforts are made to reduce the consumption of fossil fuels and to develop means for producing carbon-based fuels sustainably. Photochemical reduction of inert CO₂ could in principle conveniently recycle greenhouse gasses back into valuable fuels.

Even though CO₂ reduction and water oxidation could in theory be achieved at a potential difference as low as 1.06 V (Equation 2.1 and 2.3), the potential needed in practice is much higher for several reasons:¹⁸ (1) The overpotentials are either exceedingly high,²⁸ (2) metal catalyst surfaces become poisoned and deactivated by the reaction products,²⁹ (3) considerable kinetic challenges occur for the conversion of CO₂ into more complex products, since it is a multi-proton-coupled electron transfer process (see Equations 1.3 – 1.6),³⁰ (4) the product selectivity of CO₂ conversion is very low, so almost always a mixture of products is formed.^{18,25} These drawbacks make the use of CO₂ less favorable as it comes to testing the underlying fundamental aspects of a PEC cell. Therefore, H₂ is a good model compound to produce in order to develop the concept of the PEC cell. As a consequence, we focus in this review on the production of H₂.

2

2.2.2 Choice of semiconductor material

Figure 2.2 summarizes schematically the complex process of how light is converted into H₂. The incoming light is converted into charge carriers by the semiconductor, but part of the incident light is blocked or scattered in multiple ways, either by inherent reflectance from the semiconductor surface (1), bubble formation (2), absorption by the electrolyte (3), or by the catalyst material (4). The remaining light is absorbed by the semiconductor, which generates both charge carriers (*i.e.* electrons and holes) and creates the photovoltage. Charge carriers need to be shuttled in an efficient way to their respective reaction sites, holes to oxidize H₂O (Equation 2.1) and electrons to reduce protons (Equation 2.2). Protons evolved from Equation 2.1 have to be transported from the anode to the cathode compartment in an efficient manner. In the end the evolved gasses (H₂ and O₂) can be collected and stored.

A sensitivity analysis was performed to investigate all parameters of the complex process described in Figure 2.2, to deduce the factors that could provide the largest benefits to the performance of a full system.^{31,32} Fontaine *et al.* considered the effects of five parameters, namely: semiconductor absorption fraction, semiconductor external radiative efficiency, series resistance, shunt resistance and catalytic exchange current density, on the limiting efficiency. Only ~1% absolute efficiency gains could be realized by reduction of the overpotentials for the HER catalyst, OER catalyst, or the effective transport resistance of the membrane separator, and the solution electrolyte. Fontaine *et al.* concluded that the most important material in a PEC system is the photoabsorber, *i.e.* the semiconductor(s).³² This material generates both the photovoltage and photocurrent to drive the overall reaction.

Figure 2.2 All major processes in a schematic PEC device which turn light and water into hydrogen and oxygen. (Reflected colors are chosen randomly and do not represent a physical meaning.)

Solar-driven water splitting could be achieved with either a single semiconductor with a large bandgap (>1.7 eV) or with a combination of two or three semiconductors in a tandem PEC cell consisting of an integrated oxygen-evolving photoanode and a hydrogen-evolving photocathode. To date, no earth-abundant PEC cell consisting of a single semiconductor material is known to operate above 2% overall efficiency. Compared to using a single semiconductor, a tandem configuration allows the utilization of semiconductors with smaller bandgaps, enables a more efficient usage of the solar spectrum, and more importantly, enhances the overall efficiency. Modeling helps to find the optimal bandgap material for maximum solar-to-hydrogen (STH) efficiency. It is instructive to calculate theoretical efficiency limits, which provide guidance in material choice. In theory, a PEC cell could be fabricated from a single semiconductor and still obtain efficiencies as high as 30% (see Figure 2.3A, blue line). However, actual reported efficiencies of single bandgap PEC water splitting devices are an order of magnitude lower than predicted by theoretical calculations. Most of these models take one or more specific losses into account, *e.g.* kinetic overpotentials, catalyst activities, product crossover, pH of the solution, Ohmic resistance within the cell, or even parasitic absorption of light within a water layer at the submerged photoabsorber.^{2,33-40} More importantly, all models take the Shockley-Queisser limit as input, which is not a realistic starting point, since only four materials come close to this theoretical value, *i.e.* germanium (Ge, $E_g = 0.67$ eV), silicon (Si, $E_g = 1.1$ eV), gallium arsenide (GaAs, $E_g = 1.52$

eV), and cadmium sulfide (CdS $E_g = 2.4$ eV), while all other reported materials are far below this limit.⁴¹ GaAs, Ge, and CdS are also scarce materials in the earth's crust and therefore of less interest to develop into a PEC cell.

Figure 2.3 (A) Single junction limiting efficiencies. Limiting efficiencies (η_{PEC}) versus semiconductor bandgap (E_g) for ideal case (blue solid line, $\eta_{\text{max}} = 30.6\%$, $E_g = 1.59$ eV), high-performance realistic case (green dashed line $\eta_{\text{max}} = 15.1\%$, $E_g = 2.05$ eV) and earth-abundant realistic case (red dotted line, $\eta_{\text{max}} = 5.4\%$, $E_g = 2.53$ eV). (B) High-performance realistic case for a tandem PEC cell ($\eta_{\text{max}} = 28.3\%$, $E_g = 1.59$, and 0.92 eV) and where contour lines mark every 5% and maximum efficiency points are indicated. Reproduced with permission.³² Copyright 2016, Nature Publishing Group.

Recently, this non-ideal semiconductor behavior (*i.e.* deviation from the Shockley-Queisser limit) was taken into account for both single and multi-bandgap absorbers.³² A more realistic efficiency outcome was calculated, with an optimal bandgap of 2.5 eV and an overall efficiency of 5.4%, see Figure 2.3A. CdS particles come close to this value and are widely investigated at the moment.^{42–44}

To overcome this low efficiency limit, a combination of bandgap materials can be used, which use a broader range of the light spectrum. To date, the highest efficiency PEC cells are constructed from multiple bandgap absorbers. Theoretically achievable efficiencies for dual absorber PEC devices reach as high as 41%.³² The above mentioned model, with more realistic values, shows an efficiency of 28.3% with dual semiconductors, with bandgaps of $E_g = 1.59$ and 0.92 eV (see Figure 2.3B), or for a triple bandgap device with $\eta_{\text{max}} = 17.3\%$, and $E_g = 1.91$, 1.36 , and 0.93 eV.³² One of the most important outcomes of the study of Fountaine *et al.* is that the calculated realistic efficiencies are within reach. However, the required materials with the proper bandgaps do not exist at this moment.³² Small deviations from these ideal bandgap values lead to a substantial decrease in overall obtainable efficiencies. More specifically, when another bandgap has to be chosen, a higher value is of less impact than a lower one. The iso-efficiency lines in Figure 2.3B are

more closely together at bandgap values lower than the perfect bandgap value (green dot), compared to higher values. Thus, these models give a handle to which bandgap materials should be investigated. Silicon, with a bandgap of 1.1 eV is almost ideal for the lower bandgap absorber in a dual bandgap tandem device, due to the outcome of the simulations. Moreover, it reaches the Shockley-Queisser limit, it is earth abundant, and is one of the most applied materials in micro-engineering.

2.2.3 Device design concepts

Within the debate of device configurations of tandem PEC cells, two overall schematic views are accepted to construct such devices, a wired and a wireless (*i.e.* monolithic) device, see Figure 2.4.¹⁸ Here, the major difference is in how electrons and protons are transported from the anode to the cathode. In a wired device, protons are shuttled from the anode to the cathode and electrons via a wire (Figure 2.4A). The protons in a wireless device are shuttled via a detour between anode and cathode, while the electrons pass internally. Two examples exist of a direct comparison between these concepts, and in both cases the wired device outperformed the wireless cell by a factor of 2 in efficiency.^{45,46} The exact reasoning why the efficiency of a wireless setup is lower, is still up for debate. One postulated reason is a slight chemical bias shift caused by a pH gradient in the PEC cell.^{33,47} Both of these comparative studies (*i.e.* wired vs wireless) reveal that a wireless assembly could profit substantially from a shortened proton transport path. Therefore, shortcuts could be implemented by increasing the porosity in the device.^{48,49} Moreover, both of these configurations still have considerable crossover in gasses (*i.e.* O₂ and H₂), which is both dangerous (*i.e.* explosion danger) and disadvantageous. Furthermore, the produced gasses, when they reach the opposite electrode, are converted back, which reduces efficiency, and even more importantly, the evolved gasses have to be separated subsequently and this requires extra energy input. To overcome this problem, a membrane should be embedded between the anode and cathode, to counteract the crossover.

Most functional laboratory-scale electrochemical water splitting devices work according to the above described wired principle. They show an incremental efficiency increase over the years, for both more scarce semiconductors (*e.g.* InP, GaAs, etc.) and more earth abundant semiconductors (*e.g.* Si, Cu₂O, BiVO₄, etc.).⁵⁰ Two noteworthy PEC cells include a tandem PEC cell constructed from AlGaAs/Si and a RuO₂ catalyst, with a STH efficiency of 18.3%.⁵¹ Although the efficiency of this cell is high, the cost involved in fabricating is too, and therefore it does not qualify for mass production. Secondly, an all earth abundant hetero-type dual photoelectrode, constructed from BiVO₄ - Fe₂O₃/Si was reported to have a STH efficiency of 7.7%.⁵² Especially the latter example is interesting, due to the use of earth-abundant materials. All of these devices generate a mixture of O₂ and H₂, and all PEC cells suffered from one or more disadvantages.

Figure 2.4 Schematic representation of proton and electron transport in (A) wired and (B) monolithic electrode assemblies. A = anode; C = cathode. Reproduced with permission.¹⁸ Copyright 2014, The Royal Society of Chemistry.

These developments have led to five key requirements when designing a PEC cell: (1) integrating PV and electrolysis functions into a single integrated tandem PEC cell, (2) protecting the semiconductors in PEC cells from corrosion in the harsh electrolyte environment, (3) introducing low-cost earth-abundant semiconductors and catalysts to suppress the cost when applying to the terawatt (world) scale, (4) improving the active area and optical absorptivity, and (5) keeping the reaction products O_2 and H_2 separated.

From the above stated results (*i.e.* bandgap engineering, wire(less) device, and key requirements), two conceptual device concepts have evolved. The first is a membrane embedded wireless assembly. Nocera and coworkers introduced a more popular name, “The Artificial Leaf”.^{45,47,53,54} A conceptual view is given in Figure 2.5, and the device targets the practical generation of solar fuels.⁵⁵ All of the components used in the device are off-the-shelf products and can be easily assembled into a functional device. The membrane allows protons to cross but acts as a molecular barrier for reagents and reaction products (*i.e.* H_2 and O_2). This architecture has two major disadvantages. Firstly, the distance protons have to travel from the anode to the cathode is substantial and secondly, the membrane itself is not photoactive and reduces the overall efficiency. The cationic transport over these macroscopic distances imposes tremendous Ohmic losses.³⁴ The trade-off between product separation and proton transport distance restricts the size of an artificial leaf. A computational model has shown that electrode widths of 25

mm already leads to several hundreds of mV overpotential. Haussener *et al.* calculated the different losses of such a device when it is scaled from the cm^2 range to m^2 range, by introducing arrays of such a device.³⁴ The total size of each individual leaf should not exceed $10 \times 10 \text{ mm}^2$ to avoid the above mentioned potential losses.

Figure 2.5 Schematic illustration of a fully monolithically (wireless) integrated intrinsically safe, solar-hydrogen system prototype. Reproduced with permission.⁵⁵ Copyright 2015, the Royal Society of Chemistry

To overcome the disadvantages of the embedded wireless device, all of the components have to scale down to the order of micrometers. Lewis *et al.* proposed an architecture that would satisfy all five of the key requirements for a PEC cell, see Figure 2.6.⁵⁶ This concept mimics the thylakoid membranes performing photosynthesis in natural leaves and is referred to as a “solar membrane”.¹⁸ The proposed device consists of a stack of two different semiconductor micro/nanowire materials (red and blue, respectively) to take full advantage of the energy distribution of the sunlight, and the top absorber has a higher bandgap than the bottom absorber (as explained in Section 2.2.2). Both absorbers would be highly structured, for multiple reasons: (1) A structured surface reduces the light reflection of a material and therefore increases the absorption of photons and thus the current generation to form chemical fuels. (2) The increased surface area is able to hold high mass loadings of an electrocatalyst without compromising light absorption. High mass loadings enhance the activity of the electrocatalyst and thus lower the overpotential to drive the required half-reaction. (3) High surface areas diminish the absolute energy carrier density generated by the underlying semiconductor and therefore reduce the stress imposed on the electrocatalyst. Moreover, earth-abundant catalysts can be used, since the catalyst material does not have to be a high performance catalyst (such as Pt or IrO_2). An electrocatalyst for the oxygen evolution reaction (OER, Equation 2.1) is used in conjunction with one or multiple light absorbers, and another electrocatalyst for the production of the required fuel, *e.g.* the hydrogen evolution

reaction (Equation 2.2). A membrane allows for the robust separation of products, thereby ensuring intrinsically safe operation of the system. The membrane in between the two micro/nanowire arrays minimizes any Ohmic resistance losses by allowing the protons to move along a pathway parallel to that traversed by the photo-generated charge carriers in a solid. The solar membrane concept offers assemblies with good light harvesting capabilities and the possibility to fine-tune each side individually.

Figure 2.6 (A) Schematic of a microwire-based membrane-bound solar fuels generator. The device is illuminated from the top. The photoanode material absorbs blue light and effects water oxidation. The photocathode material absorbs red light and drives the reduction of water or carbon dioxide. The photoanode and photocathode material are in Ohmic contact, and both photoelectrodes are decorated with catalysts for the reaction of interest. The membrane allows for the transfer of ions and separates the product. (B) A cross-sectional scanning electron microscopy image of the final dual microwire-array structure. Reproduced with permission.⁵⁷ Copyright 2011, Royal Society of Chemistry.

Until now, a working PEC cell according to this principle has not yet been demonstrated, due to the complex nature of the device. However, Lewis and coworkers did extensive work on parts of this conceptual idea: Si microwires (MWs) were fabricated by vapor-liquid-solid (VLS) growth.^{58,59} By spin-on-glass, a radial emitter was introduced, and a 7% energy-conversion efficiency was recorded under simulated solar light.^{60,61} By coating the microwires with platinum particles, an effective H₂ half-cell was constructed.⁶² This half-cell exhibited a 6% ideal regenerative cell efficiency.⁶³ A set of Si microwires was embedded into a polydimethylsiloxane film and removed from the substrate, with the periodicity intact.⁶⁴ Even though the microwires comprised of only 4% by projected area of the microwire–polymer composite, the microwire arrays absorbed ~85% of the incident photons.⁶⁵ A dual microwire array structure was synthesized by fabricating two sets of free-standing membrane-embedded microwires (p-Si and n⁺-Si), followed by laminating these polymer-embedded arrays together.⁵⁷ A poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT:PSS) intermediate layer was used to “glue” the two sets of microwires while ensuring electrical contact (see Figure 2.6B). Furthermore, the Nafion/PEDOT:PSS/Nafion stack was still sufficiently protonconductive.⁵⁷ The latter structure was employed as a proof-of-concept, in order to

demonstrate the membrane-bound microwire design and to measure critical properties of the membranes, but was not used as a full solar-to-fuel device.

One of the key points in a solar membrane are the microwires. From a sensitivity analysis it follows that a major impact could be achieved by improving the semiconductor materials.³² As one of the materials for the microwires, silicon is a logical material to start with, for reasons mentioned in the previous paragraph. Furthermore, a large toolbox is available for microstructuring of the material.⁶⁶⁻⁶⁸ p-Si can be used directly as photocathode, since the conduction band straddles the H_2/H^+ reduction band.⁶⁹ Combined with the earth abundance and relatively low production costs, it is used extensively in the nano/micro-fabrication area. Optimization of the silicon solar cell is important for both photovoltaics and solar-to-fuel applications, since higher efficiencies will ultimately affect consumer and industrial interest in solar energy devices.

2.2.4 Charge separation

The study of p-Si as a photocathode semiconductor material is well developed. A major limiting step is a low photovoltage of p-Si. The conduction band (E_{cb}) of p-Si straddles the H^+/H_2 redox potential, as illustrated in Figure 2.7. When p-Si comes in contact with an electrolyte, both the valence and conduction bands bend downward. This in turn generates a potential drop over the material (qV_{oc}). The latter is intrinsically limited by the Si/liquid junction (*i.e.* ~ 380 mV). Depositing an n^+ layer on top of p-Si can effectively replace the Si/liquid junction with a built-in buried p/n junction and therefore significantly boosts the photovoltage of the PEC system, as shown in the band-bending scheme in Figure 2.7.

Figure 2.7 Band bending in (A) p-Si and (B) n^+/p -Si photocathodes in contact with the H^+/H_2 redox couple in solution. The top diagrams show the interfaces in the dark, whereas the bottom diagrams show the interfaces under illumination. E_{cb} is the conduction band edge, E_v the valence band edge, and E_F the Fermi level. $E_{F,p}$ and $E_{F,n}$ are the hole and electron quasi-Fermi levels, respectively, under illumination. The photovoltage (V_{oc}) is larger for n^+/p -Si samples due to increased band bending at the n^+/p interface relative to the aqueous solution/ p -Si interface. Reproduced with permission.⁶² Copyright 2011, American Chemical Society.

As stated above, the use of a p/n junction is important for the performance of a PEC cell. Since micro- and nanowires enhance the absorption, a way has to be found to introduce a p/n junction into such structures. This can be done either in a axial or radial form as is further discussed in Section 2.3.2.

2.2.5 Catalyst materials

Si has a suitable bandgap and conduction band edge position with respect to the HER, although the sluggish HER kinetic of p-Si limits the efficiency of the PEC HER. In order to design an efficient Si-based PEC system, a catalyst needs to be integrated with silicon to efficiently convert the generated photocharges to H_2 . This is mainly accomplished by decreasing the overpotential for the HER. Correspondingly, large efforts have been made to identify highly active catalyst materials.

Among the key inspirations behind the design of new hydrogen evolution catalysts are the so-called volcano plots that correlate HER exchange current densities (a measure of the effectiveness of a catalyst for the HER) for various materials with the chemisorption energy of atomic H on those materials. This trend was first recorded for metals by Trasatti in the 1970s and has been a fertile treasure map for new catalysts ever since.⁷⁰ Platinum (Pt) metal is at the summit of the volcano plot, thus making it the best HER catalyst, and its use in combination with Si will be discussed in further detail in 2.3.3. However, one of the challenges in the development of a sustainable and globally scalable PEC cell is the discovery and development of materials and architectures that allow for the replacement or minimal use of scarce elements, and Pt belongs to one the most scarce materials in the earth's crust.⁷¹ Therefore, more recent research is devoted to finding highly active earth-abundant HER catalyst materials.⁷² Many other challenges remain in effectively integrating such electrocatalysts with a semiconductor to enable efficient photocathodes. These include synthesis difficulties, chemical incompatibility and stability issues of the semiconductor-catalyst combination, conflicting light-absorption requirements, unsuitable band alignment, induced interfacial defect states and recombination sites, and inefficient charge transfer across multiple interfaces. Despite significant recent progress in developing earth-abundant, inexpensive, and nontoxic catalysts for HER, most of these materials have been investigated only as stand-alone electrocatalysts, and few of them have been integrated into photocathodes. The integration of earth-abundant catalysts will be discussed in Section 2.3.3.

2.2.6 Important parameters for a PEC cell

The performance of photocathodes toward PEC HER can be evaluated from current-voltage (JV curve) data obtained with a potentiostat in a three-electrode cell illuminated by a solar simulator. The important parameters for describing and comparing the PEC performance include open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (FF), and the saturation current density (J_{sat}), and these are depicted in Figure 2.8.

Figure 2.8 Equivalent circuit diagram for a photocathode with its most important parameters.

V_{oc} represents the maximum photovoltage at which the photocathode passes zero current under illumination and represents the maximum generated driving force for the reaction. J_{sc} is the current density measured at 0 V versus RHE and is a measure for the production rate of the fuel (*i.e.* in this case H_2). FF determines the maximum power point of a PEC cell and can be calculated from V_{oc} and J_{sc} with Equation 2.7.

$$FF = \frac{J_{mp}V_{mp}}{J_{sc}V_{oc}} \quad \text{Eq. 2.7}$$

Here, J_{mp} is the current density and V_{mp} is the voltage at the maximum power point. In other words, FF is the ratio between the largest inner and smallest outer rectangle between V_{oc} and J_{sc} in a JV curve, as seen in Figure 2.8. The FF is determined by the activity of the catalyst and represents the maximum power a photocathode can generate. The saturation current density is the maximum produced current density in a photoelectrode system and is determined by the light-harvesting ability of the semiconductor. Ideally, the overall performance of a HER photocathode can be characterized in the same manner as a solid state PV cell (*i.e.*, J_{sc} , V_{oc} , and FF), which is defined as an ideal regenerative cell (IRC) and obeys an efficiency definition (Equation 2.8).⁶³

$$\eta_{IRC} = \frac{V_{oc}J_{sc}(E_{H_2/H^+})FF}{P_{in}} \quad \text{Eq. 2.8}$$

The values of FF , V_{oc} and $J_{sc}(E_{H_2/H^+})$ in Equation 2.8 are referenced to the equilibrium potential of the half-reaction being performed at the photocathode, P_{in} is the light power input (AM 1.5G, 100 mW/cm²), and (E_{H_2/H^+}) is 0 V vs. RHE.

Generally, a key aim is to maximize the generated power output by generating (1) a large short circuit current density and (2) a high open-circuit voltage, and (3) maximizing the fill factor (FF). The first two points are determined by the light-harvesting ability of the underlying semiconductor and the ability to collect and effectively separate the photogenerated charge carriers, as is discussed in-depth in Sections 2.3.1 and 2.3.2, respectively. The last point is dictated by the catalyst material and is discussed in-depth in Section 2.3.3

2.3 Micro- and nanowired silicon structures

2.3.1 Light management in Si based PEC and PV cells

The efficiency of a PEC cell is directly related to the maximum photo-generated current (J_{sc} ; see Equation 2.8) Therefore, the reflectivity of silicon plays a major role, as is seen schematically from Figure 2.2. A polished Si surface has a high natural reflectivity (>35 %) with a strong spectral dependence, and thus, minimization of reflection losses is a prerequisite for efficient Si solar cells. Conventionally this is achieved by texturing the top surface of a Si PV cell.⁷³ The decrease in reflection directly results in a higher photon absorption and thus a higher J_{sc} , since more photons are available for charge carrier generation.

Recently, non-reflecting surfaces based on Si micro (MWs) and nanowires (NWs) have been investigated for PV applications. Especially Si NW arrays possess several unique optical properties owing to their high surface area and structural features smaller than the wavelength of light, yielding excellent anti-reflection or light-trapping properties.

Choudhury *et al.* have investigated the relationship between the diameter and the spacing of Si NWs, in the range of 200-600 and of 500-1200 nm, respectively, with a fixed height of 3000 nm.⁷⁴ As can be seen from Figure 2.9A, the absorption can vary from 0.30 to 0.65 for different combinations of wire diameter and period. Higher absorption values imply that, for those combinations of diameter and period, broadband suppression of reflectivity is achieved, and the light is well coupled into the NWs. Furthermore, the highest absorption zone, as indicated by the red colored area, follows a nearly linear relationship between wire diameter and period and can serve as worthy design rule.

Peng *et al.* have reported that Si NW arrays fabricated on single-crystal Si wafers drastically suppress light reflection (<1.4 %) over a wide spectral range (300–600 nm).⁷⁵ Furthermore, Srivastava *et al.* performed systematic investigations on the anti-reflectance property of the Si NWs with different array heights.⁷⁶ The hemispherical reflectance of Si NW arrays for different lengths, along with the reflectance of the polished planar silicon wafer, is shown in Figure 2.9B. These results clearly illustrate that Si NW arrays drastically suppress light reflection over a broad spectral range. They observed that the reflectance decreases with an increase in etching time (*i.e.* with

increasing Si NW lengths) and reaches a minimum of $\sim 1.5\%$ in the 300–600 nm range and $\sim 4\%$ in the spectral range 600–1000 nm of samples etched for 15 min or more (corresponding to the NW arrays length of $\sim 4\ \mu\text{m}$ or more). The black surface is due to these extremely low reflectance values, and therefore such surfaces are also known as ‘black’ silicon.

Figure 2.9 (A) 2D contour plot of AM1.5 weighted average absorption for different average NW diameter and spacing combinations of Si NW arrays. Reproduced with permission.⁷⁴ Copyright 2010, American Chemical Society. (B) Reflectivity (R_λ) as a function of wavelength (λ) of silicon (or sample) surface with Si wires obtained after different etching times of (1) 0 min (polished wafer); (2) 1 min; (3) 1.5 min; (4) 2 min; (5) 5 min; (6) 15 min and (7) 45 min. Inset shows the optical photograph of a polished Si wafer (right) and a textured silicon wafer (left). Reproduced with permission.⁷⁶ Copyright 2010, Elsevier

Nanocones (NCs) in amorphous silicon (a-Si:H) were investigated by Zhu *et al.*⁷⁷ Compared with flat thin films and NW arrays, the NC arrays provided excellent refractive index matching between a-Si:H and air through a gradual reduction of the effective refractive index away from the surface. As a consequence, the NC arrays exhibited enhanced absorption due to superior antireflection properties over a large range of wavelengths and angles of incidence.⁷⁸

For most the above mentioned NWs the reflectance is measured perpendicular to the surface. In real world applications (*i.e.* PV or PEC cells), the sun's incident angle changes during the day. Spinelli *et al.* have developed a new concept based on Mie resonances.⁷⁹ Mie resonant modes have large scattering cross-sections, leading to strong interaction with the incident light over a broad wavelength. Full-wafer Si nanowire arrays (150 nm height and 300 nm pitch) were fabricated using a soft-imprint technique capable of large scale, high-fidelity surface patterning. Total reflectance spectroscopy showed 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 $\pm 60^\circ$, see Figure 2.10.⁸⁰

Figure 2.10 Specular reflectivity for wavelengths of 514 nm (A), 632 nm (B) and 405 nm (C). Panels show results for s- (solid symbols) and p-polarized (open symbols) incident light. In each graph, reflectivities from a bare Si wafer (black lines), a 60-nm standard Si₃N₄ coating (red) and a coated NW array (blue) are shown. The excellent AR properties of Si NW arrays are maintained over the entire range from 0° to 60°. Reproduced with permission.⁷⁹ Copyright 2012, Nature Publishing Group.

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Compared to NWs, microwires are more easily fabricated, for example using standard photolithography. A disadvantage, however, is that MW structures are not sub-wavelength and thus reflect light differently. The reflection was decreased with increased lengths of the microwire. Work performed by Lee *et al.* showed that absorption became saturated with microwire length of 20 μm .⁸¹ The reason for this limitation in light absorption is suspected to be the reflection of light at the flat surface of the top of the microwire, which is not affected by the length of the microwire. The area of the top flat surface of the microwire array used in this study was approximately 25% of the total area (1 cm^2).

To combine benefits from micro and nanowires, Lee *et al.* have fabricated a hybrid device, which consists of MWs in combination with NWs on top and bottom (see Figure 2.11A–E).⁸¹ The planar structure showed a high reflection of 40%, whereas the microwire arrays (20 μm) demonstrated a moderate reflection of 10–20%, while that of the nano/micro hybrid structure was less than 2%, Figure 2.11E. The reduction in the reflectivity can be explained by the mitigation of the refractive index mismatch. The nanostructures are, optically speaking, homogeneous mixtures of Si and air. Thus they act like an anti-reflection coating, effectively reducing the mismatch of the refractive index of a Si substrate (refractive index = 3.5–5) and air (refractive index = 1) in a gradual manner.^{76,78,80}

Figure 2.11 (A) Schematic overview (a) showing the process steps for fabricating the nano/micro hybrid structure. (b) Schematic of selective chemical etching at the top surface of Si microwires. (c) Low-magnification SEM image of the nano/micro hybrid structure. The high-magnification SEM images of (d) the bottom region and (e) the top region of the nano/micro hybrid structure. (B) Total reflectance spectra of planar Si (black solid line), microwires (green solid line), and nano/micro hybrid structures (blue solid line). Reproduced with permission.⁸¹ Copyright 2016, Royal Society of Chemistry.

2.3.2 p/n junctions in highly structured Si PV devices

Recently, wire arrays of silicon have gained attention for solar-energy applications because of their increased light-harvesting properties, compared with flat surfaces (see Section 2.3.1). This is due to their higher surface area and efficient light trapping by multiple interactions of light within the gaps between the wires, even at relatively small wire aspect ratios. Furthermore, if the micro- and nanowires have a radial junction, the effective junction area is increased, which leads to enhanced charge-carrier generation and separation. Finally, and perhaps most importantly, the radial junction decouples the charge transport and light-incidence direction.

To produce an actual PV cell, a p/n junction is required. Elbersen *et al.* reviewed the different methods that exist to create such junctions.⁸² When transferring doping methods developed for flat Si to Si MW or NW arrays, the doping depth becomes critical. Especially in early work on NW arrays, the NWs were heavily doped and utilized purely for their antireflective property only in a silicon wafer PV cell.^{75,76,78} Consequently, the NWs get fully doped, effectively burying the junction in the underlying base. Thus, the as-prepared Si NW PV cells are similar to a conventional planar p/n junction solar cell with the Si NW arrays acting as an antireflection coating for enhanced optical absorption as discussed above. Therefore the performance of these NW arrays was only marginally better than that of their flat counterparts. Peng *et al.* constructed a NW array PV cell with a V_{oc} of 548 mV, a J_{sc} of 26 mA/cm², and an overall efficiency of 9.31%.⁷⁵ The low conversion efficiency was mainly attributed to the surface or interfacial recombination, high series resistance, and low current-collection efficiency of the front-grid electrodes. Fang *et al.* tackled the latter problem by improving the electrical contacts and reported

on a Si NW array PV cell with an efficiency of 11.4% (*i.e.* V_{oc} of 580 mV and J_{sc} of 27 mA/cm²).⁸³ Further improvements were made by not directly contacting the NWs, but selectively growing NWs and contacting the flat Si next to the NW arrays. Using this method, Kumar *et al.* reported on a Si NW array PV cell with an efficiency of 13.7%, which had J_{sc} of 37 mA/cm² and a V_{oc} of 544 mV.⁸⁴ Overall this cell was improved with 1% compared to its flat counterpart (*i.e.* V_{oc} = 588 mV, J_{sc} of 29 mA/cm² and η of 12.6%).

A recent review of Battaglia *et al.* on conventional PV cells pointed out the importance of emitter formation.⁸⁵ For high energy efficiencies, lightly doped emitters and highly doped regions in connection with the metal contacts are required. Chen *et al.* were the first to report on this specific difference and compared a two-step doping process (*i.e.* lightly doped emitter and highly doped metal contact) vs. a single doping process (*i.e.* everything highly doped).⁸⁶ Through this approach, an electrode-contact enhancement was achieved which increased the FF. Furthermore, they observed a 40.2% increase in J_{sc} in their two-step-doped PV cells as compared to those fabricated by the one-step diffusion process. Um *et al.* reported on the same fact, and deduced the increase was due to an increase in blue light response of the PV cell.⁸⁷

The doping depth of MWs is more easy to control, without completely overdoping the MWs, due to their relatively large size. Therefore, for MWs it has been confirmed that radial *p/n* junctions are possible and measureable.²⁴ Yet, structured silicon photovoltaic cells with either radial or basal *p/n* junctions show poor cell efficiencies compared with even commercially available wafer silicon photovoltaics, the efficiency of which can reach 15–21%. Even though it was observed that Si MW/NWs reduce the reflectance of solar cells significantly, this optical gain did not improve the performance of the PV cells.^{88,89} The main cause is the low V_{oc} as compared with the state-of-the-art commercial PV, which reaches V_{oc} values as high as 750 mV.⁹⁰ All of the given MW/NW array PV cell examples discussed above have a lower V_{oc} as compared to their flat counterparts. Two main reasons are put forward to explain this low V_{oc} . The first is fundamentally imposed by the increased surface area of a wire geometry. The increased junction area in structured PV cells lowers the total absorbed flux. A wire geometry has a larger roughness, and thus receives a lower flux per unit area of exposed Si (*i.e.* per outer wire area, not per footprint of Si). According to the Shockley diode equation, the V_{oc} of a PV cell is a logarithmic function of the absorbed solar flux (I_L) and of the reverse saturation current (I_0) of the diode (see Equation 1.9). Since $I_L \gg I_0$, the voltage decreases by 59 mV for every decadic decrease of I_L (*i.e.* decadic increase of surface roughness). An increase by a factor of 10 (or much more) is easily obtained by micro/nanostructuring the Si surface, and thus the maximum reported 750 mV can never be obtained and is already reduced to a maximum of 691 mV (or lower).

$$V_{oc} = \frac{k_b T}{q} \ln \left(\frac{I_L}{I_0} + 1 \right) \quad \text{Eq. 2.9}$$

A second cause is found in recombination. The V_{oc} is the voltage at which the forward bias diffusion current is exactly equal to the short circuit current. The forward bias diffusion current is dependent on the amount of recombination in a p/n junction, and increasing the recombination increases the forward bias current. Consequently, high recombination increases the forward bias diffusion current, which in turn reduces the V_{oc} . Therefore the rate of recombination is directly related to the dark saturation current (I_0). This small current flows through the p/n junction, and is constant (independent of reverse bias voltage) and is generated by drift of the thermally generated carriers. The higher the rate of recombination events, the greater I_0 . Veldhuizen *et al.* showed this increase in I_0 , with increasing MW length, as shown in Figure 2.12, whereby the longer MW arrays clearly show a higher dark current density under zero applied bias.⁹¹

Figure 2.12 Current density-voltage characteristics of solar cells with different micropillar lengths, dark conditions. Reproduced with permission.⁹¹ Copyright 2017, Elsevier.

Different types of recombination events occur in Si PV cells in both planar and MW/NW arrays. WW/NW arrays with radial p/n junctions have a high aspect ratio which leads to a strongly increased surface area with concomitantly enhanced surface recombination.^{60,61,92-95} To overcome this problem, the surface can be passivated by an insulating layer. By passivating the Si surface, a reduction in the amount of surface trap states is observed^{96,97} (*i.e.* reduction of the amount of dangling silicon bonds, which is proportional to the total surface area of the micropillar array). Shin *et al.* have reported on radially doped silicon micropillars of 10 μm in length and pointed out the importance of a proper surface passivation.⁹⁴ Lee *et al.* have investigated the importance and influence of surface passivation on MW array PV cells.^{81,98} They constructed a Si PV cell,

which consisted of a hybrid structure of NWs on top of MW arrays, with a V_{oc} of 584 mV, J_{sc} of 39.5 mA/cm² and an overall η of 17.6%.

Furthermore, by radially doping the MW or NW arrays, the junction area is increased. This increase in junction area also enhances recombination events. Oh *et al.* identified different regimes of junction doping concentration, in which each recombination mechanism dominates (*i.e.* bulk or surface). By optimizing the dopant concentration throughout the cell, they were able to design and fabricate an independently confirmed 18.2%-efficient NW array PV cell, with a V_{oc} of 628 mV and a J_{sc} of 36.3 mA/cm². By introducing surface passivation in the form of aluminum oxide (Al₂O₃), Savin *et al.* increased the efficiency even further to 22.1%, whereby the improvement mainly was due to increase of the V_{oc} to 667 mV.

For photocathodes is the generated photovoltage as important as the photocurrent (see Equation 1.8). As discussed in Section 2.2.4, the photovoltage of a semiconductor/electrolyte is less than a buried p/n junction, due to the inherent limited difference between the E_{cb} and the H⁺/H₂ redox potential. However, p-Si MW and NW array photocathodes do have a positive influence on the obtained photovoltage at a semiconductor/electrolyte interface. Despite the imposed lowered photovoltage due to an increase in absolute surface area introduced by the MW/NW arrays.⁹⁹⁻¹⁰¹ Photocathodes with a buried p/n junction out-perform the p-Si/electrolyte junction, as is seen in Table 2.1 and Table 2.2. However, The obtained photovoltages are substantially lower as reported above (*i.e.* 667 mV for a microwire PV cell vs. 540 mV for a high performance photocathode). The difference in $E_{F,p}$ and $E_{F,n}$ for a solid state p/n junction is almost maximized for high-aspect-ratio Si PV cells. Therefore, techniques and knowledge should be transferred from the field of PV cells to the field of Si photocathodes.

2.3.3 Catalysts on micro- and nanowire arrays

p-Si has a suitable bandgap and conduction band edge position for the hydrogen evolution reaction (HER), but the low photovoltage and sluggish HER kinetics of p-Si limit the efficiency of PEC-HER. The former issue of p-Si can, however, be solved partly by using Si with a buried junction to enhance the band bending, as addressed in Section 2.2.4 and explained in depth in Section 2.3.2. After successful charge separation, electrons provide H₂ at the interface of a photocathode. However, it is widely documented that bare Si has sluggish kinetics towards HER and usually generates a negligible photocurrent at 0 V vs. RHE. Improving the HER kinetics at the surface of a photocathode is essential to increase the PEC performance. This can be accomplished by using a (co-)catalyst placed on top of the semiconductor. To avoid blocking of the light harvesting by the semiconductor, the electrocatalyst used in integrated photocathodes should have a good optical transparency.

The sluggish HER kinetics for p-Si is perfectly illustrated in Figure 2.13A. Here, p-type Si NWs were put in contact with an electrolyte and scanned for its activity under 1 sun illumination. A large overpotential was required to activate the material. To enhance this, Pt nanoparticles were deposited on p-Si, upon which the *IV*-curve shifted towards positive potentials. Huang performed simulations on p-Si photocathodes covered with Pt particles as catalyst.¹⁰² Figure 2.13B shows an ideal photodiode in contact with an electrolyte (red), with a V_{oc} of 243 mV, a J_{sc} of 30 mA/cm², and a *FF* of 77. The green solid curve is the calculated Butler-Volmer characteristic of p-Si covered with Pt nanoparticles, and the dashed green is the same curve shifted by 243 mV. The actual photocathode (blue) is a superposition of the activity of the used catalyst and the underlying PV cell. The photodiode mainly dominates the onset potential (243 mV) and maximum current density ($J_{sat} = 30$ mA/cm²), but the *FF* is dominated by the activity of the used catalyst. The *FF* of the photocathode is reduced to 33% and therefore also reduces the overall efficiency significantly, by result of Equation 2.8. The performed simulations show great similarities with the actual fabricated and measured p-Si/Pt photocathode, Figure 2.13A.¹⁰²

Figure 2.13 (A) Current density vs. voltage data for p-Si (dot), p-Si/Ni (solid) and p-Si/Pt (dashed) electrodes. The data were collected using a SCE as reference in potassium hydrogen phthalate buffer (pH 4.5) under 1 sun AM 1.5 illumination. (B) Simulation of current density vs. voltage data for: (a) diode in the dark, (b) diode under AM 1.5 illumination after correcting for the reflection loss, (c) Calculated metal dark catalysis, (d) Photodiode-metal electro-catalysis under AM 1.5 illumination after correcting for the reflection loss, (e) Metal dark catalysis shifted by the V_{oc} of the illuminated photodiode. Reproduced with permission. Reproduced with permission.¹⁰² Copyright 2014, Elsevier.

The simulations demonstrate the main problem for most H₂ photocathodes. The catalyst material determines the *FF* of the *IV* curve and thereby the efficiency. Pt is the best performing H₂ catalyst in acidic environments. Therefore, the best performing Si based H₂ photocathodes to date, with the highest *FF* values are constructed with platinum (Pt) as H₂ catalyst. In the above given example, Pt nanoparticles of random size and total

loading were deposited on the p-Si NWs. Kemppainen *et al.* investigated more in depth the importance of mass loadings of catalyst deposition.¹⁰³ They produced nanoparticles (with a diameter of ~ 5 nm) and deposited them on planar n^+/p Si. At low mass loadings, *i.e.* <100 ng/cm², the efficiency of the photocathode was dominated by a low FF , as is seen in Figure 2.14A-B. As a comparison, an overlay was produced with an ideal PV cell (grey dashed) and a simulated IV curve with the imposed catalyst on top (green dashed). The simulations show the same trend as the actual measured data, further indicating the limitation imposed by the catalyst. By increasing the mass loading of the catalyst up to a 1000 ng/cm², the activity was no longer limited by the catalyst, since the IV curve of the photocathode overlapped with the curve of the ideal PV cell. Moreover, the J_{sc} in all of these experiments was ~ 22.5 mA/cm², independently of the catalyst loading. This indicates that the catalyst did not interact or block the incoming light, since the particles are below the wavelength of the incoming light and because they were deposited in a thin, discontinuous layer.

Figure 2.14 Measured IV curves of (A) 10, (B) 50, (C) 200 and (D) 1000 ng/cm² Pt loadings on TiO₂-covered p^+ - p -Si PV cell (black lines) and the simulated IV curves for the same loadings including the calculated HER overpotentials (η) (green dashed lines). The IV -curve for an ideal PV cell with $n = 1$ (grey dashed line) is shown for comparison. Reproduced with permission.¹⁰³ Copyright 2015, The Royal Society of Chemistry.

The photocurrent in the above example was limited by the use of planar structures and can be improved by the introduction of MW or NW arrays, as shown in Section 2.3.1. Sim *et al.* investigated different NW arrays with various NW lengths, and found NWs with a length of ~ 29 μ m had the highest performance as photocathode.⁹⁹ Upon coating these

NW arrays with Pt nanoparticles, a photocurrent of 16.4 mA/cm^2 at 0 V vs. RHE was obtained, while 12.3 mA/cm^2 was observed for a planar structure with the same mass loading of Pt. More interestingly, under the same conditions, the FF increased from $\sim 20.2\%$ for a planar structure to $\sim 27.9\%$ for a NW array, indicating a higher activity for the NW arrays.⁹⁹ However, the overall efficiency was only 1.20%, which was due to the low photovoltage of 260 mV.

Boettcher *et al.* investigated the difference between Pt-covered p-Si MW arrays with radial p/n junctions.⁶² First of all, MW arrays with a p/n junction showed a clear shift in V_{oc} (*i.e.* 0.16 V for p-Si MWs and 0.54 V for n^+/p -Si MWs), which is discussed in Section 2.3.2. More importantly, the FF of the photocathodes with a buried p/n junction increased substantially, from 18% for p-Si MWs to 71% for the n^+/p -Si MWs. They attributed this difference in FF to the presence of a thin oxide barrier at the Pt-Si interface, formed during Pt deposition, that impeded interfacial charge transport. Upon introducing a metallurgical n^+/p -junction, this was resolved. The high FF and V_{oc} produced the highest overall efficiency to date of 5.8%.⁶²

Passivation of the surface is equally important as the catalyst loading. Passivation of PV cells decreases the recombination at the surface, which is increasingly more important for nano- and microstructures, with their enhanced surface area. Dai *et al.* investigated samples with and without surface passivation by using two different deposition techniques, atomic layer deposition (ALD) and electroless deposition (ELD) of Pt nanoparticles.¹⁰⁴ The addition of a Pt catalyst resulted in photocathodes with fill factors of 28 % and 55% as measured on Si NWs decorated with ELD Pt and ALD Pt, respectively. The major difference between these two samples is the deposition of the catalyst. Whereas Pt deposition by ALD on Si nanowires was predominantly possible on preoxidized NWs, Pt particles prepared by ELD was only possible on oxide-free Si NWs. It is not entirely clear how the preformed amorphous SiO_2 aids in the Pt nanoparticles growth. However, Dai *et al.* suggested the oxidized Si reacted with MeCpPtMe_3 (ALD Pt-precursors), which was necessary for a high yield of Pt growth.¹⁰⁴

Even a thin oxide surface will passivate the Si NW surface and will improve the charge collection at the Pt catalyst, by decreasing the total amount of surface trapping/recombination, and leads to an improved FF .¹⁰⁵ A complete overview of all MW and NW arrays with Pt as catalyst is given in Table 2.1.

Table 2.1 A survey of micro- and nanowire-based, H₂-producing half-cells with Pt as catalyst. Measurements done under AM 1.5G in their best performing electrolyte.

Configuration	V_{oc} (mV)	J_{ph} (mA/cm ²)	FF (%)	η_{IRC} (%)	ref
n ⁺ /p-Si MWs	540	15.0	71	5.8	62
n ⁺ /p-Si MWs	510	20.2	49	5.0	106
n ⁺ /p-Si MWs	440	14.0	46	2.8	107
n ⁺ /p-Si MWs	441	13.2	47	2.7	108
p-Si NWs	380	21.2	30	2.5	109
n ⁺ /p-Si MWs	330	15.0	30	1.5	110
p-Si NWs	420	19.9	45*	3.8	100
p-Si NWs	370	16.5	44	2.6	111
p-si NWs	310	29.2	26*	2.4	112
p-Si NWs	280	19.6	17	1.6	113
p-Si NWs	310	9.0	55	1.5	104
p-Si NWs	250	20.7	25*	1.3	114
p-Si MWs	480	12.8	20*	1.2	99
p ⁺ -Si MWs	265	11.7	31	1.0	115

When photocathodes are to be employed on a terawatt scale, Pt cannot be used as catalyst, due to its costs and its limited presence in the earth's crust.⁷¹ In the past decade, significant progress has been made in the exploration of new earth-abundant, inexpensive, and nontoxic catalysts for HER, including molybdenum sulfide,^{116,117} first-row transition metal dichalcogenides,^{118,119} molybdenum carbide and boride,^{120,121} tungsten carbide,¹²² nickel phosphide (Ni₂P),¹²³ cobalt phosphide (CoP),¹²⁴⁻¹²⁶ and nickel molybdenum (NiMo).^{106,115,127-130} The edge sites of molybdenum sulfide (MoS_x) are analogous to the active center of the nitrogenase enzyme, while some surface cations of the first-row transition metal dichalcogenides resemble the ligand number and symmetry of active centers in hydrogenases (NiFe-hydrogenase, FeFe-hydrogenase, or Fe-hydrogenase).^{116,131} The electronic structures of group VI transition metal carbides are similar to those of Pt-group metals.¹³² Metal (Ni or Co) and P in metal phosphides have charged properties similar to those of the hydride and proton acceptors in NiFe-hydrogenase and its analogues.¹³³ These reports suggest that mimicking the coordination or electron structures of active sites of high-performance noble metal catalysts or

enzymes is an efficient approach to the development of new non-precious HER catalysts.¹³¹

However, there are more important factors for assessing whether an electrocatalyst is well-suited for incorporation onto Si MW or NW arrays. Firstly, at the mass loadings needed to provide high activity under solar illumination, the catalyst must not significantly absorb incident light. Secondly, optimally any light reflected by the catalyst should be directed toward the wire array to produce additional photocurrent. Thirdly, the electrocatalyst must also remain active when integrated with silicon as semiconductor. Lastly, in a full solar-driven water-splitting tandem structure, the catalyst on the absorber should ideally be transparent, yet all of the earth-abundant catalysts mentioned above are opaque. Taking all of these aspects into account, the most attractive and active materials these days are: NiMo,¹³⁴ CoP,¹³⁵ and MoS_x.¹³⁶ Most of these materials can be deposited either by electrodeposition or spun as a slurry between/over the wire arrays. All reported systems with a catalyst other than Pt on Si NW or MW arrays are tabulated in Table 2.2 and the more noteworthy examples are discussed below.

One of the most employed deposition techniques of catalyst materials on nano- and microwires is electrodeposition. The dynamics of electrodeposition of many materials depend on the surface chemistry of the substrate, which is in particularly true for a semiconductor (*i.e.* Si, GaAs, InP).¹²⁸ In the absence of templating approaches, electrodeposition on semiconductors results in random coverage of a substrate with a catalyst layer. Such coverage is desirable for “dark” electrocatalysis, where usually the substrate is inactive compared to the catalyst coating, and maximal coverage by the catalyst layer is important. McKone *et al.* have investigated the activity of NiMo, compared to Pt, for various deposition times onto planar p⁺-Si.¹¹⁵ From Figure 2.15A it becomes clear that by increasing the deposition time of NiMo, the activity increases substantially, note the difference between 30 s (blue) and 90 s (red) deposition time. At high mass loadings of NiMo, the activity becomes comparable with electroless Pt deposition, especially at low current densities (*i.e.* <20 mA/cm²). However, for semiconductor photocatalysis, conformal coverage of a catalyst will attenuate light absorption. McKone *et al.* measured an optimized photocathode with NiMo as catalyst, and compared it to Pt (see Figure 2.15B).¹²⁸ These results clearly demonstrate the influence of catalyst loading: Both tested samples have a comparable *FF*, indicating NiMo (dashed blue line) has a comparable activity to Pt (dashed black line), although samples with NiMo had a lower *J_{sc}* in all tested cases. This suppresses the maximum obtainable efficiency of these cells considerably. This clearly evidences the negative influence on the light absorption capabilities of the underlying p-Si.

Table 2.2 A survey of micro- and nanowire-based, H₂-producing half-cells with earth-abundant catalysts. Measurements done under AM 1.5G in their best performing electrolyte.

Configuration	V_{oc} (mV)	J_{ph} (mA/cm ²)	FF (%)	η_{IRC} (%)	ref
NiMo					
n ⁺ /p-Si MWs	450	14.3	48	2.9	106
n ⁺ /p-Si MWs	485	10.3	45	2.2	108
n ⁺ /p-Si MWs	349	13.5	12	0.6	102
p ⁺ -Si MWs	145	7.0	35	0.4	115
Other					
p-Si NWs/Ni ₁₂ P ₅	400	21.0	36	3.0	131
p-Si NWs/CoP	407	15.6	27	2.9	113
p-Si NWs/FeP	370	13.9	45	2.8	137
p-Si NWs/NiCoSe _x	250	37.5	26*	2.5	112
p-Si NWs/NiB	440	15.6	36	2.5	109
p-Si NWs/CoB	450	19.5	29	2.5	109
p-Si NW/N-GQS	210	35.0	32	2.3	138
p-Si NWs/MoS ₃	360	24.9	28*	2.3	111
p-Si NWs/a-WS ₃	400	19.0	30*	2.0	139
n ⁺ /p-Si MWs/CoP	480	17.0	24	1.9	107
n ⁺ /p-Si MWs/MoS ₂	300	15.0	30	1.4	110
p-Si MWs/Mo ₃ S ₄	150	9.3	--	1.2	140
p-Si NWs/NiSe _x	225	20.5	26*	1.2	112
p-Si MWs/CoMoS _x	192	17.2	23	0.7	112
p-Si NWs/CoSe _x	140	15.3	26*	0.6	112
p-Si MWs/CoSe ₂	200	9.0	25*	0.5	141
p-Si MWs/C ₃ N ₄ /CoSe ₂	195	4.9	25*	0.2	142

* data not available and estimated from the figures within the source

Figure 2.15 (A) Electrochemical data of the HER activities of various catalysts on planar p⁺-Si electrodes. The total deposition times for electrodeposited catalyst films are specified. Data were collected at pH = 4.5, and are referenced to the RHE potential. Reproduced with permission.¹¹⁵ Copyright 2011, Royal Society of Chemistry. (B) Polarization curves at pH 4.5 for hydrogen evolution by electrodeposited Ni-Mo (blue) and Pt (black) onto p-Si (dashed lines) and n⁺p-Si (solid lines) microwire substrates under 100 mW/cm² white light illumination from a tungsten-halogen light source. Reproduced with permission.¹²⁸ Copyright 2013, Royal Society of Chemistry.

To overcome the problem of conformal electrodeposition on NW or MWs, a slurry of nanoparticles can be employed and spin coated across the MW arrays. Roske *et al.* investigated the difference between specific mass loadings of spincoated Pt (0.5 mg/cm²) and CoP (2 mg/cm²) nanoparticles at MW arrays.¹⁰⁷ Due to the lower turnover frequency of CoP relative to Pt, higher mass loadings of CoP are required to produce similar geometric area-based HER activities as those obtained from Pt. MW arrays, compared with planar surfaces, therefore can beneficially accommodate the higher CoP mass loadings and provide a performance comparable to Pt in the range of 30 – 100 mW/cm² illumination intensities. MWs with CoP nanoparticles produced by Roske *et al.* produced 17 mA/cm² as compared to 14 mA/cm² for Pt-loaded MWs. Although the current was higher in the case of CoP, the overall efficiency was still suppressed as witnessed by a lower *FF* of 24% for CoP loaded MWs, as opposed to 46% for Pt-loaded MWs.

Shaner *et al.* improved this idea and changed the CoP nanoparticles by NiMo/TiO₂ nanoparticles.¹⁰⁶ They designed, fabricated and experimentally verified a broadly applicable photocathode architecture that circumvents the trade-off between catalytic activity (*FF*) and optical absorption of the underlying semiconductor (here, n⁺/p-Si). They claim that the combination between high activity of the catalyst (NiMo), specific deposition at the bottom, and a high dielectric scattering layer (TiO₂ nano particulates) results in the best performing homojunction to date, with a *J_{sc}* of 14.3 mA/cm², a *V_{oc}* of 0.42 V, and a *FF* of 48%. Modeling of this specific example indicated that still higher efficiency values could be obtained by optimization of the MW growth and doping process, in conjunction with optimization of the deposition procedures used for the catalyst and optical scattering layers.

Another interesting catalyst is MoS_x. Earlier work in the 1970s on bulk MoS₂ suggested that this material would not be a particularly active HER catalyst. Nevertheless, since the seminal theoretical work by Hinnemann *et al.*, suggesting promising HER catalytic activity from MoS₂ nanostructures, various approaches have been developed in the past few years to significantly enhance its HER catalytic activity, making it a highly competitive HER catalyst.¹¹⁶ One of the most noteworthy examples has been presented by Huang *et al.*, who demonstrated for the first time a substantially higher photocurrent with an earth-abundant catalyst (MoS₃) as compared to Pt.¹¹¹ They produced flakes of MoS₃ on p-Si NWs by electrodeposition, and, after tuning the mass loading of the catalyst, the photocathode exhibited a J_{sc} of ~ 25 mA/cm² as compared to 16 mA/cm² for optimized Pt-coated p-Si NWs under AM 1.5G illumination.¹¹¹

2

All of the examples given above use optically opaque catalyst materials, which block the incoming light and therefore reduce the maximally obtainable photocurrent. An attempt to circumvent this problem is by clever catalyst position engineering. Huang *et al.* designed a 3D p-Si/NiCoSe_x completely enclosed core/shell nanowire architecture using a facile photo-assisted electrodeposition method of NiCoSe_x alloy and demonstrated the highest recorded J_{sc} for a p-Si photocathode to date.¹¹¹ A stable photocurrent density of ~ 37.5 mA/cm² at 0 V (vs. RHE) for solar-driven H₂ generation was achieved. The enhanced PEC performance of the p-Si/NiCoSe_x core/shell NW array photocathode was attributed to the perfect combination of the high light harvesting of 3D Si NW array and the active NiCoSe_x electrocatalyst with good optical transparency. The fully covered p-Si/NiCoSe_x core/shell structure offers a new strategy for designing more efficient photocathodes for photoelectrochemical solar energy conversion. Although the J_{sc} was high, the FF was only 26% and needs to be improved when employed as high performance Si photocathode.

2.4 Conclusions and outlook

The last decade an increase in research activities on high-aspect-ratio, Si-based photoelectrochemical systems for solar water splitting has occurred. In this chapter, silicon NW and MW arrays have been reviewed in depth because they show great promise to be used as photocathode.

The underlying principle of a Si photocathode shows great resemblance to a Si PV cell, and therefore improvements made in the latter area could directly be implemented in the field of Si photocathodes, with respect to structuring, doping, contacting, and passivation. NWs and MWs are easily fabricated by a large range of techniques. These structures reduce inherently the reflectivity of silicon tremendously and offer therefore the possibility to enhance the light absorption and thus the overall efficiency. The obtainable current density in high-aspect-ratio Si PV cells is almost maximized, although the overall efficiency is limited by the open circuit potential, which is created by a junction. The presence and functionality of junctions can be proven by means of simple

JV measurements, although it is still difficult to reliably select the proper design settings for high-aspect-ratio structures, due to the numerous variations in the literature with respect to the fabrication methods, the doping profile and technique, as well as wire (diameter, height, pitch) and array dimensions and order. Lately, more detailed doping process are developed and slowly but surely the V_{oc} for high-aspect-ratio PV cells reach values as high as that of planar PV cells.

For Si photocathodes, Pt is still the most used HER catalyst, due to its tremendously high activity at low loadings. High-aspect-ratio Si photocathodes show also great output when this catalyst is used. Lately a transition of Pt-based photocathodes to earth-abundant catalysts is observed. Earth-abundant catalyst show great enhancements with respect to the activity. The major drawbacks are the high mass loadings ($>1 \text{ mg/cm}^2$) required to be as active as Pt, and the optically opaque nature of the materials. High-aspect-ratio structured Si, such as Si microwire arrays provide an alternative approach to ameliorating the negative correlation between the *FF* and J_{sc} . In such systems, a relatively high loading of catalyst can be positioned over the wire or at the base of a high-aspect-ratio microwire array, leaving a major proportion of the array accessible for light absorption while still obtaining a high catalytic activity. J_{sc} and *FF* have been greatly improved, but the overall efficiency is held back by a low V_{oc} as compared to Si PV cells.

The overall efficiency of a Si photocathode is greatly enhanced by the introduction of a n^+/p -junction. To date, little investigation is done on the doping of highly structured Si photocathodes, although research has shown its importance for improving the V_{oc} . Future developments will bring new insights on how to enhance the understanding, the fabrication and the performance of Si micro-/nanowire-based PEC cells.

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Chapter 3

Effects of Pillar Height and Junction Depth on the Performance of Radially Doped Silicon Pillar Arrays for Solar Energy Applications

The effects of pillar height and junction depth on solar cell characteristics were investigated in order to provide design rules for arrays of such pillars in solar energy applications. Radially doped silicon pillar arrays of 4 μm diameter and 6 μm pitch in a hexagonal packing were fabricated by deep reactive ion etching of silicon substrates followed by the introduction of dopant atoms by diffusion from a phosphorus oxide layer conformally deposited by low pressure chemical vapor deposition. Increasing the height of the pillars led to doubling of the efficiency from 6% for flat substrates to 12% for 40 μm high pillars with a 900 nm junction depth, because of an increase of the total junction area and lower optical reflection. For higher pillars, the current density and efficiency decreased, which is attributed to the presence of larger amounts of defect states at the surface introduced during the etching process. This effect is counteracted by an Al_2O_3 passivation layer on the pillar surface. An optimum in efficiency of 13% was found for a junction depth of 790 nm for 40 μm pillar height. At increased junction depths, the efficiency decreased due to the ever thinner undoped core of the pillars, leading to the observation that pillars with a diameter of 4 μm and a junction depth of 1.2 μm became less efficient than flat silicon substrates.

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3.1 Introduction

Silicon is a widely used material in the field of photovoltaics and solar-to-fuel devices, because of its outstanding electrical properties and the large toolbox available for structuring of the material.¹⁻³ Combined with the earth abundance and relatively low production costs, it is used extensively in the nano/micro-fabrication area. Previous studies in the field of photovoltaics have shown large improvement in solar cell performance, such as a lower reflectivity of silicon, structuring by means of wet and dry etching as well as various methods to introduce dopants, on both structured and random arrays.⁴⁻⁹ One of the recent developments is the shift from planar to radial p/n junctions using nano- or micropillars.^{10,11} The advantage of pillars with a radial $p-n$ junction for use in solar panels, and more specifically in solar-to-fuel devices, is two-fold. First, the radial junction decouples the direction of light incidence and charge transport processes, reducing the recombination losses. Secondly, the high surface area for a given footprint is ideal for catalysis and light absorption, as a lower reflectivity results in improved light absorption.¹²⁻¹⁴ Already a few examples of full-scale (lab) devices for solar-to-fuel conversion have been reported, where hydrogen is produced in an electrolyte using a silicon solar cell functionalized with proper catalysts.^{15,16} Optimization of the silicon solar cell is important for both photovoltaics and solar-to-fuel applications, since higher efficiencies will ultimately affect consumer and industrial interest in solar energy devices.

Pillar dimensions (*i.e.* height, width and density) and p/n junctions in the pillars (radial vs axial, depth and doping levels) have effects on all the performance parameters discussed above (light absorption, charge separation and surface area) which ultimately determine device efficiency. Yet, the relationships between fabrication and performance aspects are difficult to predict and decouple. For example, increasing the height of the pillars inherently increases the total junction area present in the solar cell, and possibly decreases the reflectivity of sunlight.⁹ Previous publications, which focus on pillars with diameters of up to a few μm , have shown a positive effect of increased pillar heights on the efficiency of solar cells.^{10,17,18} Voigt *et al.* have used simulations to predict the most efficient pillar radius (in the range 62-4000 nm) and height (range 3-384 μm)¹⁷ and found an optimum of 2 μm for the pillar diameter with a corresponding height of 96 μm . Another important aspect in the design of the pillar array is the diameter-over-pitch (D/P) ratio. A D/P ratio between 0.5-0.8 has been shown to have the highest theoretical and experimental efficiencies for various systems.¹⁸⁻²⁰ The radial junction depth variation in micropillars can be varied by tuning the doping process, and a trend of improved *JV* characteristics for thinner junctions, down to 50 nm, has been shown in simulations.²⁰ A thin junction leads to less recombination, which implies that the outer highly doped shell of a radially doped micropillar should be kept thin, but also should keep its carrier separation functionality. Pillars with a deep junction may suffer from bulk recombination,

which negatively affects the efficiency of the solar cell.²¹ Clearly, an optimal radial junction depth exists for any given configuration of a solar cell (*i.e.* pillar diameter, pitch, height and specimen footprint) that yields the highest overall efficiency. To date, no studies have shown the joint optimization of pillar height and junction depth.

Here, we show the optimization of the electrical performance of radially doped arrays of micropillars with a fixed diameter, pitch and footprint by variation of the pillar height and junction depth (x_j), etched in a flat solar cell. Moreover, the trends in the measurements are compared to theoretical calculations. Microsized pillar arrays were chosen over nanowires, to increase the control over the radial junction inside the pillars. Arrays were used with a pillar diameter of 4 μm in combination with a pitch of 6 μm ($D/P = 0.67$), and heights in the range of 0 to 60 μm , and compared to their flat counterparts, *i.e.* a flat silicon solar cell with the same junction characteristics. A full range of junction depths, from shallow (~ 140 nm) to deep junctions (~ 1640 nm), has been realized using low pressure chemical vapor deposition (LPCVD) for the creation of the required dopant source, *i.e.* a thin layer of phosphorus oxide. Preliminary experiments are discussed to further improve the efficiency of pillar array-based solar cells by depositing a passivation coating on the surface of the micropillars.

3.2 Results and discussion

After DRIE fabrication of the micropillars, a few samples were broken and cross sections were imaged in a scanning electron microscope (Figure 3.1). Due to the nature of the etching process on high aspect ratio structures, a slight tapering occurred at about 33% from the top of the pillars. This effect was more pronounced for the 60 μm pillars (18 min etching), where the diameter decreased approximately 500-600 nm, compared to 100-200 nm in the case of 40 μm micropillars (12 min etching). The pillars were broad enough to prevent overdoping of the pillar arrays, which would annihilate the beneficial effect of a radial p/n junction.

Figure 3.1 Cross-sectional SEM images of micropillar arrays with a height of (A) 40 μm and (B) 60 μm .

The combinations of drive-in temperature and time used here led to junction depths between 140 and 1640 nm, as predicted by FEM simulations.⁷ Junction depths were experimentally verified by ball grooving and staining experiments on five different flat samples (140, 790, 900, 1170 and 1550 nm). Since the phosphorus surface concentration upon drive-in is relatively low, transport of phosphorus into silicon can be described by Fick's law of diffusion.²² Two examples of the ball grooving and staining experiments (900 and 1170 nm) are shown, Figure 3.2.

Figure 3.2 Microscope images of ball grooving experiments after staining with chromium oxide for 30 s, on two different samples; (A,B) 1050 °C, 15 min and (C,D) 1050 °C, 30 min. Images B and D display the measurements of the two diameters.

Ball grooving and staining experiments were used to verify the junction depth. Figure 3.1 shows two typical examples of stained grooves, including the measurement of the two diameters required for calculating the junction depth. The junction depth was calculated using Equation 3.1:

$$x_j = \frac{a^2 - b^2}{8 * R} \quad \text{Eq. 3.1}$$

Where a and b are the outer and inner diameter and R is the radius of the ball. For the two examples below, this results in junction depths of 899 nm (1050 °C, 15 min, A/B) and 1166 nm (1050 °C, 30 min, C/D).

The influence of the height of silicon micropillars with incorporated radial p/n junctions was investigated by analyzing their electrical properties. Figure 3.3 shows the JV characteristics of samples with seven different pillar heights, from 0 to 60 μm . All samples had a junction depth of 900 nm. The large increase in both current density (J_{sc}) as well as open circuit voltage (V_{oc}) for a sample with 10 μm high pillars compared to a flat sample (Figure 3.3A) indicates that even a shallow structure already drastically improves the light absorbing properties of the solar cell. This can be explained by both an increase in total junction area and a decrease in reflectivity. The latter is supported by previously reported work by various groups, who showed that the reflectivity of polished, flat silicon (ca. 35%) decreases to values below 10% by even the smallest amount of micro/nano structuring.^{1,23} The parameters J_{sc} and V_{oc} were plotted as a function of the pillar height (Figure 3.3B), along with their respective fill factor (FF) and efficiency, as shown in Figure 3.3C. A monotonous increase of V_{oc} is visible, from 400 mV for flat samples to 460 mV for 60 μm high pillars. This is attributed to the increase of the total surface area – and concomitantly of the junction area – of the solar cell on the given footprint, which is 5 times higher for 10 μm high pillars and increases to 22 times for the 60 μm high pillars. The J_{sc} values, after a gradual increase with pillar height up to 40 μm , decrease again for larger pillar heights, which was unexpected as in simulations this effect does not occur, and longer pillars obtain higher currents.¹⁷ The decrease is reflected in the overall efficiency: since the FF remains fairly constant, the efficiency exhibits a maximum for a pillar height of 40 μm . We conclude that for these pillar arrays, with a 4 μm diameter, 6 μm spacing and a junction depth of 900 nm, the optimum pillar height is 40 μm .

We attribute the decrease in current density for heights above 40 μm to surface recombination by an increasing number of defect states at the, equally increasing, outer surface of the silicon pillars. These defects have been induced by the dry etching method in combination with the circular pillar design, because of which the sidewalls of the pillars are not terminated by a low-index crystallographic plane of silicon. This has led to defects at the surface of the silicon pillar compared to (100) silicon.²⁴ In addition, the working principle of the applied ‘Bosch’ process, which is a cyclic process involving gas pulses of SF_6 (etching gas) and C_4F_8 (passivation gas), has led to scalloping of the pillar sides,²⁵ which further increases the amount of defect states.²⁴ Cryogenic etching would lead to pillars with a lower sidewall roughness without scallops, however, this method did not produce good quality micropillars with heights above 20 μm at the pitch used here.

Figure 3.3 (A) *JV* measurements of n-doped (900 nm junction depth) p-type base substrates for different pillar heights. Each line is the average of at least four different samples prepared with the same settings. (B) *JV* and V_{oc} voltage as a function of the pillar height; shaded areas indicate the 1σ range (determined from at least 4 different samples). (C) Corresponding *FF* and efficiencies of the values shown in B. (D) *JV* measurements on samples with 60 μm high pillars before and after ALD deposition of 11 nm Al₂O₃.

To reduce surface recombination, a passivation layer (11 nm) of Al₂O₃ was deposited by atomic layer deposition (ALD) on a sample with 60 μm pillars, after initial *JV* analysis of the same specimen. The passivation layer resulted in increased J_{sc} (Figure 3.3D), V_{oc} and *FF*. The increase in J_{sc} may also be explained by the anti-reflective properties of the Al₂O₃ layer, however, the ALD layer is sufficiently thin (11 nm) that its possible anti-reflective properties are negligible.²⁶ The *JV* curves were fitted to determine the shunt (R_{sh}) and series (R_s) resistances, and the V_{oc} . Upon application of the passivation layer, R_{sh} was found to increase from 308 to 1064 Ω cm² and R_s decreased from 3.1 to 2.4 Ω cm², whereas the V_{oc} barely changed. These improvements show that surface defects indeed play an important role for arrays with higher pillar, and that a conformal coating of Al₂O₃ can be used to reduce the impact of the defects.

Subsequently, the junction depth was varied by changing the drive-in temperature between 900 - 1100 °C and the drive-in time between 5-60 min using pillar arrays with the optimum pillar height of 40 μm. Figure 3.4 shows *JV* measurements for twelve different junction depths. Junctions made at 900 or 950 °C (Scheme 3.1A) did not give proper charge separation, most likely due to too low dopant concentrations (<2×10¹⁹

atoms/cm³ surface concentration for 1050 °C as determined by SIMS, see Figure 3.5), resulting in a low FF . At higher doping temperatures, the surface concentration increases sufficiently to prevent resistance losses at the surface, as proven by the high FF . In case of a drive-in temperature of 1000 °C, both the R_{sh} and R_s decreased significantly with the drive-in time, resulting in a proper solar cell with higher current densities and correspondingly increased V_{oc} (Figure 3.4A). The increase in J_{sc} and V_{oc} for thicker junctions continued until a junction depth of 790 nm (Figure 3.4B). For junctions $\geq$ 790 nm the current density dropped, and also V_{oc} decreased slightly, but not as pronounced as J_{sc} (Figure 3.4C). The R_{sh} and R_s remained fairly constant for larger junction depths, due to which the FF remained constant as well at about 70% (Figure 3.4D). For x_j values $\geq$ 790 nm bulk recombination became significant, resulting in lower efficiencies.

Figure 3.4 JV measurements of various n-doped p-type base micropillar arrays for different junction depths. Each line represents the average of at least four different samples prepared with the same settings. (A) JV data for junction depths between 140-790 nm. (B) JV data for junction depths between 790-1640 nm. (C) JV and V_{oc} as a function of the junction depths shown in A and B, shaded areas indicate the 1 σ range. (D) Corresponding FF and efficiencies of the values shown in (C).

Figure 3.5 SIMS measurement of a flat sample, doped with LPCVD of phosphorus at 1050 °C, for 15 min. The dotted line indicates the base boron concentration of the used wafer, prior to doping, estimated by a 4-point probe measurement.

For junctions above 1.55 μm J_{sc} dropped even below the current density of flat samples (22 mA/cm^2 , see Figure 3.1B). Some insight in this behavior can be obtained by calculating the doping profile plus the depletion zone in the radially doped pillars. For p/n junctions as used here, the donor density (N_D) is much larger than the acceptor density (N_A), therefore the depletion zone W_{dep} can be approximated by Equation 3.2:

$$W_{dep} \approx \sqrt{\frac{2\epsilon_{Si}\Phi_{bi}}{q N_A}} \quad \text{Eq. 3.2}$$

where ϵ_{Si} is the permittivity of silicon, Φ_{bi} is the built-in potential (V), q is the electric charge and N_A is the acceptor density (atoms/cm^3). The built-in voltage is defined as Equation 3.3:

$$\Phi_{bi} = \frac{k T}{q} \ln \frac{N_D N_A}{n_i^2} \quad \text{Eq. 3.3}$$

Where k is the Boltzmann constant, T is the temperature (K), and n_i is the intrinsic carrier concentration (atoms/cm^3). Equation 3.2 gives a built-in potential of 0.67 V for a base doping level of $2 \times 10^{15} \text{ atoms}/\text{cm}^3$. W_{dep} largely depends on N_A , and since the used substrates have a resistivity of 5-10 Ωcm , the depletion zone was calculated to be in the range of 584 to 808 nm. Because the doping level of the introduced n-type dopants is much higher than the base p-type doping, the depletion zone can be expected to be located mainly from the junction depth inward into the core of the pillar. This implies that 4- μm pillars with junctions deeper than 1.2 – 1.4 μm will have no p-type core left. This agrees well with the experimental data for junction depths of 1.37 μm and higher (Figure 3.3B). Summarizing, our pillar arrays, in combination with LPCVD phosphorus doping, show an optimal x_j value of approx. 800 nm. Simulations have shown that thinner junctions should perform better.^{20,21} To make such thinner junctions experimentally with

good diode quality, a doping method should be used which gives a higher dopant surface concentration.

3.3 Conclusions

The solar cell performance of radially n-doped silicon pillar arrays was studied as a function of the pillar height and junction depth. Compared to flat samples, pillar arrays gave rise to a large increase in current density, from 22 mA/cm² for flat samples (6% efficiency) up to 37 mA/cm² for 40 µm pillar arrays (12% efficiency, 900 nm junction). However, for heights of 50 and 60 µm, J_{sc} decreased, which is attributed to increased numbers of surface defect states, resulting from the deep reactive ion etching process. This effect was counteracted by an Al₂O₃ passivation layer. The LPCVD process for phosphorus doping did not give proper diodes for shallow radial junctions. The optimum junction depth found experimentally was 790 nm (13% efficiency for 40 µm high pillars). For deeper junctions, a steady decrease of J_{sc} was observed, which is explained by the narrowing p core of the pillars, resulting in efficiencies poorer than flat Si surfaces for junction depths exceeding approx. 1.2 µm. Further research towards more efficient silicon pillar array solar cells should focus on the fabrication of shallower junctions, <600 nm, using a more effective doping technique, in combination with optimized passivation and anti-reflective coatings. In addition, future research should also verify what the optimal pillar configuration is (*e.g.* nano/micro-scale), combined with different D/P ratios.

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3.5 Materials and methods

3.5.1 Fabrication of radial *p/n* junctions in silicon micropillar arrays

Radial *p/n* junctions were prepared as previously reported, and shown in Scheme 3.1.⁷ In summary, p-type silicon {100} substrates (5-10 Ω cm, 525 µm thickness, single side polished, Okmetic Finland) were covered with 100 nm silicon nitride (SiN_x). On the front side, after removal of SiN_x, the substrate was patterned with arrays of hexagonally packed dots (4 µm diameter, 6 µm pitch, 0.5x0.5 cm² cell size on a specimen of 2 x 2 cm²) by standard photolithography (Olin 907-17 photoresist). This pattern was transferred into the silicon by deep reactive ion etching (CF-chemistry, Adixen AMS100SE), and the height of the pillar arrays was controlled by the etching time, where the etching rate of silicon was ca. 3.2 µm/min. After removal of the photoresist layer and residual fluorocarbons

using an oxygen plasma, a *ca.* 400 nm thick phosphorus oxide layer was deposited by LPCVD (Tempress tube furnace), using phosphine (PH_3) as dopant precursor.

Dopant transfer into the pillars by diffusion was performed at temperatures ranging from 900 to 1100 °C and various drive-in times (5-60 min) under a stream of N_2 . The combination of drive-in time and temperature determines the radial junction depth in the pillars. After the thermal diffusion step, the phosphorus oxide was removed by immersion in BHF (NH_4F -buffered aqueous HF) for 10 min, and the silicon nitride from the backside of the substrate was stripped in 50% aqueous HF (30 min). Values of the junction depth were predicted by FEM (Finite Element Modelling, COMSOL Multiphysics 4.2) simulations and verified with ball grooving and staining.⁷

Scheme 3.1 Schematic fabrication process. (A) Removal of topside silicon nitride, followed by photolithography. (B) Deep reactive ion etching of Si. (C) Low pressure chemical vapor deposition of phosphorus oxide. (D). Drive-in diffusion of phosphorus, resulting in radial p/n junctions. (E) Removal of silicon nitride and deposition of metal front and back contact.

3.5.2 Atomic layer deposition

To reduce the reflectivity of the micropillar arrays, a layer (42 nm) of aluminum oxide (Al_2O_3) was conformally coated on several samples, using a thermal ALD process at 100 °C (Picosun P-300S reactor). Trimethyl-aluminum (TMA) and H_2O were used as precursors and N_2 was the carrier gas, yielding a growth rate of 0.83 Å per cycle (after initial growth stabilization). The time for one complete Al_2O_3 ALD cycle was 9.3 s, where each cycle was defined as: 0.1 s TMA exposure, 4 s N_2 purge, 0.2 s H_2O exposure, and 5 s N_2 purge.

3.5.3 JV measurements

To ensure Ohmic contact to the solar cells, 1 μm aluminum/silicon alloy (99% Al, 1% Si) was sputtered (Oxford PL 400) on the front and backside of each specimen, where on the front side a shadow mask was applied to protect the pillar arrays from coating. In this

way, a rectangular electrode is formed around the pillar array. To measure the photovoltaic characteristics, the samples were positioned perpendicular to a 300 W xenon arc light source with an intensity of 1 sun (AMG 1.5). *JV* measurements were recorded on a VersaSTAT 4 potentiostat for a linear voltage sweep from -0.7 to 0.7 V at a rate of 0.2 V/s. For each setting (pillar height or junction depth) at least four different samples were measured.

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Chapter 4

Photo-Electrical Characterization of Silicon Micropillar Arrays with Radial p/n Junctions Containing Passivation and Anti-Reflection Coatings

In order to assess the contributions of anti-reflective (AR) and passivation effects in microstructured silicon-based solar light harvesting devices, thin layers of aluminum oxide (Al_2O_3), silicon dioxide (SiO_2), silicon-rich silicon nitride (SiN_x), and indium tin oxide (ITO), with a thickness ranging from 45 to 155 nm, were deposited onto regularly packed arrays of silicon micropillars with radial *p/n* junctions. Atomic layer deposition (ALD) of Al_2O_3 yielded the best conformal coating over the micropillars. The fact that layers made by low pressure chemical vapor deposition (LPCVD; SiO_2 and SiN_x) were not conformally deposited on the sidewalls of the Si micropillars did not influence the photoelectrical efficiency. For ITO, a change in composition along the micropillar height was measured, which led to poor performance. For Al_2O_3 , deconvolution of the contributions of passivation and anti-reflection to the overall efficiency gain exhibited the importance of passivation in micro/nano-structured Si devices. Al_2O_3 coated samples performed the best, for both n/p and *p/n* configured pillars, yielding (relative) increases of 116% and 37% in efficiency of coated versus non-coated samples for p-type and n-type base micropillar arrays, respectively.

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4.1 Introduction

Solar-to-fuel (S2F) is the concept of turning solar energy into a storable fuel. These fuels, which can be sustainably produced in liquid or gaseous form, may offer several benefits, such as improved grid stability by providing a solution to solar intermittency, enhanced energy security, compatibility with existing infrastructure, and climate change mitigation.

To fabricate a fully integrated, efficient S2F device based on photo-electricity, a set of semiconductors must be combined with a proper electrocatalyst. One approach is the use of a two-photon absorber in tandem to gain sufficient solar-to-fuel efficiency, which consists of a set of semiconductors with bandgaps of approximately 1.7 eV and 1.0 eV.^{1,2,3} Si is suitable as one of the semiconductors, since it has a bandgap of 1.1 eV, is being used as a material in photovoltaic (PV) cells intensively for many decades,⁴⁻⁶ is earth abundant, stable, non-toxic, and is cost-effective to produce. A popular geometry for a S2F device is based on nano/micropillar arrays.⁷⁻¹² A pillar array ensures effective harvesting of photons and effective photocurrent collection, while also providing a large surface area for catalytic reactions. Silicon nano/micro-engineering process flows have enabled the fabrication of more complex structured silicon solar cells, and in particular the development of 3D micropillar structures with radial p/n junctions.¹³⁻¹⁸ The efficiencies of these silicon micropillar arrays depend on various parameters. In our previous work an optimum was found for pillars with a length of 40 μm and a junction depth of close to 1 μm .¹⁸

In order for S2F devices ever to be viable, the underlying photon-absorber needs to be an efficient PV cell. Micropillar arrays with radial p/n junctions have a high aspect ratio which leads to a strongly increased surface area with concomitantly enhanced surface recombination.¹⁹⁻²⁵ Shin *et al.* have reported on radially doped silicon micropillars of 10 μm in length and pointed out the importance of a proper surface passivation.²³ Yet, even with a passivation layer, reported efficiencies of silicon nano- and micropillar PV cells rarely exceed 5%.²³ Previously we showed the feasibility of radially doped silicon micropillars of 40 μm in length, with efficiencies well above 5%.¹⁶⁻¹⁸ Yu *et al.* have simulated the effect of surface passivation on nanopillar solar cells.²⁶ Their results suggest that surface passivation and p/n junction placement are important factors in the design of nanowire solar cells. In the current study, we aim to improve the efficiency of Si micropillar PV cells by applying a passivation and anti-reflection (AR) coating. We will discuss the deposition and in-depth characterization of various surface coatings (aluminum oxide (Al_2O_3)^{20,27,28}, silicon-rich silicon nitride (SiN_x)^{27,29,30}, silicon dioxide (SiO_2)^{27,29,30}, and indium-doped tin oxide (ITO)³¹⁻³³) on Si micropillar arrays with a radial p/n junction, to function as a passivation, anti-reflective and possibly also as a conductive layer. In order to function as an AR coating, the thickness has to be optimized separately for each material. To obtain a starting point of the AR coating thickness, we have

developed a finite element model in combination with an analytical model. This model is experimentally validated by depositing layers with different thickness around the predicted optimal value. On the pillared samples, the conformality of the deposited layers is addressed by measuring the material thickness on the sidewalls of the silicon micropillars. The electrical characteristics of the coated PV cells are evaluated and compared to uncoated samples to assess the efficiency gain. For Al_2O_3 as a coating, we are able to discriminate between the passivation and AR effects of the coating on the efficiency of a PV cell.

By applying a coating of a certain thickness over a micro-structured PV cell, an improved efficiency is targeted by reducing reflection and surface recombination. We optimize the thicknesses of applied coatings to obtain the maximum efficiency for PV cells. Si micropillar arrays with radial p/n junctions were fabricated as described before.¹⁸ Briefly (Figure 4.1), micropillars of 40 μm were etched by deep reactive ion etching. Radial junctions were fabricated by doping with either phosphorous or boron oxide at 1050 $^\circ\text{C}$ for 15 min. Subsequently, a coating was deposited by means of ALD (Al_2O_3), LPCVD (SiO_2 , SiN_x) or sputtering (ITO). Finally, the pillar arrays were masked to etch away the deposited coating on the flat surface regions and contact the underlying junction by aluminum.

Figure 4.1 Fabrication of silicon micropillar arrays with a radial junction. (A) Deposition of a passivation layer by either ALD (Al_2O_3), LPCVD (SiO_2 , SiN_x) or sputtering (ITO), followed by contact formation by masking of the pillar arrays by photoresist, and removal of the coating on the contact points and deposition of aluminum front and back contacts by sputtering. (B) The finalized micropillar array with radial p/n junction and covered with 106 nm of SiO_2 . The scale bar is 20 μm .

4.2 Results and discussion

4.2.1 FEM simulations of reflectivity

To predict the optimal AR coating thickness, we developed a finite element method (FEM) simulation in combination with an analytical model. This model solely calculates the reflectivity of the micropillar PV cell, and does not include passivation losses/gains. A typically fabricated and simulated pillar geometry is depicted in Figure 4.2A and B, respectively.

The reflectivity of flat silicon can be calculated analytically by the Fresnel equations. An infinite flat silicon substrate reflects 35% of the incoming light (Figure 4.2C, analytical). By adding an anti-reflective coating (ARC), the reflectivity can be reduced at a specific wavelength (Figure 4.2C, flat with ARC). The optimal thickness of the AR coating can be calculated by considering a combination of two spectra as a function of the wavelength, namely the photon flux,³⁴ and the absorbance ($= 1 - \text{reflectivity}$) (Figure 4.2C) of the sample. By multiplying these spectra, the theoretical photon absorbance of the silicon cell is obtained (Figure 4.2D). In fact, the surface area underneath each curve in Figure 4.2D is directly related to the expected current density output of a complete PV cell. The thickness of an AR coating has to be such that it minimizes the reflectivity at the maximum photon flux. More specifically, the total amount of absorbed photons can be maximized by adjusting the minimum in the reflectivity curve (Figure 4.2C, flat with ARC).

Figure 4.2: (A) SEM image of a realized and (B) simulated pillar geometry of the COMSOL simulation. (C) The reflection of a flat silicon surface based on Fresnel's analytical equations and FEM simulations. Furthermore, FEM simulation results are given of the reflectivity of microstructured surface. The results also include the analytical reflection of a flat silicon surface when only 34% of the light is reflected. (D) The photon absorbance spectra of flat silicon, a bare pillar array, both with and without a coating of 106 nm SiO₂.

The reflectivity of micropillar arrays cannot be calculated in a straightforward manner by an analytical model. Therefore we used FEM simulations to calculate the reflectivity of micropillar arrays. FEM is a powerful tool to simulate structures over a broad wavelength spectrum. According to these simulations (Figure 4.2C, 40 μm high pillars), the reflectivity

of flat silicon is lowered substantially upon the addition of pillars with a height of 40 μm . Since the diameter of the pillars is an order of magnitude larger than the wavelength range of the incoming light, the top surface of the pillars will reflect light as being a flat surface. For hexagonally packed micropillars with a diameter of 4 μm and a pitch of 6 μm , the total surface area of the tops of the pillars encompasses 34% of the footprint of 5 x 5 mm^2 . Therefore at most 66% of the light is completely absorbed, while 34% is reflected as if it hits a flat surface of polished silicon. Figure 4.2C includes a curve of 34% reflectivity of the analytically calculated reflection of a flat surface: this curve is in reasonable agreement with the FEM simulation done for the 40 μm high pillars. Furthermore, total reflectance spectra measurements of similar micropillar arrays done by Lee *et al.*, agreed very well with our predicted outcome.³⁵ Therefore, we conclude that light absorption for this given hexagonal packing of the pillar array is limited by the packing density of the pillars within the footprint: for the array configuration used here, a pillar height of 40 μm ensures maximum light absorption.¹⁸

Since the tops of the micropillars reflect light as if it was an infinite flat surface, a (conformal) anti-reflective coating is applied to lower the reflectivity even further (Figure 4.2, 40 μm high pillars with ARC). The thickness was calculated in the same manner as for an infinite flat sample, but with the assumption that micropillar silicon arrays already reflect 66% less light than an infinite flat sample (Figure 4.2C). In Table 4.1 are the calculated and measured values for the optimum anti-reflective properties.

Table 4.1: Simulated and measured optimal coating thicknesses of various AR coating materials.

Material	Optimal thickness (nm) ^a	Thickness on p-type (nm) ^b	Thickness on n-type (nm) ^b
Al_2O_3	91	90 ± 1	89 ± 1
SiN_x	71	71 ± 3	65 ± 6
SiO_2	106	110 ± 4	106 ± 7

^a Simulated by FEM

^b Measured by ellipsometry on flat surfaces next to micropillar arrays

Comparison of the absorbance gain upon applying an AR coating (Figure 4.2D) indicates that the relative gain is less for a pillared array than on a flat sample. This is again attributed to the effect that the AR coating only reduces reflection of the tops of the micropillars, while it is actively contributing to the absorbance of a flat substrate over the full footprint.

4.2.2 Anti-reflection coatings

We use the outcome of the FEM simulations for the optimal AR coating thickness (Al_2O_3 91 nm, SiO_2 106 nm, SiN_x 71 nm, and ITO 71 nm; Table 4.1) as initial input for the optimization of the micropillar arrays in absolute efficiency.

These coatings were chosen because the deposition techniques ALD (Al_2O_3) and LPCVD (SiO_2 and SiN_x), are known to conformally coat high-aspect ratio structures (p- and n-type base, pillar height: 40 μm). Moreover, ITO was applied by sputtering to investigate its capability as a triple function coating, *i.e.* for passivation, anti-reflection and conduction. Initially, the thickness of each coating was chosen according to the outcome of the FEM simulations (see above). Table 4.1 shows the theoretical (FEM) and the measured (ellipsometry, on flat areas next to the micropillar arrays before removal for Al/Si contacting) of the optimal thicknesses of the deposited AR coatings with respect to the highest current density (see below). The ellipsometry measurement is fitted with a material selective model to obtain the thickness of each coating in a nondestructive manner. The beam diameter is 300 μm , therefore the thickness of each coating is not measured on top the micropillar arrays, but in close proximity of the micropillar arrays. 25 points around the micropillar arrays are taken for the error calculation.

In order to inspect the conformality of the AR coating layers, coated pillars were cut in half along the z-direction using focused ion beam (FIB) etching (Figure 4.3). These results clearly show that deposition of Al_2O_3 (90 nm) by ALD resulted in a perfectly conformal coating over the entire height of the pillars. In contrast, both LPCVD materials (*i.e.* SiO_2 (110 nm) and SiN_x (65nm)) exhibited a gradient in thickness along the pillar height. At the bottom of the pillar the coating was almost twice as thick as at the top. However, it is well-known that LPCVD coatings in deep microstructures, if they are non-uniform, will in fact exhibit a thicker coating at the top side compared to the bottom side of the trench.³⁶ Therefore we attribute the thickness variation instead to undesired removal of SiO_2 or SiN_x during FIB etching, which cannot be excluded and is more pronounced at the top region of the pillars, because of the concomitantly higher exposure times upon FIB etching of the pillar. Therefore, we presume that the original LPCVD deposition before FIB was also conformal for these materials. Sputtering of ITO (88 nm) caused a conformality problem in the scallops that result from the fabrication process of the micropillars (DRIE; Bosch process, highlighted in Figure 4.3), due to the high directionality of the material flux during ITO deposition. This resulted in a shadowing effect on the upper part of the scallop. Further down the height of the pillar less scalloping is visible leading to more homogeneous coating.

Figure 4.3: Cross-sectional HR-SEM images showing the coating layers of Al_2O_3 (90 nm), SiN_x (65 nm), SiO_2 (110 nm), and ITO (88 nm), along the sides of pillars that have been cut in half orthogonally to the substrate by FIB to be able to inspect the conformality of the AR coatings along the pillar height. The HR-SEM images for Al_2O_3 , SiO_2 and SiN_x are false colored manually in Photoshop to aid the visualization of the coatings. The image of sputtered ITO was recorded by ESB. The micropillar on the left is completely coated with ALD Al_2O_3 .

As indicated above, an ITO coating has a three-fold function, and in order to fulfill its third function, the electrical resistance through the film has to be minimized. The conductivity mainly depends on the composition of the indium:tin ratio.³⁷ One way to verify and visualize the composition level along the height of the pillar is by energy selective backscattered (ESB) SEM imaging. ESB visualizes the contrast between the coating and the silicon micropillar and discriminates between elements of which the coating is composed. Figure 4.3 shows that the ITO composition changes from top to bottom, which is observed by the reduced ESB brightness along the length of the pillar from top to bottom. We expect that this composition change is accompanied by a decrease of conductivity along the pillar, which was confirmed by the *JV* measurements described below. Furthermore, conformal coating is a requirement for good passivation. Based on these considerations, we conclude that ITO as deposited here does not fulfil the criteria of a good coating on micropillars.

4.2.3 JV measurements

In previous work, we have already shown the benefits of bare micropillar arrays with radial junctions over flat surfaces with respect to PV efficiency.^{17,18} Therefore, here we assess solely the effects of the applied coatings on micropillar arrays with a fixed pillar length and junction depth. As a reference we added a comparison of the performance of flat and micropillar samples, with and without an AR coating (Figure 4.4A).

JV measurements were performed on both non-coated (bare) and coated silicon micropillar arrays with radial junctions. To verify the predicted optimal thickness by the FEM simulations (see above), layers with different thickness were applied to pillared p-type silicon (n-emitter). Current density outputs were measured for Al_2O_3 , SiO_2 and SiN_x , and these revealed optimal thicknesses of 90 ± 1 , 110 ± 4 and 71 ± 3 nm, respectively (Figure 4.4B). These values are in excellent agreement with the values (91, 106 and 71 nm, respectively) predicted by the simulations.

Figure 4.4: (A) An overview of the effect of the addition of 106 nm SiO_2 onto a bare flat sample and onto a micropillar sample. (B) Current density output as a function of the ellipsometric thickness (measured outside the pillar area) of the anti-reflection coating for pillared p-base samples (P-doped at 1050 °C for 15 min) coated with several thicknesses of Al_2O_3 , SiO_2 or SiN_x . The error bars indicate the 1σ error range. For each data point, at least 4 specimens were measured (both current density and ellipsometric thickness). Connector lines serve solely as a guide to the eye.

All pillared samples coated with an optimized AR coating showed an improvement in current density compared to the bare pillar arrays (Figure 4.5). For the p-type base samples (n-emitter, Figure 4.5A), SiO_2 and SiN_x showed a larger increase than Al_2O_3 (Table 4.2). We contribute this increase to a combination of effects. Firstly, all investigated coatings have a refractive index (n) lower than Si and therefore each material will act as an anti-reflection coating. Secondly, Al_2O_3 , SiO_2 and SiN_x passivate the silicon surface by reducing the amount of surface trap states via chemical passivation,^{38,39} *i.e.* the reduction of the amount of dangling silicon bonds, which is proportional to the total surface area of the micropillar array. Thirdly, SiN_x and SiO_2 introduce a positively charged interface,⁴⁰ due to which the minority carriers (holes) in the n-emitter are electrically shielded from

the surface and thus from remaining trap states, an effect that is known as field effect passivation.^{25,41} In contrast, Al_2O_3 induces a negatively charged interface,^{25,40} due to which the minority carriers (holes) are attracted towards the surface and thus into possible remaining trap states. This limits the increase in J_{sc} upon the use of Al_2O_3 . The reason for the large increase of V_{oc} for the Al_2O_3 sample is unknown, but it is considered likely that the chemical passivation induced by the ALD technique is more effective than that of the LPCVD methods and that this counteracts the negative effects of a negatively charged interface upon Al_2O_3 deposition. All coatings give a significant improvement of efficiency compared to the bare arrays, yielding efficiencies up to 13.2% (for Al_2O_3 coated pillar arrays; Table 4.2).

Figure 4.5: J/V current measurements on A) p- and B) n-type base micropillar arrays with radial p/n junctions, in the absence and presence of a coating with an optimal thickness (corresponding to Figure 4.4B).

Table 4.2: J/V characteristics for various coatings on 40 μm high p- and n-type base micropillar arrays

Sample	η (%)**	J_{sc} (mA/cm²)*	V_{oc} (V)	FF (%)
p-base bare	6.6±1.3 / (---)	29.9±3.0 / (---)	0.41±0.01	54±0.7
p-base Al_2O_3	13.2±1.0 / (12.2)	36.6±2.7 / (35.9)	0.47±0.01	73±0.1
p-base SiN_x	10.2±1.4 / (8.1)	39.4±3.4 / (35.7)	0.42±0.02	62±0.8
p-base SiO_2	10.2±1.2 / (7.7)	40.9±1.5 / (34.0)	0.44±0.02	57±0.4
n-base bare	7.5±0.8 / (---)	23.5±2.4 / (---)	0.45±0.01	68±0.2
n-base Al_2O_3	10.1±0.7 / (8.1)	33.8±0.8 / (28.2)	0.46±0.01	70±0.5
n-base SiN_x	9.5±0.9 / (8.5)	28.9±2.9 / (28.1)	0.45±0.01	72±0.2
n-base SiO_2	8.6±0.8 / (8.1)	26.1±2.0 / (26.3)	0.46±0.01	72±0.3
n-base ITO	7.4±1.0 / (7.5)	27.0±2.2 / (27.2)	0.43±0.01	63±0.3

* Values in between brackets are theoretical current densities, calculated by means of Figure 4.2C. The surface area of this graph is directly proportional to the current density. Now only improvements due to the respective anti-reflective coating are taken into account and no passivation effects

** The efficiencies in between brackets are calculated with the corresponding current density* in between brackets

In case of the n-type base samples (p-emitter, Figure 4.5B), opposite effects are observed. The increase in J_{sc} was the highest for Al_2O_3 , compared to the SiO_2 and SiN_x layers, which is due to the negatively charged Al_2O_3 interface with c-Si which now repels the minority carriers. In contrast, the adverse effect of the positively charged interface upon coating of the pillars with SiO_2 or SiN_x was most pronounced for samples with SiO_2 as passivation coating. The negative field effect passivation for SiN_x can be diminished by annealing, as done at 825 °C in this study, which reduces the negative charge density at the interface of c-Si and SiN_x .³² Similar to the p-type base samples, an Al_2O_3 , SiO_2 or SiN_x coating on p-emitters resulted in an improvement of the overall efficiency compared to bare micropillars (efficiency up to 10.1% (for Al_2O_3)). Contrary to the other coatings, ITO-coated n-type base micropillar arrays performed slightly worse than bare samples in terms of efficiency (Table 4.2). Although the ITO layer yielded a small improvement in current density (Figure 4.5B), the V_{oc} and FF became lower (Figure 4.5B and Table 4.2), which counteracted any improvement of the efficiency.

When comparing p- and n-type base specimens, p-type base samples gave a higher J_{sc} for identical coatings, whereas for n-type samples the V_{oc} and FF were higher. The increase in J_{sc} for coated p-type base samples was higher than for coated n-type base samples, for which reason the p-type specimens had a higher overall efficiency. The large differences between the recorded V_{oc} and J_{sc} for identical applied coatings cannot be explained easily, but these are likely caused by fabrication parameters such as a different doping technique (LPCVD vs SSD), different base concentrations (1-10 (p-type) vs 5-10 Ω cm (n-type)), doping profiles, and thicknesses of the base wafers (525 μ m (p-type) vs 380 μ m (n-type)).

4.2.4 Deconvolution of the contributions of passivation and anti-reflective properties

To assess the improvement in efficiency upon applying a coating and to discriminate between the contributions of passivation and anti-reflection, a set of bare p-type base samples was first analyzed electrically. Subsequently, the same bare pillar arrays were passivated by ALD with a thin layer of Al_2O_3 (11 nm) and again electrically analyzed, after which the thickness, of the previously passivated samples, was increased to 91 nm to function as AR layer. Such an analysis of JV measurements to discriminate between the passivation and anti-reflection effects of LPCVD-based coatings (SiO_2 and SiN_x) is not possible on the same sample, since the required temperature for the investigated LPCVD processes (well above 400 °C) will cause detrimental roughening of the already deposited aluminum contacts, which will result in short-circuiting, and hence destruction of the junction.⁴²

The main effect of the first applied Al_2O_3 layer (*i.e.* 11 nm) is a slight increase in current density, which we attribute to the presence of less surface trap states at the sides of the

pillars, as a consequence of which less surface recombination occurs (Figure 4.6A). The positive effect of passivation is also visible in a plot of the bias-dependent local ideality factor (LIF; Figure 4.6B). The local ideality factor is heavily affected by the amount of defect sites.⁴³⁻⁴⁵ The total amount of surface area of a sample, thus the amount of surface defect sites, is drastically increased due to the realization of a micropillar array. This is clearly visible by means of the enlarged local ideality factor when comparing a bare flat sample and a bare micropillar array (Figure 4.6B).⁴⁵ In fact, if the footprint of the pillared sample is increased, so does the local ideality factor.⁴⁴ Upon applying a coating layer of 11 nm Al_2O_3 , the LIF reduces drastically. Interestingly, the LIF value did not further diminish upon increasing the layer thickness to 91 nm, because all defect states were already passivated by the initial 11 nm Al_2O_3 . Nevertheless, increasing the coating thickness to 91 nm resulted in a higher current density (Figure 4.6A), which is due to the anti-reflective property of an Al_2O_3 layer of such thickness. Thus, a layer thickness of *ca.* 11 nm solely functions as a passivation layer and the efficiency is increased from 6.6 to 10.9%, whereas a 91 nm thick aluminum oxide layer additionally acts as an anti-reflection coating, as a consequence of which the overall efficiency is increased to 13.2%. This indicates that both passivation and anti-reflective properties are important in the improvement of pillar arrays, but that the largest relative improvement arises from passivation.

Figure 4.6: (A) Silicon micropillar array with a radial p/n junction passivated with 11 nm Al_2O_3 and with an anti-reflection coating of 91 nm Al_2O_3 . (B) The local ideality factor for a bare micropillar array sample (black), a bare flat sample (grey), and after coating of the micropillars with 11 nm of Al_2O_3 (red) and subsequent increase in layer thickness to 91 nm (blue).

Both LPCVD materials – SiO_2 and SiN_x – exhibited a non-conformal coating thickness on the sidewalls of the pillars (see Figure 4.3). At the top surface of the pillars a targeted and highly uniform thickness of the AR coating is essential in order to obtain optimal AR behavior. On the sidewalls, however, these aspects – *i.e.* coating thickness and uniformity – are less critical, since light entering the spacing between the pillars will be absorbed fully by the pillars. Thus, the function of the coating at the sidewalls of the pillars is primarily for passivation. Therefore a thickness of a few nanometers is sufficient, without

stringent thickness uniformity requirements. Therefore, the quality of the coating at the interface is of uttermost importance film (*i.e.* defect free, pinholes, correct composition, etc). This is reflected in the performance of the Al_2O_3 . The explored LPCVD coatings fulfill the specifications to act as AR coating on the top surface of the pillars and as passivation layer at the sidewalls, as evidenced by the following. First of all, the photon absorbance for micropillar arrays with an AR coating can be calculated for each optimized AR coating thickness. The total photon absorbance is directly correlated to the current density, and therefore, the theoretical improvement in current density and the corresponding theoretical efficiencies (Table 4.2 in brackets) of the micropillar arrays can be calculated, taking solely the AR effect into consideration. It is clear from the table that the experimentally measured efficiency gains are higher than predicted by these calculations, indicating a clear passivation effect additional to the AR effect. Secondly, the anti-reflective character has no relation with changes in FF and V_{oc} . From Table 4.2, however, it becomes clear that every chosen coating material leads to an improvement of these parameters. Third and last of all, when a coating acts both as a chemical and as a field effect passivation layer, the difference in measured and calculated efficiency is significantly higher (Table 4.2). Thus, in the case of a n-type emitter, coatings of SiO_2 and SiN_x both contribute field and chemical passivation to the efficiency gain ($\Delta\eta = \sim 2\%$), as opposed to Al_2O_3 as a coating, whereby only chemical passivation contributes to the efficiency gain ($\Delta\eta = \sim 1\%$). In case of a p-type emitter, an Al_2O_3 coating induces both field and chemical passivation ($\Delta\eta = \sim 2\%$), as opposed to SiO_2 and SiN_x coatings, which only establish chemical passivation ($\Delta\eta = < 1\%$) (see Table 4.2)

4.3 Conclusions

In this work, the deposition and functionality of different anti-reflection and passivation coatings has been investigated. The optimal thicknesses for silicon oxide, silicon-rich silicon nitride and aluminum oxide as AR coating were predicted using FEM simulations and empirically verified on micropillar silicon PV cells. The different layers were deposited on arrays of silicon micropillars with radial p/n junctions (both p- and n-type base) using different techniques (ALD of Al_2O_3 , LPCVD of SiO_2 and SiN_x , sputtering of ITO), and the obtained coatings were analyzed and characterized by HR-SEM imaging and JV measurements. A coating made by ALD was conformal over the complete height of the pillar, whereas in the case of LPCVD and sputtering, the coatings exhibited a thickness gradient along the sidewalls. Sputtering of ITO was not able to fill the scallops at pillar sidewalls, leading to a discontinuous coating layer. Moreover, a change in composition was visible for ITO by ESB imaging, implying that the material loses its conductive properties. JV measurements showed that an Al_2O_3 coating of 91 nm improved the overall efficiency the most (*i.e.* to 13.2% for p-type and 10.1% for n-type, respectively). Also upon use of LPCVD SiO_2 (110 nm) or SiN_x (71 nm) the overall efficiencies of micropillar arrays

improved significantly, for both p- and n-emitters. It can be concluded that atomic layer deposition is most suited for the deposition of anti-reflection and passivation layers on high length-to-spacing aspect ratio micropillars arrays to be used as PV cells.

The absorbance of pillar arrays is primarily determined by the projected area of the spacing between the pillars. As such, the anti-reflective properties of the coating influence primarily the tops of the pillars, which is only a fraction compared to the reflective area of a flat cell. In contrast, the increase in surface area of pillars vs. flat surfaces causes more recombination and thus also a larger effect of passivation. All-in-all, the work described here shows that surface passivation induced by a coating is a more important parameter, compared to anti-reflective properties, for improving the efficiency of microstructured Si solar light harvesting devices. This provides a clear design parameter for future S2F devices, for which Si micropillar arrays, with their low bandgap of 1.1 eV and an efficiency well above 10%, can become an important component.

4.4 Acknowledgements

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4.5 Materials and methods

4.5.1 Fabrication of radial p/n junctions in silicon micropillar arrays

Scheme 4.1 gives a schematic representation of the fabrication and coating of an array of micropillars with radial *p/n* junctions. P- and n-type Si {100} substrates, with a resistivity of 5-10 Ωcm for p-type and 1-10 Ωcm for n-type, 100 mm diameter, 525 μm (p-type) and 375 μm (n-type) thickness, single side polished (Okmetic Finland), were used for micropillar array fabrication as previously reported.¹⁷ In short, substrates were cleaned and covered with 100 nm silicon-rich silicon nitride (SiN_x), via LPCVD. The silicon nitride on the front side of the wafer was removed by reactive ion etching (RIE, Adixen AMS100DE), and cleaned by means of oxygen plasma (30 min) and piranha (mixture of sulfuric acid and 30% aqueous hydrogen peroxide, 3:1 (v/v), 20 min). By means of standard photolithography, squares (5x5 mm²) with hexagonally packed circles (4 μm diameter, 2 μm spacing, *i.e.* 6 μm pitch) were defined in a photoresist polymer (Olin 906-12). Silicon micropillars (40 μm in height) were etched into the silicon substrate by deep reactive ion etching (DRIE, Bosch process) and the substrates were cleaned subsequently

in oxygen plasma (30 min) and piranha (20 min) to remove the photoresist and fluorocarbon residues.

Scheme 4.1 Schematic fabrication process. (A) Deep reactive ion etching of a silicon wafer with a photoresist pattern on the front side and silicon-rich silicon nitride on the backside. (B) Deposition of the dopant oxide by either SSD (boron) or LPCVD (phosphorus). (C) Formation of the radial junction, by a drive-in step at 1050 °C for 15 min. (D). Deposition of a passivation layer by either ALD (Al_2O_3), LPCVD (SiO_2 , SiN_x) or sputtering (ITO). (E) Removal of the silicon nitride and deposition of aluminum front and back contacts by sputtering.

P/n and *n/p* junctions were formed by the deposition of boron oxide (using solid source dotation, SSD) and phosphorus oxide (LPCVD), respectively. For SSD of boron, boron nitride wafers were placed in between the silicon target wafers and, under a flow of 6000 sccm O_2 , a boron oxide layer was formed on the silicon surface. In case of the LPCVD of phosphorus, a mixture of 330 sccm PH_3 and 50 sccm O_2 was supplied for 45 min at 350 mTorr in order to deposit the phosphorus oxide on the silicon surface. The formed dopant oxide layers were then annealed at 1050 °C for 15 min to accomplish diffusion of the dopant into the silicon micropillars, to form the proper radial junction. Prior to the deposition of the passivation layers, the dopant oxide was stripped in buffered hydrogen fluoride solution (BHF, 10 min), upon which the wafers returned to their hydrophobic state. Subsequently, the wafers were cleaned by immersion in fuming 99% nitric acid (HNO_3 , 2×5 min), boiling 69% nitric acid (10 min) and immersion in 1% aqueous hydrofluoric acid (HF) to remove the native oxide (1 min).

The passivation layers were applied using different methods as described in detail below. In short, sputtering was chosen as a control, because the directionality of this deposition technique is expected to lead to a non-conformal coating on high aspect ratio microstructures, which then can be compared with the highly conformal methods of LPCVD and ALD. Al/Si Ohmic contacts to the pillars were realized by selectively removing the surface coating around the array by completely filling the spaces between the pillars with photoresist, which also covered the tops of the pillars. Hereto, HMDS was spin-

coated in between the pillars (4000 rpm, 2 min), and subsequently AZ9260 photoresist was spin-coated (1000 rpm, 4 min). The samples were dried overnight in air at 10^{-3} mbar at room temperature. Hereafter the samples were exposed to photolithography (3×10 s UV exposure, 10 s delay between exposure cycles) and developed (8 min), see Figure 4.7. Al_2O_3 and SiO_2 were both stripped by wet etching in BHF (etch rates: 180 nm/min and 210 nm/min, respectively), SiN_x was stripped by RIE (Adixen AMS100DE). Subsequently the photoresist mask layer and fluorocarbon residues were removed using oxygen plasma (Tepla360). Finally, Ohmic contacts ($1 \mu\text{m}$; Al/Si, 99/1%) were sputtered (Oxford PL400) onto the back side of the wafer, as well as onto the frontide. The latter sputter run was done by means of a shadow mask to prevent deposition on and between the pillars.

Figure 4.7: SEM images of the selective coverage of the pillar array with photoresist. The slight off set in alignment was done deliberately to visualize that the spacings between the pillars are completely filled with photoresist

4.5.2 Atomic layer deposition

To reduce the reflectivity and to passivate the micropillar arrays, a layer of aluminum oxide was conformally coated onto the pillar arrays. Al_2O_3 films were deposited in a Picosun P-300S reactor by a thermal ALD process at 100°C . Trimethyl-aluminum (TMA) and H_2O were used as precursors and N_2 as the carrier gas, yielding a deposition rate of $0.83 \text{ \AA}$ per cycle (after initial deposition stabilization). The time for one complete Al_2O_3 ALD cycle was 9.3 s, where each cycle was defined as: 0.1 s TMA exposure, 4 s N_2 purge, 0.2 s H_2O exposure, and 5 s N_2 purge.

4.5.3 Low pressure chemical vapor deposition

The deposition of silicon oxide and silicon nitride films was done by LPCVD. SiO_2 was deposited at 725°C with a 50 sccm tetraethyl orthosilicate flow (200 mTorr, 8.1 nm/min deposition rate). For SiN_x , flows of 50 sccm SiH_2Cl_2 and 150 sccm NH_3 were used at a pressure of 250 mTorr at 825°C (6.6 nm/min deposition rate).

4.5.4 Sputtering

Indium tin oxide (ITO) was deposited by means of an in-house built sputter device. The silicon wafer was placed on a rotating chuck (5 rpm), 44 mm from the ITO source, in a low-pressure reactor chamber (5.5×10^{-3} mbar) with a 40 sccm flow of argon. The ITO

source had an angle of 45° with respect to the wafer surface. By means of a DC power of 50 W and a 20 sccm argon flow at the gun ITO was sputtered (2.6 nm/min deposition rate).

4.5.5 Ellipsometry

The thickness of each deposited coating was measured by ellipsometry (Woollam M-2000UI) in the range of 245 - 1690 nm. Spectral resolutions were 1.6 nm (245-1000 nm) and 3.2 nm (1000-1690 nm), and a beam diameter of 300 μm was used.

4.5.6 Focused ion beam structuring

FIB structures were made with a Nova 600 Dual Beam – SEM/FIB setup. A Ga^+ liquid metal ion source was used to mill away approximately half of a single pillar, along the pillar length with respect to the footprint of an array, with a beam current of 0.92 nA and a 10 kV extraction voltage.

4.5.7 *JV* measurements

To measure the photoelectrical characteristics of the coated Si micropillars, samples were positioned perpendicular to a 300 W xenon arc light source, which is filtered to modify its output to AM 1.5G spectrally. Upon installation of the lamp, the lamp was calibrated by VLSI Standards Incorporated. Before every measurement the lamp was checked by a calibrated Si solar cell, supplied by VLSI Standards Incorporated, for spectral mismatch. *JV* measurements were recorded on a VersaSTAT 4 potentiostat using a linear voltage sweep from -0.7 to 0.7 V at a rate of 0.2 V/s. For each variation in sample (*i.e.* type of coating and/or layer thickness) at least 4 specimens were measured. Averages are given in each figure and standard deviations are listed in the accompanying table.

4.5.8 Finite element modeling of the reflectivity of silicon micropillars

The reflectivity of a close packed micropillar array was simulated using a finite element modeling (FEM) package (COMSOL Multiphysics 4.4). The simulation was performed by a parametric sweep (10 nm step) in the wavelength domain of visible light (400 – 1100 nm). The pitch and diameter of the micropillars were set to 6 and 4 μm respectively, and the height of the micropillars was varied between 0 and 40 μm (the latter is similar to the experimentally realized pillar arrays). The slab of silicon underneath the micropillar array was limited to 1 μm . The footprint of the fabricated arrays was 5 mm x 5 mm, which is orders of magnitude larger than the wavelength of the incoming light. Therefore, we only simulated one pillar of which the outcome was periodically repeated in the lateral directions. For this reason the side boundaries of the simulation had a Floquet periodicity. The incoming light was a plane wave in the *z*-direction and had an input power of 1 W.

The maximum free triangular mesh size in the used materials (silicon and air) was set to $\frac{1}{5}$ of the minimum wavelength in the material.

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Chapter 5

Textured and Micropillar Silicon Heterojunction Solar Cells with Hot-Wire Deposited Passivation Layer

The passivating quality of hydrogenated amorphous silicon thin films is essential for achieving high open-circuit voltages in silicon heterojunction solar cells. This work reports our progress towards the use of hot wire chemical vapor deposition for fabricating these passivation layers. We have achieved 19.4% energy conversion efficiency for a solar cell with a conventional alkali-etched pyramidal texture. Next, we tested radial heterojunction devices that consist of up to 20- μm high micropillar arrays. Proper passivation of these devices is challenging, since the structures feature an enlarged surface area and vertical walls. We have made use of the ability of hot wire chemical vapor deposition to deposit conformal thin films at high deposition rate. The micropillar solar cells show only limited reduction of open-circuit voltage in comparison to a flat reference solar cell and have an improved overall performance. We created additional stacked multijunction silicon based junctions on top of the micropillars to increase the open-circuit voltage of the solar cells for future applications, such as water splitting devices, in which a higher potential is required.

5

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5.1 Introduction

The highest solar cell efficiencies using crystalline silicon are obtained for cells employing the silicon-heterojunction (SHJ) concept. These cells benefit from excellent passivation of interface defects at the surfaces of crystalline Si wafers. Commonly, hydrogenated amorphous silicon (a-Si:H) is used to render the surface dangling bonds of the wafers electrically inactive by saturating these bonds with atomic hydrogen that is present in ultra-thin films of such materials. These films have to be very thin (~ 4 nm) and conformal as they bring about parasitic absorption. Plasma enhanced chemical vapor deposition (PECVD) is the most common method for the fabrication of a-Si:H for SHJ devices, hence the majority the research on this topic has focusing on this method. Despite the high performance obtained worldwide for SHJ cells with PECVD a-Si:H,¹⁻⁴ hot wire chemical vapor deposition (HWCVD) is an interesting alternative method for the deposition of the a-Si:H films. This method offers various advantages over PECVD such as a high concentration of hydrogen radicals at the surface available for passivation.⁵ Due to the almost complete absence of ions or electric field, there is improved conformality at high deposition rates and no risk of ion bombardment damage to the wafer interfaces.⁶ Additionally, HWCVD is a suitable in-line deposition technique and can lead to lower cost-of-ownership in the mass fabrication of SHJ cells.⁷

5

We have developed a HWCVD process for thin, highly passivating a-Si:H layers on n-type crystalline silicon (c-Si) wafers. These layers are suitable to be used with p-type nanocrystalline silicon oxide (nc SiO_x:H) layers that feature better optical transmission than conventional a-Si:H p-type emitter layers. We have applied our process to fabricate SHJ solar cells with a random pyramid texture and cells with a micropillar front texture. The micropillar or microwire concept is widely considered for photovoltaic applications due to its potential for enhanced absorption and carrier collection.⁸⁻¹⁰ Micropillar solar cells are not only considered for solar electricity but also for the production of solar fuels by means of photoelectrochemical water splitting as they feature a large reaction surface.¹¹ To passivate the c-Si surface of the pillars in our study, that have vertical walls up to 20 μm high, we fully exploit the conformality of HWCVD. To boost the operating voltage of our devices we added extra amorphous silicon-based radial junctions on top of the SHJ solar cells, to achieve voltages that are high enough for photoelectrochemical water splitting.

5.2 Results and discussion

5.2.1 Randomly textured SHJ cells

For the cells on pyramidal texture, the J - V characteristics showed a strong “S-shape” behavior before annealing, which is an indication of a low amount of active doping centers in the p-layer.¹² Figure 5.1 shows both the J - V and EQE characteristics of the best performing solar cell after the annealing treatment. The energy conversion efficiency (η) of this solar cell exceeds that of all previously reported efforts in which HWCVD was used as deposition method for the passivation layers in a similar structure.^{12,13} The J - V characteristics were scaled, to match the short circuit current density (J_{sc}) value that is extracted from the EQE measurements which was only 5% lower than the J_{sc} value as measured with the solar simulator. The average open-circuit voltage (V_{oc}) of the best five cells was 704 mV, which is exemplary for the excellent passivation capabilities of the 4-nm thick a-Si:H passivation layer. The V_{oc} is known to increase for larger solar cell areas due to a relative reduction of the resistive load imposed by the dark perimeter of the cell. This was reflected by a ~ 20 -mV V_{oc} increase upon removal of the shadow mask.

Figure 5.1 (A) Current density-voltage characteristic and (B) External quantum efficiency results of a typical silicon heterojunction solar cell with a-Si:H passivation layers deposited by HWCVD. The series resistance (R_s) and the parallel or shunt resistance (R_{sh}) were derived from the tangent to the current density at the V_{oc} and J_{sc} positions, respectively.

5.2.2 Micropillar SHJ cells

We continued by testing the capabilities of HWCVD to passivate silicon wafers with more extreme morphologies. To this end we fabricated heterojunction solar cells with several types of micropillar arrays on its front-facing side. Figure 5.2 gives an overview of 20 μm long micropillars with three different hexagonal pitches (*i.e.* 8 μm , 10 μm , and 15 μm pitch, respectively). Each of these micropillars has a heterojunction solar cells grown conformally over the micropillars as described above.

Table 5.1 shows the electric characteristics of the SHJ solar cells as compared to a simultaneously fabricated flat cell. The J_{sc} , as determined by EQE measurements, increased upon introducing the micropillars due to geometric light trapping and/or better current collection. Interestingly, a larger inter-pillar spacing distance also benefitted the J_{sc} value. This can be attributed to reduced light scattering from the top of the micropillars, as due to the larger pitch, less micropillars are present per unit projected area. The optimum packing density is not known at this stage in our research.

Figure 5.2 Micropillars of 20 μm in length with different pitches: (A) 8 μm , (B) 10 μm and, (C) 15 μm . The scale bars are 20 μm .

Table 5.1 Results of silicon heterojunction solar cells with a micropillar front texture with different spacings compared to that of a flat reference cell. The length of the micropillars was 20 μm .

Spacing (μm)	V_{oc} (mV)	J_{sc} (mA/cm ²)	FF (%)	η (%)	R_s ($\Omega\cdot\text{cm}^2$)	R_{sh} ($\text{k}\Omega\cdot\text{cm}^2$)
flat	648	33.85	71.4	15.66	2.14	5.24
8	628	33.90	73.8	15.70	1.53	1.53
10	627	34.56	74.0	16.05	1.61	2.75
15	632	34.93	75.1	16.59	1.73	2.29

The V_{oc} of the micropillar devices was about ~ 20 mV lower than that of the flat reference. This is only a small decrease considering the increase of surface area and inevitably higher surface recombination that is introduced by the pillars. The fill factors of the devices with micropillars were higher than that of the flat reference cell, which is partly expressed by a lower series resistance in these devices. This could be an indication of more efficient carrier collection caused by shorter collection paths of holes in the pillars.

The current densities were nevertheless lower than that of the previously presented device with random pyramid texture. Given the relatively large dimensions of the micropillars, we expect that further current density gains can be achieved by adding features with dimensions that are closer to or below the wavelength of light. Furthermore, the length of the pillars could be increased to help the absorption. Elbersen *et al.*⁹ showed the effect of pillar length on the J_{sc} of these structures. It was found that a length of 40 μm was optimum for light trapping in homojunction micropillar structures.

However, increasing the length of the micropillars beyond 20 μm is challenging with the chosen deposition techniques, in particular the sputter technique for the ITO contact layer.

In order to inspect the conformality of the different layers, coated pillars were cut in half along the z-direction using FIB etching and imaged by HR-SEM as shown in Figure 5.3. In this configuration, the single heterojunction with a total thickness of ~ 25 nm is not visible in the HR-SEM. The ITO coating is clearly visible at the top of the micropillar in the HR-SEM image. Due to the directionality of the sputtering technique used to deposited ITO, a gradient of ITO is observed along the micropillar length. One way to better verify and visualize the composition thickness along the height of the pillar is by energy selective backscattered (ESB) SEM imaging. ESB visualizes the contrast between the coating and the silicon micropillar and discriminates the materials accurately. The insets of Figure 5.3 show that the ITO thickness changes from top to bottom, which is observed by the reduced ESB brightness along the length of the pillar from top to bottom. At the bottom the thickness of ITO is less than 10 nm and has a flaky structure. We expect that this change in thickness and composition is accompanied by a decrease of conductivity along the pillar. The latter limits the collection of the photogenerated charges. Increasing the length of the micropillar would only aggravate this problem even more. For these reasons we did not increase the length of the micropillar even further.

Figure 5.3 Cross-sectional HR-SEM images showing a micropillar of 20 μm that has been cut in half, orthogonally to the substrate, by FIB to be able to inspect the conformality of the different coatings along the pillar height. The insets are magnifications of the top, middle and bottom of the micropillar, in order to inspect the ITO layer. The sputtered ITO was recorded by ESB.

5.2.3 a-Si:H/SHJ tandem cells

Micropillars arrays are one of the proposed geometries to use as photoelectrochemical cell in a solar to fuel device. However, many photoelectrochemical reactions, such as water splitting, require a higher operating voltage than that obtained with a single junction cell. To increase the operating voltage, we created a-Si:H n-i-p radial junctions on top of SHJ cells with a micropillar array. The obtained SHJ/a-Si:H n-i-p tandem structures basically resemble earlier so-called “honeymoon” tandem cells that have been fabricated with either diffused junction c-Si solar cells,^{14,15} or SHJ solar cells as bottom cells.^{16,17} As absorber layer a 350-nm thick a-Si:H intrinsic HWCVD layer was used. Although it is expected that this layer will not provide enough current to match that of the bottom SHJ cell, an increase in the thickness will likely result in a reduction of FF rather than a substantial increase of current density due to collection length limitations.¹⁸ Therefore, we did not attempt to achieve current matching in this n-p SHJ/n-i-p tandem cell. For the a-Si:H top cell, the same p-layers were used as in the SHJ emitter. Figure 5.4A shows the J - V curves under AM1.5 conditions of representative tandem cells with various pillar lengths (spacing $\sim 15 \mu\text{m}$) compared to a flat device with Table 5.2 providing further details. Although all spacings of pillars led to functional devices, the increase of pillar length caused a decrease of the FF and the V_{oc} . Due to the larger surface area of the micropillars, the dark current increases, which leads to a reduced V_{oc} . This decrease can also be understood when considering the J - V curves measured under dark conditions in Figure 5.4B. Even though it is not straightforward to derive a physical meaning from all aspects of the dark J - V curves of multijunction devices,¹⁹ the higher saturation currents that are observed for the longer pillar lengths are an indication of shunting paths in the top cells.

Figure 5.4 Current density-voltage characteristics of SHJ/a-Si:H tandem solar cells with micropillar surface under AM1.5G (A) and dark (B) conditions. The current densities under dark conditions are plotted on a logarithmic scale.

Table 5.2 Electrical characteristics of the SHJ/a-Si:H tandem solar cells. The spacing of the micropillars was ~ 15 μm .

Spacing (μm)	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF (%)	η (%)	R_s ($\Omega \cdot \text{cm}^2$)	R_{sh} ($\text{k}\Omega \cdot \text{cm}^2$)
flat	1521	11.21	70.1	11.96	7.99	4.16
3	1507	11.59	67.6	11.81	7.27	2.92
6	1457	11.02	56.0	8.99	11.0	1.89
10	1139	11.29	44.1	5.67	25.8	0.38

The performance of the flat and 3 μm micropillar device is however significantly better than recent efforts on SHJ/a-Si:H tandem devices.^{16,17} The V_{oc} of these cells is in good agreement with the sum of individual sub-cells (~ 650 mV for the SHJ and ~ 850 mV for the a-Si:H solar cell adds up to ~ 1500 mV). EQE measurements show that all devices were current-limited by the a-Si:H top cell, as expected. The pillar length did not have a large influence on the current densities that are generated by the top cells. Instead, a current density gain of the SHJ bottom cell was observed as the pillar length increases. This effect is most profound in the device with 10 μm pillars as shown in Figure 5.5, where its EQE response is compared to that of the flat tandem solar cell. A similar effect was observed in thin film silicon based tandem solar cells fabricated on a nanorod morphology.²⁰ The interference fringes caused by the optical contrast between c-Si and a-Si:H layers as seen in the flat device are almost absent in the pillar device due to enhanced absorption.

Figure 5.5 External quantum efficiency of the SHJ/a-Si:H tandem solar cell with 10- μm long pillars (solid line) compared to that of a flat tandem (dashed line) under short circuit conditions. The response of the top and bottom cells were measured separately by applying infrared and blue bias LED illumination, respectively.

A micropillar of 10 μm was cut in the z-direction by FIB etching, in order to inspect conformity by HR-SEM of the different deposited layers (see Figure 5.6). The a-Si:H absorber layer is clearly visualized, due to the different morphology of the amorphous material from the crystalline silicon. A small difference in deposited thickness is visible

between the top and side of the micropillar. Additionally, the layer thickness is gradually smaller along the micropillar length. This indicates a diffusion limitation of a-Si:H precursors during deposition.

Figure 5.6 Cross-sectional HR-SEM images showing a micropillar of 10 μm with a SHJ/a-Si:H tandem structure that has been cut in half, orthogonally to the substrate, by FIB to be able to inspect the conformality of the different coatings along the pillar height. The insets are magnifications of the top, middle and bottom of the micropillar, in order to inspect the ITO layer. The sputtered ITO was recorded by ESB.

5.2.4 a-Si:H/a-SiGe:H/SHJ triple junction cell

To fabricate a fully integrated solar-to-fuel device, literature states a set of semiconductors must be combined with a proper electrocatalyst. Here, unbiased photoelectrolysis requires at least 1.23 V of photovoltage from semiconducting materials, without taking significant losses into account, *e.g.* kinetic overpotentials needed to drive the hydrogen- and oxygen-evolution reactions or mass-transport.²¹ The best of our tandem devices had a voltage at maximum power point (V_{mpp}) that barely exceeds this value. For this reason, we briefly explored the possibility of adding an extra junction in the device architecture. A 120-nm thick hydrogenated amorphous silicon germanium (a-SiGe:H) layer was added as a middle cell absorber of an a-Si:H/a-SiGe:H/SHJ triple junction device. The best results were obtained using a sample which was 5 μm long, 4 μm in diameter and with 15 μm pitch of the micropillars: $V_{\text{oc}} = 1821$ mV, $J_{\text{sc}} = 6.14$ mA/cm², $FF = 65.6\%$, $\eta = 7.33\%$. Although the current matching of this device is not optimized, the higher V_{mpp} (1472 mV) is better suited for photoelectrochemical water splitting without the use of a bias voltage.

Figure 5.7 shows of a HR-SEM image of cross section of a micropillar with a triple junction grown on top of it. All of the individual grown absorber layers are clearly visualized. Especially 120 nm of a-SiGe:H and 80 nm of ITO are bright in the HR-SEM. The top absorber of Intrinsic a-Si:H is darker in color. Both of the TRJs are distinguishable due to their different (crystal) structure which is most pronounced at the top and bottom of the micropillar and clearly sandwich the a-SiGe:H layer (see magnifications). For intrinsic a-Si:H a gradient in thickness is visible along the micropillar length. From the top to the bottom of the micropillar the thickness of the a-Si:H layer gradually decreases. This is due to the directionality of the deposition technique. The same trend holds for the TRJ. This layer is clearly visible on top of the c-Si micropillar and a-SiGe:H layer and at the bottom next to the micropillar. At the side of the micropillar this layer is hardly visible. This depletion of layers is a good indication of why longer micropillars perform poorly.

Figure 5.7 Cross section HR-SEM image of a micropillar solar cell with a SHJ/a-SiGe:H/a-Si:H triple junction structure. The insets show magnifications of the top, middle and lower part of the micropillar.

5.3 Conclusions

We have demonstrated the quality of hydrogenated amorphous silicon passivation layers deposited by hot wire chemical vapor deposition for silicon heterojunction solar cells with demanding surface morphologies. The high open-circuit voltages and 19.4% energy conversion efficiency on solar cells with a common random pyramid texture demonstrate the high quality of the passivation layer. The conformal nature of HWCVD avoids the need of post-texturization treatments to round off the sharp features in random pyramidal textures. This opens new avenues for the production of silicon heterojunction cells with thin intrinsic layers.

Utilizing the same conformal nature, we created radial heterojunctions on c-Si micropillar arrays with pillar heights of 20 μm that show only limited loss of open-circuit voltage despite the increase of surface area. For future use in photoelectrochemical fuel production devices, we fabricated multijunction solar cells with a silicon heterojunction as bottom cell and a-Si(Ge):H alloy n-i-p top cell(s), resulting in open-circuit voltages that are high enough for water splitting. The performance of SHJ/a-Si:H tandem cells was better than recent tandem structures of this type.

5.4 Acknowledgments

The work in this chapter was done in close collaboration with the University of Eindhoven. Pim Veldhuizen is greatly acknowledged for all of the fruitful discussions and performed deposition experiments. Paula Bronsveld of ECN is acknowledged for supplying the random pyramid textured c-Si wafers. Mark Smithers is thanked for the HR-SEM images.

5.5 Material and methods

5.5.1 SHJ fabrication

All silicon thin films were deposited in a multi-chamber system that consists of separate reactors for n-type, p-type, and intrinsic silicon films to avoid cross-contamination. The intrinsic films were deposited by HWCVD at a rate of ~ 0.4 nm/s using two heated (1700°C) parallel 0.3-mm tantalum filaments at a distance of 35 mm from the substrate. Figure 5.8 shows a top view of the opened reactor. Further details about this process can be found elsewhere.²² The doped layers were deposited by 13.56 MHz PECVD at a low rate of < 0.1 nm/s to promote conformal deposition. The n-type c-Si wafers in this study were cleaned for 2 min in a 1% HF solution. The dangling bonds on both sides of the c-Si surface were passivated with a-Si:H passivation layers with a thickness of 4 nm, deposited at a temperature of 130°C . These a-Si:H layers were made at a process pressure of 2 Pa and using undiluted silane as precursor gas. An a-Si:H n-type back surface field (BSF) layer of 20 nm was deposited at a temperature of 200°C on what is to be the rear side of the solar cell. On the other side, a triple-layer p-type emitter was deposited at a temperature of 160°C . The core of this emitter consists of a 10-nm thick hydrogenated nc-SiO_x:H p-layer.²³ This material has a higher optical band gap ($E_g = 2.3$ eV) and a considerably lower refractive index at a photon energy of 2 eV ($n_{2\text{ eV}} = 2.7$) compared a non-oxide film ($E_g = 2.1$ eV, $n_{2\text{ eV}} = 3.8$). Whereas the oxygen in this layer opens up the band gap, making the layer more transparent, it also delays the formation of crystallites that are desired for efficient doping and sufficient conductivity. The layer is therefore preceded by 5 nm of nc-Si:H (p) to provide an early onset of crystallization. The top of the stack is a highly conducting 3-nm thick nc-Si:H p-layer that can form an Ohmic contact with the

transparent indium tin oxide (ITO) front electrode. The ITO front electrodes were 80 nm thick and deposited by magnetron sputtering on the front and rear side. All solar cells were overacted by thermally evaporated layers of 300-nm thick Ag back contacts and front contact grids.

Figure 5.8 Top view of the opened HWCVD reactor. Two tantalum filaments span the reactor interior. Insulated spacers are used to tension the filaments. The rectangle indicates the position of the sample in a sample holder which is located 35 mm above the filaments. A shutter plate is slid between the filaments and the sample to prevent film growth during the initiation and completion of the deposition process.

5.5.2 Texturing

Silicon heterojunction cells were fabricated on pyramidal texture and on micropillar arrays. The pyramidal texture was fabricated using 160- μm thick n-type silicon Czochralski wafer with $\langle 100 \rangle$ orientation as the base material. The texture etch was a conventional random-pyramid texture on both sides, created with a (isopropanol-free) KOH chemical etch. Instead of the smoothening treatment that is often done for SHJ wafers reduce risk of localized recombinative paths situated at the pyramid valleys,^{24,25} only an HNO_3 cleaning etch treatment was used which did not alter the pyramidal texture. This leaves a less smooth surface than using a full smoothening treatment. The solar cells have an active area of 0.69 cm^2 . After fabrication, the cells were annealed in a nitrogen atmosphere at 190°C for 3 h.

Figure 5.9 (A) Schematic cross sections a c-Si wafer during the micropillar fabrication process. (a) A photoresist pattern is applied on a c-Si (n) wafer with a 200-nm thick SiO₂ layer using UV-lithography. (b) The pattern is transferred into the SiO₂ layer by reactive-ion etching and subsequently into the wafer by cryogenic deep reactive-ion etching. (c) The photoresist and SiO₂ layers are removed by oxygen plasma treatment. (B) Scanning electron microscopy (SEM) image showing ~20-μm-long micropillars, directly after fabrication and before removal of the mask.

Arrays of silicon micropillars with various lengths, and spacings, of 4 μm diameter were fabricated by growing a hard mask of 200 nm silicon dioxide (SiO₂) on the n-type c-Si wafer using wet oxidation at 1100°C for 30 min.⁹ By means of standard UV-lithography, the pattern of the pillar arrays was defined in photoresist (Olin 907-17), and post-baked for 10 min at 120°C after exposure and development. Subsequently, this pattern was transferred into the SiO₂ by reactive-ion etching (Adixen DE). Although both the SiO₂ and photoresist layer acted as mask during cryogenic deep reactive-ion etching (DRIE) of the micropillars, the SiO₂ is more resilient to the DRIE process and therefore enables better defined micropillar features. The micropillars were etch via cryogenic (-100°C) deep reactive ion etching (DRIE; Adixen MS100SE, 1000 W) of silicon, using sulfur hexafluoride (SF₆, 200 sccm) for etching silicon and O₂ (30 sccm) for passivating the sidewalls. After etching, the remaining photoresist and SiO₂ was removed via oxygen plasma (Tepla360) and BHF, respectively. Figure 5.9A schematically shows the fabrication process of the micropillar arrays and Figure 5.9B shows a side view scanning electron microscopy (SEM) image of ~20-μm long micropillars. The SEM image reveals that the pillars have a tapering that is stronger at their base.

5.5.3 SHJ micropillar fabrication

SHJ solar cells were created on these micropillar arrays using the same layer stack as for the random pyramid texture. The cell area of these solar cells was reduced to an active area of 0.13 cm² to allow a higher quantity of pillar variations within the same deposition run. A schematic cross section of the micropillar-based SHJ device is shown in Scheme 5.1A.

5.5.4 Tandem cell micropillar fabrication

For tandem solar cells, a 20-nm phosphorus-doped nc-Si:H n-layer was grown on top of the nc-Si(O):H (p) emitter of a SHJ cell. Together, these layers form the tunnel recombination junction (TRJ) that is needed for a proper connection between the two sub-cells. The individual layers of the TRJ have low dark current activation energies ($E_a = 0.009$ eV and 0.011 eV for the nc-Si:H n-type and p-type layer, respectively), which facilitates the tunneling efficiency.¹⁷ As absorber layer, a 350-nm thick a-Si:H intrinsic HWCVD layer with a band gap of 1.86 eV was fabricated. This intrinsic film was deposited in a similar manner as the a-Si:H passivation layers of the SHJ devices, except at an increased substrate temperature of 270°C. On top of this absorber layer, a nc-Si(O):H (p) emitter was grown as previously described. Thin (<3 nm) PECVD intrinsic a-Si:H buffer layers were fabricated at the i/n and i/p interface in order to improve the contact between these layers. This process is described elsewhere.²⁶ A schematic representation of such a device is given in Scheme 5.1B.

5.5.5 Triple cell micropillar fabrication

For triple junction solar cells, we used the previously discussed SHJ structure and created a 20-nm phosphorus-doped nc-Si:H n-layer on top of the nc-Si(O):H (p) emitter to form a TRJ. A hydrogenated amorphous silicon germanium (a-SiGe:H) layer of 120 nm was deposited with HWCVD as a middle cell absorber. The band gap of this layer was graded to facilitate the extraction of photo-generated charge carriers. The band gap was varied from 1.86 eV to 1.37 eV and back by varying the germanium content as described elsewhere.²⁷ The material with the lowest band gap was 60 nm thick and positioned 15 nm from the front interface. At the rear side of the film, a 45-nm thick graded-band gap layer was used. On top of the a-SiGe:H layer, a nc-Si:H (p)/nc-Si:H (n) stack was added to construct a second TRJ between the top (a-Si:H) and middle cell (a-SiGe:H). As top cell, a 350 nm intrinsic a-Si:H was grown with a 20 nm nc-Si(O):H p-type layer. Again, thin PECVD buffer layers were used at i/n and i/p interfaces of the middle and top cell. A schematic representation is given in Scheme 5.1C.

Scheme 5.1 Schematic cross-sections of a micropillar-array (A) SHJ cell, (B) a-Si:H/SHJ tandem cell, and (C) a-Si:H/a-SiGe:H/SHJ triple junction cell. The dimensions of the wafer and micropillar are not to scale. Insets show the composition of the thin films that are used in the design. The nc-Si(O):H (p) layers consists of a nc-SiO_x:H film that is sandwiched between two nc-Si:H (p) layers. The a-SiGe:H sub-cell uses a single nc-Si:H p-type layer for its high conductivity. Ag contact grids (not shown) are used as front electrode. The thin PECVD buffer layers in the tandem and triple junction cells are not shown. For the SHJ cells with random pyramid texture the same layer stack was used as in (A).

5.5.6 Current density-voltage measurements

The current density-voltage (J - V) characteristics of the solar cells in this study were measured at 25°C under a WACOM dual source solar simulator (class AAA) calibrated to the AM1.5G spectrum. A shadow mask was used to prevent current collection from outside the active area of the cells. The current densities are presented with respect to the active area of the solar cells (the area that is not covered by the contact grid). The external quantum efficiency (EQE) was measured under short-circuit conditions in the range of 290–1200 nm using a xenon lamp and a monochromator. The EQE of the multijunction devices was acquired using colored LED bias light to measure the response of the sub-cells separately.

5.5.7 Imaging

Focused ion beam (FIB) structures were made with a Nova 600 Dual Beam – high resolution (HR-) SEM/FIB setup. A Ga⁺ liquid metal ion source was used to mill away approximately half of a single pillar, along the pillar length with respect to the footprint of each array, with a beam current of 0.92 nA and a 30 kV extraction voltage.

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Chapter 6

Spatial Decoupling of Light Absorption and Catalytic Activity of Nickel-Molybdenum at High-Aspect-Ratio Silicon Micropillar Arrays

Earth-abundant catalysts for the hydrogen evolution reaction (HER), for example NiMo, are generally opaque and require high mass loadings to obtain high catalytic activity, which in turn leads to parasitic light absorption and thus limits H₂ production. Here, we show the fabrication of a highly efficient HER photocathode by decoupling light absorption and catalytic activity on the microscale on a Si micropillar array. Hereto, NiMo was spatioselectively electrodeposited on the upper $\sim 2\ \mu\text{m}$ of Si micropillars with a radial n⁺/p junction. This was achieved by covering SiO₂-coated micropillar arrays with photoresist and selective back-etching of the photoresist layer by O₂ plasma and the exposed SiO₂ by BHF, respectively. Hereafter NiMo was selectively deposited on the freshly exposed emitter by electrodeposition. This configuration allowed the application of high mass loadings of the NiMo catalyst while retaining a high photocurrent of the underlying PV cell. The best performing micropillar array devices exhibited a short-circuit photocurrent density of 34.9 mA/cm², a photovoltage of 480 mV, and a fill factor of 44% under AM 1.5G of simulated solar illumination, which resulted in a photon-to-hydrogen efficiency of 7.5%. This efficiency is close to that of the highest performance devices reported today, and well above that of devices with earth-abundant catalysts.

6

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6.1 Introduction

A good solar-to-fuel (S2F) device is efficient both in harvesting a large part of the energy in incident solar radiation and in transforming this into chemical energy. For achieving the former, silicon (Si) is a popular, well performing, photon absorber and has been studied for many decades as a material for photovoltaic purposes. However, Si as a photocathode has a considerable disadvantage, due to its poor kinetics for the hydrogen evolution reaction (HER).¹ To surpass this problem, Si requires a catalyst to achieve efficient solar energy conversion. Nickel molybdenum (NiMo) is an earth-abundant catalyst which is almost as active as platinum (Pt).²⁻⁴ However, NiMo is opaque and requires high mass loadings to obtain high catalytic activities. High mass loadings of NiMo lead to parasitic optical absorption losses of the photon absorber (Si) underneath, limiting the photon current density (J_{ph}) and concomitantly the efficiency (η) of the device.^{4,5}

The proposed route to obtain high efficiencies for systems consisting of semiconductors coated with a catalytic material is by spatially and functionally decoupling the optical absorption and the catalytic activity of the photocathode. This allows for simultaneous achievement of high values of the fill factor (FF), the J_{ph} and the open circuit potential (V_{oc}). Shaner *et al.* obtained high FF values in a Si photocathode, by covering the bottom area between the micropillars with NiMo/TiO₂ nanoparticles.⁵ Their best performing Si homojunction microwire array photocathodes demonstrated an ideal regenerative cell efficiency, η_{irc} , of 2.9%.^{5,6} The design was limited in efficiency due to a low J_{ph} of 14.3 mA/cm², while a passivated Si PV cell can easily generate ~40 mA/cm².⁷

6

The fabrication and design parameters of Si micropillar arrays (*e.g.*, doping process, micropillar length, pitch, diameter, etc.) are of utmost importance to realize high PV efficiencies.^{8,9} Furthermore, the front surface of a flat Si PV cell accounts for 11% of the electron losses within the cell, due to recombination. In micropillar arrays the absolute front surface area increases strongly, up to ~17 times, by the surface topography, stressing the need for proper surface passivation by an insulator (*e.g.*, silicon dioxide (SiO₂), silicon nitride, or aluminum oxide).^{7,8} Here, we describe the spatial and functional decoupling of light absorption and catalytic activity of hydrogen-producing, NiMo-covered Si photocathodes. Our team has already reported extensive work on the characterization and optimization of hexagonally packed radially doped Si micropillar PV cells with respect to junction depth and pillar height.⁸⁻¹¹ In the current work, we show how to convert these micropillar arrays in highly efficient HER half-cells. Radially doped micropillar arrays are passivated by SiO₂, which increases the efficiency of the solar cell.^{8,9,11} SiO₂ is spatioselectively removed from the top sides of the micropillar arrays, to act as masking layer, and the freshly exposed Si top is subsequently covered with either Pt, Ni, or NiMo by electrodeposition as catalyst for H₂ production. NiMo was chosen, because it is known to be a top-performing earth-abundant catalyst, and its performance

is compared to Pt, which is one of the best performing HER catalysts. The catalyst layers are visualized by high resolution scanning electron microscopy (HR-SEM). Both the photoelectrical and photoelectrochemical performances are assessed and compared to pillar arrays onto which the catalyst was deposited over the entire surface of the pillar arrays.

6.2 Results and discussion

Substrates with arrays of silicon micropillars (4 μm diameter, 40 μm length, and 6 μm pitch) with radial junctions (p-type base and 900 nm n^+ -type emitter) were fabricated according to a procedure reported before, and the length was chosen to provide optimal light absorption.^{8,9} These substrates were processed in two ways. To deposit a catalyst over the entire surface of the Si micropillar arrays (Figure 6.1A), the arrays were subjected to electrodeposition as is. For spatioselective deposition at the tops of the micropillars (Figure 6.1B), the pillars were first conformally covered with SiO_2 , followed by a photoresist layer. The photoresist layer was back etched in O_2 plasma to expose the tops of the pillars and the exposed SiO_2 layer is etched in BHF, subsequently (see SI for more detailed fabrication aspects).

For samples A, dense, continuous, bright Ni films are readily formed on various conducting substrates by electrodeposition, see Figure 6.1C. The composition of the deposited Ni films was confirmed by x-ray diffraction (XRD) analysis.¹² The homogeneous electrodeposition of Ni over 3D microstructures, such as Si micropillars, has been described before.¹³ The addition of a relatively low concentration of Na_2MoO_4 (24 mM) to the NiSO_4 (1.3 M) deposition bath alters the growth morphology significantly.^{14,15} HR-SEM images reveal that electrodeposition of NiMo in the range of 10 s to 180 s does not form continuous thin films on bare Si micropillar arrays, but isolated particles are deposited all over the surface (Figure 6.1E). The difference in growth between the two electrocatalysts is attributed to the low current efficiency, below 5%, of NiMo deposition, as compared to nearly 100% under the conditions used for Ni deposition from the sulphate solution.^{2,16-19} Furthermore, the NiMo particles were slightly agglomerated at the tops of the micropillars, whereas at the bottom individual particles were evenly distributed over the surface. This difference in growth is due to the electrochemical cell design, in which the counter electrode is closer to the top of the micropillar arrays than to the bottom, giving a stronger electric field and therefore enhanced growth at the tops of the micropillars.¹³

Figure 6.1 Electrodeposition of earth-abundant catalysts (NiMo or Ni) on Si micropillar arrays with a radial junction. Fabrication process for (A) completely exposed micropillars or (B) micropillars passivated by SiO₂ with exposed tops. HR-SEM images of (C) Si micropillar arrays with n⁺/p junctions with fully exposed micropillars (sample A) after Ni electrodeposition of 30 s of Ni, and (D) with top-exposed Si micropillars (sample B) with Ni on the top of the micropillar. HR-SEM images of (E) NiMo over the complete micropillar (sample A, 30 s deposition) and (F) NiMo solely on the tops of the micropillar (sample B, 180 s deposition). The scale bars are 1 μm.

6

For samples B, we selectively removed SiO₂ from the tops of the micropillars (see SI). Subsequent electrodeposition allowed the spatioselective deposition of a catalyst, *i.e.* Pt, Ni, or NiMo, on the freshly exposed n⁺-Si emitter. Figure 6.1D shows the selective deposition of a bright and continuous Ni film on the bare n⁺-Si micropillar tops, with a similar quality as obtained for the deposition on fully exposed pillars (Figure 6.1C). Figure 6.1F presents Si micropillars with high mass loadings of NiMo solely at the upper ~2 μm. The results confirm that the insulating layer of SiO₂ effectively inhibits the transfer of electrons at the pillar surface below the exposed tops during the electrodeposition process, thereby restricting catalyst deposition solely to the top side of the micropillar arrays. Similar to what was observed for NiMo deposition on samples A (Figure 6.1E), this catalyst did not form smooth films, but gave closely packed agglomerated particles. However, due to the smaller exposed areas, for equal deposition times, denser NiMo particle films (Figure 6.1F) were formed on the top-exposed pillars than on fully exposed pillars.

The crystal structure of the deposited NiMo films was confirmed by X-ray diffraction (XRD).¹² Figure 6.2A shows the XRD pattern of 30s electrodeposited Ni on a flat Si, here the (111), (002), and (022) peaks are observed at 44.56°, 51.92°, and 76.50°, respectively and no interfacial phases are detected.¹² The high intensity peak at 69.13° is p-Si (400). Figure 6.2B shows the XRD pattern of 180s electrodeposited NiMo on flat Si. The (111), (002) and (022) peaks of NiMo are at 43.96°, 51.21°, and 75.35°, respectively and the (400) peak of Si is at 69.13°. The shift of the peaks is visualized in the combined XRD pattern of Figure 6.2C, which confirms the incorporation of Mo-atoms in the Nickel structure. To confirm the alignment of the XRD apparatus, a combined figure of the Si signal is given Figure 6.2D. Here, no shift is observed between the two different Si-substrates. This is in line with the reported information that molybdenum cannot be deposited as a pure metal from an electrodeposition bath and only occurs in co-deposition with another metal like nickel.¹⁷⁻¹⁹ Research done by Suzuki *et al.* indicated that this NiMo alloy has 9% of molybdenum incorporated in the structure, *i.e.* Ni_{0.91}-Mo_{0.09}.²⁰

Figure 6.2: XRD patterns of electrodeposited nickel (30s) and alloyed nickel molybdenum films on flat silicon, with their characteristic peaks and relative intensities marked. (A) Ni/Si,¹² (B) NiMo/Si,²⁰ (C) an overlap of the Ni and NiMo pattern, and (D) an overlap of the Si peak in each pattern.

6.2.1 Photoelectrical (JV) measurements

The micropillar arrays with a radial n⁺/p-junction were also fabricated as a solid-state Si PV cell. This allows for the assessment of the effects of the addition of Ni or NiMo on the light harvesting capabilities, without interference of other factors, such as electrolyte, bubble formation, and contact resistances. JV measurements were performed on both bare and catalyst-coated Si micropillar arrays with fully (samples A) or partially (samples B) exposed pillars (Figure 6.3). Characteristic values of V_{oc} , J_{sc} , FF , and η , are given in Table 6.1.

Figure 6.3 Photoelectrical JV measurements of Si micropillar arrays with radial n⁺/p-junctions without and with electrodeposited Ni or NiMo at given deposition times on fully exposed Si micropillars (A) and spatioselectively on tops-exposed arrays (B), measured at AM 1.5G illumination. Each line is the average of at least four different samples prepared with the same settings.

Table 6.1 JV characteristics for the Si micropillar arrays with radial n⁺/p-junctions, without or with Ni or NiMo as catalyst, as determined from the JV graphs shown in Figure 6.3.

Route	Device	Dep. time (s)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	η (%)
A	Bare Si	--	0.46	37.6	65	11.1
	NiMo (10 s)	10	0.46	35.5	64	10.3
	NiMo (15 s)	15	0.46	32.8	64	9.7
	NiMo (30 s)	30	0.46	29.4	60	8.0
	NiMo (180 s)	180	0.44	4.2	63	1.1
B	Bare Si	--	0.49	41.8	60	12.5
	Ni (30 s)	30	0.49	33.5	53	9.3
	NiMo (180 s)	180	0.49	35.0	58	9.9

For samples A, the addition of NiMo as a catalyst did not significantly influence the FF or V_{oc} of the JV curve (see Figure 6.3A and Table 6.1A). It solely blocked and/or scattered the light in an unfavourable manner, as a consequence of which J_{sc} rapidly decreased for

increasing deposition time of NiMo. When the deposition time was increased to 180 s, hardly any light was converted into photo-current and the efficiency dropped to 1.1%. When Ni was deposited for only 30 s, a dense layer had already formed (Figure 6.1C), and also no photo-current could be measured.

For samples B, the Si micropillar arrays were passivated by SiO₂ and the upper ~2 μm of SiO₂ was spatioselectively removed. SiO₂ does not only form an electrical barrier that prevents catalyst deposition during the electrodeposition step, it also passivates the Si surface, preventing charge carrier recombination and thus enhancing the PV efficiency.²¹⁻²³ *JV* measurements performed after removal of the SiO₂ from the tops of the pillars showed a decrease in *FF* as compared to the non-passivated, fully exposed samples A, which was due to a higher contact resistance in the former sample.²⁴ Nevertheless, the *V*_{oc} and *J*_{sc} values were substantially higher, resulting in an increased efficiency of 12.5% (see Table 6.1B) for the Si micropillar arrays with SiO₂.

As expected, high mass loadings of electrodeposited Ni (30 s) or NiMo (180 s) only affected the *J*_{sc}, due to blocking of light absorption (see Figure 6.3B). Since the areas between the micropillars remain free, the effect on light absorption is much less severe for samples B than for samples A. Whereas no photo-activity was observed in the case of 30 s of Ni deposition on a complete micropillar (sample A), a high *J*_{sc} of 33.5 mA/cm² was observed for samples with spatioselective deposition of Ni (sample B). Likewise, 180 s of deposition of NiMo yielded a *J*_{sc} of 35.0 mA/cm² for sample B as opposed to 4.2 mA/cm² for sample A. The slightly higher photocurrent density for NiMo as opposed to Ni in samples B is attributed to the fact that NiMo has a more open, granular structure than Ni (see Figure 6.1E and F). For sample B, longer deposition time gave higher mass loadings of the catalyst on the micropillars, yet the decrease in *J*_{sc} was minimal as compared to the results for samples A. We did not increase the deposition time beyond 30 s and 180 s for Ni and NiMo, respectively. For Ni, already a dense layer had been obtained at 30 s, while 180 s of NiMo deposition already yielded a catalytic activity comparable to Pt, as is discussed below.

6.2.2 Dark electrochemical (*JE*) measurements

Figure 6.4 shows the dark *JE* measurements for HER electrocatalysis on n⁺-Si micropillar array substrates, without catalyst or completely covered with Ni, NiMo, or Pt as catalyst (sample A). Although the band edge position of p-Si straddles the H⁺/H₂ redox couple, almost no catalytic activity is observed over a large overpotential range for bare Si micropillars, which underlines the requirement for a catalyst. The addition of a smooth, continuous Ni film on the surface already improves the catalytic activity substantially (see Figure 6.4 Ni (30 s)). A relatively small addition of Na₂MoO₄ (<2 mol% Mo to Ni) to the plating bath solution increases the HER activity in an acidic environment even more. Such

a NiMo alloy on n^+ -Si micropillar arrays gives JE responses that exhibit increasing catalytic activities with increasing deposition time. Increasing the deposition times beyond 180 s does not have any further effect, as is seen by increasing the deposition time to 240s. Furthermore these layers show a catalytic activity in close similarity to Pt (see Figure 6.4).

Figure 6.4: Dark JE behavior for electrodes with the noted compositions. The Si micropillars were radially doped (n^+/p) and completely covered with the noted catalyst (sample A). All of the samples were evaluated in 0.1 M $H_2SO_4(aq)$.

6.2.3 Photoelectrochemical (JE) measurements

JE measurements under illumination were performed for fully exposed Si micropillar arrays without catalyst, with a complete coating of NiMo catalyst (samples A), and for tops-exposed samples with spatioselective catalyst deposition (samples B) (Figure 6.5) in 0.1 M H_2SO_4 . It was reported, however, that NiMo does not exhibit infinite stability under these acidic conditions.⁴ Here we want to compare our results with the state-of-the-art NiMo photocathode developed by Shaner *et al.*, which was measured in 0.5 M H_2SO_4 over the course of several CV scans.⁵ All of the relevant values (*i.e.* V_{oc} , J_{ph} , FF , plateau current density, and η_{irc}) are tabulated in Table 6.2. Ideally, a well performing photocathode has the same characteristics (*i.e.*, J_{ph} , or J_{sc} , V_{oc} , and FF) as the underlying PV cell. Therefore, ideal regenerative cells (IRCs) are fully analogous to the above described and measured solid-state PV cells, and the efficiency (η_{irc}) of these systems is described by a similar equation as used to describe the efficiency of a PV device, see Equation 6.1.⁶

$$\eta_{IRC} = \frac{V_{oc} J_{ph}(E_{H_2/H^+}) FF}{P_{in}} \quad \text{Eq. 6.1}$$

The values of FF , V_{oc} and $J_{ph}(E_{H_2/H^+})$ in Equation 1 are referenced to the equilibrium potential of the half-reaction being performed at the photocathode, and P_{in} is the light power input (AM 1.5G, 100 mW/cm²).

Figure 6.5 Current density J_{ph} versus potential behaviour of Si micropillar array devices with radial n^+/p -junctions without and with electrodeposited metal catalyst at given deposition times on fully exposed Si micropillars (A) and spatioselectively on top-exposed arrays (B), measured at 1 sun illumination. Data was collected at pH 1 in H_2SO_4 and referenced to the RHE potential.

Table 6.2 JE characteristics for the Si micropillar arrays with radial n^+/p -junctions, with Ni, NiMo, or Pt as catalyst, as determined from the JE graphs shown in Figure 6.5. The values of FF , V_{oc} and J_{ph} are referenced to the equilibrium potential of the half-reaction occurring at the photocathode.

Route	Device	Dep. time (s)	V_{oc} (V)	J_{ph} (mA/cm ²)	FF (%)	PC^* (mA/cm ²)	η_{IRC} (%)
A	NiMo (10 s)	10	0.28	16.7	13	36	0.58
	NiMo (15 s)	15	0.30	16.5	12	32	0.57
	NiMo (30 s)	30	0.31	15.1	11	29	0.51
	NiMo (180 s)	180	0.46	2.7	45	3.0	1.04
B	Ni	30	0.47	22.3	9	35.6	0.89
	NiMo	180	0.48	34.9	45	35.5	7.54
	Pt	30	0.48	36.5	51	37	9.15

* Plateau current (PC) measured at -0.5 V vs RHE of Figure 6.5

Bare Si micropillar arrays only produced H_2 at a large overpotential (see Figure 6.5A and B) which once more exemplifies the need for a HER catalyst. For samples A, incorporating NiMo as catalyst, with a deposition time as short as 10 s, enhanced the H_2 production tremendously. This is witnessed by an increase in photo-current (J_{ph}) at 0 V vs RHE as compared to a bare sample. At a high overpotential the underlying PV cell limits the J_{ph} (i.e. J_{ph} reaches a plateau), and the J_{ph} value matches well with the J_{sc} measured as a solid-state PV cell (see Table 6.1A, Table 6.2A plateau current densities). The FF increased substantially for a photocathode sample when coated with NiMo ($\sim 12\%$ FF), although the values are significantly less than the values reached for the solid-state PV cell ($\sim 65\%$ FF). Only when the deposition time is increased significantly (180 s), the FF increases to 45%. Furthermore, the V_{oc} of samples A with deposition times up to 30 s is lower (~ 0.30 V vs RHE) than that of the PV cell (~ 0.45 V). The V_{oc} shifts to 0.46 V vs RHE when the

deposition time is increased (180 s). Interestingly, even though the J_{ph} is the lowest (2.7 mA/cm²) for the 180 s deposition time, the η_{IRC} (1.0%) is the highest of all samples A.

Figure 6.5B presents the JE measurements of the micropillar arrays with and without the spatioselectively deposited catalysts Ni, NiMo, and Pt (samples B), recorded under illumination. Table 6.3B contains the compiled parameters of Figure 6.5B. Again, Si micropillar arrays with spatioselectively etched SiO₂ without a catalyst exhibits a negligible J_{ph} at a potential of 0 V vs RHE. In contrast, deposition of either Ni, NiMo or Pt at the top of the micropillar arrays leads to a substantial increase of J_{ph} at 0 V vs RHE. Furthermore, the V_{oc} values for samples with locally deposited catalysts are substantially higher (~0.48 V vs RHE) than those observed for samples A with the catalyst deposited along the complete micropillar length (~0.30 V vs RHE). The values for V_{oc} , FF and J_{ph} are in good agreement with the solid state PV cell data (see Table 6.1B and Table 6.2B).

Ni as catalyst gives a lower FF compared to NiMo or Pt, which makes Ni a less appropriate HER catalyst. The lower catalytic activity was already observed in the dark JE measurements (Figure 6.4). For comparison, Pt was also deposited on the top-exposed micropillars. Pt is one of the best performing HER catalysts, which was already observed in the dark JE measurements (Figure 6.4). The η_{IRC} for the samples B with the Pt catalyst is 9.1%. A disadvantage of Pt is that it is a rare and precious metal, in contrast to Ni and Mo, which are earth-abundant. The use of NiMo as a catalyst enhances the photoelectrochemical output tremendously as compared to Ni, as seen in Figure 6.5B. The increase is mainly reflected in the FF of the curve, which increases from 9% for Ni to 45% for NiMo. The best performing micropillar array with NiMo has a V_{oc} of 0.48 V, J_{sc} = 34.9 mA/cm² and a fill factor of 45%, which results in η_{IRC} = 7.5%.

As noted above, NiMo does not exhibit infinite stability under strong acidic conditions.⁴ To assess the durability of this catalyst we measured the potential vs RHE at a constant current density of 10 mA/cm² in a buffered (pH 4.0) electrolyte of 0.2 M potassium hydrogen phthalate for 72 h under AM 1.5G light (see Figure 6.6A). The average applied potential appeared stable over the entire period of time, and the potential only oscillated, most likely due to hydrogen bubble formation and detachment. The H₂ production for patterned NiMo (180 s) Si micropillar samples B in Figure 6.6B was measured by gas chromatography (GC). Here, the n⁺/p junction was biased by contacting the emitter of the Si micropillar photocathode and applying a bias to generate either 5, 10 or 20 mA of current output. The calculated and measured amounts of H₂ produced match excellently, indicating a nearly 100% faradaic efficiency.

Figure 6.6: (A) Supplied potential of a spatio-selectively deposited NiMo catalyst on Si micropillars under continuous operation of 10 mA/cm² and AM 1.5G simulated sunlight. (B) Calculated (lines) versus real (markers) hydrogen production using patterned Si micropillar photocathode, biased at 5, 10 or 20 mA.

The main difference between samples A and B in the use as a photocathode is observed in the *FF*. The *FF* of a photocathode is a reflection of the apparent catalytic activity, which is controlled by two factors. First of all, the catalytic activity is a function of catalyst loading. At low mass loadings, not enough active sites are present to produce hydrogen efficiently.⁴ Secondly, a low catalytic activity can be caused by a pinch-off effect, which has been described for Ni particles (< 50 nm) on an n-type semiconductor by Garcia-Esparza *et al.*²⁵

The η_{IRC} value observed for our best performing device is about a factor 3 higher than that reported before for a device with NiMo as catalyst.⁵ The higher efficiency observed for the photocathodes studied here is attributed to several aspects. Firstly, we used a well-developed Si micropillar array PV cell, with optimal junction depth (~900 nm) and micropillar height (40 μm).⁹ Secondly, passivating the micropillar array by a SiO₂ coating provided a further increase of the efficiency of the substrate.⁷ Lastly, we achieved decoupling of the electrolyte-semiconductor interface by the SiO₂ coating (*i.e.*, effectively burying the underlying junction). In this way, direct contact between the Si and the electrolyte is avoided, thus preventing a possible “pinch-off” effect. Overall, the catalytic performance for samples B is solely determined by the catalyst on the n⁺-Si tops and the light absorption by the underlying Si micropillar substrate.

To highlight the importance of catalysts on silicon micro- and nanopillars as hydrogen producing half-cells, we have subdivided the existing results into three categories: with NiMo, with Pt, or with any other catalyst. The three best performing systems are given in Table 6.3. The efficiencies, if not given in the original literature reference, were calculated according to Equation 6.1. From Table 6.3 it becomes clear that our system outperforms any other half-cell constructed from either Si micro or nanopillars.

Table 6.3 Compilation of micro and nanowire-based hydrogen producing half-cells. Measurements done under AM 1.5G simulated sunlight in their best performing electrolyte.

Configuration	V_{oc} (mV)	J_{ph} (mA/cm ²)	FF (%)	η_{IRC} (%)	ref
NiMo					
n⁺/p-Si MWs	480	34.9	45	7.5	Here
n ⁺ /p-Si MWs	420	14.3	48	2.9	⁵
n ⁺ /p-Si MWs	485	10.3	45	2.2	¹⁵
Pt					
n⁺/p-Si MWs	480	36.5	48	9.1	Here
n ⁺ /p-Si MWs	540	15.0	71	5.8	²⁶
n ⁺ /p-Si MWs	510	20.2	49	5.0	⁵
Other					
p-Si NWs/Ni ₂ P ₅	400	21.0	36	3.0	²⁷
p-Si NWs/CoP	407	15.6	27	2.9	²⁸
p-Si NWs/FeP	470	13.9	45	2.8	²⁹

6.3 Conclusions

We have designed, fabricated and experimentally verified a broadly applicable photocathode architecture that circumvents a trade-off between catalytic activity and optical absorption, which control FF and J_{ph} , respectively. By spatially and functionally decoupling light absorption and catalytic activity on high-aspect-ratio silicon micropillars with a radial n⁺/p-junction, efficient solar-driven water reduction has been achieved. This was demonstrated by an architecture which consisted of a high mass loadings of catalyst (*e.g.* NiMo or Pt) deposited selectively and specifically on the top part of micropillar arrays. The best performing Si n⁺/p-junction micropillar array photocathodes investigated here involve Pt as the catalyst, and demonstrate an efficiency of $\eta_{IRC} = 9.1\%$. When the Pt catalyst on the micropillar tops is replaced by a layer of NiMo, the photocathode reaches an unprecedentedly high efficiency, $\eta_{IRC} = 7.5\%$, for an all earth-abundant HER half-cell. Due to the versatility of this configuration, catalyzed reactions are not limited to H₂ formation, and other electrodeposited catalysts can be used.

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6.5 Materials and methods

6.5.1 Fabrication of radial n⁺/p junctions in silicon micropillar arrays

Scheme 6.1 gives a schematic representation of the fabrication and passivation of an array of micropillars with radial n⁺/p junctions. P-type Si{100} substrate, with a resistivity of 5-10 Ωcm , 100 mm diameter, 525 μm in thickness, single side polished (Okmetic Finland), were prepared as previously reported.^{8,9} In short, substrates were cleaned according to a standard procedure, and covered with 100 nm silicon-rich silicon nitride (SiN_x) via LPCVD. The SiN_x on the front side of the wafer was removed by reactive ion etching (RIE, Adixen AMS100DE), and the substrate was cleaned by oxygen plasma (30 min). By means of standard photolithography, squares ($5 \times 5 \text{ mm}^2$) with hexagonally packed circles (4 μm diameter, 2 μm spacing, *i.e.* 6 μm pitch) were defined in a photoresist polymer (Olin 906-12). Silicon micropillars (40 μm in height) were etched into the silicon substrate by deep reactive ion etching (DRIE, Bosch process) and the substrates were cleaned subsequently in oxygen plasma (30 min). n⁺/p junctions were formed by the deposition of phosphorus oxide (LPCVD). A mixture of 330 sccm PH_3 and 50 sccm O_2 was supplied for 45 min at 350 mTorr in order to deposit a phosphorus oxide glass on the silicon surface. The substrate was annealed at 1050 $^\circ\text{C}$ for 15 min to accomplish diffusion of the dopant into the silicon micropillar array, to form the proper radial junction. Prior to the deposition of the passivation layer, the dopant oxide was stripped in buffered hydrogen fluoride solution (BHF, 10 min), upon which the wafers returned to their hydrophobic state (Scheme 6.1A). Subsequently, the wafers were cleaned by immersion in fuming 99% nitric acid (HNO_3 , $2 \times 5 \text{ min}$), boiling 69% nitric acid (10 min) and immersion in 1% aqueous hydrofluoric acid (HF) to remove the native oxide (1 min). The 100 nm passivation layer of SiO_2 was applied by LPCVD and is described in more detail below (Scheme 6.1B). After selective removal of the surface passivation coating from the tops of the micropillars (Scheme 6.1C,D), a NiMo alloy was deposited on the micropillars by electrodeposition (Scheme 6.1E), for more details see below. Finally, Ohmic contacts (1 μm ; Al/Si, 99/1%) were sputtered (Oxford PL400) onto the back side of the wafer (Scheme 6.1E).

Scheme 6.1 Schematic fabrication process: Pillar array obtained after deep reactive ion etching of a silicon wafer with a photoresist pattern on the front side and silicon-rich silicon nitride on the backside, followed by the deposition of the dopant oxide by LPCVD (phosphorus). (A) Formation of the radial junction, by a drive-in step at 1050 °C for 15 min. (B) Deposition of a passivation layer of SiO₂ by LPCVD. (C) Filling of the pillar arrays with photoresist, followed by controlled retraction by O₂ plasma. (D) Selective removal of the passivation layer by BHF wet etching. (E) Deposition of aluminum back contacts by sputtering and catalyst by electrodeposition.

6.5.2 Low pressure chemical vapor deposition of SiO₂ passivation layer

Conformal deposition of a silicon oxide (SiO₂) film was done by means of LPCVD. SiO₂ was deposited at 725 °C with a 50 sccm tetraethyl orthosilicate flow (200 mTorr, 8.1 nm/min deposition rate). The total thickness of SiO₂ was set to 100 nm.

6.5.3 Local removal of SiO₂ from the tops of micropillar arrays

In order to selectively remove SiO₂ from the tops of the micropillars, the following protocol was applied. HMDS (hexamethyldisilazane) was spin-coated in-between the pillars (4000 rpm, 2 min), and subsequently AZ9260 photoresist was spin-coated (1000 rpm, 4 min). The samples were dried overnight at 10⁻³ mbar at room temperature. Next, the photoresist was removed around the micropillar arrays by masking the arrays with squares of 5×5 mm². The samples were exposed to light (3 × 10 s UV exposure, 10 s delay between exposure cycles) and developed (7 min). The remaining photoresist within the micropillar arrays was exposed to light with a blank mask (3 × 10 s UV exposure, 10 s delay between exposure cycles). The resist layer between the micropillars was reduced in thickness using reactive ion etching for ~30 min (100 sccm O₂, 100 mTorr, 25 W, 10 °C), until the desired height of photoresist around the micropillars was obtained (Figure 6.7A). SiO₂ was selectively removed from the exposed tops by wet etching in BHF (~1 min, etch rate 210 nm/min). The remaining photoresist layer was stripped by 10 min ultra-

sonication in acetone, followed by 10 min ultra-sonication in isopropanol and spin drying. The selectively etched micropillar arrays clearly showed exposed tops (Figure 6.7).

Figure 6.7: (A) HR-SEM images of Si micropillar arrays with photoresist between the micropillars, which is etched by O₂ plasma. (B) Si micropillar array with selectively removed SiO₂ from the tops by etching (A) in BHF.

6.5.4 Catalyst deposition

Onto the freshly exposed Si tops of the micropillar arrays, catalysts were deposited by electrodeposition. The Ni–Mo catalyst was deposited in a two-electrode setup. The electrodeposition bath consisted of an aqueous solution of 1.3 M nickel(II) sulfate, 0.5 M boric acid, and 25 mM sodium molybdate in Milli-Q water. The electrodeposition of Ni–Mo catalyst on the Si micropillars was performed at a constant current of 20 mA/cm² for 10 to 250 s.

For the deposition of nickel as catalyst, a two-electrode setup was used. The electrodeposition bath consisted of 1.3 M nickel(II) sulfate, and 0.5 M boric acid, in Milli-Q water. The electrodeposition of Ni catalyst on the Si micropillars was performed at a constant current of 20 mA/cm² for 30 s.

Platinum was deposited from an aqueous solution of 5 mM hexachloroplatinic acid (H₂PtCl₆) and 0.5 M sodium sulfate (Na₂SO₄), potentiostatically at –0.7 V. Charge densities of 130 mC/cm² were supplied.

6.5.5 *JV* measurements

To measure the electrical characteristics of the coated Si micropillars, samples were positioned perpendicular to a 300 W xenon arc light source, with an intensity of 1 sun (AM 1.5G). The active sample size was 5x5 mm². *JV* measurements were recorded on a VersaSTAT 4 potentiostat using a linear voltage sweep from –0.7 to 0.7 V at a rate of 0.2 V/s. For each catalyst (*i.e.* Pt, Ni, and NiMo deposition) at least 4 samples were measured. The presented figures give the average per catalyst.

6.5.6 *JE* measurements

The coated micropillar photocathodes were photoelectrochemically tested using a potentiostat (VersaSTAT 4) in a three-electrode system, where the micropillar photocathode with an exposed projected surface area of 0.28 cm² acted as the working electrode, a platinum wire mesh as the counter electrode and an Ag/AgCl electrode as the reference electrode. The electrolyte used was 0.1 M aqueous sulfuric acid (H₂SO₄). Linear sweep voltammetry measurements were done at a scan rate of 50 mV/s. Photocurrent measurements were performed perpendicular to a 300 W xenon arc light source, with an intensity of 1 sun (AM 1.5G). All current–potential curves are presented as measured (without correction).

6.5.7 Gas chromatography

The reactor was connected to a GC (Compact GC, Interscience), equipped with a Parabond Q column (10 m) and a TCD detector to determine the amount H₂ in the argon carrier gas. Argon was flowed with 5 mL/min through the electrolyte and sampled every 90 s for the presence of H₂.

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Chapter 7

Optimization of Spatially Decoupling Light Absorption and Catalytic Activity of Nickel-Molybdenum on Passivated High-Aspect-Ratio Silicon Microwire Arrays

To enhance the performance of photoelectrodes for use in solar-to-fuel devices, catalysts are often applied to the surface of the photoabsorber material, *e.g.* silicon (Si). Earth-abundant catalysts for the hydrogen evolution reaction (HER), *e.g.* NiMo, are generally opaque and require high mass loading to obtain high catalytic activity. This, in turn, leads to parasitic light absorption when the electrode is illuminated from the front electrolyte side, and thus limits H₂ production. Here, we show the fabrication of a highly efficient HER photocathode by decoupling light absorption and catalytic activity on each individual Si microwire photocathode in a larger array of such microwires. The essential improvement made here, compared to work of others, is that the Si microwires are partially covered with a passivating coating, and partially with a catalyst that is in electrical contact with the light-absorbing semiconductor. To this end, NiMo was spatioselectively electrodeposited over a distance in the range of 2–36 μm from the top of 40- μm long Si microwires which possess a radial n⁺/p junction. This was achieved by exactly tuned etching of the antireflective SiO₂ coating from a defined top section of these microwires, followed by selective electrodeposition of the catalyst material on the freshly exposed n⁺-Si emitter. This configuration shows high mass loading of the opaque catalyst, while retaining a high photocurrent in the PV cell. By varying the fraction of catalyst coverage and the pitch of the microwires, it was possible to deconvolute the contributions of catalytic activity and light absorption to the overall device performance. This insight facilitated the fabrication of microwire array devices that exhibit a near-ideal short-circuit photocurrent density of 35.5 mA/cm², a photovoltage of 495 mV, and a fill factor of 62% under AM 1.5G illumination, resulting in an unprecedented photon-to-hydrogen energy efficiency of 10.8%.

7

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7.1 Introduction

A good solar-to-fuel (S2F) device is efficient both in light harvesting and in transforming the photogenerated electricity into chemical bonds. Silicon (Si) is a popular, well performing photon absorber. However, Si as a photocathode has poor kinetics for the hydrogen evolution reaction (HER)¹ and therefore requires a catalyst to achieve efficient solar to hydrogen (STH) conversion. Unfortunately, for state-of-the-art earth-abundant catalysts (*e.g.* NiMo), the high mass loading that is needed for sufficient catalytic activity also results in significant parasitic light absorption upon frontside illumination, which reduces the efficiency of such photocathodes.

One promising route to obtain high efficiencies for systems consisting of semiconductors coated with a catalytic material is by spatially and functionally decoupling the optical absorption and the catalytic activity of the photocathode. Si microwire arrays provide an approach to overcome the negative correlation between the catalytic activity, which is directly related to the fill factor, FF , in terms of photovoltaic (PV) cells, and light absorption, J_{ph} . Both Shaner *et al.* and Roske *et al.* obtained high FF values in Si microwire photocathodes, by covering the bottom area between the microwires with NiMo/TiO₂ or cobalt phosphide nanoparticles, respectively.^{2,3} Their best performing Si homojunction microwire array photocathodes showed an ideal regenerative cell efficiency, η_{irc} , of 2.9% and 2.8% respectively.²⁻⁴ These efficiencies, obtained in designs without surface passivation, were restricted by light absorption, evidenced by a limited photocurrent (<15 mA/cm²), whereas passivated Si PV cells easily generate ~40 mA/cm².^{5,6} Surface passivation suppresses recombination of charge carriers at the surface. This becomes increasingly important as the absolute surface area increases, which is the case especially for high-aspect-ratio structures.

Chen *et al.* identified, by studying ultramicroelectrode arrays of platinum (Pt) disks on n⁺-Si, that placing catalyst islands as far as 12 μ m apart did not significantly increase the kinetic overpotential of the HER, but that beyond that distance catalyst performance went down.⁷ Although this study was limited to a 2D surface, it is clear that the spacing of separate catalyst islands can strongly influence the catalyst performance of any photocathode. Because this might also hold for the 3D photocathodes discussed in the present paper, the influence of microwire pitch on the performance of these devices is investigated.

In this contribution we describe the spatial and functional decoupling of light absorption and catalytic activity of frontside-illuminated Si microwire array photocathodes. Radially doped microwire arrays are passivated by SiO₂, which increases the efficiency of the underlying PV cell.^{6,8,9} SiO₂ is spatioselectively removed from the top sides of the microwire arrays. The remaining, insulating SiO₂ layer acts as a masking layer in a

subsequent process step in which the freshly exposed Si top is covered with an electrodeposited catalyst for H₂ production. The influence of the size of the catalyst-covered region and the spacing between the microwires on the performance of the resulting photocathodes was investigated, by measuring their photovoltaic (*JV*), electrochemical and photo-electrochemical (*JE*) characteristics. Variation and comparison of the different device parameters results in a deeper understanding of the limiting factors in photocathode performance, leading to an optimised design with an unprecedented solar-to-hydrogen half-cell efficiency of >10%.

7.2 Results and discussion

To decouple and vary the contributions of light absorption and catalytic activity of microwire arrays covered with NiMo, we developed a fabrication route to spatially control the coverage of NiMo over a microwire. Figure 7.1A gives a schematic illustration of the investigated parameters; the microwire pitch and the catalyst coverage. Substrates with arrays of silicon microwires (4 µm diameter, 40 µm length) with radial junctions (p-type base and 900 nm n⁺-type emitter) were fabricated according to a procedure reported before.^{8,9} Previously the pitch of the microwires was fixed at 6 µm.^{6,9,10} In the present paper we investigate the light absorption capabilities of microwires with a pitch of 8, 10, 12, 14, 19, and 24 µm. The pitch between the microwires was controlled by standard photolithography using a different patterning mask. For electrodeposition of the catalyst, a conformal silicon dioxide (SiO₂) layer was selectively etched back to specific heights (2, 9, 18, 25, and 36 µm) from the top of the microwire, thereby exposing the underlying Si emitter (n⁺-Si) of the microwires (Figure 7.2).

Figure 7.1 (A) schematic illustration of the investigated parameters, microwire pitch and catalyst coverage. SEM images of electrodeposition of an earth-abundant catalysts (NiMo) on Si microwire arrays with a radial junction. The microwires are passivated by SiO₂ on the lower part, while NiMo was electrodeposited at the top (B) 2 μm, (C) 9 μm, (D) 18 μm, (E) 25 μm, and (F) 36 μm on the upper part of the microwire, with varying pitches. Scale bars: (B) 2 μm, (C-F) 10 μm.

Figure 7.1B-F presents scanning electron microscopy (SEM) images of microwire arrays where sections ranging from 2 to 36 μm in length of the 40 μm long microwires are covered by NiMo, fully independent of the pitch of the microwire (*i.e.* Figure 7.1: 2 μm (B), 9 μm (C), 18 μm (D), 25 μm (E), and 36 μm (F)). All SEM images in Figure 7.1 show that no deposition occurred at the lower parts of the microwire arrays, which was covered with SiO₂. The remaining SiO₂ layer effectively blocks the electrons during electrodeposition. NiMo was only deposited on the freshly exposed n⁺-Si emitter. This well-controlled selective deposition enables us to effectively investigate how the activity of the catalyst is related to both the pitch and to how big a section of the Si microwire is covered with catalyst.

Figure 7.2 overview SEM image of passivated n^+/p Si microwires, (A) where the top of the microwire is free of SiO_2 , while the remaining microwire is covered by SiO_2 . (B) Zoom-in SEM image of a microwire of (A). (C) Zoom-in SEM image of (B). (D) SEM overview image of microwires of which 36 μm of the SiO_2 layer of the 40 μm microwire is retracted.

The morphology of the deposition changed upon varying the height of the catalyst-covered sections. The difference in growth can be explained by the following reasons. Firstly, the deposition current efficiency of Ni–Mo is low (*i.e.* below 5%), due to H_2 formation during deposition.^{11,12} The addition of boric acid to the deposition bath suppresses the evolution of H_2 gas, but does not completely prevent the effect. We expect that the formation of H_2 bubbles hinders the homogeneous deposition of NiMo and roughens the deposition, especially at the confined spaces at the bottom. Secondly, we deposit under a fixed current, therefore the local current density varies between devices, dependent on the pitch and the exposed microwire area. This may lead to differences in growth rates. There might also be effects of reactant/product mass transport limitation in the solution, which could lead to concentration gradients, and/or a deposition current density that varies along the length of the microwire.

7.2.1 Photovoltaic (JV) measurements (bare)

The influence of the pitch on the performance of passivated Si microwires with incorporated radial n^+/p junctions was investigated by analysing their photovoltaic

properties, *i.e.*, V_{oc} , J_{sc} , and FF . Except the varying pitch, every microwire in the array had a diameter of 4 μm , a length of 40 μm , a junction depth of ~ 900 nm, and was passivated by 100 nm SiO_2 (see Materials and Methods for details). Figure 7.3A shows the current-voltage (JV) graphs of samples with six different microwire pitches.

From these overviews it can be seen, firstly, that the V_{oc} does not vary significantly upon changing the pitch of the microwires. Secondly, an increase in J_{sc} is observed for increasing pitch. This indicates that the reflectivity is reduced by the lower density of microwires, which improves the light absorbing properties of the PV cell. The trend in increase of J_{sc} directly leads to an increase in η , as they are related by Equation 7.1.

$$\eta = \frac{V_{oc} J_{sc} FF}{P_{in}} \quad \text{Eq. 7.1}$$

The parameters J_{sc} and η were plotted as a function of the microwire pitch in Figure 7.3B, and the same increasing trend is observed. The non-consistent increase in η for pitch 14 and 24 μm is related to a decrease in FF (see Table 7.1). The FF was lower for these samples due to a higher contact resistance (R_s), as is visible in Figure 7.3A by the lower slope around the V_{oc} . All mentioned parameters are summarized in Table 7.1.

Figure 7.3 (A) JV measurements of microwire substrates without catalyst, for varying pitches as indicated. Each line is the average of at least four different samples prepared with the same settings. (B) J_{sc} and η as a function of the microwire pitch for the samples shown in (A).

Table 7.1 JV characteristics for various pitches on the 40 μm high microwire arrays of Figure 7.3A.

Pitch	η (%)	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)
8	14.6 $\pm$ 1.0	38.5 $\pm$ 2.7	0.54 $\pm$ 0.01	72 $\pm$ 0.1
10	15.2 $\pm$ 1.4	39.5 $\pm$ 3.4	0.54 $\pm$ 0.02	72 $\pm$ 0.8
12	15.5 $\pm$ 1.2	41.1 $\pm$ 1.5	0.54 $\pm$ 0.02	73 $\pm$ 0.4
14	16.3 $\pm$ 0.8	42.2 $\pm$ 2.4	0.54 $\pm$ 0.01	68 $\pm$ 0.3
19	17.2 $\pm$ 0.7	43.4 $\pm$ 0.8	0.55 $\pm$ 0.01	73 $\pm$ 0.5
24	16.9 $\pm$ 0.9	43.5 $\pm$ 2.9	0.53 $\pm$ 0.01	68 $\pm$ 0.2

7.2.2 Photovoltaic (JV) measurements (with catalyst)

The fully finished microwire photocathodes with the spatioselectively deposited catalyst were measured as PV cells, without the electrolyte, as seen in Figure 7.4A-E (*i.e.* Figure 7.4: 2 μm (A), 9 μm (B), 18 μm (C), 25 μm (D), and 36 μm (E)). For spatioselectively deposited NiMo on the microwires there was only a minor influence of the presence of the catalyst on the FF or V_{oc} of the samples. To assess the impact of the wire coverage and pitch on the PV performance of the samples, the J_{sc} is plotted in a contour plot, see Figure 7.4F. From Figure 7.4F it becomes apparent that J_{sc} increases with increasing pitch and with decreasing degree of catalyst coverage (a pitch of 24 μm and coverage of 2 μm yields the highest J_{sc} of 40.36 mA/cm²). Conversely, lowering the microwire pitch and increasing the coverage leads to a lower current density (a pitch of 8 μm and coverage of 36 μm yields the lowest J_{sc} of 14.62 mA/cm²). For the largest investigated pitch (24 μm) only 2.5% of the footprint is covered with Si microwires. As only the microwires are spatioselectively functionalized, the addition of an opaque catalyst and the height over which it is deposited have little impact on the light absorption for these devices, and hence the highest J_{sc} is observed for the largest tested pitch. As the pitch decreases, the density of Si microwires increases accordingly, and therefore the amount of deposited NiMo. For the smallest tested pitch (8 μm), 22% of the footprint area is occupied by Si microwires and thus a higher fraction of the geometric surface is catalyst. Therefore, more light is blocked and lower J_{sc} values are observed. Also, the dependence of the catalyst-covered wire height is more pronounced because of the higher wire density, resulting in the lowest current density at the lowest pitch and highest catalyst coverage.

Figure 7.4: JV measurements of microwire substrates spatioselective functionalized with NiMo for varying pitches (as stated) and catalyst coverage as is seen in Figure 7.1B to F, (A) 2 μm , (B) 9 μm , (C) 18 μm , (D) 25 μm , and (E) 36 μm . Each line is the average of two different samples prepared with the same settings. (F) Contour plot of the current density J_{sc} as a function of wire coverage and pitch.

7.2.3 Dark electrochemical (J_E) measurements

The electrocatalytic activity of NiMo as a function of the deposition time was assessed (section 6.2.2). The HER catalytic activity of NiMo was essentially unchanged when the nominal deposition time was >180 s for microwire arrays with a pitch of 8 μm and the top 2 μm covered with NiMo. The deposition time for each sample in this study was corrected for absolute surface area of exposed silicon. In that way it was tried to achieve approximately the same catalyst layer thickness in all cases. The deposition time as a function of pitch and exposed wire area is given in Table 7.2.

Table 7.2 Deposition time (D_t) of NiMo catalyst on microwire arrays for every microwire pitch/coverage combination.

Pitch	f_c (%)	D_t (s) 2 μm	D_t (s) 9 μm	D_t (s) 18 μm	D_t (s) 25 μm	D_t (s) 36 μm
8	22.7	180	270	540	630	1080
10	14.5	65	195	390	455	780
12	10.1	45	135	270	315	540
14	7.4	33	99	198	231	396
19	4.0	18	54	108	126	216
24	2.5	12	36	72	84	144

The study of Chen *et al.* with Pt microdisks (diameter of 6 μm) of varying pitch on a flat substrate was limited to 2D and only varied the filling fractions (f_c) of the catalyst.⁷ Their defined f_c is directly related to the pitch of the Si microwires when only the tops of the microwires are taken into account. In our study, the partial and tunable covering the sidewalls of the Si microwires provides an additional control parameter. Therefore, it is important to know how the electrocatalytic activity of NiMo depends on the pitch (*i.e.* f_c) and coverage height of the microwires.

The dark current-potential graphs of the patterned microwire arrays with varying pitches and coverage heights were determined experimentally by only contacting the emitter, n^+ -Si, through the front side aluminium contact, as working electrode. Figure 7.5A-E show the current density as a function of the potential vs. RHE for samples with varying pitch (as stated) and varying catalyst coverage (*i.e.* Figure 7.5: 2 μm (A), 9 μm (B), 18 μm (C), 25 μm (D), and 36 μm (E)). As the pitch increases from 8 μm (f_c of 22%) to 24 μm (f_c of 2.5%) the activity of NiMo decreases. At a pitch of 24 μm and 2 μm coverage, the current density is only 4.5 mA/cm^2 at 50 mV overpotential, as opposed to 13.5 mA/cm^2 at a pitch of 8 μm and a coverage of 2 μm .

Figure 7.5: Plot of current density vs. potential, obtained for Si microwire arrays with varying pitch as stated and the upper (A) 2 μm, (B) 9 μm, (C) 18 μm, (D) 25 μm and, (E) 36 μm functionalized with NiMo, performed in the dark in an electrochemical cell, containing 0.1 M H₂SO₄. (F) Contour plot of current density at 50 mV vs RHE as a function of wire coverage and pitch, as interpolated (cubic spline) from measurements on varying devices.

Chen *et al.* found a similar trend for Pt ultramicroelectrode arrays on n⁺-Si.⁷ A f_c down to 10% had nearly the same activity as 100% flat Pt.⁷ A clear deviation was observed for f_c < 6.3%, which is comparable to a microwire pitch larger than 14 μm (see Table 7.2). In our system, the activities of microwires with pitches of 14, 19, and 24 μm almost overlap (see Figure 7.5A).

To summarize the effects of pitch and coverage, current densities of all combinations are plotted at one potential, *i.e.* 50 mV vs RHE (see red line in Figure 7.5A to E), as shown in Figure 7.5F. Clearly, a trade-off is visible between the NiMo coverage and microwire pitch

on the electrocatalytic activity. Firstly, smaller pitches are better, independently of covered height (every trajectory from right to left at any coverage, Figure 7.5F). Secondly, to overcome the limited activity of NiMo at larger pitches (*i.e.*, at the lower right corner of Figure 7.5F), a higher coverage of the microwire is required (*i.e.* upper right corner of Figure 7.5F). At smaller pitches, however, already low coverages provide sufficient amounts of catalyst (*i.e.*, at the lower left corner of Figure 7.5F), witnessed by an almost constant current density when increasing the coverage.

7.2.4 Photoelectrochemical (*JE*) measurements

JE measurements under illumination were performed for Si microwire arrays with spatioselective catalyst deposition in 0.1 M H₂SO₄. Although it has been reported that NiMo has limited stability under these acidic conditions,¹³ this electrolyte was used to provide comparable conditions with the state-of-the-art NiMo photocathode developed by Shaner *et al.*²

In the case of well performing catalysis this photocathode has the same characteristics (*i.e.*, J_{ph} or J_{sc} , V_{oc} , and FF) as the underlying PV cell. Therefore, ideal regenerative cells (IRC) are fully analogous to the above described and measured solid-state PV cells (Equation 7.1), and the efficiency (η_{IRC}) of these systems is described by a similar equation as used to describe the efficiency of a PV device, see Equation 7.2.⁴

$$\eta_{IRC} = \frac{V_{oc} J_{ph}(E_{H_2/H^+}) FF}{P_{in}} \quad \text{Eq. 7.2}$$

The values of FF , V_{oc} and $J_{ph}(E_{H_2/H^+})$ in Equation 7.2 are referenced to the equilibrium potential of the half-reaction occurring at the photocathode, and P_{in} is the light power input (AM 1.5G, 100 mW/cm²). From Equation 7.2 it becomes clear that both the FF and J_{ph} play an important role in the overall efficiency of a hydrogen half-cell. Via the performed photovoltaic (*JV*) measurements the impact of the catalyst loading on the light absorption capabilities (J_{ph}) of the underlying Si microwire arrays is known (Figure 7.4E). Furthermore, the impact of 5 mm of electrolyte solution on top of the cell has been calculated and reduced to a maximum photocurrent of 42.8 mA/cm².¹⁴ This loss is mainly due to the absorption by water at wavelengths >1000 nm. Since Si is an indirect bandgap semiconductor, its absorption in this region is poor, meaning the light absorption by water has no significant impact on the total generated photocurrent.¹⁵

Figure 7.6A-E show the current-potential (*JE*) graphs obtained from half-cell measurements, for varying pitches (as stated), and varying catalyst coverage (*i.e.* Figure 7.6: 2 μ m (A), 9 μ m (B), 18 μ m (C), 25 μ m (D), and 36 μ m (E)). By combining light absorption (J_{ph}), catalytic activity (FF), and open circuit potential (V_{oc}) we can calculate the efficiency of the HER half-cell. The contour plot Figure 7.6F shows the overall device

efficiency η_{IRC} vs. pitch and wire coverage and visualizes two limiting domains. Firstly, the overall efficiency is dominated by the FF in the lower right corner of Figure 7.6F, which is a direct consequence of the limited amount of active catalyst, as explained in Figure 7.5F. In detail, a photocathode behaves as the superposition of the catalyst behavior in the dark, *i.e.* Figure 7.5F, and the underlying PV cell, *i.e.* Figure 7.4F. Because the resistances of the PV cells are found to be lower than those of the catalytic behavior, we conclude that the FF of a photocathode is mainly determined by the resistance the catalyst imposes on the underlying PV cell. Green developed an analytical approximation to calculate the FF , when the values of R_s , V_{oc} , and I_{sc} are known.¹⁶ Here, R_s was obtained for each variation by linearizing every data series in Figure 7.5A-E, in the range between 0 and 50 mV. The calculated (FF_s) and measured (FF) fill factor values are tabulated in Table 7.3. In all cases, the calculated values correspond very well to the measured ones, thus supporting that limitation by the catalyst is the main contributor to the fill factor.

Table 7.3 Cell characteristics from Figure 7.5A-E and Figure 7.6A-E, for various pitches and catalyst coverages

Coverage: 2 μm						
	8 μm	10 μm	12 μm	14 μm	19 μm	24 μm
R_s (Ω/cm^2)	3.67	3.71	3.98	5.73	7.43	10.26
FF (–)	60.69	59.33	62.32	43.18	37.67	35.86
FF_s (–)	61.20	58.20	59.37	45.37	35.36	31.52
Coverage: 9 μm						
R_s (Ω/cm^2)	3.72	3.79	4.89	5.07	7.47	10.57
FF (–)	57.88	59.02	57.50	46.20	35.93	33.19
FF_s (–)	60.87	60.06	59.73	46.39	36.33	36.50
Coverage: 17 μm						
R_s (Ω/cm^2)	4.50	4.16	3.75	2.78	4.14	4.42
FF (–)	58.25	52.54	63.29	58.69	50.52	50.68
FF_s (–)	65.45	50.25	63.37	60.42	50.11	50.72
Coverage: 22 μm						
R_s (Ω/cm^2)	5.54	4.20	4.38	3.38	4.37	4.82
FF (–)	62.38	62.15	57.33	63.61	59.14	62.18
FF_s (–)	61.27	63.73	62.92	62.00	59.05	60.87
Coverage: 35 μm						
R_s (Ω/cm^2)	5.02	4.70	4.62	4.96	4.20	4.75
FF (–)	54.66	55.62	61.75	53.96	64.91	60.67
FF_s (–)	62.01	60.99	58.50	56.63	58.71	60.22

Secondly, in the upper left corner of Figure 7.6F of the overall efficiency is limited by light absorption. This is a direct consequence of reduced light absorption of the microwire array, since the catalyst blocks the incoming light, as is clear from Figure 7.4F. Between these two zones, a region of optimal performance is found where both the catalysis and the light absorption perform close to their maximum. In this zone, a pitch of 12 μm and a spatioselective coverage of 2 μm on the upper part of the 40 μm long Si microwires results in the highest efficiency, of 10.8%.

Figure 7.6 *J-E* measurements of microwire photocathodes with varying pitch as stated and the upper (A) 2 μm , (B) 9 μm , (C) 18 μm , (D) 25 μm and, (E) 36 μm functionalized with NiMo, performed under simulated solar light, in an electrochemical cell, containing 0.1 M H_2SO_4 . Each line is the average of two different samples prepared with the same settings. (F) Contour plot of the *FF* as function of wire coverage vs. pitch for all tested combinations.

7.3 Conclusions

We have designed, fabricated and experimentally validated a broadly applicable photoelectrode architecture. By spatially and functionally decoupling light absorption and catalytic activity on high-aspect-ratio silicon microwires with a radial n^+/p -junction, efficient solar-driven hydrogen evolution has been achieved. This was shown by investigating high-aspect-ratio buried radial n^+/p junction Si photon-absorber microwires, of which a upper part was covered with an opaque catalyst and the remaining surface was passivated.

Two factors have been identified as limiting for the performance of photocathodes with opaque catalysts, insufficient catalyst loading (FF) and parasitic light absorption (J_{ph}) by the catalyst. The first was found to dominate when the microwire arrays had a large pitch and only small parts of the wires were covered by catalyst. The second was found at a low pitch and high catalyst coverage, where the performance was clearly limited by the light absorption performance of the underlying Si microwire photon absorber

The photocathode configuration presented here has been functionally assessed upon frontside illumination in an acidic electrolyte. Obviously, the relevance of the spatioselective catalyst deposition method presented here is depending on an overall device configuration in which frontside illumination is used. Therefore implementation of the photocathode in a full device is logically relevant in a wired device geometry.

We have demonstrated that, by careful design at the microscale, the chosen architecture provides high performance. The concept should also be applicable to other material combinations, provided that fabrication methods can be found to achieve similar structuring at the right scale, with those materials. The best-performing all earth-abundant HER half-cell investigated here consisted of a NiMo catalyst on the upper $2\ \mu\text{m}$ of microwires with a pitch of $12\ \mu\text{m}$, which demonstrated a η_{IRC} of 10.8 %.

7.4 Acknowledgements

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7.5 Materials and methods

Silicon microwires with radial n^+/p junctions were fabricated as reported before, but without the use of silicon dioxide as a hard mask.^{6,8,9} In short, cleaned silicon substrates (Okmetic) were covered with a 100 nm thick silicon-rich silicon nitride layer (SiRN) using low-pressure chemical vapor deposition (LPCVD). The SiN_x layer was removed from the front side using reactive ion etching, leaving a protective SiN_x layer at the back side. After

cleaning, a photoresist layer (OiR 906-12) on the front side was patterned by standard photolithography, resulting in $0.5 \times 0.5 \text{ cm}^2$ hexagonal arrays of circles ($4 \text{ }\mu\text{m}$ diameter, with $8 \text{ }\mu\text{m}$, $10 \text{ }\mu\text{m}$, $12 \text{ }\mu\text{m}$, $14 \text{ }\mu\text{m}$, $19 \text{ }\mu\text{m}$, or $24 \text{ }\mu\text{m}$ pitch) for each $2 \times 2 \text{ cm}^2$ sample. This resist layer functioned as a mask during deep reactive ion etching of silicon using the Bosch process. This process resulted in microwires with a length of approximately $40 \text{ }\mu\text{m}$. The samples were cleaned by an O_2/CF_4 plasma before further processing.

7.5.1 Local removal of SiO_2 over a defined length of Si microwire arrays

Scheme 7.1 gives a schematic representation of the fabrication and passivation of an array of microwires with a radial n⁺/p junctions and spatioselective catalyst deposition. In order to selectively electrodeposit a catalyst on microwires, a SiO_2 layer is used as masking layer for the electrodeposition of the catalyst. First, microwires are coated with three layers deposited by LPCVD, where each layer will form a hard mask for patterning the underlying layer. First, 100 nm of SiO_2 is deposited (400 mTorr , 40 sccm of tetraethoxysilane (TEOS) and 30 sccm of N_2 at $725 \text{ }^\circ\text{C}$, 10 min), followed by 60 nm of silicon-rich silicon nitride (SiRN; 150 mTorr , 77.5 sccm of SiH_2Cl_2 , 20 sccm of NH_3 and 150 sccm of N_2 at $850 \text{ }^\circ\text{C}$, 12 min), followed by 180 nm of polycrystalline silicon (250 mTorr , 50 sccm of SiH_4 and 250 sccm of N_2 at $590 \text{ }^\circ\text{C}$, 55 min). Lastly 134 nm of SiO_2 is formed by wet thermal oxidation ($900 \text{ }^\circ\text{C}$, 45 min) which consumes part of the polysilicon layer (see Scheme 7.1).

The first outer layer of SiO_2 is selectively removed from the top of the wires by ion beam etching under an angle (Oxford Ionfab 300Plus system – $2 \times 10^{-4} \text{ Torr}$; neutralizer: 5 sccm argon, 100 mA ; RF plasma: 125 W ; beam: 5 sccm argon, 50 mA , acceleration 300 V , angle of the beam with respect to surface normal 70° , substrate rotating at 5 rpm ; etching time: 10 min) and the rate of silicon removal was monitored using secondary ion mass spectrometry (SIMS). Subsequently the sample was etched for 5 min in 1% aqueous HF solution (see Scheme 7.1A).

Retraction of polysilicon ($\pm 500 \text{ nm/min}$) was done in 25% aqueous tetramethylammonium hydroxide (TMAH) solution at $70 \text{ }^\circ\text{C}$, for times varying between 4 and 72 min depending on the required height of the catalyst (see Scheme 7.1B). Next, the outer SiO_2 is removed by etching for 150 s in BHF ($12.5 \text{ wt. \% HF}$ in NH_4F), followed by SiRN etching, 25 min at $180 \text{ }^\circ\text{C}$ in 85% aqueous H_3PO_4 solution (see Scheme 7.1C). The polysilicon is removed by etching for 1 min in the TMAH solution as described above, and the pattern is transferred to the inner SiO_2 layer by etching for 2 min in BHF (see Scheme 7.1D). Finally the SiRN is removed by etching 25 min in a hot concentrated H_3PO_4 solution. After each wet etching step the wafers were thoroughly rinsed in deionized water, and then directly transferred to the next wet etching bath.

Scheme 7.1 Schematic outline of the process for spatioselective formation of a passivation layer and deposition of the catalyst. On the radially doped silicon microwires several layers are formed by LPCVD: silicon oxide, silicon nitride, and polysilicon. The outer part of the polysilicon is then thermally oxidized. (A) The thermal silicon oxide is opened at the top by inclined ion beam etching. (B) the polysilicon layer is retracted in hot TMAH solution to the desired height. (C) The thermal silicon oxide is removed in buffered HF solution, and the silicon nitride is etched in hot phosphoric acid solution. (D) The polysilicon is stripped in hot TMAH solution, and the LPCVD silicon oxide is etched in buffered HF solution. (E) The silicon nitride is stripped in hot phosphoric acid solution. An electrical back side contact is formed by sputtering aluminum. Finally the catalyst is deposited selectively by electrodeposition.

7.5.2 Electrical contacts

To ensure Ohmic contact to the solar cells, 1 μm aluminum/silicon alloy (99% Al, 1% Si) was sputtered (Oxford PL 400) on the front and backsides of each specimen, where on the front side a shadow mask was applied to protect the wire arrays from coating. In this way, a square electrode is formed around the wire array. Directly before coating all native silicon oxide was stripped from the silicon surface by etching for 1 min in 1 wt. % aqueous HF solution.

7.5.3 Catalyst deposition

NiMo was deposited by electrodeposition directly after forming the Ohmic contacts as described above, to limit formation of a new oxide layer on the silicon as much as possible. The Ni–Mo catalyst was deposited in a two-electrode setup, by solely contacting the $\text{n}^+\text{-Si}$ emitter through the aluminum contact on the front. The counter electrode was a Pt mesh. The electrodeposition bath consisted of an aqueous solution of 1.3 M nickel(II) sulphate hexahydrate, 0.5 M boric acid, and 25 mM sodium molybdate in Milli-Q water. The samples were covered with a ring so that only a circular area of 6 mm diameter was exposed to the electrolyte. Electrodeposition of Ni–Mo catalyst on the Si microwires was

performed at a constant current of 5.5 mA (20 mA/cm^2 with respect to projected sample area not covered by the ring) for time periods described in Table 7.2.

7.5.4 *JV* measurements

To measure the electrical characteristics of the coated Si microwires, samples were positioned perpendicular to a light source. *JV* measurements were recorded on a VersaSTAT 4 potentiostat using a linear voltage sweep from -0.7 to 0.7 V at a rate of 0.2 V/s . The light intensity was calibrated to 1 sun at the position of the sample, using the calibrated light source described below.

7.5.5 *JE* measurements

The coated microwire photocathodes were photoelectrochemically tested using a potentiostat (VersaSTAT 4) in a three-electrode configuration, where the microwire photocathode with an exposed projected surface area of 0.28 cm^2 acted as the working electrode (WE), a platinum wire mesh as the counter electrode (CE) and an Ag/AgCl electrode as the reference electrode (RE). The electrolyte used was 0.1 M aqueous sulfuric acid (H_2SO_4), pH 1. For dark *JE* measurement, the $\text{n}^+\text{-Si}$ emitter was contacted as the WE, directly through the aluminum contact on the front. For each sample, 5 full cyclic voltammetry measurements were done at a scan rate of 10 mV/s .

For *JE* measurements under illumination, the backside p-Si base was contacted through the aluminum contact on the back. Five full cyclic voltammetry measurements were done at a scan rate of 10 mV/s . Samples were positioned perpendicular to a solar spectrum light source. The light intensity was calibrated to 1 sun at the position of the sample.

The water layer on top of the sample was 15 mm thick. The absolute light absorption by the solution would lead to a decrease of 4 mA/cm^2 if it is assumed that every photon leads to an electron. The absorption was calculated by the Lambert-Beer relation and integrated over the solar spectrum in the range of $300 - 1200 \text{ nm}$ (see Figure 7.7).¹⁴

Figure 7.7 Plot of the ASTM reference pattern (black) and calculated transmittance through 15 mm of water (red). Each graph was integrated in the range of 300 to 1200 nm to calculate the maximum photo-current.

7.5.6 Light source and calibration

The light source that was used is a 300 W xenon arc light source, fitted with Air Mass filter (AM 1.5G) from Newport, Oriel Instruments. Upon installation, the lamp was calibrated by Newport. Before every measurement the lamp was checked by a calibrated reference solar cell (91150V). The 91150V reference cell and meter consists of a readout device and a 2 x 2 cm calibrated solar cell made of monocrystalline silicon and a KG5 window. The cell is equipped with a thermocouple assembled in accordance with IEC 60904-2. The certification is accredited by NIST to the ISO-17025 standard. It reads solar simulator irradiance in sun units, whereby one sun is equal to 1000 W/m² at 25 °C and AM 1.5 Global Reference.

The solar simulator was checked for spectral mismatch by a spectrometer (AvaSpec-ULS2048XL-EVO) fitted with a CC-VIS/NIR, slit size of 10 μm, 1.4 nm resolution in the range of 300 - 1050 nm, an integration time of 8 ms, and averaged over 60 scans. The spectral scan and an ASTM reference pattern are given in Figure 7.8. The current density (assuming 100% IPCE) of the calibrated lamp and the ASTM spectrum match very well, 40.1 mA/cm² and 40.8 mA/cm² respectively, in the range of 300-1050 nm.

Figure 7.8 Spectral irradiance plot of an ASTM reference pattern (red) and of the solar simulator used for the measurements in this paper (black).

7.6 References

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Chapter 8

Nickel Silicide Interlayers Render Si Microwire Photocathodes Stable in Alkaline Electrolyte

Most of the photoanodes that are commonly applied in solar fuel research (*e.g.* Fe_2O_3 , BiVO_4 , TiO_2 , or WO_3) are only active and stable in alkaline electrolytes. Silicon (Si)-based photocathodes on the other hand are mainly studied under acidic conditions, due to their instability in alkaline electrolytes. This mismatch in suitable electrolytes leads to an incompatibility especially when a photoanode and –cathode are integrated into a solar-to-fuel device. Here, we show the fabrication of a highly efficient Si microwire photocathode that is made stable in alkaline solutions by incorporating a nickel silicide (NiSi) interlayer between the catalyst and the Si microwires. Spatiotemporal electrodeposition of nickel (Ni) on top of the Si microwires appeared insufficient to shield the underlying Si from the electrolyte, and microwires were etched within 1 h of operation. NiSi, an alloy of nickel and silicon, is stable in alkaline electrolytes. More importantly, the in-diffusion of nickel into the Si structure upon thermal annealing enables the formation of a defect-free NiSi interlayer, even when the electrodeposition of the Ni precursor on top of the microwires provides particle growth and leaves pinholes. After subsequent electrodeposition of a catalyst (nickel molybdenum, NiMo) on top of the NiSi layer, a highly active, alkaline stable, Si-based photocathode was obtained. The best performing, all earth-abundant microwire array devices exhibited a short-circuit photocurrent density of 29.8 mA/cm^2 , a photovoltage of 554 mV, and a fill factor of 61% under AM 1.5G of simulated solar illumination, which resulted in a photon-to-hydrogen efficiency of 10.1% in 1 M KOH.

8.1 Introduction

In a complete photoelectrochemical cell, a photocathode and anode are coupled together, preferably in one electrolyte, which is either acidic or alkaline. A major shortcoming of PEC cells that operate in an acidic electrolyte is the limited range of materials for the oxygen evolution reaction (OER) catalyst.¹⁻³ The vast majority of PEC cell-compatible OER catalysts in acidic electrolyte is based on oxides of ruthenium (Ru) and, especially, iridium (Ir) which are very scarce noble metals,⁴ with annual production capacities far below that of Pt.^{1,5} Hence, pricing and availability of Ru and Ir can be considered as a major issue for the large-scale application of PEC cells in acidic electrolyte. Furthermore, McCrory *et al.* benchmarked many known OER and HER catalysts in both acidic and alkaline electrolytes and found the average overall overpotential at 10 mA/cm² for the HER and OER together in acidic electrolyte to be ~1.26 V (1 M H₂SO₄), as opposed to ~0.63 V (1 M NaOH) in alkaline medium.² To date, a number of different reaction mechanisms have been proposed for the OER in acidic or alkaline electrolytes, based on kinetic studies⁶⁻⁸ or density functional theory (DFT) calculations.⁹⁻¹¹ However, none of the OER mechanisms proposed for heterogeneous catalysts has yet been experimentally validated regarding the required overpotential of the OER in acidic or alkaline electrolytes.¹ Therefore, there is a strong drive to produce HER photocathodes that are stable, active, and earth-abundant in alkaline medium.

Our previously fabricated n⁺/p-Si microwire array photocathodes with spatioselectively deposited nickel molybdenum (NiMo) have shown one of the highest reported efficiencies (*i.e.* $\eta_{\text{irc}} = 10.8\%$, $V_{\text{oc}} = 495$ mV, $I_{\text{sc}} = 35.5$ mA/cm², and $FF = 62\%$) in acidic electrolyte.¹² Crystalline Si has a high stability in acidic medium, but it is etched quickly (~2 $\mu\text{m}/\text{h}$) in alkaline solutions. Unfortunately NiMo does not provide a conformal coverage over the entire Si structure, and thus the underlying Si substrate will be etched in an alkaline electrolyte, reducing the lifetime of Si/NiMo microwire photocathodes substantially. This problem can potentially be overcome by introducing an intermediate closed layer between the catalyst and the n⁺-Si emitter. Such a layer should be (i) deposited spatioselectively only on the interface between the silicon and the NiMo overlayer, (ii) electrically conductive between the n⁺-Si emitter and the catalyst on top, (iii) stable in alkaline solution, and (iv) defect free.

Electrodeposition of a metal is an excellent choice for the first three requirements. Many metals can be spatioselectively deposited on the top side of Si microwires (i) by electrodeposition,¹³ of which metallic nickel (Ni) (ii) can be grown in a conformal manner over high-aspect-ratio structures and is stable between pH 5 and 14 (iii).¹⁴ However, literature shows that these layers are not defect free, since electrodeposition usually progresses via particle growth, inherently leaving pinholes as a result,¹³ through which the Si can still be etched by the alkaline electrolyte.

In order to comply with the fourth requirement for defect-free layer formation, we envisaged the use of a Ni layer that is transformed into nickel silicide (NiSi) at locations where it is in contact with Si, in a self-aligned and repairing process. NiSi is an effective and proven masking material for selective Si etching in KOH, in which it is not being etched at a noticeable rate, and NiSi is highly conductive.^{15,16} More importantly, the formation mechanism of NiSi provides the opportunity to repair possible defects introduced in the preceding step of the electrodeposition of Ni, thus complying with all four requirements stated above. NiSi is the product resulting from Ni diffusion into the underlying Si substrate, which follows Fick's diffusion law. Through this process, pinhole defects in the Ni layer inherent to the electrodeposition process, can be corrected, as long as the pinholes are smaller than twice the diffusion distance.

Here we show the chemical resistivity and applicability of NiSi as an interlayer for the protection of Si microwires in alkaline electrolyte. We compare its performance to electrodeposited Ni. Furthermore, we apply the NiSi interlayer in a photocathode that is functional in alkaline medium, by the fabrication of a Si microwire array with a radial n⁺/p-junction, the spatioselective formation of a conformal interlayer of NiSi, and the subsequent electrodeposition of NiMo as a highly active and stable HER catalyst in alkaline medium.² As we have demonstrated previously, by the spatioselective functionalization of the Si microwire with a catalyst, light blocking due to the catalyst is kept to a minimum.¹² The activity and stability of the photocathode are assessed for prolonged periods of time under strong alkaline conditions.

8.2 Results and discussion

8.2.1 Development of a NiSi interlayer

Microwires with a radial n⁺/p junction of ~900 nm, a diameter of 4 μm, a length of 40 μm, and a range of pitches between 6 and 19 μm were fabricated as previously reported (see Materials and Methods).¹⁷⁻²⁰ The fabrication scheme of the microwire arrays with spatioselectively deposited Ni or NiSi interlayers is schematically depicted in Scheme 8.1. First, the conformal silicon rich silicon nitride (SiN_x) layer deposited all over the microwires was retracted to ~100 nm below the top of the microwires, thereby exposing the underlying n⁺-Si emitter (see Chapter 7.2 for detailed scanning electron microscope (SEM) images). Ni was electrodeposited spatioselectively only at the tops of the microwire array because of the good conductivity of the emitter exposed at the top, and the electrical insulation provided by the SiN_x layer elsewhere on the pillar and between the pillars.

Scheme 8.1. Fabrication scheme for alkaline-stable photocathodes, starting from a microwire array with a spatioselectively etched SiN_x protection layer, which acts as a masking layer for (A) the electrodeposition of Ni on top of the wires, followed by either (B) direct electrodeposition of NiMo on top of the Ni-covered microwire array, or (C) formation of NiSi by RTA and removal of the remaining Ni by wet etching, followed by (D) electrodeposition of NiMo on top of the NiSi-covered microwire array.

To achieve conformal Ni deposition, the use of additives to the electrolyte solution plays a major role. Here, two types of organic additives (*i.e.* saccharin and sodium dodecyl sulfate (SDS)) were used simultaneously. The incorporation of sulfur atoms from the saccharin results in smoother, more ductile deposits.²¹ SDS reduces the pitting caused by clinging of H_2 bubbles to the substrate which intervene with the Ni formation.²¹

NiSi is a widely studied material in solid-state devices for electronic applications, owing to its properties: a broad temperature range (400 – 700 °C) in formation (as opposed to other silicides, *e.g.* TiSi, CoSi, RhSi), a low resistivity ($\sim 10\text{--}18\ \mu\Omega\ \text{cm}$), and ease of fabrication.^{22,23} NiSi has been found to grow by a diffusion-controlled mechanism, whereby the Ni atoms diffuse through the growing NiSi layer with an activation energy between ~ 1.75 and $1.85\ \text{eV}$.²³ The pre-exponential factor, D_0 , for the diffusion of Ni is mainly dependent on the pre-treatment of the Si sample before Ni deposition (*e.g.* with native oxide, or stripped in 1% HF) and is in the range of $1\text{--}2\ \text{cm}^2/\text{s}$.²⁴ Vallei *et al.* developed a model to interpret spectroscopic ellipsometry data, used to investigate the thickness of the formed NiSi in a non-invasive manner.²⁵ Here, we used this model to study the etch rate of NiSi in 1 M KOH by ellipsometry.

Here, we fabricated microwire arrays with spatioselectively deposited NiSi by means of rapid thermal annealing (RTA, 485 °C and a holding time of 30 s; see Scheme 8.1C) of pre-fabricated Ni-covered Si microwire arrays. After the RTA step, the residual Ni layer was etched in a piranha solution (*i.e.* 3:1 v/v H_2SO_4 : 30% aq. H_2O_2). The thickness of the NiSi layer was measured on a flat area of the substrate next to the microwire array by ellipsometry, which resulted in a thickness of $\sim 78\ \text{nm}$, which is in good agreement with the parameters given above (D_0 of $2\ \text{cm}^2/\text{s}$ and an activation energy of $1.8\ \text{eV}$). Furthermore, the conductivity after the formation of NiSi was measured by a four-point

probe measurement, which resulted in a resistivity of $33 \mu\Omega \text{ cm}$ which is only slightly higher than that reported in literature ($10\text{--}18 \mu\Omega \text{ cm}$).²³

The etching of Si in aqueous potassium hydroxide (KOH) is well studied and documented, although often the applied etching baths are highly concentrated ($> 20 \text{ wt.}\%$) and used at elevated temperature ($> 60 \text{ }^\circ\text{C}$). Here we used 1 M KOH ($2 \text{ wt.}\%$) at room temperature, because that would be closer to the intended operating condition of a solar fuel device, and we tested the chemical resistivity of each material individually. The necessity of protecting Si becomes clear from Table 8.1: Si etches at a high rate, although doping of the microwires reduces the etch rate significantly.²⁶ Even at these reduced etch rates, unprotected microwire arrays would be etched completely within one day. In contrast, both Ni and NiSi show a very high chemical resistivity under these conditions.

Table 8.1 Etch rates in 1 M KOH of different materials used in the fabrication process

	n-Si	n ⁺ -Si	n ⁺⁺ -Si	SiN _x	NiSi	Ni
Etch rate	2.13 $\mu\text{m/h}$	0.75 $\mu\text{m/h}$	0.12 $\mu\text{m/h}$	0.2 nm/week	< 0.1 nm/week	< 0.1 nm/week

SEM images were acquired after immersing the array samples in a 1 M KOH solution for 24 h, with either Ni or NiSi as the interlayer. Figure 8.1A and B show SEM images of a sample that was only protected by a spatioselective Ni layer on top of the microwire. Figure 8.1A shows an overview of the array, and most of the microwires were affected, etched, or completely removed. Figure 8.1B shows a zoom-in of Figure 8.1A, and only hollow sleeves of SiN_x are visible whereas the Ni caps are absent.

Figure 8.1 SEM images of Si microwire arrays after 24 h in 1 M KOH: (A) with a Ni interlayer (without annealing to NiSi, scale bar is 250 μm); (B) a zoom-in of (A), which shows the remaining hollow SiN_x sleeves (scale bar is 10 μm); (C) with a NiSi interlayer (scale bar is 100 μm); (D) a zoom-in of (C) (scale bar is 20 μm). (The white spots in (D) are alkaline residues formed after taking the sample out of solution).

For samples with a slightly larger Ni capping layer (upper $\sim 2\ \mu\text{m}$), released Ni caps were found at the bottom of the substrate (see Figure 8.2). Scallops resulting from the fabrication process of the microwires are clearly visible within the caps, further indicating the stability of Ni under the alkaline test conditions, confirming that only the Si has been etched while leaving the Ni structure intact. These results indicate that the instability of the Si structures occurs at the interface between SiN_x and Ni, or at possible pinholes in the Ni layer.

8

Figure 8.1C shows an overview of microwires with a NiSi interlayer after 24 h in 1 M KOH. All of the microwires are still intact, which indicates that NiSi provides continuous protection of the underlying silicon under the harsh alkaline conditions. Figure 8.1D shows a close-up of the microwires in Figure 8.1C, clearly confirming that the microwires are undamaged.

Figure 8.2 SEM images of spatioselectively deposited Ni on top of Si microwires. (A) Microwire array with Ni on the upper ~2 μm , (B) Zoom in of (A), viewed from the bottom side. (C,D) Ni caps after immersion of the substrates in 1 M KOH. The inside clearly shows the scallops resulting from the microwire fabrication process, indicating conformal coverage of the Ni by electrodeposition. (E) Zoom-out of the microwire array after deposition in 1 M KOH, and affected microwires are clearly visible.

Defects within the Ni layer are clearly detrimental for the stability of the underlying Si microwire array. Even though we optimized the Ni deposition parameters, pinholes are most likely still present within several of the millions of microwires/ cm^2 . Even a single pinhole could eventually lead to dissolution of the complete silicon device, and should therefore be prevented. Annealing the sample by RTA does not only form a chemically resistive NiSi layer, it may also (i) repair defects within the layer and (ii) seal off the interface at the top edge of the SiN_x protection layer, both attributed to the diffusion process of the Ni atoms into the Si material at the Ni-Si interface. In order to show the above mentioned effects, we produced two test structures. Figure 8.3A and B shows SEM images in order to visualize the repair of defects (i) and Figure 8.3C to E to seal interface between the protective SiN_x layer and underlying Si (ii).

Figure 8.3 SEM images of a cross-section of a microwire (broken wires visible on the left side in both images), with scallops resulting from the fabrication process: (A) After Ni sputtering, and (B) after subsequent annealing of the sample and stripping off the residual Ni layer (bright contrast implies a conductive layer). Scale bars are 300 nm. (C) Microwire with a spatioselective electrodeposited Ni layer. Scale bar is 2 μm . (D) Cross sectional image after Ni diffusion and stripping off the residual Ni layer. Scale bar is 2 μm . (E) Zoom-in of the interface between Si, SiN_x and NiSi of (D). Scale bar is 200 nm.

Figure 8.3A shows a cross-section of a Si microwire with sputtered Ni and Figure 8.3B after annealing the sample by RTA. Sputtering of Ni (bright contrast in Figure 8.3A) resulted in a non-conformal layer over the Si microwire array, in particular at the side walls where scallops are present, thus providing induced defects. The top of a scallop causes a shadowing effect for the incoming sputtered material and, as a result of the high directionality of the material flux during sputtering, no material is found within the troughs of the scallops. Such defects in the Ni layer would lead to attack of the exposed Si under the harsh alkaline conditions. After annealing and stripping the remaining Ni layer, a conformal NiSi layer is visualized by the SEM image in Figure 8.3B. Ni not only diffused orthogonally inward, but also into the troughs of the scallops where no Ni source was present at the Si interface, thereby forming a conformal and closed NiSi layer. The diffusion distance of approx. 100 nm is apparently sufficient to seal the defects induced by the scalloping.

Figure 8.3C shows a SEM image of a 5 μm long microwire, whereby the upper 2.5 μm was spatioselective functionalized with electrodeposited Ni, and the lower 2.5 μm is SiN_x . Figure 8.3D shows a cross-sectional image of a spatioselective functionalized Si microwire after Ni diffusion, of which Figure 8.3E shows a zoom-in at the interface of Si, SiN_x and NiSi. A conformal layer of NiSi is formed completely over the top of the microwire (light grey), as in Figure 8.3B. More importantly, the zoom-in (Figure 8.3E) clearly visualizes that a NiSi layer is formed in-between the Si and SiN_x layer. Ni has apparently diffused downward in-between the conformal SiN_x layer and the Si microwire, thereby effectively protecting the underlying Si against the alkaline electrolyte. Generally, as long as the defects are smaller than twice the diffusion distance of Ni during the RTA step, defects occurring in the preceding Ni deposition step will be repaired.

8.2.2 Photocathodes with a NiSi interlayer

After the successful development of the NiSi interlayer for providing alkaline-stable Si microwire arrays, NiMo was deposited as a catalyst on top of microwire arrays with Ni as well as NiSi as interlayer. Electrodeposition was employed in order to cover all microwires with a catalyst layer. NiMo was deposited by contacting the n^+ -emitter, as was performed for the preceding Ni deposition step. Successful structures of NiMo-coated wires with Ni and NiSi interlayers are shown in Figure 8.4. The deposition of NiMo on both substrates (*i.e.* Figure 8.4A for Ni, Figure 8.4B for NiSi) resulted in an open granular structure. This highlights even further the necessity for a sealed interlayer, as NiMo alone is not adequate to protect the underlying Si microwire.

Figure 8.4 SEM images of Si microwire arrays with NiMo as a catalyst, with (A) Ni and (B) NiSi as interlayer. Scale bar is 2 μm .

The emitter in a Si microwire photocathode is n-type, and NiSi forms a Schottky barrier on n-Si of 0.67 eV.²⁷ It is therefore important to overcome this barrier, since it decreases the performance of a photocathode tremendously by introducing an extra resistance. Wong *et al.* showed that this barrier can be reduced to as low as 0.07 eV, by applying an n-type, antimony (Sb) doping step.²⁷ Here, instead of Sb, we investigated the role of the

P dopant concentration on the barrier. Three planar samples were prepared with different dopant levels, n-Si (10^{16} cm^{-3}), n⁺-Si (10^{19} cm^{-3}) and n⁺⁺-Si (10^{21} cm^{-3}), with NiSi on top.

Figure 8.5A shows the current–voltage (*JV*) characteristics of NiSi on n-Si, with three different doping levels. All the measured devices had an active area of $1 \times 1 \text{ cm}^2$. At low doping levels, *i.e.* n-type (10^{16} cm^{-3}), a typical Schottky characteristic was observed for the formed junction (see solid line in Figure 8.5A). At a higher doping level, *i.e.* n⁺-type (10^{19} cm^{-3}), the effective barrier height was reduced significantly. Indeed, the forward current increased substantially, but a deviation from linear behavior is still observed around 0 V. By further increasing the doping level, to n⁺⁺-type (10^{21} cm^{-3}), the barrier height was lowered further, and Ohmic behavior was observed over the range of -2 to 2 V. The effective barrier height values were not extracted since low-temperature conditions (*i.e.* <100 K) are required to ensure accurate measurements.²⁸

Figure 8.5. Plots of current density vs. potential for (A) planar Si devices with NiSi interlayers at three different n-type Si doping levels, and (B) planar Si devices with and without NiMo catalyst on a Ni or NiSi interlayer, at different doping levels as in (A).

Figure 8.5B shows the dark *JE* measurements for HER electrocatalysis at planar Si substrates, tested in 1 M KOH. Again, the influence of the doping level of n-Si is included. Although the band edge position of Si straddles the H^+/H_2 redox couple, planar Si shows almost no catalytic activity over a large overpotential range (not shown in Figure 8.5B), which underlines the requirement for a catalyst. Furthermore, unprotected n-Si is etched rapidly ($\sim 2 \mu\text{m/h}$) under these conditions (see Table 8.1). The addition of a smooth Ni film on the surface improves the catalytic activity substantially, as shown in Figure 8.5B. By electrodepositing NiMo on top of the already deposited Ni, the activity is increased even further (see Figure 8.5B, NiMo-Ni on n⁺⁺-Si). However, from the above mentioned KOH immersion experiments, it is known that Ni alone does not protect the interface of the Si microwires, and NiSi is required to preserve the microwires.

NiSi was prepared as described above, on samples with different doping levels. After removal of the remaining Ni, NiMo was deposited on top (see Scheme 8.1D) and the resulting dark *JE* behavior was characterized (Figure 8.5B). For n-Si and n⁺-Si, the activity was less than for the NiMo-Ni (on n⁺⁺-Si) sample. This is due to the Schottky barrier formed at lower doping levels, as described above. By increasing the doping level this barrier is overcome, and the activity of NiMo-NiSi on n⁺⁺-Si appeared to be the same as NiMo on a metallic Ni layer. Therefore a doping level of 10²¹ cm⁻³ was applied for the n-emitters.

Previously, we optimized Si microwire photocathodes with respect to (optimum values between brackets): doping depth of the emitter (900 nm), microwire length (40 μm), pitch (12 μm), and catalyst coverage (upper ~100 nm).^{12,19} Here, we used these settings to fabricate a microwire array photocathode, but now with an emitter doping level of 10²¹ cm⁻³ to ensure Ohmic contact between the catalyst and the NiSi interlayer, while using NiMo as the HER catalyst. *JE* measurements for Si microwire arrays with spatioselectively deposited NiMo catalyst on a NiSi interlayer were performed in a 1 M KOH electrolyte under AM1.5G illumination, and the results are presented in Figure 8.6A. The photocathode is characterized as an ideal regenerative cell (IRC), which is fully analogous to a solid-state PV cell, and therefore the efficiency (η_{IRC}) of these systems is described by a similar equation, see Equation 8.1.²⁹

$$\eta_{IRC} = \frac{V_{OC} J_{ph}(E_{H_2/H^+}) FF}{P_{in}} \quad (8.1)$$

Figure 8.6 (A) *JE* measurements of microwire photocathodes with a NiSi interlayer and functionalized with NiMo catalyst, see Scheme 8.1C/D. The average of four different samples prepared with the same settings is shown. (B) Recorded current density under supplied potential of such a Si microwire array photocathode under continuous operation at 10 mA/cm² and AM 1.5G simulated sunlight.

The values of *FF*, *V_{OC}* and *J_{ph}(E_{H₂/H⁺}*) in Equation 8.1 are referenced to the equilibrium potential of the half-reaction being performed at the photocathode, and *P_{in}* is the light power input (AM 1.5G, 100 mW/cm²). All relevant values of the photocathode are presented in Figure 8.6A. To our knowledge this half-cell gave the highest *V_{OC}*, *I_{SC}* and *FF*

values reported so far for a photocathode in highly alkaline conditions, with an overall efficiency of 10.1%.

The NiMo catalyst is expected to have infinite stability under highly alkaline conditions. To assess the durability of this catalyst in the microwire configuration, we measured the current density at a constant potential vs RHE. An applied bias of 500 mV vs RHE resulted in a current density of $\sim 10 \text{ mA/cm}^2$ and was maintained for 72 h under AM 1.5G light (see Figure 8.6B). These values for potential and current density are in good agreement with the JE measurement given in Figure 8.6A. The average recorded current density was stable over the entire period of time, and the current only oscillated slightly, which is most probably due to H_2 bubble formation and detachment. Furthermore, the Si microwire arrays were unaffected by the immersion in 1 M KOH for prolonged periods of time, which indicates the excellent passivation properties of the NiSi interlayer, positioned between the Si microwires and the NiMo catalyst.

8.3 Conclusions

We have designed, fabricated and experimentally validated a broadly applicable photoelectrode architecture that circumvents not only the trade-off between catalytic activity and optical absorption, but also provides stability in harsh alkaline electrolyte. For the latter reason, an interlayer of NiSi was developed to effectively shield the underlying Si microwire from the alkaline electrolyte, in which Si microwires normally are being etched rapidly. By annealing a sample with spatioselectively electrodeposited Ni, pinholes within the Ni layer were repaired effectively by Ni diffusion during the NiSi formation step. To ensure Ohmic behavior between the microwire array and the NiSi interlayer, a high doping level of the Si emitter layer is required to overcome an undesirable Schottky barrier. Lastly, by spatially decoupling light absorption and catalytic activity on high-aspect-ratio silicon microwires with a radial n^+/p -junction, a highly efficient, *i.e.* $\eta_{\text{IRC}} = 10.1\%$, solar-driven Si photocathode that is stable in alkaline electrolyte was achieved, which maintained a constant activity for several days of operation.

Our future research will focus on the integration of these Si microwires with spatioselective catalyst deposition in a full solar-to-fuel device. The improved chemical resistivity of these Si microwires in alkaline electrolyte should enable the identification of a suitable combination with a higher bandgap photoanode.

8.4 Materials and methods

8.4.1 Fabrication of radial n⁺/p junctions in silicon microwire arrays

Silicon microwires with radial n⁺/p junctions were fabricated as reported before, but without the use of silicon dioxide as a hard mask.^{17,19,20} In short, cleaned silicon substrates (Okmetic) were covered with a 100 nm thick silicon-rich silicon nitride layer (SiRN) using low-pressure chemical vapor deposition (LPCVD). The SiN_x layer was removed from the front side using reactive ion etching, leaving a protective SiN_x layer at the back side. After cleaning, a photoresist layer (OiR 906-12) on the front side was patterned by standard photolithography, resulting in 0.5 x 0.5 cm² hexagonal arrays of dots with a pitch of 12 μm, for each 2 x 2 cm² sample. This resist layer functioned as a mask during deep reactive ion etching of silicon using the Bosch process. This process resulted in microwires with a length of approximately 40 μm or 5 μm (depending on the etching time), and the samples were cleaned by an O₂/CF₄ plasma before further processing.

Doping was performed on freshly cleaned substrates by depositing a dopant-containing oxide layer (SOD 509, Filmtronics), followed by a thermal drive-in step to diffuse the dopant into the silicon. In case of n⁺/p junctions, p-type substrates were covered with a phosphorus oxide layer by depositing a spin-on dopant. Thermal diffusion was performed at 900 °C for 15 min under nitrogen flow.

8.4.2 Local removal of SiN_x from the tops of microwire arrays

In order to electrodeposit selectively a catalyst on the tops of the microwires, a SiN_x layer was used as patterning layer for the electrodeposition of the protective NiSi cap and of the catalyst. Microwires were coated with four layers deposited by LPCVD, hereby each layer is a protective layer for the subsequent underlying layer upon patterning. First, 70 nm of SiN_x was deposited (150 mTorr, 77.5 sccm of SiH₂Cl₂, 20 sccm of NH₃ and 150 sccm of N₂ at 850 °C), followed by 100 nm of SiO₂ (400 mTorr, 40 sccm of TEOS and 30 sccm of N₂ at 725 °C), followed by 180 nm of amorphous silicon (250 mTorr, 50 sccm of SiH₄ and 250 sccm of N₂ at 590 °C), and lastly ~100 nm of SiO₂ by wet thermal oxidation (900 °C, 45 min) (see Scheme 8.2).

The first outer layer of SiO₂ was selectively removed by ion beam etching (Oxford Ionfab 300Plus system – 2x10⁻⁴ Torr; neutralizer: 5 sccm argon, 100 mA; RF plasma: 125 W; beam: 5 sccm argon, 50 mA, acceleration 300 V; etching time: ~10 min) and the rate of silicon oxide removal was monitored using SIMS. Subsequently the sample was etched for 5 min in 1% aqueous HF solution (see Scheme 8.2A).

Retraction of polysilicon (500 nm/min) was done in 25% aqueous tetramethylammonium hydroxide (TMAH) solution at 70 °C for 1 min (see Scheme 8.2B) in the case of 40 μm

microwires or 5 min for 5 μm long microwires. Next, the outer SiO_2 and inner SiO_2 were simultaneously removed by etching 2 min in BHF (see Scheme 8.2C). The polysilicon was removed by etching 1 min in the TMAH as described above, and the pattern was transferred to the underlying Si microwire layer by etching SiN_x 25 min at 180 $^\circ\text{C}$, 85% aqueous H_3PO_4 solution (see Scheme 8.2D). Finally the SiO_2 was removed by etching 2 min in BHF solution (see Scheme 8.2E).

Scheme 8.2 Schematic outline of process for spatioselective formation of a passivation layer and the catalyst. On the radially doped silicon microwires several layers are formed by LPCVD: silicon nitride, silicon oxide and polysilicon. The outer part of the polysilicon is then thermally oxidized. (A) The thermal silicon oxide is removed from the top by inclined ion beam etching. (B) the polysilicon layer is retracted in hot TMAH solution to the desired height. (C) The thermal silicon oxide is removed in buffered HF solution, and the LPCVD SiO_2 is etched in BHF solution. (D) The polysilicon is stripped in hot TMAH solution, and the LPCVD SiN_x is etched in hot H_3PO_4 solution. (E) The SiO_2 is stripped in BHF solution, an electrical back side contact is formed by sputtering aluminium.

8.4.3 Protective Ni and NiSi deposition

To ensure Ohmic contact to the solar cells, 1 μm aluminum/silicon alloy (99% Al, 1% Si) was sputtered (Oxford PL 400) on the front and backsides of each specimen, where on the front side a shadow mask was applied to protect the wire arrays from coating. In this way, a rectangular electrode was formed around the wire array.

Onto the freshly exposed Si tops of the microwire arrays, Ni was deposited by electrodeposition, Scheme 8.1A. Ni was deposited in a two-electrode setup, by solely contacting the emitter ($\text{n}^+\text{-Si}$) while the counter electrode was a platinum mesh. The electrodeposition bath consisted of an aqueous solution of 1.3 M nickel(II) sulfate, 0.5 M boric acid, 3.5 μM sodium dodecyl sulfate, and 3 μM saccharin in Milli-Q water. The electrodeposition of Ni on the Si microwires was performed at a constant current of 20 mA/cm^2 for 30 s.

A NiSi alloy was fabricated by RTA, Scheme 8.1C. A sample with a Ni cap was processed in an RTA setup (Surface Science Intergration – Solaris 150). Using a purge of 60 s in N₂, a heating ramp of 25 °C/s was applied, then a holding temperature of 400 °C for 30 s, followed by natural cooling to room temperature. The unreacted Ni was removed by etching in piranha (H₂SO₄:H₂O₂ - 3:1) for 2 min.

8.4.4 Catalyst deposition

Onto the freshly prepared NiSi tops of the microwire arrays, NiMo was deposition by electrodeposition, Scheme 8.1D. The NiMo catalyst was deposited in a two-electrode setup, by solely contacting the emitter (n⁺-Si) while the counter electrode was a platinum mesh. The electrodeposition bath consisted of an aqueous solution of 1.3 M nickel(II) sulfate, 0.5 M boric acid, and 25 mM sodium molybdate in Milli-Q water. The final pH was 4.4. The electrodeposition of NiMo catalyst on the Si microwires was performed at a constant current of 20 mA/cm² for 90 s.

8.4.5 NiSi formation on n-type Si with different dopant levels

Two cleaned n-type silicon (n-Si, 10¹⁶) substrates (Okmatic) were covered with a 100 nm thick silicon-rich silicon nitride layer (SiN_x) using low-pressure chemical vapor deposition (LPCVD) (150 mTorr, 77.5 sccm of SiH₂Cl₂, 20 sccm of NH₃ and 150 sccm of N₂ at 850 °C). The SiRN layer was removed from the backside using reactive ion etching (RIE) (Adixen AMS100DE; octafluorocyclobutane (C₄F₈) and methane (CH₄)), leaving a protective SiN_x layer at the front side. Three wafers (one bare extra) were covered with phosphorus oxide by a LPCVD process (350 mTorr, 330 sccm PH₃ and 150 sccm O₂, 650 °C). A drive-in step of 15 min at 1050 °C in an atmospheric oven was used to dope the backside of n-Si to 10¹⁹ cm⁻³ and the bare wafer on both sides. The remaining dopant oxide layer was removed by immersing the wafers in buffered hydrogen fluoride (1:7, HF:NH₄F), followed by oxidation at 800 °C for 15 min and etching in 1% HF (15 min), rinsing and drying. One cleaned wafer was again covered with SiN_x and the front side was etched by RIE. Afterwards a spin-on dopant (SOD 509, Filmtronics) was spun on the front side at 4000 rpm, 30 s, and dried at 200 °C for 30 min. The doping was achieved by a drive-in temperature of 900 °C, and a drive-in time of 15 min in an atmospheric oven, to reach a doping level of 10²¹ cm⁻³. The remaining dopant oxide layer was removed by immersing the wafers in buffered hydrogen fluoride (1:7, HF:NH₄F), oxidation at 800 °C for 15 min and etching in 1% HF (15 min), rinsing and drying. The SiN_x layer of all wafers was removed by immersion in 50% HF for 30 min and the wafers were rinsed and dried.

On the three different wafers, 200 nm of Ni was sputtered at the front side and 1 μm of Al/Si (99%/1%) at the backside. NiSi was formed as stated above. From every wafer, 1x1 cm² were cut and three different test structures were thus obtained as schematically shown in Figure 8.7.

Figure 8.7 Three different structures to test the Schottky barrier height of Figure 8.5A. (A) only the backside overdoped, to ensure Ohmic contact with n-Si. (B) overdoped front and backside to 10^{19} cm^{-3} . (C) Overdoped backside to 10^{19} cm^{-3} and front side to 10^{21} cm^{-3} .

8.4.6 *JE* measurements

The Schottky barrier was tested in a four-electrode setup, in order to eliminate the contact resistance of the potentiostat (VersaSTAT 4) from the measurement. The tested planar surface was $1 \times 1 \text{ cm}^2$. In all three tested cases, the working electrode and secondary electrode were placed at the NiSi side (see Figure 8.7), and the reference and counter electrode at the Al/Si side (see Figure 8.7).

The coated microwire photocathodes were photoelectrochemically tested using a potentiostat (VersaSTAT 4) in a three-electrode system, where the microwire photocathode with an exposed projected surface area of 0.28 cm^2 acted as the working electrode, a platinum wire mesh as the counter electrode and an Ag/AgCl electrode as the reference electrode. The electrolyte used was 1 M potassium hydroxide (KOH), pH 14. For dark *JE* measurement, solely the emitter (n^+ -Si) was contacted. For each sample, five full cyclic voltammetry measurements were done at a scan rate of 10 mV/s .

For *JE* measurement under illumination, solely the backside base (p-Si) was contacted. Five full cyclic voltammetry measurements were done at a scan rate of 10 mV/s . Samples were positioned perpendicular to a light source. The water layer on top of the sample was 5 mm. The absolute light absorption by the electrolyte was 3 mA/cm^2 as calculated from the Lambert-Beer law in the range of $300 - 1200 \text{ nm}$.³⁰

The light source is a 300 W xenon arc light source, fitted with an Air Mass filter (AM 1.5G) of Newport, Oriel Instruments. Upon installation of the lamp, the lamp was calibrated by Newport. Before every measurement the calibration was checked by a reference solar cell and meter, $2 \times 2 \text{ cm}$ with a fused silica window calibrated by Newport.

The solar simulator was checked for spectral mismatch by AvaSpec-ULS2048XL-EVO fitted with a CC-VIS/NIR, slit size of $10 \mu\text{m}$, 1.4 nm resolution in the range of $300 - 1050 \text{ nm}$, an integration time of 8 ms , and averaged over 60 scans. The current density of calibrated lamp and ASTM match very well, 40.1 mA/cm^2 and 40.8 mA/cm^2 respectively, in the range of $300\text{-}1050 \text{ nm}$.

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Chapter 9

A Stand-Alone Membrane-Embedded Microporous Photoelectrochemical Cell

Wireless photoelectrochemical (PEC) devices promise an easy device fabrication concept together with reduced losses by removal of wiring. However, new losses occurs, primarily in the form of ionic resistances caused by long proton diffusion distances between anode and cathode. These can potentially be solved by creating micro-porosity in the devices, but such pores may lead to gas crossover. Therefore, to develop an efficient, scalable, and technologically safe PEC cell, a cation-exchange membrane is mandatory to separate the gaseous products and minimize the recombination losses in the system. As a result, strong acidic electrolytes are required to reduce the solution transport losses in the cell and to obtain high transfer rates for protons through the membrane. The efficiency limits, gas crossover behavior, formation of local pH gradients near the electrode surfaces, and safety characteristics have been evaluated experimentally as well as by use of multi-physics modeling for a wireless PEC cell that operates with bulk electrolyte solutions in 1 M H_2SO_4 . The membrane-embedded microporous PEC cell utilized a triple Si junction cell as the light absorber, Pt and IrO_2 as electrocatalysts for the hydrogen (HER) and oxygen-evolution reactions (OER), respectively. Although the solar-to-electrical efficiency of the stand-alone triple-junction was **10.8%**, the solar-to-hydrogen (STH) conversion efficiency for the integrated membrane PEC cell was limited under steady-state operation to 7%. The latter was mainly due to absorption losses by the incorporation of micropores and catalyst microdots. Furthermore, the introduction of a Nafion® membrane ensured an intrinsically safe PEC cell, by reducing the total gas crossover to <0.1%, while without a cation exchange membrane, a crossover of >6% was observed. Lastly, the potential losses due to a pH gradient formation near the electrode surfaces were both practically and theoretically evaluated for different salt compositions at 1 M concentration. Only in a pure electrolyte of 1 M H_2SO_4 , a pH gradient-free system was observed thus completely avoiding potential losses.

9.1 Introduction

Development of a photoelectrochemical (PEC) cell has received increasing attention for large-scale solar energy conversion and storage applications. The primary components of a PEC cell include photoabsorbers, electrocatalysts, membrane separators, electrolytes, and the supporting structures. In short, photoabsorbers capture and convert the incident photons and generate the required photovoltage and –current to drive the required fuel-forming reactions. Electrocatalysts lower the kinetic overpotentials and therefore affect the efficiency and selectivity of the fuel-forming reactions. A membrane separator prevents product crossover, to avoid explosive/flammable product mixtures (*e.g.*, H_2/O_2 mixtures). Lastly, an electrolyte facilitates ion transport between the cathode and anode compartments. However, to develop an efficient and intrinsically safe PEC cell, (i) concentration-overpotential losses, (ii) electrolyte resistive losses, (iii) the rates of gas crossover, and (iv) the catalytic activity, which is negatively correlated with the light-limited photocurrent, must be minimized simultaneously.¹

The theoretical voltage to split water in a PEC cell is 1.23 V.² The upper limit on the tolerable losses strongly depends on the photoabsorber characteristics. For example, if the PEC device is driven by a solar cell operating with an open circuit potential (V_{oc}) of 1.9 V and a maximum power potential (V_m) of 1.7 V, then the maximum tolerable potential loss can be $1.9 - 1.23 = 670$ mV, however at the maximum operating point a loss of only 470 mV is acceptable. The overpotentials needed to drive the hydrogen and oxygen evolution reaction at 10 mA/cm^2 are already 80 and 340 mV, respectively.³ Thus all other potential losses should be within the range of 250 and 50 mV at an operating current of 10 mA/cm^2 , which would correspond to a solar-to-hydrogen efficiency of at least 12.3%.

The constraints mentioned above create contradictory geometric design parameters. The design parameters for the construction of a PEC cell have been modelled extensively with respect to: the optimal band gap combination for photoabsorbers, the overall kinetic overpotential for electrocatalysts, the permeability and conductivity properties for membrane separators, and the conductivity and pH requirements for the electrolyte solution.⁴⁻⁷ Although these simulations help tremendously paving the way towards efficient PEC cells, practical measurements are essential to find the actual geometric design parameters to fabricate a full stand-alone PEC cell.

9

Within the discussion of possible device concepts, both wired and wireless devices are envisioned as possible contenders.⁸ The wireless design has the upper hand, first of all, due to the simplified cell design by eliminating electrical contacts and wires through integration of all components in a flat assembly.⁹ More importantly, the electronic conductivity is much higher ($\sim 10^5 \text{ S/cm}$), than ionic conductivity ($< 1 \text{ S/cm}$). Therefore, Newman showed by a simple analysis that, in order to keep Ohmic losses within the

device low, a short ionic pathway between the two electrodes is a necessity.¹⁰ LeRoy *et al.* pointed out for a wired device that an increase of gas volume between the electrodes (*i.e.*, at a short electrode distance) will lead to a higher electrical resistance, an efficiency decrease of water electrolysis, and the lodging of bubbles between the electrodes.^{11,12} A wireless device overcomes these problems, by separating the production of the evolved gasses in two separate compartments. However, short ionic pathways are still required in a wireless device between the anode and cathode to reduce the overall resistance.

Bosserez *et al.* investigated an option for reducing the ionic pathway microporous silicon electrode (*i.e.*, not photoactive), with the aim to provide such ionic shortcuts and gain more insight into the potential losses due to the electrolyte. Less than 100 mV potential loss was found at 7.84 mA/cm² in 1 M KOH at a porosity of ~7% and a micropore pitch of 250 μ m.¹³ However, two problems evolved for this conceptual device. Firstly, a substantial H₂ crossover to the O₂ compartment of ~20% was measured. Whether the crossover occurred by mass transfer of dissolved gasses or by transport of bubbles was not elucidated. The observed gas crossover is far above the lower flammable limit (4% in O₂) and the lower explosion limit (17% O₂), and therefore not intrinsically safe nor useful in a functioning S2F device.¹⁴ Secondly, a possible change of local pH (*i.e.*, pH gradient) around the electrodes was neglected, while these pH gradients can add to a severe increase in required potential to drive the reaction.¹⁵

To overcome the crossover of reaction products, micropores could be filled with a molecular barrier material (*e.g.*, cation or anion exchange membrane) to prevent crossover of gaseous products. However, Hernández-Pagán *et al.* showed that for several near-neutral pH electrolytes with either an anion or cation exchange membrane, a severe pH difference develops between the anode and cathode compartment, which led to an extra required potential up to 341 mV within 6 h of operation.¹⁵ Even with diurnal cycling (*i.e.* 8h on, 16 h off), a significant gradient was observed after 3 cycles.¹⁵ Modestino *et al.* showed that circulation of the anode and cathode compartment in a near-neutral electrolyte was an absolute necessity, otherwise the performance of the device rapidly came to a halt.¹⁶ A pump was required to perform this circulation, which requires energy to operate, and thus suppresses the overall obtainable STH efficiency. Singh *et al.* simulated a wired device in a strong acid (*e.g.*, 0.1 M H₂SO₄) in combination with a cation exchange membrane and showed the rapid formation of a pH gradient at operating current densities >8 mA/cm².¹ However, to date no practical data has been shown on the existence and in situ formation of a pH gradient for a wireless devices configuration, with an exchange membrane incorporated.

Another point of concern is that electrocatalysts block the incoming solar light and thereby reduce the overall generated photocurrent, and thus the fuel production. Chen *et al.* showed that patterning electrocatalysts on the surface of photoabsorbers in a solar-

fuel generator could provide a viable approach to minimize this parasitic absorption by catalyst films and still maintain a high overall efficiency.¹⁷ However, this study only presented practically the dependence of the filling fraction of the catalyst on the surface and resulting catalytic activity, without studying the impact for the underlying photoabsorber.

All of these studies presented significant results to solve one or more of the requirements to produce an efficient and intrinsically safe PEC cell. Here we show how to fabricate a stand-alone membrane embedded microporous photoelectrochemical cell architecture, and overcome all of the above stated drawbacks, such as pH gradient, ionic conductivity, light absorption losses, and product crossover. We employ a nanometer-scale, thin membrane to reduce the resistance caused by the membrane. Furthermore, by patterning of the catalyst at the illumination side to prevent parasitic light absorption losses. The influence of porosity on the device performance is studied by experimental (photo)electrochemistry as well as analytical and finite-element models.

9.2 Results and discussion

Figure 9.1A shows the targeted microporous photoelectrochemical cell with an embedded membrane. The starting substrate was a triple PV cell, in order to generate sufficient potential for the oxygen (OER) and hydrogen evolution reactions (HER).¹⁸ The top cell was constructed from amorphous silicon (a-Si), the middle cell from nano-crystalline silicon (nc-Si), and the base cell from a wafer of silicon (n-Si).¹⁸ In order to reduce the overall ionic transport losses between the anode and cathode, micropores were etched through the silicon substrate, with a porosity of ~7%.¹³ The diameter of the micropores was limited to 50 μm , due to the employed deep reactive etching (DRIE) process. Therefore, micropores with a pitch of 166 μm were etched into the triple PV cell, as is visualized in Figure 9.1B, to yield a porosity of 7%.

Since etching completely through the Si substrate exposes bare silicon, which would be etched very rapidly in alkaline electrolyte¹⁹, we were forced to perform our analysis in acidic electrolyte to maintain stability of the silicon material. McCrory *et al.* benchmarked many known OER and HER catalysts in alkaline and acidic electrolytes and showed that the only viable combination in acidic electrolyte to date is iridium oxide (IrO_2) and platinum (Pt)³, which is the reason why we chose these electrocatalysts in our membrane PEC cell. The illuminated side of our triple PV cell is p-type doped, and therefore we sputtered IrO_2 at the front side as OER catalyst and used a blanket layer Pt backside as HER catalyst. Chen *et al.* presented the importance of microdot arrays with respect to the parasitic light absorption of the catalyst for the underlying light absorber (*i.e.*, IrO_2 in our case) and the catalyst activity. Therefore we fabricated arrays of microdots of IrO_2 , with a diameter of 2 μm and a periodicity of 11, 16, 22 μm . Arrays of micropores and IrO_2

microdots are clearly visualized in a microscope image (Figure 9.1C) of the fabricated device.

Figure 9.1 (A) Schematically depicted stand-alone, microporous PEC cell with embedded membrane, with all different components highlighted. (B) Top view cross-sectional SEM and (C) light microscopy images of the illuminated side of a stand-alone microporous PEC cell made according to the scheme shown in A. Micropores (50 μm) through the Si substrate and 2 μm IrO_2 microdots are visible with a pitch of 16 μm . Scale bars indicates 50 and 100 μm for (C) and (D), respectively. (D) SEM image of the backside of a stand-alone microporous PEC cell made according to the scheme shown in A. The backside is fully platinized, and micropores are filled with Nafion[®]. Scale bar indicates 500 μm .

A molecular barrier material is required to separate the evolved gasses. Nafion[®], a perfluorosulfonic acid polytetrafluoroethylene copolymer, is commonly used as the membrane separator material in proton exchange membrane fuel cells and can easily be dropcasted from various solvents.^{20,21} A Nafion[®] layer was dropcasted at the backside of the device, and excessive Nafion[®] was removed after solvent evaporation (see Figure 9.1A and D). As a result, Nafion[®] is only present within the micropores. A cross sectional SEM image shows a thin membrane of ~ 100 nm in thickness within the Si micropores, as is seen in Figure 9.2.

Figure 9.2 Cross-sectional SEM image of micropores filled with a thin Nafion® membrane. Scale bar is 100 μm .

9.2.1 Operational PEC cell

Both the micropores and IrO_2 microdots may result in absorption losses for the underlying PV cell which needs to be assessed. Figure 9.3A shows the current–voltage characteristics of an unmodified (bare) triple PV cell before and after etching micropores into the surface. Although the open-circuit voltage exhibited a minimal change after etching, the short-circuit current density decreased from 8.5 mA/cm^2 to 7.9 mA/cm^2 , due to a reduction in total surface of photo-absorber by the micropores. This relative reduction of $\sim 7.1\%$ is in close agreement with the porosity of 7% induced by the micropore formation. Upon introducing IrO_2 microdots on the microporous surface, a further decrease in current density is observed. Microdots ($2 \mu\text{m}$ diameter) with a filling fraction of 5 and 10%, decreased the current density to 7.4 mA/cm^2 and 6.9 mA/cm^2 , respectively. Here, the filling fraction (f_c) is defined as the ratio of the geometric area of the catalyst to the total geometric area of the photoelectrode. These values correspond to a decrease of 6.3% and 11.7% in current density, respectively, which agree reasonably well with the employed filling fractions of catalyst. All relevant values are summarized in Table 9.1.

Figure 9.3 (A) Photoelectrical J/V measurements of a bare Si triple cell, a cell with 7% micropores, and microporous cells with a filling fraction of IrO_2 microdots of 5 and 10%. (B) Dark J/E behavior for electrodes with different filling fractions of IrO_2 microdots. The inset shows a zoom-in of the range in which the photocathode operates, $<10 \text{ mA/cm}^2$.

Table 9.1 *JV* characteristics for the various triple PV cells shown in Figure 9.3

Sample	η (%)	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)
Bare	10.8	8.57	1.92	66.17
With pores	9.3	7.86	1.90	62.09
With pores and f_c of 5%	8.5	7.42	1.87	61.18
With pores and f_c of 10%	7.8	6.92	1.86	60.38

Chen *et al.* showed that low filling fractions (<10%) of catalyst islands (Pt) do not have to lead to a significantly reduced performance of a photocathode.¹⁷ Therefore, we assessed the activity of the IrO₂ dots with different filling fractions (i.e. f_c of 2.5, 5, and 10%) on top of Si, as seen in Figure 9.3B. An f_c of 2.5% of IrO₂ on top of Si shows a significantly reduced activity, as compared to a fully covered surface, most likely due to mass transport limitations, as suggested by Chen *et al.*¹⁷ In contrast, filling fractions of 5 and 10% provide substantial activities, especially in the range up to 10 mA/cm², as is seen in the inset of Figure 9.3B. Compared to 100% coverage, approx. 50% of the activity is retained when reducing the coverage to 5%.

The PEC performance of the device was characterized by operation of the microporous device as a photocathode in a three-electrode voltammetry configuration (triple PV cell with Pt backside as working electrode, Pt counter electrode, and Ag/AgCl reference electrode), as indicated in Figure 9.4A. Figure 9.4 plots the current density obtained from the photocathode as a function of the applied potential. The obtained current densities from the measured devices correspond well with the current densities obtained when measured as a PV cell (Figure 9.3A). A stand-alone operating current is obtained by overlaying the potential-current relation of the IrO₂ OER catalyst of Figure 9.3B. The obtained stand-alone currents are 5.7 and 5.1 mA/cm², for filling fractions of 5 and 10% of IrO₂ microdots, respectively. Notably, although a higher filling fraction leads to a higher catalytic activity, the impact on maximum current density was more severe for the overall efficiency, due to stronger light blocking of the catalyst at the higher catalyst coverage. Therefore, a lower overall STH efficiency (6.2%) was obtained than for an f_c of 5%, which gave an STH efficiency of 7%.

Figure 9.4 (A) Schematically depicted setup to measure the photocathode behavior. (B) Current density versus potential photocathode behavior for two different stand-alone, membrane embedded microporous PEC cells, with different filling fractions of catalyst. Overlay of the catalyst activity of the two different filling fractions of IrO_2 (from Figure 9.3B). Red dots indicate the stand-alone operating potential and current.

9.2.2 pH gradient formation in microporous PEC devices

The occurrence of a concentration overpotential due to the build-up of a pH gradient is a widely investigated topic.^{1,9,16,22-24} In most cases a concentration gradient is resolved by recirculating the anode and cathode compartments, although substantial gas crossover is inevitable in this manner.^{13,25}

For these reasons we investigated the influence of the effect of pH gradient formation at a constant salt concentration of 1 M salt, but with different starting pH. To exclude possible limitations imposed by the current-potential characteristics of a triple PV cell, we produced a dummy Si microporous substrate with platinum electrodes on both sides and Nafion® embedded in the micropores, as schematically depicted in Figure 9.5A. This Si microporous substrate had the same porosity ($\sim 7\%$) and micropore diameter ($50\ \mu\text{m}$) as the microporous PEC cell with embedded membrane described above. A Nafion® membrane was introduced in the micropores to prevent gas crossover, see Figure 9.5B. In order to measure the pH near the surface of the device, we constructed a homemade pH meter, as depicted in Figure 9.7. The pH is measured near the surface by means of an IrO_2 wire vs. a reference electrode. The potential of an IrO_2 surface vs. a reference electrode is dependent on the pH of the electrolyte, is very sensitive, has a fast response upon pH change, and is stable over prolonged periods of time and many cycles of pH switching.^{26,27}

Figure 9.5 (A) Schematic overview of a microporous dummy device for investigating the formation of a pH gradient upon water splitting. (B) SEM image of a micropore of a device schematically depicted in A, filled with a Nafion® proton exchange membrane, with an uncovered SiN_x ring visible and Pt at the outside. Scale bar indicates 25 μm. (C) pH in the cathode (solid) and anode (dotted) compartments, and their overall difference, measured over time. (D) pH in the cathode compartment over time, with varying starting electrolytes.

Figure 9.6 Schematic setup used to measure the pH change in the cathode compartment.

Upon applying a constant current density of 8.13 mA/cm^2 over the anode and cathode in sodium sulfate electrolyte (*i.e.*, $1 \text{ M Na}_2\text{SO}_4$ with a pH of 5.8), the pH at the cathode rapidly increased within minutes to a pH of ~ 11 (solid line), see Figure 9.5C. At the anode, the pH decreased within the same time to a very low pH of ~ 0.7 (dotted line). Within minutes, a pH gradient of more than 10 units (dashed line) was established over the device. Such a difference would lead to an increase in potential required to drive the complete PEC cell of $>590 \text{ mV}$. For comparison, the catalytic overpotentials for highly active catalysts, such as IrO_2 for the OER and Pt for the HER in acidic electrolyte as were benchmarked by McCrory *et al.*, were 360 mV and 52 mV , respectively.³ The potential loss due a pH gradient can thus be even higher, and therefore severely suppresses the overall operating current density. The large induced overpotential is understandable, since the majority of carriers will be Na^+ and SO_4^{2-} within the electrolyte, and not the produced or consumed protons. Therefore, a depletion and accumulation of protons will occur in the anode and cathode compartments, respectively.

By decreasing the starting pH, an increase in transportation of protons is expected, and therefore a decrease in pH gradient. A competition between Na^+ and H^+ diffusion is thereby expected. We tested different electrolyte composition of Na_2SO_4 and H_2SO_4 , however keeping the overall ion concentration at 1 M . Figure 9.5B shows the results of the pH change over time, with different starting compositions as stated by addition of a specific amount of H_2SO_4 . Upon lowering the starting pH, a longer period of time was required before depletion of protons in the cathode compartment became evident. Even for $0.9 \text{ M Na}_2\text{SO}_4$ and $0.1 \text{ M H}_2\text{SO}_4$ a pH increase of 0.3 units was measured after 20 min . Not until a pure electrolyte of $1 \text{ M H}_2\text{SO}_4$ was used, a stable pH over time was observed, as is seen in Figure 9.5B.

The crossover of gaseous products is another major concern for a membrane-free solar-driven water-splitting device. Figure 9.7 shows the time evolution of the gas compositions in the anode compartment of two devices, with and without Nafion®, as determined by GC measurements. On average $\sim 6.5\%$ of crossover of H_2 into the anode compartment was observed for 100 min of operation when Nafion® was not present within the micropores. H_2 crossover is most likely due to gas bubbles moving through the open micropores, which results in the observed step increases in concentration of H_2 in the anode compartment. In contrast, when Nafion® was present in the micropores, only $<0.1\%$ crossover of H_2 into the anode compartment was observed. This indicates the importance of the incorporation of a molecular barrier in the PEC design.

Figure 9.7 Time evolution of the measured hydrogen crossover in the oxygen compartment (anode), with Nafion® as molecular barrier (triangle) and without Nafion® (square).

9.2.3 pH gradient simulation

To gain more insight in the influence of the development of a pH gradient, an analytical and a COMSOL model were developed. A simple model already provides insight into the evolution of a pH gradient over the anode and cathode compartment. In order to estimate the length scale at which pH gradient formation becomes an issue, a 1D, infinite parallel plate model was developed, in which an electrolyte is placed between cathode and anode and a steady-state proton gradient was established. In this case, 1D Fick's first law in steady state can be used, which simplifies to Equation 9.1:

$$J = -D \frac{\Delta C}{x} \quad \text{Eq. 9.1}$$

Here, D is the diffusion constant of protons, x is the distance between the electrodes, ΔC is the proton concentration difference between anode and cathode, and J the proton flux. Here, the proton flux is directly related to the operating current density (J_{op}), and therefore the proton concentration is given by Equation 9.2:

$$\Delta C = \frac{J_{op} * x}{D * F} \quad \text{Eq. 9.2}$$

Here F is the Faraday constant. The concentration gradient can be maximally twice the electrolyte concentration (C_{el}), and therefore the critical dimension, x_{crit} , at which the concentration at the anode becomes zero, is given by Equation 9.3:

$$x_{crit} = \frac{2 * C_{el} * F}{J_{op}} \quad \text{Eq. 9.3}$$

At an operating current density of 8.13 mA/cm^2 (*i.e.*, 10% STH efficiency) and an electrolyte proton concentration of 0.1 M , x_{crit} is $\sim 2 \text{ mm}$. However, a zero proton concentration at the cathode, would result in an infinite overpotential. When allowing an overpotential on the order of the overpotential required for Pt to produce hydrogen (52 mV), a separation distance of $\sim 1.7 \text{ mm}$ is allowed. When the proton concentration of the electrolyte is reduced, then the maximal electrode separation to allow the same overpotential is reduced with the same factor, *i.e.*, a C_{el} of 0.01 M results in a $\sim 170 \text{ }\mu\text{m}$ maximal separation distance. Most operational lab-scale PEC devices are constructed on the order of 1 cm^2 , with macroscopic slits at the sides through which the electrolyte solutions in either compartment can mix. This analytical model already highlights one of the major problems: the large separation distance of the anode and cathode.

The above described model assumes parallel plates and only diffusion of protons. This model includes neither the migration of protons in an electric field, nor the fact that anode and cathode are not parallel, as is the case in a real PEC device, in particular a wireless one. To gain more insight in the geometric design parameters, a COMSOL model, which does include the actual device geometry, diffusion, and migration, was developed to assess the pH gradient formation. Firstly, a setup found in literature was simulated as in as seen in Figure 9.8A.²² During (simulated) operation, a pH gradient develops near the surfaces of the electrodes. Figure 9.8A shows the calculated pH profile for the system after 15 min of simulated operation at 8.13 mA/cm^2 with a starting H^+ concentration of 0.1 M . Although the electrolyte was a strong acid, the pH at the surface of the photocathode was around ~ 8.5 , and the pH at the surface of the photoanode was ~ 0.7 . The simulation shows great similarities with simulations done by Jin *et al.*, who performed it at near-neutral pH.²² The average voltage loss due to such a pH gradient would be 462 mV (*i.e.* 59 mV/pH decade).

Figure 9.8 Cross-sectional pH profiles in the non-microporous PEC device (A) and in a microporous device with 60 slits/cm (B) from COMSOL Multiphysics simulations after 15 min operation at 8.13 mA/cm² starting in homogeneous 0.1 M H₂SO₄. (C) Zoom in of (B) (D) Simulated pH over time at one of the cathode slits for different numbers of microslits within the device.

By introducing microslits (slits with a width of 50 μm) in the device with a certain pitch, a pH gradient can be mediated, by reducing the distance over which protons are transported. A similar simulation was performed as described above, although several microslits (*e.g.*, 60 slits/cm) are introduced in the system. Figure 9.8B shows the results after 15 min of simulated operating time. A substantial decrease in pH gradient is observed within the system. The pH at the anode and cathode, measured at the electrode surfaces (see green dots in Figure 9.8C), were ~ 0.80 and ~ 1.2 , respectively. This almost completely suppressed gradient is mainly attributed to a shortened proton transport distance from the anode to the cathode. More insight is generated by changing the amount of microslits in the system. From Figure 9.8D it becomes clear that from 60 microslits/cm a steady state pH is obtained after ~ 10 min of simulated operating time. Increasing the amount of microslits (*e.g.* 100 microslits/cm) does not resolve into a substantial decrease in pH at the cathode. The above modelled system is 2D (*i.e.* microslits instead of micropores), but it indicates again, as seen for the 1D analytical model as well, that the shortest distance between the electrodes is of crucial importance. In an actual, 3D PEC cell, therefore, micropores can offer such diffusion short-cuts, and at a much lower overall porosity than microslits. *E.g.*, a microslit of 50 μm width and 166

μm pitch would result in a 30% porosity, and thus 30% less light absorption. In contrast, micropores of 50 μm and 166 μm pitch result in 7% porosity, and thus only 7% less light absorption. Moreover, both the simulations and measurements show the importance of porosity and the use of a pure electrolyte for the device stability during operation.

Most important lesson resulting from both simulations is that the proton diffusion distance between cathode and anode is the crucial device parameter. If the distance is too long, a pH gradient will build up that causes a detrimental overpotential. All in all, both models provide basic design rules for a microporous device: (i) at highly acidic electrolytes, pore separations can be on the order of 100 μm , a higher degree of porosity is unnecessary; (ii) more weakly acidic electrolytes have concomitantly more stringent design requirements.

9.3 Conclusions

We have designed, fabricated and experimentally validated a membrane-embedded microporous PEC cell architecture that circumvents the ionic transport losses, the formation of a pH gradient, and gas crossover in a PEC cell. By introducing micropores into a Si-based substrate, all three losses are reduced and kept within the limit of 250 mV. Together with the research of Bosserez *et al.* and our performed simulation on pH gradient formation, a micropore pitch < 250 μm is required, and an overall porosity of $\sim 7\%$ ensures low ionic losses of <100 mV in acidic conditions.¹³ Therefore, our final device was constructed of micropores with a diameter of 50 μm and a pitch of 166 μm . Crossover of the co-evolved gasses (*i.e.* H_2 and O_2) is solved by the incorporation of Nafion[®] proton exchange membrane within the micropores.

The formation of a pH gradient between the anode and cathode compartment in 1 M Na_2SO_4 was observed within minutes of operation, thereby increasing the potential to split water by > 500 mV. By increasing the acidity of the electrolyte to a pH of 2.5, a significant decrease in pH gradient was observed, however it still increased over time. Not until a pure electrolyte of 1 M H_2SO_4 was employed, a stable pH was obtained over time.

A fully stand-alone PEC cell was fabricated according to these design principles. We have demonstrated that, by careful design at the microscale, the chosen architecture provides a high performance. The micropore concept should also be applicable to other material combinations, provided that fabrication methods can be found to achieve similar structuring at the right scale. The best-performing stand-alone microporous membrane-embedded PEC cell investigated here, demonstrated a STH efficiency of $\sim 7\%$.

Our future research will focus on the incorporation of all earth-abundant materials, especially for the chosen catalyst materials. Furthermore, as shown by McCrory *et al.* by

benchmarking 24 OER catalyst, the activity of the OER catalyst is higher in alkaline electrolyte.³ The currently shown microporous PEC cell is instable in alkaline electrolyte, due to bare Si, which etches rapidly in alkaline medium. Therefore, the stability of the present microporous PEC cell should be increased for alkaline conditions.

9.4 Materials and methods

9.4.1 Triple PV cell

The triple PV cell structure consists on a hybrid thin film a-Si:H/nc-Si:H tandem and silicon heterojunction cell, resulting in a triple junction. The c-Si wafers (Topsil, n-type, {111} FZ, $\sim 280\ \mu\text{m}$), were cleaned using a sequence of 99 % HNO_3 at room temperature for 10 min, 69.5 % HNO_3 at 95 °C for 10 min. Subsequently, a dip in 0.55 % HF was performed at room temperature to remove the oxide film. The thin film silicon layers were fabricated by plasma enhanced chemical vapor deposition (PECVD). Silane (SiH_4), hydrogen (H_2), carbon dioxide (CO_2), phosphine (PH_3) and diborane (B_2H_6) were used as precursor gases.

9.4.2 Sputtering

A transparent conductive oxide, hydrogenated indium oxide (IO:H), was sputtered on both sides of the finished triple junction cell, in order to improve the charge extraction of the underlying materials. The deposition was conducted at room temperature with a power of 135 W and 30 μbar of H_2O partial pressure, and then annealed at 175 °C for 150 min.

Ir microdots were fabricated by means of lift off. Squares ($10 \times 10\ \text{mm}^2$) with cubic packed circles (2 μm diameter, varying pitch) were defined in a photoresist polymer (Olin 906-17). Iridium (Ir) was deposited by means of an in-house built sputter device. The silicon wafer was placed on a rotating chuck (5 rpm), 44 mm from the Ir source, in a low-pressure reactor chamber ($5.5 \times 10^{-3}\ \text{mbar}$) with a 40 sccm flow of argon. The Ir source had an angle of 45° with respect to the wafer surface. By means of a DC power of 50 W and a 20 sccm argon flow at the gun Ir was sputtered (2.6 nm/min deposition rate). Subsequently, microdots were obtained by lift-off, by immersing the wafer in acetone in an ultrasonic bath for 20 min, followed by immersing the wafer in iso-propanol, in an ultrasonic bath for 20 min. The electrochemical growth of IrO_2 from Ir was carried out in a 0.5 M H_2SO_4 solution with a Versastat 4 potentiostat. For a 0.5 M H_2SO_4 solution, the optimal switching potentials are $V_U = 1.25\ \text{V}$ and $V_L = -0.25\ \text{V}$ versus RHE, a sweeping rate of 150 mV/s, for a time of 20 s.²⁶

A full Pt backside was sputtered by means of an in-house built sputter device. The silicon wafer was placed on a rotating chuck (5 rpm), 44 mm from the Pt source, in a low-pressure reactor chamber ($6.6 \times 10^{-3}\ \text{mbar}$) with a 145 sccm flow of argon. The Pt source

had an angle of 90° with respect to the wafer surface. By means of a DC power of 200 W Pt was sputtered (5.0 nm/min deposition rate).

9.4.3 Deep reactive ion etching

The IO:H on the front side of the wafer was removed by reactive ion etching (RIE, Adixen AMS100DE), and cleaned by means of oxygen plasma (30 min). By means of standard photolithography, squares (10x10 mm²) with cubic packed circles (50 µm diameter, 166 µm pitch) were defined in a photoresist polymer (Olin 906-35). Silicon micropores (~280 µm) were etched into the silicon substrate by deep reactive ion etching (DRIE, Adixen AMS100SE, C₄F₈ pulsed process) and the substrates were cleaned subsequently in oxygen plasma (30 min) and piranha (20 min) to remove the photoresist and fluorocarbon residues.

9.4.4 Membrane dropcasting

10 mL Nafion® (20 wt%, Sigma Aldrich) was added to 10 mL dimethylformamide (DMF). By evaporation at a rotavap, at 10⁻³ mbar and 80 °C the lower aliphatic alcohols and water content was removed. 100 µL was dropcasted at the backside of a microporous structure and dried at a hotplate with a temperature of 60 °C. After solvent evaporation, Nafion® covering the Pt backside was removed by a razor blade, so that only the micropores are closed with Nafion®

9.4.5 Gas chromatography

The reactor was connected to a GC (Compact GC, Interscience), equipped with a Parabond Q column (10 m) and a TCD detector to determine the amount of H₂ in the argon carrier gas. 10 mL/min argon was flowed through the electrolyte and sampled every 130 s for the presence of H₂.

9.4.6 COMSOL modelling

The modelling of the system was performed by COMSOL 5.3, by means of the electrochemistry module in 2D (A typical geometry is given in Figure 9.8B), with as main model the tertiary current. The net molar flux of each species in the electrolyte, N_i , is the sum of the fluxes due to migration, diffusion and convection, such that:

$$N_i = -D_i \nabla c_i - z_i u_i F c_i \nabla \phi_l + v c_i \quad \text{Eq. 9.4}$$

where ϕ is the electric potential, v is the velocity, c_i is the concentration, D_i is the diffusion coefficient, z_i is the charge number, $u_i = D_i/RT$ is the mobility where R is the ideal gas constant and T is the absolute temperature, and F is the Faraday constant. The conservation of mass requires that:

$$R_i = \frac{\partial c_i}{\partial t} + \nabla \cdot \mathbf{N}_i \quad \text{Eq. 9.5}$$

where R_i is the net rate of formation of the i^{th} species due to bulk ionic reactions such as buffer and water-dissociation kinetics. The predominant source of convection in this system was due to product bubbles, which was neglected in the modeling. Electroneutrality was assumed at every point in the simulation space, such that:

$$\sum_{i=1}^n z_i c_i = 0 \quad \text{Eq. 9.6}$$

The charge-transfer kinetics at the electrodes were represented according to the Butler–Volmer model as:

$$\mathbf{n} \cdot \mathbf{i}_l = i_R = i_0 \left[e^{\frac{\alpha_a F (\phi_s - \phi_l - E_0)}{RT}} - e^{\frac{\alpha_c F (\phi_s - \phi_l - E_0)}{RT}} \right] \quad \text{Eq. 9.7}$$

Parameter	Description	Value
i_0 (OER)	OER exchange current density	$1.4\text{E-}^3 \text{ A/m}^2$
α_a (OER)	OER anodic transfer coefficient	1.7
α_c (OER)	OER cathodic transfer coefficient	0.1
i_0 (HER)	HER exchange current density	10 A/m^2
α_a (HER)	HER anodic transfer coefficient	1
α_c (HER)	HER cathodic transfer coefficient	1
E_0	Equilibrium potential	1.229 V
T	Reaction temperature	298 K
D_{H^+}	Diffusion Coefficients H^+	$9.3\text{E}^9 \text{ m}^2/\text{s}$
$D_{\text{HSO}_4^-}$	Diffusion Coefficients HSO_4^-	$1.3\text{E}^9 \text{ m}^2/\text{s}$

D_{Na^+}	Diffusion Coefficients Na^+	$1.9E^9 m^2/s$
$D_{SO_4^{2-}}$	Diffusion Coefficients SO_4^{2-}	$1.0E^9 m^2/s$
I_{lim}	Limiting photocurrent	$20 mA/cm^2$
S_w	Conductivity electrolyte	$0.5 S/cm$

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Summary

Silicon (Si) is an attractive semiconductor material for a wide range of applications. Particular advantages result from the larger surface area of silicon microwires, and from surface functionalization with different materials that can be employed to tune the functionality of the substrate towards a desired application. For example, silicon can be used in photovoltaic (PV) cells, or it can be employed as one of the materials in a so-called solar-to-fuel (S2F) device, solely by changing the surface functionalization. In a simplistic view, a S2F device is constructed by adding electrocatalysts to a PV cell. However, to produce an efficient S2F device, silicon has to be modified in several manners, both regarding its structure (*e.g.* shaping into microwires) and using additional materials (*e.g.* catalysts, protective layer, junction, anti-reflection coating, etc.). This thesis discusses the use of silicon as a base material for a S2F device, employing structuring and modification.

To improve the efficiency of a S2F device that is based on a PV cell, the efficiency of the underlying PV cell is of utmost importance. Many parameters can be varied in a Si microwire array to enhance the efficiency as PV cell. Chapter 3 has reported on different fabrication aspects of designing microwire PV cells, regarding the microwire height and the radial junction depth. The height of the microwires was varied between 0 (flat) and 60 μm , and showed the highest PV cell efficiency for a length of 40 μm . Although increasing the length is beneficial for improving the light absorption, increasing the height of the microwires beyond 40 μm resulted in a decrease of the overall efficiency. The latter is most likely due to the fact that longer Si wires have an increased surface area which introduces more defect states, leading to a higher recombination rate. The junction depth was varied between 140 and 1640 nm, and an optimal junction depth was found at 790 nm. Si microwires with a shallower junction depth showed increasing leakage currents, with decreasing junction depth. This severely affected the fill factor and thereby the overall efficiency. By increasing the junction depth beyond 790 nm, a decrease in current density was observed which suppressed the overall efficiency. An increased junction depth introduces more defects in the Si emitter and thus increases the recombination rate.

The efficiency of Si microwire PV cells was further improved by the addition of passivation and anti-reflection layers, which has been discussed in Chapter 4. As mentioned in Chapter 3, the overall increased surface area leads to defects at the surface (*i.e.*, surface defect states) that enhance charge recombination. Surface defect states were reduced by applying a thin insulating layer (of, *e.g.*, Al_2O_3 , SiN_x , or SiO_2) conformally over the

microwires. The effect of this reduction of the density of defect states was indirectly confirmed by an increase of the overall efficiency of a Si microwire PV cell. By increasing the layer thickness, such an insulating layer also acted as an anti-reflective coating. For each of the above mentioned materials, an optimal layer thickness was found, which resulted in an increased overall efficiency. The effectiveness of these layers is, among other things, determined by the conformal character of the layers. The 3D conformal deposition was investigated by cutting a microwire orthogonally to the substrate, by means of focused ion beam etching. For both p- and n-type base samples, Al_2O_3 gave the highest increase in PV efficiency.

Silicon as a single absorber does not generate enough photovoltage to perform the required fuel production. In Chapter 5, a method to increase the photovoltage of Si microwires was discussed. Silicon heterojunction (SHJ) devices were fabricated on Si microwire arrays with a height up to 20 μm . The wire morphology ensures a high surface area which may be used for photoelectrochemical reactions. However, the enlarged surface area, and especially the vertical walls, in the device complicates the required passivation. The ability of hot-wire chemical vapor deposition (HW-CVD) to deposit conformal thin films at high deposition rates makes this technique suitable for depositing an a-Si:H passivation layer. Microwire arrays with heights of 20 μm showed only limited loss of open-circuit voltage despite the increase of surface area in comparison with a flat SHJ PV cell, while an increase in current density led to an increased overall efficiency. For use in photoelectrochemical fuel production devices, multi-junction PV cells were fabricated with a silicon microwire heterojunction as bottom cell and a-Si(Ge):H alloy n-i-p top cell(s), resulting in a photovoltage sufficient for solar fuel production.

In Chapter 6, a new type of Si microwire photocathode architecture was presented. Here, we designed, fabricated and experimentally validated a broadly applicable photocathode architecture that circumvents a trade-off between catalytic activity and optical absorption. By spatially and functionally decoupling light absorption and catalytic activity on high-aspect-ratio Si microwires with a radial n⁺/p-junction, a highly efficient hydrogen-producing half-cell was constructed. More interestingly, we showed it is possible to produce such an efficient photocathode with all earth-abundant materials. Due to the versatility of the proposed configuration, catalyzed reactions are not limited to H₂ formation as fuel, also other electrodeposited catalysts can potentially be used for different reaction products.

Chapter 7 has discussed the further optimization of the Si microwire photocathode. Two competing factors were identified that limited the performance of Si photocathodes with opaque catalysts, *i.e.*, insufficient catalyst loading and parasitic light absorption by the catalyst. A parameter sweep was performed by varying both the catalyst coverage over a microwire array and the microwire pitch. The fill factor dominated the overall efficiency

of a photocathode in a negative manner when the microwire arrays had a large pitch, and only small parts of the wires were covered by catalyst. The light absorption dominated the overall efficiency in a negative manner at a low pitch and high catalyst coverage. By careful design at the microscale, the chosen optimal parameters provided, compared to the best one presented in Chapter 6, an even further increased high-performance hydrogen half-cell. The concept of optimizing the spatial and functional decoupling of light absorption and catalyst deposition should also be applicable to other semiconductor material combinations.

The fabricated Si microwire photocathodes in Chapters 6 and 7 were characterized in acidic electrolyte. In Chapter 8, a fabrication method for Si microwires that are stable in harsh alkaline electrolyte has been discussed. An interlayer of nickel silicide (NiSi) was developed to effectively shield the underlying Si microwire from the alkaline electrolyte, in which Si microwires normally are being etched rapidly. Ohmic behavior was ensured between the microwire array and the NiSi interlayer, by a high doping level of the Si microwire emitter. Crucial design parameters found in Chapter 7 were employed to fabricate a highly efficient photocathode, which was also stable in alkaline electrolyte.

In Chapter 9, a membrane-embedded microporous PEC cell architecture was designed, fabricated and experimentally validated that circumvents the ionic transport losses, the formation of a pH gradient, and gas crossover in a PEC cell. By introducing micropores into a Si-based substrate, all three losses are reduced and kept within the limit of 250 mV. Our final device was constructed of micropores with a diameter of 50 μm and a pitch of 166 μm . Crossover of the co-evolved gasses (*i.e.* H_2 and O_2) is solved by the incorporation of a Nafion[®] proton exchange membrane within the micropores. It was demonstrated that, by careful design at the microscale, the chosen architecture provided a high performance. The best-performing stand-alone microporous membrane-embedded PEC cell investigated here, demonstrated a STH efficiency of $\sim 7\%$.

To conclude, silicon microwires with radial p/n junctions were fabricated and optimized with respect to various parameters, *i.e.*, junction depth, microwire height and pitch, and passivation and anti-reflection layers. The investigated microwires proved to be a very suitable template for the development of a hydrogen half-cell, *i.e.*, a photocathode, in a silicon-based S2F device. The increased surface area of Si microwires is beneficial for both the light absorption capabilities and the catalyst activity. A strong dependence on the overall efficiency has been found on catalyst loading, both catalyst coverage in combination with microwire pitch. By careful design of the parameters mentioned above, a highly efficient, earth-abundant, Si-based photocathode has been fabricated that can function in both acidic and alkaline electrolytes. Lastly, a full wireless S2F was constructed, and experimentally validated. Micropores within a Si triple PV cell provided

ionic short cuts, which decreased the overall ionic potential losses, and prevented a pH gradient within the device.

Silicon is the only earth-abundant semiconductor with maximized potential, both in photocurrent and photovoltage. In order to construct a full, stand-alone S2F device, our designed photocathode has to be coupled to an earth-abundant photoanode. Bismuth vanadate (BiVO_4) is to date one of the best functioning earth-abundant photoanode materials in literature. As a proof-of-concept, we have fabricated a full S2F device, by combining a backside-illuminated photoanode of BiVO_4 and a frontside-illuminated photocathode (c-Si) in combination with a bipolar membrane. A bipolar membrane enables us to use different electrolytes in the anode and cathode compartments. In this manner the photoanode and photocathode operate within their best performing electrolyte. Figure S1A schematically depicts the fabricated S2F device.

Figure S1 (A) Schematic setup for a full S2F device with the different absorbances and losses in light through every layer. (B) Absorbance spectra of the BiVO_4 layer (solid line) and the employed bipolar membrane (dashed line). The AM 1.5G photon flux spectrum (dotted line) is shown as well. (C) Current density (J_{ph}) vs. potential (vs. RHE, (V)) for the Si microwire photocathode and the BiVO_4 photoanode. The inset shows a section of the same graph magnified around the operating point. (D) Stability of unbiased water splitting (at 0.0V versus counter electrode) over the course of an hour.

Part of the light illuminated at the backside of the photoanode is absorbed by the BiVO_4 film and by the bipolar membrane (see Figure S1B), and the remaining light is available for the c-Si microwire array photocathode. BiVO_4 only uses a fraction of the solar

spectrum. For the bipolar membrane, the absorption rapidly decreases with increasing wavelengths, and the membrane shows $\sim 15\%$ absorbance for wavelengths > 600 nm. The maximum photon current generated by a frontside-illuminated c-Si photocathode, after subtracting the absorption of the BiVO_4 layer ($\sim 6.5 \text{ mA/cm}^2$) and bipolar membrane ($\sim 9 \text{ mA/cm}^2$) is 29 mA/cm^2 in the range of 300 to 1100 nm. The latter is at a maximum absorbance within the c-Si microwires and without influence of the catalyst on top of the c-Si microwires.

The performance of the photocathode was assessed with the BiVO_4 photoanode and a bipolar membrane in front of the c-Si photocathode. A clear decrease in photocurrent is observed for the photocathode when compared with the values reported in this thesis, but this is understandable seen the photocurrent losses induced by the two overlayers (*i.e.*, by BiVO_4 and the membrane). The plot in Figure S1C shows the crossover point for unbiased water splitting, and an inset highlights this point at ~ 513 mV vs. RHE. For this basic, wired S2F device, we observed a stable, unbiased water splitting efficiency of 2.1% over the course of an hour (Figure S1D). However, from this analysis it becomes clear that that the resulting unbiased performance is primarily limited by the performance of the BiVO_4 photoanode, and mainly by the photovoltage.

Furthermore, to date, no other earth-abundant photoanode (*e.g.* TiO_2 , WO_3 , a-Si, or Fe_2O_3), with optimized photovoltage and photocurrent, is readily available to be coupled effectively to a silicon photocathode. Therefore more research is required to optimize the properties of photoanodes. Furthermore, new types of earth-abundant semiconductors need to be found and investigated, in order to expand the possibilities of semiconductor combinations (*i.e.*, photocathode and –anode) in a full S2F device, and thus to maximize the solar-to-fuel efficiency. The findings described in this thesis offer new perspectives for the development of stabilized silicon microwire systems with tailored functionalities to be applied in photoelectrochemical and electrochemical conversion processes.

Samenvatting

Silicium (Si) is een aantrekkelijk halfgeleidermateriaal voor uiteenlopende toepassingen. Silicium kan bijvoorbeeld zowel in de fabricage van zonnecellen als in een zogenaamd zonlicht-naar-brandstof- ('solar-to-fuel', S2F-) apparaat worden gebruikt, eenvoudig door het oppervlak verschillend te functionaliseren. Een S2F-apparaat zou simpelweg geproduceerd kunnen worden door electrokatalysatoren aan een zonnecel toe te voegen, echter, om een efficiënt S2F-apparaat te produceren moet het silicium op verschillende manieren gemodificeerd worden, zowel structureel (bv. in de vorm van micropilaren om o.a. het oppervlak te vergroten), als door de toevoeging van extra materialen (bv. katalysatoren, een bescherm laag, een junctie, een anti-reflectie laag, etc.). Dit proefschrift beschrijft hoe silicium als basismateriaal gebruikt kan worden voor een S2F-apparaat, waarbij zowel structurering als functionalisering gebruikt wordt.

Om de efficiëntie van een S2F-apparaat, dat bestaat uit een zonnecel met Si-micropilaren, te verhogen is de efficiëntie van de onderliggende zonnecel uitermate belangrijk. Vele parameters van een Si-micropilaar-zonnecel kunnen worden gevarieerd om de efficiëntie als zonnecel te verhogen. Hoofdstuk 3 beschrijft verschillende fabricage-aspecten van belang voor het ontwerpen van zonnecellen met micropilaren, met name de lengte van de micropilaar en de diepte van de radiale junctie. De lengte van de micropilaren is gevarieerd tussen 0 (vlak) en 60 μm en zonnecellen met micropilaren vertoonden de hoogste efficiëntie bij een pilaarlengte van 40 μm . Hoewel de lichtabsorptie verbeterde met langere micropilaren, vertoonden micropilaren langer dan 40 μm een afname van de algehele efficiëntie. De lagere efficiëntie van de langere pilaren is toegeschreven aan het toenemend aantal oppervlakte-defecten bij toenemende pilaarlengte, hetgeen tot meer recombinatie leidt. De junctiediepte werd gevarieerd tussen 140 en 1640 nm, en een optimale junctiediepte werd gevonden bij 790 nm. Si-micropilaren met een dunnere junctie dan 790 nm gaven geen correct werkende diode en vertoonden een hogere lekstroom. Dit heeft een grote invloed op de 'fill factor' en daarmee op de algehele efficiëntie. Voor juncties dieper dan 790 nm werd een afname in stroomdichtheid waargenomen, welke wederom de algehele efficiëntie onderdrukte. Een verhoogde junctiediepte introduceert meer defecten in de Si-emitter en verhoogt daarmee de recombinatie.

De efficiëntie van micropilaar-zonnecellen kan nog verder verhoogd worden d.m.v. passivatie en anti-reflectielagen, zoals beschreven is in Hoofdstuk 4. Micropilaren verhogen het totale effectieve oppervlak van het Si-substraat, waardoor meer defecten op het Si-oppervlak ontstaan (zogenaamde oppervlakte-defecten). Oppervlakte-defecten

verhogen de recombinatie van ladingdragers. Deze defecten konden worden verminderd door een dunne isolerende laag, ook wel een passivatielaag genoemd, van Al_2O_3 , SiN_x of SiO_2 over de micropilaren aan te brengen. Het effect was een vermindering in de dichtheid van defecttoestanden, met als indirect gevolg een toename van de algehele efficiëntie van de Si-micropilaar-zonnecel. Door de laagdikte te vergroten, werkte een dergelijke passivatielaag ook als een anti-reflectielaag. Voor elk van de bovengenoemde lagen is de optimale laagdikte gevonden en dit verhoogde wederom de efficiëntie van de zonnecel. De effectiviteit van deze lagen wordt o.a. bepaald door de conforme bedekking van de pilaren door de laag. De bedekkingsgraad van verschillende lagen over de micropilaren is onderzocht door de micropilaar in de lengte doormidden te snijden d.m.v. een gefocusseerde ionenstraal. Voor zowel p- als n-gedoteerde zonnecellen bleek een laag van Al_2O_3 de grootste efficiëntieverbeteringen voor zonnecellen te leveren.

Puur silicium als zonnecel levert niet genoeg foto-spanning om water te splitsen in waterstof en zuurstof. In Hoofdstuk 5 is een methode besproken om de foto-spanning van Si-micropilaren te verhogen. Functionele Si-heterojuncties (SHJ) werden gefabriceerd op substraten dicht bezet met Si-micropilaren met een lengte tot 20 μm . De micropilaren zorgen voor een vergroot oppervlak dat kan worden gebruikt voor foto-elektrochemische reacties. Het vergrote oppervlak, en in het bijzonder de verticale wanden, compliceren echter de vereiste passivering. 'Hot-wire chemical vapor'-depositie (HW-CVD) is in staat om conforme dunne films met hoge snelheid te deponeren. Dat maakt deze techniek geschikt voor het deponeren van een a-Si:H-passiveringslaag. Substraten met micropilaren met een lengte van 20 μm vertoonden een beperkt verlies van open-circuitspanning, ondanks de toename van het oppervlak in vergelijking met een vlakke SHJ-zonnecel, terwijl een toename in stroomdichtheid leidde tot een verhoogde algehele efficiëntie. Voor het gebruik in S2F-apparaten werden multi-junctie-zonnecellen geproduceerd met een Si-micropilaar-heterojunctie als onderste cel en a-Si(Ge):H-legering, in n-i-p configuratie, als topcel(len), hetgeen resulteerde in voldoende foto-spanning voor het splitsen van water.

In hoofdstuk 6 is een nieuw type fotokathode-architectuur beschreven. We hebben een breed inzetbare fotokathode-architectuur ontworpen die een suboptimaal compromis tussen katalytische activiteit en optische absorptie omzeilt, deze gefabriceerd, en experimenteel gevalideerd. Door lichtabsorptie en katalytische activiteit ruimtelijk en functioneel te ontkoppelen op Si-micropilaren met een radiale n^+/p -junctie, werd een zeer efficiënte waterstof-producerende halfcel gemaakt. Nog belangrijker, we toonden aan dat het mogelijk is zo'n fotokathode te maken met alleen materialen die in overvloed op aarde aanwezig zijn. Vanwege de veelzijdigheid van de voorgestelde architectuur is de reactie niet beperkt tot waterstof alleen als reactieproduct. Simpelweg het veranderen van het katalysator-materiaal maakt andere reactieproducten mogelijk.

In hoofdstuk 7 is de ontworpen Si-fotokathode verder geoptimaliseerd. Twee belangrijke factoren zijn gevonden die de prestatie van Si-fotokathodes beperkten, namelijk onvoldoende katalysatormateriaal en parasitaire lichtabsorptie door het katalysatormateriaal. Deze parameters werden beide onderzocht door zowel de katalysatorbedekking over de micropilaren te variëren alsook de hart-hart-afstand (periode) tussen de micropilaren. Een 3D-plot van de algehele efficiëntie, met op de assen de katalysatorbedekking en de periode van de micropilaren, liet twee limiterende zones zien. Ten eerste, de algehele efficiëntie van een fotokathode was laag als de micropilaren een hoge periode hadden en een lage katalysatorbedekking, hetgeen leidde tot een lage 'fill factor'. Ten tweede, de lichtabsorptie domineerde de algehele efficiëntie op een negatieve manier bij een kleine periode en een hoge katalysatorbedekking. Door zorgvuldig de periode en de katalysatorbedekking op elkaar af te stemmen op de microschaal kon de algehele efficiëntie van een waterstof-producerende halfcel nog verder verhoogd worden t.o.v. van de fotokathode beschreven in hoofdstuk 6. Het hier gepresenteerde concept zou ook toepasbaar moeten zijn voor andere halfgeleidermateriaalcombinaties.

De in Hoofdstukken 6 en 7 gefabriceerde Si-micropilaar-fotokathodes zijn allemaal getest in een zuur elektrolyet. In hoofdstuk 8 is een fabricagemethode beschreven hoe Si-micropilaren gestabiliseerd kunnen worden in basisch milieu. Een tussenlaag van nikkelsilicide (NiSi) is ontwikkeld om de onderliggende Si-micropilaar te beschermen tegen het alkalische elektrolyet. Door de emitter van de micropilaren hoog te doteren werd Ohms gedrag tussen het NiSi en Si mogelijk. De ontwerpparameters gevonden in Hoofdstuk 7 werden gebruikt om een zeer efficiënte fotokathode te vervaardigen, die ook stabiel was in een sterk basisch elektrolyet.

In Hoofdstuk 9 is een architectuur voor een microporeuze foto-elektrochemische (FEC) cel met een membraan beschreven. Deze FEC-cel is gefabriceerd en experimenteel gevalideerd, en er is aangetoond dat hoge ladingstransport-verliezen, vorming van een pH-gradiënt, en ongewenst gastransport op deze manier worden vermeden. Door microporiën in een Si-gebaseerd substraat te introduceren, werden alle drie de verliezen binnen een limiet van 250 mV gehouden. Onze laatste architectuur bestond uit microporiën die een diameter van 50 μm hadden en een periode van 166 μm . Uitwisseling van de ontwikkelde gassen (d.w.z. H_2 en O_2) wordt voorkomen door een proton-uitwisselingsmembraan (Nafion®) in de microporiën te plaatsen. Er is aangetoond, door zorgvuldig ontwerp op de microschaal, dat de gekozen architectuur een hoge efficiëntie had. De best presterende microporeuze FEC-cel die hierin werd onderzocht gaf een STH-efficiëntie van $\sim 7\%$.

Samenvattend, Si-micropilaren met radiale p/n-juncties zijn gefabriceerd en geoptimaliseerd met betrekking tot verschillende parameters, zoals junctie-diepte,

hoogte van de micropilaren, periode, en passivatie- en antireflectielagen. De onderzochte micropilaren bleken een zeer geschikt substraat te zijn voor de ontwikkeling van een waterstof-half-cel, een zogenoemde fotokathode. Het verhoogde oppervlak van de Si-micropilaren is gunstig voor zowel lichtabsorptie als de activiteit van de katalysator. Er is een sterk verband gevonden tussen de hoeveelheid katalysatormateriaal op de micropilaar-fotokathode in combinatie met de periode van de micropilaren, en de algehele efficiëntie. Door zorgvuldig de hierboven genoemde parameters te kiezen, is een zeer efficiënte fotokathode op basis van Si-micropilaren vervaardigd die kan functioneren in zowel zure als alkalische elektrolyten. Tenslotte is een volledige S2F-apparaat gefabriceerd en experimenteel gevalideerd. Microporiën in een Si-triple-zonnecel voorkwamen een pH-gradiënt en beperkten de totale potentiaalverliezen tot een minimum.

Tot op heden is silicium het enige, veel voorkomende halfgeleidermateriaal met gemaximaliseerde fotostroom en foto-spanning. Alleen silicium is niet voldoende om een S2F-apparaat te produceren vanwege een te lage foto-spanning om water te splitsen. Om een volledig S2F-apparaat te produceren moet de door ons ontworpen fotokathode worden gekoppeld aan een foto-anode, hierbij in acht nemend dat de foto-anode-materialen ook overvloedig op aarde aanwezig moeten zijn. Bismutvanadaat (BiVO_4) is tot op heden één van de beste foto-anode-materialen. Als haalbaarheidsstudie hebben we een volledig S2F-apparaat geproduceerd. We hebben een BiVO_4 -foto-anode en een Si-micropilaar-fotokathode gecombineerd, om op deze manier genoeg foto-spanning te genereren om water te splitsen. Een bipolair membraan stelt ons in staat om verschillende elektrolyten in de anode- en kathodecompartimenten te gebruiken. Op deze manier werken de foto-anode en de fotokathode elk in hun best presterende elektrolyet. Figuur S1A geeft schematisch het geproduceerde S2F-apparaat weer.

Figuur S2 (A) Schematische opstelling van een volledig S2F-apparaat met de verschillende lichtabsorpties en -verliezen voor elke laag. (B) Absorptiespectra van de BiVO₄-laag (zwarte lijn), het bipolaire membraan (streeplijn) en een AM 1.5G foton-spectrum (stippellijn). (C) Stroomdichtheid (j_{ph}) tegen de potentiaal (versus RHE, (V)) voor een Si-micropilaar-fotokathode en de BiVO₄-foto-anode. De uitvergroting toont een deel van dezelfde grafiek rond het kruispunt van de twee lijnen. (D) De stabiliteit van watersplitsing gedurende een uur.

Een deel van het invallende licht wordt geabsorbeerd door de BiVO₄-film en gedeeltelijk door het bipolaire membraan (zie figuur S1B). Het resterende licht is beschikbaar voor de Si-micropilaar-fotokathode. BiVO₄ absorbeert slechts een fractie van het invallende zonnenspectrum, zoals te zien is in Figuur S1B. Voor het bipolaire membraan neemt de absorptie snel af met toenemende golflengten en het membraan vertoont een absorptie van ~15% voor golflengten >600 nm. De maximale fotostroom gegenereerd door een micropilaar-fotokathode, na aftrek van de absorptie van de BiVO₄-laag (~6.5 mA/cm²) en het bipolaire membraan (~9 mA/cm²), is 29 mA/cm². Dit is de fotostroom bij maximale absorptie van het overblijvende zonnenspectrum en zonder invloed van de katalysator bovenop de micropilaren.

Een duidelijke afname in fotostroom is waargenomen voor de Si-micropilaar-fotokathode in de bovenstaande opstelling, in vergelijking met de waarden die in dit proefschrift worden beschreven. Dit is begrijpelijk, gezien de fotostroomverliezen die worden veroorzaakt door de twee bovenlagen (d.w.z. door BiVO₄ en het membraan) en verder nog door parasitaire absorptie van de katalysator. De plot in figuur S1C toont het kruispunt voor autonoom watersplitsen, op een foto-spanning van ~513 mV vs. RHE. Dit

eenvoudige S2F-apparaat had een stabiel watersplitsingsrendement van 2.1% gedurende een uur (Figuur S1D). Uit de bovenstaande analyse wordt duidelijk dat het resulterende rendement voornamelijk wordt beperkt door de prestaties van de BiVO_4 -foto-anode en daarbij vooral door de gegenereerde foto-spanning.

Tot op heden is er geen andere foto-anode, gemaakt van veel op aarde voorkomende elementen (bijvoorbeeld TiO_2 , WO_3 , a-Si of Fe_2O_3) met een geoptimaliseerde foto-spanning en/of fotostroom, die gecombineerd met onze Si-fotokathode autonoom water kan splitsen. Daarom is er meer onderzoek nodig om de eigenschappen van foto-anodes te optimaliseren. Verder moeten er nieuwe typen halfgeleiders worden gevonden en onderzocht, uiteraard gemaakt van elementen die ruimschoots op aarde aanwezig zijn. Dit alles om de mogelijkheden van halfgeleidercombinaties (voor fotokathode en -anode) in een volledig S2F-apparaat uit te breiden en zo de efficiëntie van de zonlicht-naar-brandstof-omzetting te verhogen. De bevindingen beschreven in dit proefschrift bieden nieuwe perspectieven voor de ontwikkeling van silicium-micropilaar-gebaseerde systemen met op maat ontworpen functionaliteiten die onder meer kunnen worden toegepast in foto-elektrochemische en elektrochemische processen.

Dankwoord

Je wilt niet weten hoe erg ik heb zitten twijfelen om hier gewoon alleen – Bedankt – neer te zetten. Hoe kan je nou iedereen beter bedanken dan dat?

Als het om mensen bedanken gaat, staan mijn professoren, Jurriaan en Han, stipt bovenaan. De vrijheid die ik van jullie gekregen heb, om mijn onderzoek te mogen volbrengen, is ongekend. Heel prettig is de samenwerking die tussen jullie bestaat. Mijn onderzoek was breed, of thans, ik heb het breed aangepakt. Hierdoor zat ik zowel met chemische, fysische en fabricage-technische problemen. Het merendeel van de tijd had één van jullie wel een suggestie voor een oplossing of verwezen jullie me naar het juiste persoon voor het probleem: "Ja, je weet wel, diegene met die enorme wenkbrauwen. Kun je niet missen." Vooral voor de eindfase wil ik jullie beiden bedanken. Schrijven is niet mijn sterkste punt en dat zal waarschijnlijk nooit veranderen. Soms had ik het idee dat ik er echt bijna was, dat ik het heel goed gedaan had. Maar dan kreeg ik een mailtje: "Ik heb nog wat kleine puntjes..." Gehele tekst rood gekleurd door track-change aanpassingen. Desalniettemin, zonder jullie had ik het niet gekund!

Naast de begeleiding van de professoren, heeft Roald mij enorm geholpen. Je was al aanwezig tijdens het onderzoek van Rick en destijds had ik al veel met je gediscussieerd over: hoe verder, wat mist er in de literatuur en wat is een mogelijke volgende stap? Daarnaast heb je een grote bijdrage geleverd in het lezen, bediscussiëren en corrigeren van mijn artikelen. Uiteraard was je er ook op persoonlijk gebied. We hebben vaak genoeg gelachen. Als het niet op de squashbaan of in de Starbucks was, dan was het wel op een terrasje onder het genot van een heerlijk biertje.

Janneke en Rick, zonder jullie had ik nooit zo'n mooie start kunnen hebben. Rick, ik kwam in jouw laatste jaar op ongeveer hetzelfde project te werken. Ik kan me geen betere start wensen dan deze. Een werkend substraat (a.k.a. "the pillars of Rick") om verder mee te gaan en binnen een jaar tijd waren er twee papers de deur uit. Menigee binnen de vakgroep is daar jaloers op, gok ik. Datzelfde substraat heeft me later nog een aantal mooie papers opgeleverd! Janneke, zonder jouw vrijdagmiddag experimenten had ik nu twee hoofdstukken minder gehad. Ik sta er nog steeds van te kijken dat zo'n simpel testje tot een geweldig paper heeft geleid. Na je promotie werden, onder andere, je sublieme baksels erg gemist. Maar bovenal de afwezigheid van de opgewekte "Goedemorgen!" als ik binnen kwam.

Pieter, je startte een maand na mij op hetzelfde project en we hebben een hoop discussies gehad in het begin over waar we moesten beginnen. We zouden wel even de

wereld gaan verbeteren en het grote gegeven probleem oplossen. Hoe moeilijk kan het nou zijn...? Nou daar zijn we achter gekomen. Verschillende conferenties, discussies, open dagen en papers later, moet ik eerlijk bekennen dat de oplossing me nog niet geheel duidelijk is. Ik weet wel dat onze samenwerking, voor mij, niet beter had kunnen zijn. De drukte en spontaniteit die ik in mij heb zitten, compenseer jij volledig met rust en bedachtzaamheid.

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