Electrochemical coating
of micro-structured silicon
for photoelectrochemical water splitting

Alexander Milbrat

ELECTROCHEMICAL COATING
OF MICRO-STRUCTURED SILICON
FOR PHOTOELECTROCHEMICAL
WATER SPLITTING

Alexander Milbrat

Members of the committee:

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Prof. dr. ir. J.W.M. Hilgenkamp University of Twente

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Prof. dr. H.J.M. Bouwmeester University of Twente

The research described in this thesis was performed in a collaboration of the PhotoCatalytic Synthesis and Molecular NanoFabrication groups, both part of the MESA+ Institute for Nanotechnology at the University of Twente.

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DISSERTATION

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by

Alexander Milbrat

born April 10, 1987
in Fergana, Uzbekistan

This dissertation has been approved by the promotor:

Prof. dr. G. Mul

University of Twente

Prof. dr. ir. J. Huskens

University of Twente

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Chapter 1

Introduction and motivation

1.1 Towards a clean energy society

Since the beginning of the industrial revolution in the 17th century, the worldwide economy and thus wealth is growing.^[1] However, this growth is mostly powered by fossil fuels, such as coal, natural gas and crude oil. Nowadays, fossil fuels contribute for more than 80% of the total world energy consumption, distributed over various sectors, such as electricity generation, transportation, industrial processes and heating.^[2] Through burning of fossil fuels, deforestation and changes in land use, CO₂ levels in the atmosphere have increased from 280 parts per million (ppm) at the beginning of the industrial revolution by more than a third to 407 ppm today.^[3, 4] CO₂ is a greenhouse gas. Its emission causes global warming which leads to rising of the sea level and longer, more intense heat waves.^[5] Also, burning fossil fuels, especially coal, increases pollution.^[6] Pollution, mainly caused by industrial emissions, vehicle exhaust and toxic chemicals, is estimated to be responsible for 9 million premature deaths in 2015, which constitutes 16% of all premature deaths worldwide.^[6]

In order to significantly slow down or stop global warming and reduce pollution, humanity needs to reduce the dependence on fossil fuels by transitioning to the use of renewable energy sources. So far, the focus has been on electricity production, which accounts for about one-third of the total primary energy consumption.^[7] The numbers of installed wind power plants and photovoltaic installations are growing as these sources are becoming the cheapest energy sources on many parts of the planet.^[8] In 2016, more than half of the added global electricity generating capacity was from renewable sources,^[8] and this number is increasing with decreasing prices. The learning curve for photovoltaics has caused the price for modules to decrease by 24% with each doubling of the cumulative module production over the last 36

years.^[9] On a yearly basis, the photovoltaic module prices drop by between 5 and 7%.^[10] However, the integration of wind and photovoltaics into the existing electricity infrastructure is a challenge as their electricity output is variable and hardly controllable, and very often does not match the demand. Germany, one of the early adopters and supporters of renewable energy produced 33% of its electricity from renewable sources in 2016.^[9] But at times when a lot of wind is blowing and the sun is shining, countries like Germany experience temporary electricity overproduction, which is evident in low or negative electricity market prices and electricity export to neighboring countries (Figure 1.1). On the other hand, many conventional power plants cannot be shut down as they are needed as a backup for times when renewables cannot meet the electricity demand. This forces the authorities to subsidize conventional power plants to keep them as a backup to stabilize the grid. Thus, it is necessary to find solutions to store renewable energy and explore energy carriers which have the same ease of handling, storage and transport as fossil fuels.

Figure 1.1 Electricity production and prices in Germany in July 2017.^[11]

1.2 Energy storage and the role of hydrogen

The sun provides the earth with about 120 000 TW of radiation, which is 8000 times the current annual worldwide energy consumption of about 15 TW.^[12, 13] Covering 0.16% of the earth land with 10% efficient solar cells would be more than sufficient to meet the world's consumption rate of fossil energy.^[13]

However, the irradiation flux at the earth's surface fluctuates with season, time of the day and weather. Also, the average amount of solar irradiation is highest at the equator and decreases towards the poles. The solar flux fluctuation over a day and a year at 50° northern latitude, which represents northern Europe and roughly the border between USA and Canada, is shown in Figure 1.2. During the day-night intermittency there is a shortage of solar energy at night, and at 50° northern latitude around 70% of the energy is received during the summer months (April to September). This means that solar energy received in the summer period needs to be stored for the winter period where it can be used for, for instance, heating.

Figure 1.2 Calculated^[14] maximal solar insolation based on the equation of the sun's position at 50° northern latitude for a day (a) and a year (b).

Thus, solar energy needs to be collected, transferred into other energy carriers and partially stored at various time frames and, eventually transported from the supplier to the consumer. The time frames in which energy needs to be stored range from milliseconds to a year. Electricity producers need to adjust their supply instantly to the demand in order to keep the grid stable and avoid blackouts. At time frames up to several days, surplus electricity is mostly stored in pumped hydro-energy storage systems.^[15] However, building pumped hydro storage needs large geologically suited areas and has a major local environmental impact. Also battery electricity storage with a rate of 100 MW and a capacity of 129 MWh has been recently installed in South Australia, and more is in planning or construction around the globe.^[16-18] Along the efforts in transport electrification, the investments in batteries are increasing which has

led to a significant price drop of more than 50% between 2013 and 2016.^[19] Also, the energy storage capacity of pumped hydro-storage, batteries and others is finite which means that very high capacities would be needed to store energy over a longer time frame than a few hours or days. Such capacities are economically not feasible as these devices generate their return *via* charging and discharging cycles, *i.e.* buying electricity when it is produced in excess and relatively cheap and selling it when the demand is higher than the supply, and electricity is relatively expensive. Instead, in order to store energy over weeks or months, technologies are needed which transfer the energy from the sun into an energy carrier which is not bound to a device and thus has no production limits.

The most energy-dense carriers are fuels. Therefore, a carrier which can function as a long-term storage is a fuel, and hydrogen is believed to be such an energy carrier or an intermediate for it.^[7, 20, 21] Hydrogen is used in the chemical industry, among others, for the production of ammonia and methanol and holds great promises to be used for electricity generation in fuel cells for transportation, back-up power, and grid stabilization.^[7, 20-22] However, about 96% of the more than 50 million metric tons of hydrogen is produced from fossil fuels.^[23] Replacing its production from renewable sources would reduce the emission of CO₂ by about 685 million metric tons as 13.7 kg of CO₂ are emitted on average with every kg of H₂ produced.^[24] Also, hydrogen can be further converted with CO₂ and water to hydrocarbons, such as methanol, using energy from renewable sources, and these can be fed back into the existing hydrocarbon economy.^[25]

1.3 Hydrogen production from water splitting

Hydrogen is a common building block in nature and the most abundant element on earth. It is present in water and all organic compounds including natural gas and oil. Since the hydrogen molecule is not present in the atmosphere, it needs to be extracted from one of the compounds of which water is the most sustainable source. The stoichiometric water splitting equation to gaseous

hydrogen and oxygen is shown in Equation 1.1 in which the water can be gaseous or liquid, depending on the process conditions.

There are three major pathways to perform the splitting of water using the energy from sunlight, *i.e.* thermolysis, electrolysis (in combination with photovoltaics (PV) or concentrating solar power technologies (CSP)) and photo(electro)catalysis.

Direct water thermolysis into hydrogen and oxygen (Eq. 1.1) occurs at temperatures above 2000 °C.^[26] Solar concentrated furnaces at laboratory and pilot scales have obtained a temperature up to 3500 °C.^[27, 28] However, these temperatures set high requirements for the selection of refractory materials and construction of equipment and bear a considerable risk of an explosion due to the evolution of oxygen and hydrogen in the same compartment.^[22] In order to reduce process temperatures and separate hydrogen and oxygen evolution, two-step thermolytic water splitting is in development. Herein, an auxiliary chemical, such as a reduced metal oxide, sulfur-iodine or copper-chlorine, catalyzes the thermolysis. In the example of a metal oxide, an endothermic reduction is performed first in which oxygen is produced (Eq. 1.2), followed by water hydrolysis and hydrogen production (Eq. 1.3).^[7, 22]

Reported redox pairs of metal oxides include Fe₃O₄/FeO, TiO₂/TiO_x, Mn₃O₄/MnO, CeO₂/Ce₂O₃, Co₃O₄/CoO, Nb₂O₅/NbO₂, In₂O₃/In, WO₃/W, CdO/Cd and others.^[22] The procedure of thermolytic water splitting, however, brings in many challenges due to high temperature heat requirements. Working fluids including water, thermal oils, molten salts, steam, air and other gases, and equipment materials of the working fluid vessel have to be able to sustain the high temperature.^[22] Especially the usage of thermal oils is problematic as they are volatile, toxic and may decompose at high temperatures.^[22]

Electrolysis of water uses energy input from an external power source in the form of a direct current to drive the oxidation (Eq. 1.4) and reduction (Eq. 1.5) reactions of water to produce oxygen at the anode and hydrogen at the cathode, respectively.

The minimum required thermodynamic potential is 1.23 V. However, to overcome overpotentials and to drive the reaction at a sufficiently high rate, cell potentials between 1.8 and 2.4 V are required.^[29] The efficiencies range between 62 and 82% for alkaline and proton exchange membrane (PEM) electrolyzers.^[29] In combination with power generation efficiencies of ~17% for photovoltaics,^[9] overall conversion efficiencies of up to 14% can be expected for these commercially available system combinations.

Photo(electro)catalysis aims to integrate solar absorbance and electrolysis into one device which is predicted to produce hydrogen at a lower price than the combination of electrolysis and photovoltaics.^[30] Herein the light absorber also acts as the electrode on which the oxidation and/or reduction reactions occur. This has the advantage that a much greater area is used for electron transfer than in electrolyzers. Thus, the current densities can be much smaller and the required overpotentials substantially lower.^[30, 31]

1.4 Scope and outline of this thesis

The research described in this thesis focuses on the development of photoelectrochemical devices for the generation of hydrogen from water splitting. In particular, it aims to utilize electrochemistry for the coating and functionalization of flat and microwire-structured silicon with metals or semiconductors.

Silicon has been chosen as a substrate because it is a nontoxic, abundant and easily available material. Silicon is the second most common element after oxygen in the earth's crust^[32] and the technology in producing highly pure silicon is established in industry due to its usage in solar cells and computer

chips. Also, it can absorb the entire range of visible and UV light with a band gap of 1.1 eV which is in the ideal range for a tandem arrangement with a second, wider band gap absorber.^[33-36] Also, silicon can be doped p- and n-type, and provides an additional voltage of ~0.5 V to the photoelectrochemical system.

Electrochemistry has been used as the main deposition technique for semiconductors and metals on Si, due to its versatility to produce a wide range of materials (such as metals, alloys, oxides, etc.) and its ability to control the nucleation and growth and thus morphology by varying the potential, the current, and/or the electrolyte composition (such as pH, solvents, additives or reagent concentrations). Also, electrodeposition allows the coating of structured substrates, ensures a good electrical contact between substrate and deposit due to electron transfer-induced growth, is compatible with ambient conditions, and is easily scalable and inexpensive to produce commercially viable and cost-effective devices.

The thesis has been structured as follows:

Chapter 2 gives a brief overview of photo(electro)chemical water splitting.

In Chapter 3, a method is presented to control the size and density of electrochemically deposited platinum particles on p-type Si by the addition of hydrogen peroxide to the electrolyte solution. Atomic force microscopy of the deposited Pt particles at various H₂O₂ concentrations gave insight into the surface area and coverage, distribution, and deposited mass of the Pt particles.

In Chapter 4, the possibility to functionalize silicon microwires with two different materials at different locations has been explored. For that purpose, an axial p/n junction has been created in Si micropillars, and two different metals, *i.e.* platinum and silver, were deposited on the bottom p-type and top n-part, respectively, without the use of a masking step.

In Chapter 5, the deactivation processes of a tungsten oxide photoanode during photocatalytic water oxidation in a phosphate buffer at different pH were investigated. Oxygen evolution on the photoanode and hydrogen evolution on a platinum cathode were followed with high time and concentration resolution by

a gas chromatograph. The electrolyte was tested for potentially evolved hydrogen peroxide and the amount of corroded tungsten. Scanning electron microscopy provided insight into the morphology of the photocatalyst, and X-ray photoelectron spectroscopy into changes of its oxidation state.

In Chapter 6, molybdenum-doped and hydrogen-annealed bismuth vanadate was deposited on microwire-structured silicon coated with indium tin oxide. The aim was to study the influence of enhanced light absorption by the structure as well as the increase of surface area and mass of bismuth vanadate at various microwire lengths and spacings. The photocatalytic performance was evaluated by the oxidation of the hole scavenger sulfite to sulfate.

Chapter 7 provides a summary of the results described in this thesis and a perspective on photoelectrochemical water splitting.

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Chapter 2

Photocatalytic water splitting

In Chapter 1 it has been explained why the direct production of fuels from solar energy is important, and how the archetypal fuel hydrogen can be produced from water splitting. Here, we focus on the principles and requirements of a system that produces hydrogen by photocatalytic and photoelectrochemical water splitting. First, the principles of photocatalytic water splitting and the necessary requirements and characteristics of a standalone water splitting device to obtain practically applicable efficiencies are described. It is explained that the combination of two or more photoabsorbers in a Z-scheme configuration is needed in such a system. Furthermore, two different types of architectures, *i.e.* particle slurry-based and thin film arrangements of semiconductors on electrodes (photoelectrochemical cells), are introduced. It is shown why the targeted arrangement of photoelectrochemical cells in this thesis is superior to particle slurry approaches.

2.1 Photocatalytic principle and material requirements

The photocatalytic principle of splitting water in an acidic environment into hydrogen and oxygen with an ideal single band gap material is schematically shown in Figure 2.1. When light hits a semiconductor with a greater photon energy than the band gap, a photon may be absorbed and lead to an excitation of an electron from the valence to the conduction band. The electron in the conduction band and remaining hole in the valence band may then migrate to the semiconductor surface and perform the reduction of protons to hydrogen and oxidation of water to oxygen and protons, respectively. The generated protons at the oxidation sites diffuse then to the reduction centers to close the charge flow cycle.

Figure 2.1 Schematic illustration of photocatalytic water splitting in an acidic environment into hydrogen and oxygen.

In order for water splitting to occur the semiconductor must meet the following minimum requirements:

- The semiconductor has to absorb photons with an energy greater than the thermodynamic water splitting potential (1.23 V) plus proton reduction and water oxidation overpotentials
- The band edge positions have to straddle the hydrogen and oxygen redox potentials and their overpotentials, *i.e.* the conduction band edge has to be more negative than the proton reduction potential and the valence band edge more positive than the oxidation potential of water
- Be stable against (photo)corrosion.

Moreover, a practically applicable standalone water splitting photocatalyst/photoelectrochemical device needs to have the following characteristics:

- Generate a voltage between oxidation and reduction centers of at least 1.23 V plus overpotentials from the interfaces of the semiconductor with the electrolyte, metals or other semiconductors in order to accelerate the migration of electrons and holes towards the surface and decrease the ratio of recombination over performance of redox reactions
- Provide efficient charge transport through the material
- Have a high light-harvesting efficiency
- Evolve hydrogen and oxygen in different compartments in order to save additional separation steps and prevent the risk of explosion
- Have a high catalytic activity (low overpotentials) towards proton reduction and water oxidation
- Be made of abundant, non-toxic and low cost materials.

To be compatible with hydrogen production from fossil fuels, the price for solar hydrogen needs to be below \$4/kg to \$2/kg.^[1, 2] This translates to solar-to-hydrogen efficiencies of rugged and long-lived (>10 years) solar water spitting systems to 10 to 15%.^[2, 3] To use as much energy from the solar spectrum as possible, William Shockley and Hans-Joachim Queisser calculated in 1961 that the optimal band gap of an ideal single p-n junction solar cell of 1.1 eV would result in a maximum efficiency of 30% when illuminated with a blackbody spectrum of 6000 K surface temperature.^[4] Later, the so-called Shockley–Queisser limit was calculated to be 33.2% at a band gap of 1.34 eV for an AM 1.5G spectrum which also takes light absorption and scattering in the atmosphere into account.^[5] Considering the minimum requirements for a semiconductor to split water and neglecting the energy losses from H₂ and O₂ evolution overpotentials and other described characteristics, a band gap of 1.34 eV should be sufficient to drive the redox reactions. However, taking the losses into account, required single material semiconductor band gaps between 2.3 and 2.0 eV have been proposed which result in solar-to-hydrogen efficiencies between roughly 7 and 18%.^[6, 7]

In order to achieve high enough practical efficiencies, two or more photon systems with two or more absorbers with smaller band gaps are required.^[2, 7, 8] Two strategies are presented in the literature on how to combine materials with different band gaps into a water splitting device, *i.e.* particle slurry-based systems, and photoelectrochemical cells. Both benefit from a Z-scheme configuration of the semiconductor materials to promote broad use of the solar spectrum and thus boost their efficiency. The Z-scheme arrangement utilizes two semiconductors with staggered band edge positions, which are by themselves not able to perform the overall water splitting reaction but have more favorable band gaps to harvest the energy from the solar spectrum more efficiently than a single semiconductor.

2.2 Dual absorber particle slurry systems

Figure 2.2 shows schematically the concept of a particle slurry-based system with a Z-scheme configuration and the use of a mediator. Upon illumination, electrons from both semiconductors are photoexcited into the conduction bands. Water oxidation is performed at one, and proton reduction at the other semiconductor. Only one band edge of one photocatalyst straddles the equilibrium potential of O_2 or H_2 and performs the corresponding reaction. The electron cycle is closed by the recombination of the photoexcited electron from the water oxidation photocatalyst with the hole of the proton reduction photocatalyst. This occurs by either the two photocatalysts having physical contact or the presence of an electron mediator, which shuttles between the two photocatalysts. In the case of a mediator, the photoexcited electrons in the water oxidation catalyst reduce the mediator which then diffuses to the proton reduction catalyst and injects an electron into its valence band. This system has the advantage that oxygen and hydrogen can be formed in different compartments when the photocatalysts are separated by a mediator permeable membrane. Typically used mediator redox couples are IO_3^-/I^- or Fe^{3+}/Fe^{2+} .^[9-11]

Figure 2.2 Schematic illustration of photocatalytic water splitting into hydrogen and oxygen in a Z-scheme arrangement with two semiconductor materials and a redox mediator in acidic environment.

The Z-scheme arrangement system with a mediator has been shown for, for instance, Pt or Ru-loaded $\text{SrTiO}_3\text{:Rh}$ as the proton reduction photocatalyst and WO_3 , BiVO_4 , BiMoO_6 or Ru-loaded $\text{SrTiO}_3\text{:Na,V}$ as water oxidation photocatalyst.^[12, 13] Also examples with physically connected materials have been reported.^[14-17] However, the efficiencies in Z-scheme mediator systems are low as the semiconductors also react with the mediator in the undesired direction, *i.e.* the water reduction photocatalyst reduces the oxidized mediator species and the water oxidation photocatalyst oxidizes the reduced form of the mediator.^[8, 9, 18] Also, the redox mediator may strongly absorb part of the illuminated light, reducing the light available for the photocatalysts.^[10] The Z-scheme particle systems without a mediator have the disadvantage that H_2 and O_2 gases evolve in the same compartment, which besides introducing the need for gas separation and bearing the risk of an explosion, also suffer from undesired back-reactions of the gases on their surfaces. In Chapter 5 we will demonstrate a loss of about 50% in hydrogen yield, when oxygen and hydrogen are produced simultaneously in the same compartment.

2.3 Photoelectrochemical cells

The first photocatalytic water splitting on a semiconductor electrode was shown by Akira Fujishima and Kenichi Honda in 1972.^[19] Herein the authors constructed an electrochemical cell with a TiO_2 electrode connected to a platinum black counter electrode.^[19] Figure 2.3 schematically shows the setup, without a membrane separating the two compartments. The authors described that a current

from the platinum electrode flowed to the TiO_2 electrode through the external circuit when the surface of the TiO_2 was irradiated.^[19] TiO_2 fulfills the minimum requirements for a photocatalyst to perform photocatalytic water splitting. The material is stable, the band gap of ~ 3.2 eV is wide enough to absorb light with the required thermodynamic potential for water oxidation and reduction reactions and the band edges straddle these potentials. However, TiO_2 is able to absorb only the UV part of the solar spectrum which is approximately 5% of the terrestrial solar radiation. Due to the n-type character of this semiconductor, holes are accelerated towards the TiO_2 surface and photoexcited electrons towards the current conductor.^[20-24] A p-type semiconductor would have shown the electron flow in the opposite direction.^[20, 23, 24] Therefore, also for PEC systems, incorporation of two semiconductors in a Z-scheme arrangement, is the way to go.

Figure 2.3 Schematic illustration of a single photoabsorber photoelectrochemical cell.

Today, photoelectrochemical cells still provide the most promising configuration for practical hydrogen production from solar water splitting.^[2, 25] This arrangement type has the potential to fulfill not only the minimum, but all described requirements and characteristics. The list of semiconductors which are viable for the use as photoabsorbers is short.^[26] However, the construction of the photocatalytic device with electrodes instead of particle systems allows the usage of protective layers (e.g. against (photo)corrosion) and thus a selection between significantly more semiconductor candidates.^[26, 27] These materials can then be chosen by taking into account their charge transport properties, abundance, high light harvesting efficiency, *etc.* High sunlight harvesting efficiencies can be achieved when a large-band gap material is layered in front of a small-band gap

material, in a Z-scheme configuration.^[28-32] Herein, the short wavelength (high energy) photons will be absorbed by the top semiconductor layer (large band gap), and the long wavelength (low energy) photons will pass through and be absorbed by the underlying semiconductor layer (small band gap). Calculations, which include losses from hydrogen and oxygen evolution overpotentials and assume a 2 cm photon path length through an aqueous electrolyte, have shown that a maximum solar-to-hydrogen efficiency of 24.5% is possible.^[32] Accordingly, the materials have to have a band gap of ~ 1.1 and ~ 1.7 eV.^[32] To increase catalytic activity towards proton reduction or water oxidation on the photoactive electrode, catalytic layers can be applied on top of the electrode which may also decrease surface defects and thus suppress electron and hole recombination.^[33-37] The H_2 and O_2 evolution occur on two different electrodes which allows the ability to separate the gases *in situ*. To increase the voltage between the two electrodes, different doping of the materials can be applied to create an inner photovoltaic cell. Figure 2.4 shows this type of a photoelectrochemical cell with an underlying silicon p/n junction. This design type is the basis of the research presented in Chapters 5 and 6. However, also other approaches building tandem devices exist, which for instance use a wireless design or hetero-type dual photoelectrodes.^[20, 25, 26, 33, 38-42]

Remarkable efficiencies have been achieved with photoelectrochemical cells. For instance, Young *et al.* obtained a 16.2% solar-to-hydrogen efficiency in 2017 by creating a tandem device photocathode consisting of a gallium arsenide (GaAs)

photovoltaic system, and a gallium indium phosphide (GaInP) photoelectrical cell covered with a very thin aluminum indium phosphide (AlInP) and GaInP layer for reduction of surface defects and protection from corrosion.^[32] May *et al.* achieved 14.0% with a similar system in 2015.^[37] However, these devices are not yet practically feasible as they need improvements in long-term durability and reduction of the costs of the device. Furthermore, the usage of more abundant and non-toxic materials is desired, which is also targeted in this thesis. With abundant, non-toxic and low cost materials and preparation methods, for example, Abdi *et al.* obtained up to 4.9% solar-to-hydrogen efficiencies by combining cobalt phosphate-coated bismuth vanadate (BiVO₄) with a gradient tungsten doping and single- or double-junction silicon solar cells.^[43]

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Chapter 3

Controlling the size and density of electrochemically deposited Pt particles on p-type Si by hydrogen peroxide

Covering p-type silicon with Pt nanoparticles is of great interest for the fabrication of a photocathode for photocatalytic hydrogen production. Controlling the Pt particle size and density is essential to achieve a high catalytic activity and thereby limit the use of the precious metal. In this study, using a simple electrodeposition method (at a charge density of 20 mC/cm^2), we reduced the average mean particle diameter from 302 nm to 60 nm, while simultaneously increasing the particle density from 0.7 to $13.0 \text{ particles}/\mu\text{m}^2_{\text{Si}}$ by addition of an optimized quantity of 81 mM H_2O_2 to the electrolyte solution. At a significantly higher H_2O_2 concentration, the deposited Pt mass reduced upon increasing charge density. These results suggest that at H_2O_2 concentrations of 81 mM and below, H_2O_2 adsorbs on the nucleated Pt particles, thus reducing adsorption and reduction of PtCl_6^{2-} on initially formed metallic Pt particles. At high H_2O_2 concentrations, however, hydroxyl radicals, which are formed during partial H_2O_2 reduction, oxidize nucleated Pt particles, thus causing their cathodic dissolution, and limiting achievable Pt coverages.

3.1 Introduction

Photocatalytic water splitting has the potential to contribute to hydrogen production from renewable resources.^[1, 2] Silicon is a promising candidate to be used as a photocathode due to its sufficiently negative conduction band edge and an almost optimal band gap of 1.12 eV to absorb the terrestrial solar spectrum efficiently.^[3] Moreover, silicon is a nontoxic, relatively stable, and second most abundant element on earth, and it is readily compatible with the silicon-based microelectronic and photovoltaic industry.^[3]

To run the hydrogen evolution reaction (HER), silicon needs to be p-type doped to achieve favorable band bending when in contact with an aqueous electrolyte. Loading with a catalyst is necessary to reduce the overpotential for proton reduction.^[4-6] In addition, the catalyst protects the silicon surface underneath from forming electrically insulating silicon oxide, and at the same time acts as conductive channel for the electron transport to the electrolyte.^[7] The insulating silicon oxide layer is thermodynamically stable over a wide range of pH and potential.^[8]

Platinum is one of the best electrocatalysts in acidic medium for the hydrogen evolution reaction.^[9] It has been shown that the deposition of Pt islands on p-Si is superior to the formation of continuous films for photoelectrochemical proton reduction.^[4, 5, 10] When the Pt film is discontinuous, a Schottky barrier between p-Si and the electrolyte is formed which generates a photovoltage and thus enhances H₂ evolution at the Pt particles.^[4, 10] In contrast, the Schottky barrier formed between Pt films and p-Si is very low or the interface is Ohmic due to negligible differences in the work functions between p-Si and Pt.^[4, 10]

However, Pt is a relatively scarce element in the earth's crust.^[11] Minimizing its deposited mass drastically reduces the cost of a solar-to-fuel device and significantly improves its optical properties by improving the transmittance of light to the silicon absorber.^[12] Nakato *et al.* have proposed the metal islands to have a 5 nm width and 20 nm separation distance when the saturation current density is fairly low, and a larger particle size and smaller distance for higher current densities.^[5] Thus, to manufacture a device with optimal performance it is

essential to be able to control the size and density of the Pt particles on a nanometer scale.^[5]

A scalable and low-cost technique for Pt particle deposition on p-Si is electrodeposition.^[4, 13-16] However, the electrochemical deposition process of Pt particles on p-Si either leads to low densities, and/or to large, μm sizes when high charge densities are applied. A commonly used method to reduce the deposited particle size is to perform the deposition under illumination.^[4, 6, 14, 15, 17] Thereby, instead of the hole injection through the valence band in the dark, photoexcited electrons reduce PtCl_6^{2-} via the conduction band, leading to a high amount of nucleation points.^[14] Also, pulsed electrodeposition has been employed in which a short high potential pulse induces the formation of many Pt nucleation points.^[18] However, as we will show in Chapter 4, the deposition under illumination or the application of a high potential pulse is not always desired.

Herein, we present a chemical method to reduce the electrochemically deposited Pt particle size to the low nm range and control their distribution density as well. To this aim, hydrogen peroxide is added to the electrolyte solution, and the influence of the H_2O_2 concentration on the obtained Pt particle morphology at variable charge density is investigated systematically.

3.2 Materials and methods

3.2.1 Pt electrodeposition

Boron-doped, p-type silicon substrates (<100>-oriented, resistivity 5-10 Ωcm , 100 mm diameter, 525 μm thickness, single-side polished, Okmetic Finland) were cleaned by immersion in 100 % nitric acid (HNO_3) (2×5 min) and in 69 % nitric acid (10 min). After quick dump rinsing in de-mineralized (DI) water, the sample was immersed in a 1 % aqueous hydrofluoric (HF) acid solution for at least 1 min to remove the silicon oxide layer, washed by quick dump rinsing in de-mineralized (DI) water, spin dried, after which the backside was sputter-coated with a 1 μm thick aluminum/silicon alloy (99 % Al, 1 % Si) (Oxford PL 400, 7000 W) to create a low resistance Ohmic contact. Subsequently, the wafer was cut into pieces of approximately $2.5 \times 2.5 \text{ cm}^2$ and mounted into a

custom-made single cell Teflon-based reactor with a volume of about 8 ml. The active surface area applied was 2.01 cm² as determined by the O-ring of the reactor. A standard three-electrode system with a platinum mesh counter electrode was used. The reactor was open to the environment and a potentiostat (PAR, VersaStat 3) served as a power source. Platinum was electrodeposited potentiostatically at -0.7 V vs. Ag/AgCl (3 M NaCl, BASi MF 2052) from an aqueous solution of 5 mM hexachloroplatinic(IV) acid (H₂PtCl₆) and 0.5 M sodium sulfate (Na₂SO₄) at room temperature. A defined amount of a hydrogen peroxide solution (H₂O₂, ≥35 %) was added to a part of the H₂PtCl₆/Na₂SO₄ solution, prior to experiments, if needed. The measured pH (Hanna Instruments pH 209) of the electrolyte was 2.55. The deposition was discontinued when the charge density amounted to either 5, 10, 20, 40, or 100 mC/cm².

3.2.2 Atomic force microscopy (AFM)

Atomic force microscopy (AFM) images were taken with a Digital Instruments Nanoscope III AFM in tapping mode and a silicon cantilever at room temperature. Particle detection and analysis was performed with the software “Gwyddion v2.37” in which the baseline of the scan was corrected and the particles masked by a threshold algorithm. The software determined the mean radius of each particle which was doubled to report the mean particle diameter.

3.3. Results and discussion

Figure 3.1a-e shows distribution histograms overlaid with normal distribution curves, corresponding to atomic force microscopy (AFM) images of potentiostatically deposited Pt particles at -0.7 V vs. Ag/AgCl (3 M NaCl) on p-type silicon. The passed charge density was varied between 5 mC/cm² and 100 mC/cm². Pt particles are highlighted in cyan and their average mean diameter, distribution density, specific surface area and deposited mass are plotted in Figure 3.2. The deposited Pt mass increased almost linearly between 5 mC/cm² and 100 mC/cm² from 13 mg/m²_{Si} to 967 mg/m²_{Si}. The stoichiometries of the two consecutive reduction reactions are shown in Equations 3.1 and 3.2.

All deposited Pt mass values, except those obtained at 5 mC/cm², are above theoretical values calculated assuming 100 % faradaic efficiencies. We attribute this error to artefacts in assessing particle sizes using atomic force microscopy. The broadening of the AFM tip causes a broadening of the laterally measured particle size.^[20] This error increases with increasing particle height, and is consistent with our results in which the Pt mass deviation between measured and theoretical values increases with increasing passed charge density (Figure 3.2b). We expect this effect to be insignificant at particle diameters below 200 nm. The deposited Pt mass is lower at 5 mC/cm² due to Pt-catalyzed hydrogen evolution, which is favored at small Pt particle sizes.

Figure 3.1 a–e) Distribution histograms with 50 nm bin size, normal distribution curves and inset AFM images, f) Si surface coverage of electrochemically deposited Pt particles at -0.7 V vs. Ag/AgCl (3 M NaCl) from a 5 mM H_2PtCl_6 , 0.5 M Na_2SO_4 solution upon variation of the passed charge density.

Figure 3.2 a) Average mean particle diameter and distribution density (from AFM), b) specific surface area and mass of electrochemically deposited Pt particles at -0.7 V vs. Ag/AgCl (3 M NaCl) from a 5 mM H₂PtCl₆, 0.5 M Na₂SO₄ solution upon variation of the passed charge density.

Apart from electrochemical reduction, an electroless Pt deposition on silicon is theoretically conceivable in which PtCl₆²⁻ is reduced by the oxidation of silicon (Eq. 3.3).

Control experiments in which we kept p-Si for a typical experiment time of 80 s in contact with the PtCl₆²⁻-containing electrolyte solution, however, showed insignificant Pt deposition of 2.6×10⁻⁸ mg/m²_{Si}. It is theoretically possible that electrochemically nucleated Pt particles accelerate the electroless Pt deposition. However, electroless Pt deposition is typically performed in a hydrofluoric acid (HF)-containing solution to etch away silicon oxide and constantly expose the silicon surface.^[21]

At 5 mC/cm² the majority of the particles had a mean diameter below 150 nm and an average mean particle diameter of 76 nm. At increasing charge densities the particles showed an asymptotic growth and reached an average mean diameter of 490 nm at 100 mC/cm² (Figure 3.1a-e and Figure 3.2a). The silicon surface coverage followed the same trend between 5 mC/cm² and 40 mC/cm² with an increase from 1 % to 8 %, respectively (Figure 3.1f). This is in agreement with the linear Pt mass, and thus volume, increase as the particles grow in a three-dimensional, semi-spherical shape. Only the surface coverage at 100 mC/cm² seems to deviate from this trend which may be attributed to the AFM

artefacts of large particles and the highest mismatch between theoretical and deposited Pt mass. Simultaneously, the Pt particle distribution density exponentially decreased from 1.6 particles/ $\mu\text{m}^2_{\text{Si}}$ at 5 mC/cm² to 0.5 particles/ $\mu\text{m}^2_{\text{Si}}$ at 40 mC/cm² and then increased to 1.1 particles/ $\mu\text{m}^2_{\text{Si}}$ at 100 mC/cm² (Figure 3.2a). This is consistent with the exponential decrease of the Pt surface area from 1.41 m²/g at 5 mC/cm² to 0.47 m²/g at 100 mC/cm² (Figure 3.2b) since small particles have a higher surface-to-volume ratio. The decrease in specific surface area and the reduction of particle density with increased passed charge density, show that existing particles tend to grow while formation of new nucleation points is limited.

The results are in good agreement with the Volmer-Weber island growth mechanism.^[13, 22] After nucleation, Pt particles tend to grow larger instead of forming further nucleation points, implying that the overpotential for the reduction of PtCl₆²⁻ is lower at the Pt surface than on the Si surface.^[13, 22] Thereby, platinum catalyzes its own deposition. The optically observed particle distribution is spatially completely random and is in agreement with many models.^[13, 22] Particles that are located closely together coalesce during growth and thus reduce particle density.

To suppress particle growth and enhance nucleation, we added between 0 and 845 mM hydrogen peroxide (H₂O₂) to the electrolyte solution and performed the potentiostatic electrodeposition, until a charge density of 20 mC/cm² was reached (Figure 3.3a-e and Figure 3.4a). The Si surface coverage dropped exponentially from 6.4 % to 0.5 % between 0 and 845 mM H₂O₂, with an exception at 81 mM H₂O₂, in which the surface coverage was 4.8 %. The average mean particle diameter decreased first from 304 nm at 0 mM H₂O₂ to 60 nm at 81 mM H₂O₂, and barely changed at higher H₂O₂ concentrations. The specific surface area increased with increasing H₂O₂ concentration from 0.8 m²/g at 0 mM H₂O₂ to 4.4 m²/g at 845 mM H₂O₂ with the strongest increase to 3.6 m²/g at 81 mM H₂O₂. The particle distribution density fluctuated between 0.2 particles/ $\mu\text{m}^2_{\text{Si}}$ and 1.0 particles/ $\mu\text{m}^2_{\text{Si}}$ in 0 mM, 15 mM, 412 mM and 845 mM H₂O₂, but is high at 81 mM H₂O₂ (13.0 particles/ $\mu\text{m}^2_{\text{Si}}$). The Pt mass dropped exponentially from 126.1 mg/m²_{Si} to 1.4 mg/m²_{Si}, with a linear H₂O₂ increase from 0 mM and

845 mM, whereas the theoretically deposited Pt maximum is $101.1 \text{ mg/m}^2_{\text{Si}}$ (Figure 3.4b).

Figure 3.3 a–e) Distribution histograms with 20 nm bin size, normal distribution curves and inset AFM images, f) Si surface coverage of electrochemically deposited Pt particles at -0.7 V vs. Ag/AgCl (3 M NaCl) and 20 mC/cm^2 from a 5 mM H_2PtCl_6 , 0.5 M Na_2SO_4 solutions at varying H_2O_2 concentrations. Note the different y-axis scale in c).

Figure 3.4 a) Average mean particle diameter and distribution density (from AFM), b) specific surface area and mass of electrochemically deposited Pt particles at -0.7 V vs. Ag/AgCl (3 M NaCl) from 5 mM H_2PtCl_6 , 0.5 M Na_2SO_4 solutions at varying H_2O_2 concentrations, at a charge density of $20 \text{ mC}/\text{cm}^2$. Faradaic efficiencies (FE) were corrected by estimating the current from H_2O_2 reduction.

Besides the catalysis of Pt deposition, nucleated Pt particles also catalyze the reduction of H_2O_2 to water (Equation 3.4).^[23]

$$E^\circ = 1.78 \text{ V}^{[19]} \text{ (Eq. 3.4)}$$

This causes a competitive and thermodynamically more favorable reduction of H_2O_2 on Pt surfaces, which is seen by increased current densities in the deposition current-time curves (Figure 3.5). The current density was highest at a H_2O_2 concentration of 81 mM. This correlates well with the observed exceptionally high Pt particle density, Si surface coverage and specific surface area found at this H_2O_2 concentration. The parasitic current from H_2O_2 reduction is approximately the difference in current between Pt deposition in H_2O_2 -free and H_2O_2 -containing solutions. Thus the amount of charges used for H_2O_2 reduction is the integrated area in the current density graph between the curves of H_2O_2 -containing and H_2O_2 -free deposition. To estimate the Pt mass at corrected faradaic efficiencies (FE), we have integrated the current density curves of the deposition from H_2O_2 -free electrolytes until the time used for deposition in H_2O_2 -containing electrolytes. The current densities at 0 mM H_2O_2 and 845 mM H_2O_2 crossed after 33 s of deposition time. In this case we integrated the graph of the current density in 845 mM H_2O_2 solution between 33 s and the end of the experiment. Resulting Pt masses match well with the measured mass up to a H_2O_2 concentration of 412 mM (Figure 3.4b). At a concentration of 845 mM H_2O_2 a

large deviation, *i.e.* only 2 % of the theoretical Pt amount after FE correction was found. This is attributed to a mechanistic change in the deposition process which we investigated in further experiments.

The deposition of Pt particles at a passed charge density of 5 mC/cm² without addition of H₂O₂ and at 20 mC/cm² with addition of 81 mM H₂O₂ led to similar deposited masses of 13 mg/m²_{Si} and 14 mg/m²_{Si}, respectively. At the same time, the mean particle diameter decreased by 20 % from 75.4 nm to 60.0 nm, the distribution density increased by a factor 8.2 from 1.58 particles/μm²_{Si} to 13.0 particles/μm²_{Si}, the specific surface area by a factor of 2.6 from 1.41 m²/g to 3.63 m²/g and the silicon surface coverage by a factor 3.7 from 1.3% to 4.8%. In the H₂O₂ concentration range between 0 mM and 81 mM H₂O₂ the equilibrium between Pt particle growth and nucleation shifts towards nucleation, by adsorption of H₂O₂ on the nucleated Pt particles, thus suppressing the adsorption of PtCl₆²⁻.

Figure 3.5 Current density vs. time curves of potentiostatically deposited Pt particles at -0.7 V vs. Ag/AgCl (3 M NaCl) from a 5 mM H₂PtCl₆, 0.5 M Na₂SO₄ solutions at varying H₂O₂ concentrations, at a charge density of 20 mC/cm².

To understand the influence of H_2O_2 on Pt particle growth and distribution density at higher H_2O_2 concentrations than 81 mM, we performed the Pt deposition in a 845 mM H_2O_2 solution and varied the deposition charge density between 80 mC/cm² and 150 mC/cm². Remarkably, the silicon surface coverage remained fairly constant at 0.7% (Figure 3.6e), while the deposited Pt mass dropped from 0.60 mg/m²_{Si} to 0.23 mg/m²_{Si}. The Pt particle distribution density decreased with increasing charge density from 16.0 particles/μm²_{Si} to 7.7 particles/μm²_{Si}. The mean particle diameter increased from 24 nm to 32 nm (Figure 3.6a-d and Figure 3.7a), and the specific surface area increased from 13.2 m²/g to 30.9 m²/g (Figure 3.7b).

The large Pt mass decreases (61.7% at charge densities of 80 mC/cm² to 150 mC/cm² and 83.0% at 20 mC/cm² to 150 mC/cm²) at increased charge densities indicate that electrons cause a H_2O_2 -induced corrosion of Pt at high H_2O_2 concentrations.

In literature, cathodic Pt dissolution in acidic media has been observed to occur through anodic and irreversible formation of surface oxide during cyclic voltammetry scans.^[24-26] Under purely cathodic conditions, when no anodic potential is applied, corrosion was reported after Pt had been exposed to air and thus formed an oxide layer.^[27] From these reports we can derive the dissolution mechanism of Pt particles at H_2O_2 concentrations above 412 mM. Potentiostatically supplied electrons induce a Fenton's reagent-type reaction in which hydroxyl radicals are formed by a partial reduction of H_2O_2 (Eq. 3.5).

These highly oxidative hydroxyl radicals oxidize the Pt particle surface and cause their cathodic dissolution. Platinum oxide is a worse H_2O_2 reduction catalyst than metallic platinum,^[28] thus explaining the current reduction during potentiostatic deposition at H_2O_2 concentrations of 412 mM and above (Figure 3.5).

Figure 3.6 a–d) Particle distribution histograms with 10 nm bin size, normal distribution curves and inset AFM images, e) Si surface coverage of electrochemically deposited Pt particles at -0.7 V vs. Ag/AgCl (3 M NaCl) from a 5 mM H₂PtCl₆, 0.5 M Na₂SO₄ and 845 mM H₂O₂ solution upon variation of the passed charge density.

Figure 3.7 a) Average mean particle diameter and distribution density (from AFM), b) specific surface area and mass of electrochemically deposited Pt particles at -0.7 V vs. Ag/AgCl (3 M NaCl) from a 5 mM H₂PtCl₆, 0.5 M Na₂SO₄ and 845 mM H₂O₂ solution upon variation of the passed charge density.

3.4 Conclusions

In conclusion, the size and density of electrochemically deposited Pt particles can be easily manipulated and adjusted by the addition of hydrogen peroxide to the electrolyte solution, and by variation of charge densities passed through the cell. Our results suggest that the dominating deposition mechanism depends on the H₂O₂ concentration and could be completely revealed by *in situ* studies. We assume that when 81 mM H₂O₂ or less is added, H₂O₂ adsorption on nucleated particles dominates, thus preventing Pt growth by suppressing PtCl₆²⁻ adsorption and consecutive reduction to metallic platinum. At concentrations of 412 mM and above, we assume high hydroxyl radical concentrations are created by partial H₂O₂ reduction, which presumably induce Pt surface oxidation and cathodic dissolution.

These results provide a synthetic means to optimize size and density of Pt particles for high solar-to-hydrogen efficiency of silicon-based photocathodes, as well as cost-effective production with a simple and scalable electrodeposition technique. Also, the understanding of Pt corrosion in a H₂O₂-containing or (unintentionally) H₂O₂-developing environment, such as in fuel cells and electrolyzers, may lead to rational measures for improvements of their stability.

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3.6 References

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Chapter 4

Spatioselective electrochemical and photoelectrochemical functionalization of silicon microwires with axial p/n junctions

Dually and spatioselectively functionalized silicon and other semiconductor nano to microwires with an axial homo- or heterojunction possess unique properties for the design of next generation devices and systems with novel functions. In this work, we present a powerful method of selectively functionalizing Si microwire surfaces by utilizing the nature of an axial p/n junction placed into the microwires. Stepwise electrochemical functionalization in light and dark was used to address the top or bottom selectively. First, we demonstrated the concept experimentally by the selective reduction of platinum on p-type and silver on n-type silicon microwires with an axial p/n junction on different samples. Subsequently, the reactions were combined, resulting in a dual functionalized microwires with an axial p/n junction, as confirmed by HR-SEM and EDX. The junction depletion layer remained unmodified which allowed its visualization and comparison with theoretical calculations.

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4.1 Introduction

Semiconductor wires and wire arrays of nano- to micrometer sizes have unique optical, electronic, electrochemical, thermal, mechanical and magnetic properties,^[1] which make them attractive structures for electronic, sensor, photonic, thermoelectric, photovoltaic, photoelectrochemical and battery applications.^[1-5] In order to tailor the wire properties for a target application, in most cases functionalization is required, for example, by deposition of catalysts,^[6] additional semiconductors,^[7] grafting with organic molecules^[8] or polymers.^[9] These modifications are commonly performed across the entire surface of the wires. Janus-type wires on the other hand, with differently functionalized top and bottom segments, may provide access to new types of devices or improve the functionality of existing ones.^[10] For instance, many applications, such as sensors,^[11] tunnel field-effect transistors,^[12-14] light-emitting diodes,^[15, 16] photovoltaics^[17-19] and photonics,^[15, 20] require or would benefit from an axial homo- or heterojunction and electrical communication between the segments with e.g. different catalytic or surface properties. The ability to create semiconductor wires and wire arrays with axial heterostructures has been demonstrated^[11-16, 18] and the feasibility of creating bi-functionalized semiconductor wires and wire arrays has been reported previously for their use in photocatalysis^[21-23] and microfluidics,^[24, 25] or as superhydrophobic surfaces^[26]. However, a combination of heterostructured wires with functionalized surfaces is rare, mainly because their preparation is complex and requires several steps. So far, bi-functionalized wires have been created by physically masking the part of the wire that was to remain unmodified.^[21-23, 26] Typically, wires are embedded completely in a polymeric material first, which is then subsequently etched back to expose parts of the wires for further functionalization. This masking process makes it difficult to control the functionalization boundary precisely, reproducibly, and homogeneously across an array, which is particularly important for, for example, axially heterostructured wires where a small misalignment could lead to failure of the device.

Herein, we show a method for the direct and spatioselective bi-functionalization of semiconductor microwires, employing the different electronic properties of an

axial junction in the dark and under illumination. As an example of the concept, we have studied silicon microwires with an axial n^+/p junction.

Figure 4.1 Schematic illustration of the spatioselective functionalization process of silicon microwires with an axial n^+/p junction: an initial silicon microwire (left) is functionalized by the electrochemical deposition of Pt in the dark on the p-Si part (a) and of Ag under illumination on the n^+ -Si part (b, c). Sequential deposition of Pt and Ag leads to a bi-functionalized silicon microwire (right) in which a depletion zone is visible between the functionalized areas. Step (d) provides an optional, but here unexplored, route.

Figure 4.1 schematically shows the concept. It starts from a silicon microwire that has an axial n^+/p junction, prepared by the n-doping of a flat p-base wafer followed by dry etching to create the microwires. The junction induces diode-like behavior upon application of a negative potential to the p-region, preventing electrons to pass from bottom to top. This allows the selective functionalization of the bottom segment by reductive electrodeposition, which is tested here by the electrodeposition of Pt nanoparticles from a hexachloroplatinic acid precursor solution (Figure 4.1a). Under illumination, the junction promotes the migration

of electrons to the n^+ -Si surface, and allows the selective functionalization of that surface, which is demonstrated here by the electrodeposition of silver (Figure 4.1b/c). The holes accumulated in the p-Si part either recombine with electrons supplied by an external source, i.e., by applying a negative bias to the base silicon, or migrate to the p-Si surface likely causing its oxidation. Performing both functionalization steps consecutively results in dually and spatioselectively functionalized arrays of microwires. As Figure 4.1 indicates, we observed (see below) an unmodified band between the functionalized segments in the final wires, attributed to a depletion zone around the junction. We provide here analytical data and theory to explain this phenomenon.

4.2 Materials and methods

4.2.1 Fabrication of silicon microwires with axial n^+ /p junction

Figure 4.2 Schematic illustration of the synthesis of silicon microwires with axial n^+ /p junctions. a) Low pressure chemical vapor deposition (LPCVD) of silicon-rich silicon nitride (SiRN) on p-type silicon substrates. b) Removal of SiRN from the front side by reactive ion etching (RIE). c) Spin coating of phosphorus spin-on-glass (P-SOG) at 6000 rpm for 30 s. d.) Thermal phosphorus drive-in at 1100 °C for 60 min. e) Definition of microwire arrays by standard UV-lithography. f) cryogenic (-100 °C) deep reactive ion etching (DRIE). g) removal of photoresist and silicon oxide and sputtering of aluminum/silicon alloy (99% Al, 1% Si).

Figure 4.2 schematically shows the fabrication of silicon microwires with axial n^+ /p junction. Boron-doped, p-type silicon substrates ($\langle 100 \rangle$ -oriented, resistivity 5-10 Ωcm , 100 mm diameter, 525 μm thickness, single-side polished, Okmetic Finland) were cleaned by immersion in 100% nitric acid (HNO_3) (2×5 min) and

in 69% nitric acid (15 min), followed by quick dump rinsing in de-mineralized (DI) water, immersion in a 1% aqueous hydrofluoric (HF) acid to remove the formed oxide shell and another quick dump rinsing cycle. After spin drying the wafers, 100 nm thick silicon-rich silicon nitride (SiRN) was deposited using low pressure chemical vapor deposition (LPCVD) on both sides of the wafer, removed from the front side with reactive ion etching (Adixen AMS100DE; octafluorocyclobutane (C_4F_8) and methane (CH_4)), followed by an oxygen plasma treatment and piranha cleaning (mixture of concentrated sulfuric acid and 30% aqueous hydrogen peroxide, 3:1 (v/v), 20 min) to remove any contamination (*i.e.* fluorocarbon traces from the DRIE-process). Subsequently, the front side was covered by a phosphorus spin-on-glass (P-SOG, Filmtronics P509), spun at 6000 rpm for 30 s, and annealed at 1100 °C for 60 min. The remaining P-SOG and SiRN layers were removed by immersion in buffered hydrogen fluoride (1:7, BHF) for 10 min, washed with DI water and dried with a nitrogen flow. By means of standard UV-lithography, six 2×2 cm² areas with an array of microwires (specifications: diameter 4 μ m, spacing 2 μ m, hexagonally stacked with a packing density of 35%) were defined in photoresist (Olin 907-17), and post-baked for 10 min at 120 °C after exposure and development. The photoresist acted as a mask layer during cryogenic (-100 °C) deep reactive ion etching (DRIE; Adixen AMS100SE, 1000 W) of silicon, using sulfur hexafluoride (SF_6 , 200 sccm) for etching silicon and O_2 (30 sccm) for passivating the sidewalls. The height of the wires was determined by the etch duration, which was set to 2 min, resulting in wire heights of approximately 7 μ m. After etching, the photoresist mask was stripped off with oxygen plasma, followed by piranha cleaning (20 min), rinsing with DI water and drying with nitrogen. Prior to selective electrodeposition experiments, the sample was immersed in 1% aqueous hydrofluoric (HF) acid solution for at least 1 min to remove the silicon oxide shell, washed by quick dump rinsing in de-mineralized (DI) water, spin dried, after which the backside was sputter-coated with a 1 μ m thick aluminum/silicon alloy (99% Al, 1% Si) (Oxford PL 400, 7000 W) to create a low resistance Ohmic contact.

4.2.2 Electrodeposition of platinum and silver

Platinum was deposited on the bottom p-Si segments from an aqueous solution of 5 mM hexachloroplatinic(IV) acid (H_2PtCl_6) and 0.5 M sodium sulfate (Na_2SO_4), potentiostatically at -0.7 V. Charge densities of 130 mC cm^{-2} were supplied. Silver was deposited on the top n-Si segments from an aqueous solution of 1 mM silver nitrate (AgNO_3) and either 0.5 M Na_2SO_4 , 0.005 M H_2SO_4 or 0.5 M H_2SO_4 as the electrolyte, with a measured pH (Hanna Instruments pH 209) of 5.3, 2.4 and 0.6, respectively. Voltages applied were -0.1 V, +0.1 V and +0.3 V. The deposition was discontinued when the charge density amounted to 25 mC cm^{-2} or after 10 min when no external potential was applied. A solar simulator with a 300 W xenon lamp and an air mass 1.5 global filter was used as a light source for experiments performed under illumination. The intensity of the simulated sunlight was adjusted to 2 suns (200 mW/cm^2) with a standard reference silicon solar cell and partially cut off at 570 nm with a cut-on filter (Newport) to avoid significant homogeneous photodecomposition of AgNO_3 in solution by shorter wavelengths.^[23] The custom-made Teflon-based reactors with a volume of about 8 ml were equipped with an optical glass window and were open to the environment. Active surface areas applied were 3.14 cm^2 for platinum and 0.28 cm^2 for silver deposition, respectively, as determined by the O-rings of the reactors. A standard three-electrode system with a platinum mesh counter electrode was used in experiments with applied potential. When no external potential was applied, a two-electrode system was constructed in which the reference electrode was connected to the platinum counter mesh. The potential was set to 0 V vs. open circuit in these cases. A potentiostat (PAR, VersaStat 4) served as a power source. All applied potentials are reported versus a Ag/AgCl (3 M NaCl, BASi MF-2052) reference electrode, and all electrochemical experiments were performed at room temperature.

4.2.3 Scanning electron microscopy (SEM)/ energy-dispersive X-ray spectroscopy (EDX)

High-Resolution Scanning Electron Microscopy (HR-SEM) images were taken with a Phillips FEI XL30 FEG-ESEM with a Secondary Electron (SE) detector or FEI Sirion FEG-SEM with a Through the Lens Detector (TLD), operated at

typical acceleration voltages of 10 kV. HR-SEM in combination with Energy-Dispersive X-ray spectroscopy (EDX) mapping was performed with a MERLIN FEG HR-SEM with an inlens SE detector and an EDX Spectrometer, and a 80 mm² detector.

4.2.4 Secondary ion mass spectrometry (SIMS)

Secondary ion mass spectrometry (SIMS) depth profiles of flat silicon specimen with n⁺/p junctions were determined with a Cameca IMS 6f ion microprobe, operated in positive mode. An O₂⁺ ion beam with the impact energy of 7.5 keV was rastered over a 250×250 μm² area of which's center a 30 μm diameter circle was analyzed. Secondary ions ³¹P⁺ and ²⁸Si₂⁺ as reference were detected. Oxygen flooding was applied to enhance the positive ion yield. Experimental crater depth was measured by optical profilometry (±5% accuracy) and used for depth scale calibration. Quantification was based on a P reference implant (±10% accuracy).

4.2.5 Staining of the n⁺/p junction

Staining of specimen with prepared n⁺/p junction was performed according the procedure described in the patent of Roman and Wilson^[1], whereby, n⁺- and p-type silicon is etched at different rates. Chromium(VI) oxide (CrO₃) (99.9%, Sigma-Aldrich) and DI water were mixed in a ratio of 1 to 3 (w/w), following an addition of a 50% aqueous HF solution (10 vol% of the starting solution). Subsequently, specimen were immersed into this mixture for a given amount of time, rinsed with DI water and dried with a stream of nitrogen.

4.2.6 Ball grooving

By means of a rotating stainless steel ball with a diameter of a 60 mm, a groove was made on a flat specimen with a n⁺/p junction. A diamond paste was applied to the ball to enhance grooving rate with which a few seconds were sufficient to expose the junction. Subsequently, the samples were cleaned with ethanol.

4.3. Results and discussion

Figure 4.3a shows platinum particles, electrodeposited in the dark, selectively on the p-type base and bottom segments of the axially doped silicon microwires. Clearly, the top n^+ -type segments have remained unmodified. A control experiment, performed at identical electrochemical conditions but applied to p-Si microwires without phosphorus n^+ -Si top segments, yielded completely covered microwires (Figure 4.3b). This confirms that the electron flow to the n^+ -Si top parts is prevented in the dark by the diode properties of the axially doped microwires. The metal was deposited as particles and not as a continuous film, which is consistent with the theory of Volmer–Weber island growth.^[27] In both samples shown in Figure 4.3, the density of the particles is higher at the top of the functionalized segment compared to the bottom, which is tentatively attributed to a diffusion limitation of the precursor in between the microwires at these densely packed arrays. A control experiment in which the distance between the pillars was increased from 2 μm to 16 μm shows optically significantly less inhomogeneity (Figure 4.10, Appendix).

Figure 4.3 Cross-sectional SEM images of a) Si microwires with a n^+/p junction and b) p-Si microwires after the electrodeposition of Pt particles at $-0.7\text{ V vs. Ag/AgCl}$ (3 M NaCl) and 130 mC cm^{-2} in the dark from a solution of 5 mM H_2PtCl_6 and 0.5 M Na_2SO_4 .

Figure 4.4 shows silver particles, electrodeposited selectively on the top n^+ -Si segments (Figure 4.4a) under illumination in 0.5 M H_2SO_4 electrolyte and at an applied potential of $+0.3\text{ V}$, and semi-selectively on the p-type base and bottom segments of the axially doped silicon microwires (Figure 4.4b) in the dark at -0.3 V . Selective photo-supported electrodeposition of silver on the top of the wires at the n^+ -Si segments was achieved in all used electrolytes (high

concentration of Na_2SO_4 and low and high concentrations of sulfuric acid) and applied potentials (no external potential, +0.3 V, +0.1 V and -0.1 V vs. Ag/AgCl (3 M NaCl)). Some deposition of silver on the bottom p-Si segments was observed in few cases (Figure 4.12, Appendix). Electrodeposition of Ag on p-Si in the dark was not as selective as that of Pt. Besides major Ag deposition on the bottom p-Si segments, minor deposition on the top n^+ -Si segments (Figure 4.4b) was observed. We assume that the formation of a Schottky junction between Ag and p-Si close to the n^+/p junction caused a leak of electrons through the n^+/p junction by a partial overlap of both junction depletion layers. Thus, an Ohmic contact between semiconductor wire segments and the functionalized material is likely important to achieve high selectivity in functionalization in the dark.

Figure 4.4 Cross-sectional SEM images of Si microwires with an axial n^+/p junction after the electrodeposition of Ag particles at 25 mC cm^{-2} from a solution of 1 mM AgNO_3 and 0.5 M H_2SO_4 at a) +0.3 V under illumination and b) -0.3 V vs. Ag/AgCl (3 M NaCl) in the dark.

To realize dually functionalized silicon microwires, we first performed the electrodeposition of platinum in the dark, followed by an immersion of the sample into a 1% aqueous HF solution (30 s), and subsequently conducted the photo-induced electrodeposition of silver. This order (Figure 4.1, steps a-b) is necessary in this case, because Ag is galvanically replaced by Pt from the Pt precursor solution otherwise (Figure 4.11, Appendix). The reverse order (Figure 4.1, steps c-d) is therefore only possible when the second metal deposited is less noble than the first. Figure 4.5 shows cross-sectional SEM images of such bi-functionalized silicon microwires with an axial n^+/p junction. The presence of silver on the top parts and platinum on the bottom parts of the microwires, shown in Figure 4.5a, was confirmed by SEM/EDX mapping (Figure 4.5b). The areas

of a silicon microwire covered by Ag or Pt particles as a function of position from the pillar top was analyzed (Figure 4.13, Appendix), and the deposition boundary of silver was observed at $2.4\ \mu\text{m}$ and that of platinum at $3.3\ \mu\text{m}$ from the top of the microwire (Figure 4.5c and Figure 4.13, Appendix). In between the metal-covered areas, the microwires exhibit an unmodified band with a width of approx. $0.9\ \mu\text{m}$. In the following these observations will be discussed in more detail.

Figure 4.5 Cross-sectional SEM images (a,c) and SEM/EDX mapping (b) of Si microwires with an axial n⁺/p junction after the electrodeposition of Pt particles at $-0.7\ \text{V}$ vs. Ag/AgCl (3 M NaCl) and $130\ \text{mC cm}^{-2}$ in the dark from a solution of 5 mM H_2PtCl_6 and 0.5 M Na_2SO_4 , followed by the electrodeposition of Ag particles at $25\ \text{mC cm}^{-2}$ under illumination from a solution of 1 mM AgNO_3 in a,b) 0.005 M H_2SO_4 electrolyte at $-0.1\ \text{V}$ vs. Ag/AgCl (3 M NaCl) and c) 0.5 M Na_2SO_4 electrolyte at $+0.3\ \text{V}$ vs. Ag/AgCl (3 M NaCl).

The mechanism of the concept of dual functionalization of axially doped microwires and the occurrence of the unmodified band in between the metal-covered areas can be explained using the theory of a p/n junction. Figure 4.6a shows band edges of a p- and highly n-doped silicon with its Fermi levels. Connecting the p- and n-type parts results in an electron flow from filled states in the n-Si conduction band to empty states in the p-Si valence band until the Fermi level of both silicon types equalizes. A depletion layer is thus formed, and this causes bending of the p-Si and n-Si bands (Figure 4.6b). The depleted areas in n-Si and p-Si become positively and negatively charged, respectively. Due to the higher doping level of n-Si, the depletion layer penetrates mostly into p-Si.

Figure 4.6 Schematic illustration of n⁺/p-Si band diagrams a) before contact, b) in contact at equilibrium, c) reverse-biased, d) under illumination.

The orientation of the diode in our concept is such that it is reverse-biased when the base is put at a negative potential. Consequently, the potential barrier in the junction prevents a significant amount of electrons to pass the junction in the dark (Figure 4.6c). These electrons, supplied by an external source, occupy the empty states in the p-Si valence band and thereby enlarge the depletion layer into the bulk or migrate to the surface of the p-type semiconductor, where they induce its

selective functionalization, i.e. the electrodeposition of platinum. We assume that in this case only electrons outside of the depletion layer are available for the reduction of Pt precursor at the silicon surface.

Upon illumination, photoexcited electrons drift across the junction from the p-Si conduction band into the n⁺-Si conduction band while holes migrate from the n⁺-Si valence band to the p-Si valence band due to the induced electric field. This diminishes the width of the depletion layer and leads to an accumulation of electrons in the n⁺-type part and of holes in the p-type material (Figure 4.6d). These accumulated electrons on the n⁺-Si side are subsequently used for the regioselective deposition of silver.

We hypothesize that the unmodified band originates from the depletion layer of the n⁺/p junction. The depletion layer width (W) of an abrupt n⁺/p junction under equilibrium conditions, is given by Equation 4.1 including 4.2:

$$W = \sqrt{\frac{2\varepsilon(N_D + N_A)\phi_{bi}}{qN_DN_A}} \quad (\text{Eq. 4.1})$$

$$\phi_{bi} = \frac{k_B T}{q} \ln \left(\frac{N_D N_A}{n_i^2} \right) \quad (\text{Eq. 4.2})$$

in which ε is the permittivity of the material (1.034×10^{-10} AsV⁻¹m⁻¹ for Si), N_D and N_A are the donor and acceptor densities (m⁻³), ϕ_{bi} is the built-in potential (V), q is the unit charge (1.602×10^{-19} C), k_B is Boltzmann's constant (1.3806×10^{-23} JK⁻¹), T is the absolute temperature (K) and n_i is the intrinsic carrier concentration (1.0×10^{16} m⁻³ at 300 K for Si). The boron doping level, N_A , of the base wafer of the specimen was determined (1.4×10^{21} m⁻³) by measuring its sheet resistance. The calculated depletion layer width depends only slightly on the heavily doped material. Based on secondary ion mass spectroscopy (SIMS) data of a phosphorus-doped specimen (Figure 4.7) we used N_D doping levels in the range of 10^{22} m⁻³ to 10^{24} m⁻³ for calculations. Consequently, the expected depletion layer width in equilibrium ranges from 0.828 μ m to 0.841 μ m, respectively. Any influences of the silicon/electrolyte junction and changes of the depletion layer width upon an applied reverse bias in the dark or under illumination are not considered, due to the unknown IR drop caused by electron flow from p-Si to the solution in the dark and to n⁺-Si under illumination. The values for the width of

the depletion layer obtained by this simplified model correspond well with experimental observations of the width of the deposition-free zone, for which typically values of $0.9 \mu\text{m}$ (Figure 4.5c) were observed.

Figure 4.7 Secondary ion mass spectroscopy (SIMS) depth profile of the phosphorus dopant concentration in a boron-doped base silicon specimen with a concentration of $1.4 \times 10^{21} \text{ atoms m}^{-3}$ (dashed line). The junction position is determined by extrapolation of the linear regime towards boron background doping concentration. Analyzed specimen is identical to the sample in **Figure 4.5c**.

According to the theory given above, the depletion layer is expected to penetrate mostly into the low-doped p-region, and therefore the junction should be positioned close to the top of the metal-free zone of the wires. In more quantitative detail, the estimated penetration depth of the depletion layer into the n^+ -Si side (W_n) is in the range of $0.104 \mu\text{m}$ to $0.001 \mu\text{m}$, while the depths at the p-Si side (W_p) amount to $0.724 \mu\text{m}$ to $0.840 \mu\text{m}$, using N_D values of 10^{22} m^{-3} and 10^{24} m^{-3} , respectively, calculated using the Equations 4.3 and 4.4:

$$W_n = \frac{N_A W}{N_A + N_D} \quad (\text{Eq. 4.3})$$

$$W_p = \frac{N_D W}{N_A + N_D} \quad (\text{Eq. 4.3})$$

Based on the observed photoelectrochemical deposition of Ag at the top 2.4 μm of the wires (Figure 4.5c), the junction is expected to be positioned at about the same height from the top of the microwires. To locate the junction position experimentally, we performed SIMS measurements (Figure 4.7), ball-grooving and staining of the junction of a doped flat wafer in a CrO_3/HF aqueous solution (Figure 4.8), and wet etching by the same staining solution of a microwired sample with an axial junction (Figure 4.9). The results are different: SIMS, ball-grooving and staining, and a diffusion model for predicting the doping profile at the drive-in settings used here,^[28] indicate the junction to be located at approx. 3.6 μm from the top. In contrast, wet etching of the doped microwires shows a transition at approx. 2.2 μm from the top (Figure 4.9). In the latter case, however, a transition becomes visible due to a higher etch rate of $\text{n}^+\text{-Si}$ compared to p-Si . Consequently, a small fraction is etched from the microwire top, suggesting that the transition is close to the Ag boundary at 2.4 μm from microwire tops. However, this may not necessarily correspond with the position of the junction. Most data indicate therefore that the junction position is deeper than indicated by the position of the metal-free deposition band. The boundary of silver deposition in the dark was observed at the same location as for deposition under illumination, i.e. at 2.4 μm from the microwire top (Figure 4.4). This is in stark contrast to the dark deposition of Pt (Figure 4.5). The difference in position of deposition between the two metals is not clear. We speculate that it might be due to electronic effects in the microwires. The formation of a Schottky contact between Ag and p-Si , of which the depletion layer partially overlaps with the n^+/p junction, may reduce the n^+/p junction depletion layer width at the microwires surface, thereby allowing Ag deposition up to the junction in the dark. Furthermore, silver deposition on the depletion layer of the n^+/p junction may be caused by the attraction of the positively charged Ag^+ ions in solution to the negatively charged depleted layer in p-Si (Figure 4.6b). In contrast, platinum ions are present as negatively charged $[\text{PtCl}_6]^{2-}$ complexes^[29] and are repelled by the depleted layer in p-Si .

Figure 4.8 Determination of a junction depth by ball-grooving and staining. Schematic illustration of a cross-section and top-view of a stained groove on a flat surface (left) and optical microscopy image of a flat silicon sample with a n^+/p junction after ball-grooving and staining in aqueous CrO_3/HF solution for 25 s (right). The junction depth (x_j) can be calculated by $x_j = \frac{a^2 - b^2}{8R}$ in which R is the radius of the ball (30000 μm).

Figure 4.9 Cross-sectional SEM image of silicon microwires with an axial n^+/p junction stained in a CrO_3/HF aqueous solution for 2 min.

To test whether the unmodified band is also observed when both deposition steps on the top and bottom segments of the axially doped wires are performed with the same metal, Pt deposition was performed under illumination. The same concentrations and electrochemical parameters were chosen as for deposition in dark. The applied potential of $-0.7\text{ V vs. Ag/AgCl (3 M NaCl)}$ is sufficiently negative to overcompensate the provided potential of the n^+/p junction under illumination (Figure 4.14, Appendix) and thus deposition occurred on both top n^+ -Si and bottom p-Si segments simultaneously (Figure 4.15, Appendix). The particles deposited under illumination were much finer than in the dark, which is in agreement with literature.^[30] Two deposition boundaries were observed, at $2.3\text{ }\mu\text{m}$ and $3.4\text{ }\mu\text{m}$ from the top, with an unmodified band of $1.1\text{ }\mu\text{m}$ in between (Figure 4.15, Appendix). The unmodified band is somewhat wider than for the Pt-Ag dually functionalized microwires. This can be attributed mainly to a higher applied reverse bias during deposition. Notably, the position of the metal-free zone is the same as for the bimetallic microwires, and the discrepancy with the data on the position of the junction remains, and cannot be attributed to the use of Ag or the two-step process used for the bimetallic wires. All in all, we conclude that the width of the metal-free band of the dually functionalized microwires corresponds well with the width of the depletion zone, but that the positions do not. The latter requires further investigation with different metals, different order of deposition steps, and different precursor ion charges, as well as modeling, to elucidate possible electronic effects.

4.4 Conclusions

In conclusion, we have developed a new method to spatioselectively functionalize semiconductor wires that have an axial p/n junction, by exploiting the differences in electronic nature of differently doped segments in the dark and under illumination. We have demonstrated separate functionalization of the n^+ - and p-type segments of silicon microwires, as well as the combined dual functionalization, with electrochemically deposited platinum particles and photoelectrochemically deposited silver particles, respectively. The presence of an unmodified band between Pt particles deposited in the dark and Ag or Pt deposited under illumination has been observed. The position of the band relative

to the junction depth is not fully clear, but its width agrees well with the width of the depletion zone around the junction. The finding of this phenomenon may help to improve fundamental understanding of interfaces between semiconductors, metals and electrolytes.

The here developed fabrication concept is highly selective, relatively simple and can potentially be applied to wires or wire arrays with semiconductor-semiconductor axial diode heterojunctions or metal-semiconductor Schottky junctions. Besides reductive electrodeposition of metals, any other reductive or electron-induced reaction, such as electrochemical grafting with organic molecules is potentially possible. Also, oxidative or electron-poor surface reactions are conceivable if an inverted junction is constructed and care is taken to prevent semiconductor surface oxidation. Thus, we believe that our method has great potential to improve the ability of creating micro-sized structures with complex compositions and engineer multifunctional devices and systems with new functions.

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4.6 References

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4.7 Appendix

Figure 4.10 Cross-sectional SEM images of p-Si microwires with a 16 μm spacing after the electrodeposition of Pt particles at -0.7 V *vs.* Ag/AgCl (3 M NaCl) and 130 mC/cm² in the dark from a solution of 5 mM H₂PtCl₆ and 0.5 M Na₂SO₄.

Figure 4.11 Cross-sectional SEM images of photo-supported electrodeposited Ag particles on top of n⁺ segments of silicon microwires with an axial n⁺/p junction at 25 mC cm⁻² from a solution of 1 mM AgNO₃ and 0.5 M H₂SO₄ a) before and b) after Pt electrodeposition at -0.7 V *vs.* Ag/AgCl (3 M NaCl) and 130 mC cm⁻² in the dark from a solution of 5 mM H₂PtCl₆ and 0.5 M Na₂SO₄.

Figure 4.12 Cross-sectional SEM images of silicon microwires with axial n⁺/p junction after photo-supported Ag particles electrodeposited on top n⁺ segments from a 1 mM AgNO₃ and 0.5 M Na₂SO₄ (left column, images a, d, g and j), 0.005 M H₂SO₄ (middle column, images b, e, h, k) or 0.5 M H₂SO₄ (right column, images c, f, i, l) electrolytes at no applied external potential (first row, images a, b, c), +0.3 V (second row, images d, e, f) +0.1 V (third row, images g, h, i) and -0.1 V (fourth row, images j, k, l). Applied potentials are vs. a Ag/AgCl (3 M NaCl) reference electrode. or 0 V vs. open circuit. Reaction was discontinued when passed charge densities reached 25 mC cm⁻² at an applied potential or after 10 min at no external potential.

Figure 4.13 Analysis of covered area by metal particles along the microwire length. a) Rasterized cross-sectional SEM image of electrodeposited Pt particles in dark conditions on bottom p-Si segments and photo-supported electrodeposited Ag particles on top n⁺-Si segments of silicon microwires with an axial n⁺/p junction. The image is identical to Figure 4c. Each raster is 0.1 μm long and 4.0 μm wide. Metal particle area was determined manually with the image processing program ImageJ. Obtained results are represented in the histogram b). Green bars correspond to Ag, blue bars to Pt and gray bars to Pt or Ag particles.

Figure 4.14 Current-voltage characteristics of a flat silicon specimen with a n^+/p junction under illumination. Identical intensities (2 suns (200 mW/cm^2 , AM 1.5) partially cut off with a 570 nm cut-on filter) were used as for photo-supported electrodeposition experiments.

Figure 4.15 Cross-sectional SEM image of electrodeposited Pt particles under illumination at $-0.7 \text{ V vs. Ag/AgCl}$ (3 M NaCl) from a solution of 5 mM H_2PtCl_6 and 0.5 M Na_2SO_4 .

Chapter 5

WO₃ photoanode deactivation during photoelectrochemical water oxidation

WO₃ photoanodes typically lose most of their photocatalytic activity within minutes to hours of operation in a photo-electrochemical cell, whereas lifetimes of 20 or more years are required for practical applications. Herein, we have investigated potential factors for this deactivation in (buffered) aqueous inorganic phosphate solutions as a function of pH. The rate of the photocurrent decay was strongest in a solution of pH 1.0, followed by pH 7.4, pH 3.0 and pH 5.0. At pH 7.4, morphology changes were observed in SEM images, and tungsten was found in the electrolyte, explaining deactivation. At lower pH the deactivation mechanism was different and was most significant at pH 1.0. Tungsten dissolution at pH 1.0 and 3.0 was negligible. XPS results confirmed the surface of WO₃ had altered insignificantly. At pH 1.0 the deactivation was permanent and could neither be recovered by an interruption of illumination and applied bias, nor by rinsing with high-purity water and resting in air. At pH 3.0 and 5.0 a partial recovery induced by these interruptions was observed. We assume that the deactivation of WO₃ photoanodes is due to a loss of number and/or activity of catalytic sites in the material with respect to water oxidation. This might be caused by the formation of peroxo species on the WO₃ surface, although significant amounts of H₂O₂, potentially formed by incomplete water oxidation, were not detected in solution.

5.1 Introduction

A promising, inexpensive and environmentally benign photoanode material for the oxidation of water is monoclinic WO_3 .^[1-3] It has a single crystal electrical conductivity ranging between $10 \Omega^{-1}\text{cm}^{-1}$ to $10^{-4} \Omega^{-1}\text{cm}^{-1}$,^[4-6] depending on stoichiometry, thus inherently good electron transport properties ($\sim 12 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$), a hole diffusion length of about 150 nm,^[6] and a reported indirect band gap between 2.6 eV and 2.8 eV^[7-9]. Such band gap allows the absorption of light in the blue range of the visible spectrum. This translates to a theoretical solar to hydrogen efficiency of 4.8% and can be further increased by staging it with an additional lower band gap absorber, such as silicon.^[10-12]

To be commercially applicable, a solar energy device has to operate for at least 20 years without a significant efficiency loss. However, WO_3 photoanodes lose most of their photoactivity within minutes to hours of operation. Its reason is not fully understood. It has been proposed that competing oxidation reactions at the surface occur.^[13-15] The valence band edge position of WO_3 is located at 2.97 V vs. NHE at $\text{pH} = 0$ ^[16] and is thus sufficiently positive not only for the desired complete oxidation of water to O_2 and H^+ (Eq. 5.1), but also for various other reactions, such as the formation of H_2O_2 (Eq. 5.2) or oxidation of the electrolyte.^[13-15] For instance, sulfates have been shown to oxidize to persulfates or chlorides to chlorine gas.^[14, 15]

Best results to improve the long-term photocatalytic performance of WO_3 photoanodes were achieved by treatment with hydrogen^[17] or covering the surface with a water oxidation catalyst such as Co-Pi,^[18] IrO_2 ^[19] or MnO_x ^[20]. In the case of Co-Pi and IrO_2 rather thick layers were needed to achieve full protection and high oxygen yield. Such catalyst layers are unfavorable if WO_3 is to be coupled with a lower band gap absorber, as they absorb the incident light either partially or completely. Thus, the origin of photocurrent loss of WO_3 photoanodes during photocatalytic water oxidation needs to be found and

understood in order to stabilize the material and to provide long-term stability for dual- or multiple-junction-based WO₃ systems.

Herein, we systematically examine the stability and performance of WO₃ photoanodes in a potassium phosphate (KPi) buffer solution at pH 1.0, 3.0, 5.0 and 7.4 by measuring time-resolved oxygen and hydrogen evolution, H₂O₂ formation, and dissolution of tungsten into the electrolyte. Furthermore, possible changes of the surface morphology and composition, in particular the oxidation of W⁵⁺ surface sites, have been analyzed and evaluated.

5.2 Materials and methods

5.2.1 Fabrication of Al₃Si/p-Si/ITO substrate

Highly boron-doped, p-type silicon substrates (<100>-oriented, resistivity 0.010 Ωcm - 0.025 Ωcm, 100 mm diameter, 525 μm thickness, single-side polished, Okmetic Finland) were cleaned by immersion in 100% nitric acid (HNO₃) (2×5 min) and in 69% nitric acid (10 min), followed by quick dump rinsing in de-mineralized (DI) water, immersion in a 1% aqueous hydrofluoric (HF) acid for at least 1 min to remove the formed oxide shell, washing by quick dump rinsing in de-mineralized (DI) water and spin drying. Subsequently, the backside was sputter-coated with a 1 μm thick aluminum/silicon alloy (99% Al, 1% Si) (Oxford PL 400, 7000 W) to create a low resistance Ohmic contact. Then, the front side was coated with indium tin oxide (ITO) in a home built reactive magnetron sputtering system (TCOater) in direct current (DC) mode, using a 90 wt% In₂O₃ – 10 wt% SnO₂ (99.99%) target of 4.00 inch diameter. A DC power of 100 W was applied. The distance between the target and the substrate was kept at 44 mm and the substrate was rotated at 5 rpm during the whole deposition process. The reactor chamber was pumped down to a base pressure of 5.0×10⁻⁷ mbar prior to sputtering and a mix of 40 sccm Ar and 1 sccm O₂ (99.5%) was introduced as reactive gas, and an Ar (99.99%) flow of 20 sccm as sputtering gas, respectively. The process pressure was 5.0×10⁻⁷ mbar and the substrate temperature during deposition was maintained at 20 °C. Before ITO was sputtered on the wafer, a pre-sputtering was carried out under the same conditions for 1 min with a shutter covering the substrate. The deposition time was 5 min.

The ITO deposition rate was found to vary from 7 nm/min in the center to 6 nm/min at the edge on the horizontal part of the wafer.

5.2.2 Electrodeposition of WO₃

The WO₃ electrodeposition procedure was derived from the publication of Hill *et al.*^[15] A 0.1 M peroxo-tungstic acid plating solution was made by first adding 1.838 g tungsten powder (12 μ m, 99.9%, Sigma Aldrich) in a 100 ml volumetric flask. Then 3 ml high-purity water (Millipore, MilliQ, R = 18.2 M Ω cm), a small Teflon covered stirring bar and 6 ml hydrogen peroxide solution ($\geq$ 35%, Sigma Aldrich) were added and the flask was hanged into a cold water bath. Under stirring, the tungsten powder was dissolved completely overnight. To decompose excess of H₂O₂, a platinum mesh, which was platinized to further increase the decomposition rate, was added and stirred in the room temperature water bath. With our platinized Pt mesh, optimal time was 20 hours. To the resulting clear pale yellow solution 55.5 g ($\triangleq$ 50 ml) ethylene glycol ($\geq$ 99.5%, Sigma Aldrich) was added and the flask was filled up with high-purity water. After vigorous stirring, the solution was transferred to a glass jar while the platinized Pt mesh was removed. The jar was slowly heated to 45 °C under stirring in a water bath. On each sample four layers were deposited potentiostatically in 2 subsequent potentials of -0.6 V and 0.2 V for 60 s each *vs.* Ag/AgCl (3 M NaCl, BASi MF 2052) reference electrode. The custom-made Teflon-based reactor with a volume of about 8 ml and a platinum mesh counter electrode was heated to 45 °C in a water bath. A potentiostat (PAR, VersaStat 3) served as a power source for electrodeposition. The active silicon/ITO surface area was 3.14 cm² as defined by the O-ring. After the deposition of each layer, the substrate was rinsed with high-purity water for 2 min, gently blow-dried with an air gun and dried in a preheated oven at 120 °C for 30 min after deposition of layer 1 to 3 or annealed at 500 °C for 2 h at a heating rate of 2 °C/min after deposition of layer 4.

5.2.3 Photoelectrochemical measurements

Photoelectrochemical measurements of individual electrodes were performed in a custom-made Teflon-based reactor with a volume of about 8 ml which was either connected to a gas chromatograph (GC) or open to the environment.

Illumination occurred through a quartz glass window and 25 mm electrolyte (front-side illumination), and the incident beam was perpendicular to the specimen surface. A solar simulator (ABET technologies model 10500 low cost solar simulator, 5 cm² beam area) with an air mass (AM) 1.5 spectrum was used as a light source. The intensity of the simulated sunlight was adjusted to 1 sun (100 mW/cm²) with a standard reference silicon solar cell. The measurements were performed in a standard three-electrode setup with a platinum mesh counter electrode and a Ag/AgCl (3 M NaCl, BASi MF 2052) reference electrode at room temperature. The reference electrode has a potential ($E_{\text{Ag/AgCl}}^0$) of +0.209 V with respect to the standard hydrogen electrode (SHE) and was confirmed with a new Ag/AgCl (3 M NaCl, BASi MF 2052) master reference electrode before measurements. All voltages reported were calculated *versus* the reversible hydrogen electrode (RHE) using the following Equation 5.3:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}}^0 + 0.059 \text{ V} \times \text{pH} + E_{\text{Ag/AgCl}} \quad (\text{Eq. 5.3})$$

A 0.1 M potassium phosphate (KPi) buffer solution with a pH of 1.0, 3.0, 5.0 or 7.4 served as the electrolyte. K₂HPO₄ and KH₂PO₄ amounts were calculated with the Henderson–Hasselbalch equation, dissolved in high-purity water in a volumetric flask and precisely pH adjusted with concentrated H₃PO₄ or KOH solutions. A potential of 1.23 eV *vs.* RHE was applied during photoelectrochemical measurements in which a potentiostat (PAR, VersaStat 3) served as a power source. The active surface areas were 1.13 cm² as determined by the O-ring.

Electrochemical control experiments were performed with a Pt sputter coated highly doped silicon wafer by applying a current density of 1 mA/cm² in a 0.1 M KPi solution (pH 3.0) without (control 1) and with (control 2) saturated sodium persulfate (Na₂S₂O₈).

5.2.4 Gas chromatography (GC) analysis

The gas composition during the photocatalytic reaction was measured with a highly sensitive gas chromatograph (CompactGC Interscience) equipped with a Pulsed Discharge Detector which allows the simultaneous detection of H₂, O₂ and N₂. The headspace volume of the reactor was roughly 1 ml and the electrolyte

was constantly purged with helium (7N) at a rate of 10 ml/min. The gas composition was sampled by a 50 μ l loop, inserted onto a Q-bond column to remove H₂O followed by a Molsieve 5Å column to separate the gaseous components.

Prior to the start of the experiment, the reactor including the sample and electrolyte was purged with helium (10 ml/min) for 1.5 h in the dark. The amount of oxygen leaked-in into the reactor was estimated by the leak-in of nitrogen and subtracted from the measured value. The correction factor was calculated from the O₂/N₂ ratio determined in the dark prior to the start of the experiment.

5.2.5 H₂O₂ determination in the electrolyte

After the photocatalytic measurements, part of the electrolyte was immediately taken and analyzed for the presence of peroxo species. Two methods, the permanganate method and the LabAssayTM Glucose method were utilized. Both procedures were derived from the publication of Daskalaki *et al.* [21]

In the permanganate method, 1 ml of concentrated H₃PO₄ (85 wt.%, Sigma Aldrich) was added to 2 ml electrolyte solution and stirred in a small glass vial. Then, 100 μ l of a 20 mM KMnO₄ standard solution (ACS reagent, $\geq$ 99.0%, Sigma Aldrich) and 2 ml of high-purity water were added and the solution stirred vigorously. Finally, the solution absorption was measured at 525 nm with a UV-Vis spectrophotometer (Thermo Scientific, Evolution 600). Always, two experiments were run in parallel of which one had 1 ml of used sample electrolyte solution from the photocatalytic measurement and the other fresh reference electrolyte solution. The purpose of the reference solution was to eliminate any lamp intensity variation between preparing the standard curve and the sample measurement. The absorption intensity of the sample solution was adjusted by the factor of the deviation between reference solution and 20 mM KMnO₄ calibration solution. For the calibration, solutions with KMnO₄ concentrations of 20, 16, 12, 8, 4, 1.6, 0.8, 0.4, 0.16, 0.08 and 0.00 mM (high-purity water) were prepared by diluting the 20 mM KMnO₄ standard solution. The standard curves in different electrolyte pH are plotted in Figure 5.1a. All glassware was treated with aqua regia (mixture of nitric acid and hydrochloric acid), rinsed well with high-purity water and dried prior of use to remove all oxidizable substances. The

amount of H₂O₂ in electrolyte solution was calculated according to the stoichiometry of the redox reaction 5.4.

H₂O₂ is known to reduce MnO₄⁻ in an acidic solution which leads to a decrease in MnO₄⁻ concentration in solution and thus its absorption.

Figure 5.1 Standard calibration curves of the a) KMnO₄ method and b) LabAssay™ Glucose method.

In the LabAssay™ Glucose method, the reagent was prepared by mixing 1 vial of Chromogen reagent with 150 ml of buffer solution from the kit and kept always in the fridge in the dark. To determine the H₂O₂ concentration, 1 ml of the reagent was added to 3 ml of electrolyte solution in a small glass vial which was then transferred to a 37 °C warm water bath and kept there for 300 s under gentle stirring. Finally, the solution absorption was measured at 505 nm with a UV-Vis spectrophotometer (Thermo Scientific, Evolution 600). Also here, always 2 experiments were run in parallel of which one had 3 ml of used sample electrolyte solution from the photocatalytic measurement and one fresh reference electrolyte solution. The reference solution was used as a blank to determine the background absorption. For the calibration, solutions of H₂O₂ (purum p.a., ≥35%, Sigma Aldrich) diluted 2.500x, 10.000x, 50.000x, 100.000x, 250.000x with the electrolyte solution and pure electrolyte solution were used. The exact amount of H₂O₂ in these solutions was determined with the permanganate method. The standard curves in different electrolyte pH are plotted in Figure 5.1b.

5.2.6 Metal determination in electrolyte

Metal traces in the electrolyte after photoelectrochemical measurements were determined with a Perkin Elmer 8300dv inductively coupled plasma optical emission spectrometer (ICP-OES) at wavelengths of 207.912 nm and 239.708 nm.

5.2.7 Scanning electron microscopy (SEM)

High-resolution scanning electron microscopy (HR SEM) images were taken with a FEI Sirion FEG SEM with a Through the Lens Detector (TLD), operated at acceleration voltages of 10 kV.

5.2.8 X-ray powder diffraction (XRD)

X-ray diffraction patterns were determined with a Bruker D2 PHASER XRD using Cu K α radiation at an acceleration voltage of 30 kV. The reference used to determine the monoclinic phase of WO₃ was JCPDS no. 43-1035.

5.2.9 Raman spectroscopy

Raman spectra were collected at ambient conditions by using a Bruker SENTERRA Raman Spectrometer equipped with a 532 nm laser and a cooled CCD detector. Measurements were performed at 10 mW laser power intensity and integration times of 2.0 s.

5.2.10 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy measurements were performed using Quantera SXM (scanning XPS microprobe) from Physical Electronics equipped with an Al K α monochromatic (1486.6 eV) X-ray source. The X-ray beam diameter had a radius of 200 μ m and 50 W power. The chamber was pumped down to a base pressure below 5×10^{-10} Torr and operated at a pressure of $\sim 3 \times 10^{-8}$ Torr. The analyzed spectra are averages of three single measurements at different locations on the sample. A Shirley-type background was subtracted from the spectrum prior to peak deconvolution and the energy scale was calibrated against adventitious carbon binding energy of 284.8 eV.

5.3 Results and discussion

Photoanodes were prepared by the cathodic electrodeposition of WO₃ films on a p-Si/ITO substrate from a peroxotungstic acid/ethylene glycol solution, followed by annealing at 500 °C in air. The deposition was performed in four steps in which a thin WO₃ layer was grown, subsequently rinsed with high-purity water for 2 min, gently blow-dried with an air gun and dried at 120 °C for 30 min. The division of the deposition in four steps was necessary to avoid cracking, flake formation, lift off and thus loss of electrical contact to the substrate upon dehydration.^[14, 22] Every step consisted of a 60 s deposition at -0.6 V *vs.* Ag/AgCl (3 M NaCl) followed a 60 s anodization at 0.2 V *vs.* Ag/AgCl (3 M NaCl). The coating had a blue color after the cathodic deposition step which is attributed to a d-d transition of partially formed W⁵⁺ in the film.^[15] The blue color disappeared during the following anodization step. After annealing, the resulting films were smooth, 2.8 μm thick, and porous, and they adhered well to the substrate (Figure 5.2c, d, e).

The XRD pattern (Figure 5.2a) of the WO₃ layers after calcination shows that the phase is purely monoclinic with highly crystalline particles. The crystallites have a mean size of 47 nm as calculated from the Scherrer equation using 0.94 for the shape factor. The Raman spectrum (Figure 5.2b) also indicates a high crystallinity with well-resolved peaks and confirms the presence of the monoclinic WO₃ phase by following the vibration assignments of Daniel *et al.*^[23] Also here, no coexistence of the hexagonal phase, which is the second stable WO₃ phase at room temperature, was observed. However, a small fraction of WO₃ was found to be hydrated.^[23] Furthermore, weak peaks at 292 cm⁻¹, 348 cm⁻¹, 418 cm⁻¹ and 577 cm⁻¹ indicate that a small amount of WO_{3-x} with W⁵⁺ was present.^[24] No peaks are observed at frequencies higher than 1000 cm⁻¹ which indicates that the samples presented in this chapter are free of hydrocarbon impurities. This is particularly important as the oxidation of hydrocarbons on the photoanode surface could contribute to parasitic photocurrents by producing oxidized hydrocarbons or CO₂. In our initial experiments we rinsed the electrodes for a few seconds with high-purity water instead of 2 min after every electrodeposition step and annealed them for 1 h instead of 2 h at 500 °C. In these samples we observed a much lower oxygen yield, hydrocarbon peaks in the chromatogram

and photocurrent densities of around 1 mA/cm^2 which were significantly higher than the values presented in this chapter. Typically, photoanodes are characterized in literature based on their photocurrents without analyzing the composition of gases. Their results may also have too high reported photocurrents since competing hydrocarbon oxidation is thermodynamically more favorable than water oxidation.

Figure 5.2 a) XRD pattern, b) Raman spectrum, c, d) top view SEM image and e) cross-sectional SEM image of a WO_3 photoanode after electrodeposition and thermal annealing.

Figure 5.3 shows chronoamperometry measurements and corresponding H_2 and O_2 evolution of WO_3 photoanodes under simulated 100 mW/cm^2 AM 1.5 solar illumination in 0.1 M potassium phosphate (KPi) buffer solution with a pH of 1.0, 3.0, 5.0 and 7.4 at an applied bias of 1.23 V vs. RHE over 5 h followed by shutting

Figure 5.3 Photocurrent stability tests of WO₃ photoanodes at 1.23 V vs. RHE in 0.1 M KPi buffer at a pH of a) 1.0, b) 3.0, c) 5.0 and d) 7.4 under 100 mW/cm² AM 1.5 simulated solar illumination. H₂, O₂ and N₂ gases were collected by a constant He purge of 10 ml/min through the reactor, separated with a GC and detected with a Pulsed Discharge Detector. The leak-in of O₂ into the reactor was estimated from the measured amount of N₂ and subtracted from the total O₂ amount. The two vertical axes are aligned such that the current density represents the theoretical amount of O₂ produced at the photoanode assuming 100% faradaic efficiency.

off the applied potential for 0.5 h. Shorter reaction times of 0.5 h, 1 h and 2 h are shown in the Appendix (Figure 5.12, 5.15 and 5.18). Both H₂ and O₂ production followed the current densities with a slight delay of roughly 8 min at a lower level than theoretically calculated. The delay between produced and detected gases is attributed to the 70 s measurement processing time of the GC and saturation of the electrolyte with H₂ and O₂. The initial photocurrent density ranged between 0.35 mA/cm² and 0.60 mA/cm² in pH 1.0, 0.22 mA/cm² and 0.33 mA/cm² in solution of pH 3.0, 0.27 mA/cm² and 0.47 mA/cm² in pH 5.0 and 0.22 mA/cm² and 0.46 mA/cm² in pH 7.4 across all experiments. The observed high fluctuations in the starting photocurrent does not allow a reliable judgement but

suggests that the electrolyte pH does not have a systematic influence on the starting photocurrent of WO_3 photoanodes. The origin of these fluctuations is not known. All presented samples in this chapter were from the same batch and did not show any fluctuation during electrodeposition of WO_3 on ITO-covered silicon substrates (Figure 5.21, Appendix). The relative rate of the photocurrent decay was the strongest at pH 1.0, followed by pH 7.4, pH 3.0 and pH 5.0, when compared at normalized photocurrent densities (Figure 5.11, Appendix). The photocurrent density seemed to level off to a plateau value at 0.04 mA/cm^2 in pH 1.0 and at 0.05 mA/cm^2 in pH 3.0 without contributing to measurable oxygen production, while the photocurrent at pH 5.0 and pH 7.4 seemed to keep decreasing towards zero. The accumulated amounts of H_2 and O_2 over time of

Figure 5.4 Integrated H_2 and O_2 gas production over time of WO_3 photoanodes operated at 1.23 V vs. RHE in 0.1 M KPi buffer at a pH of a) 1.0, b) 3.0, c) 5.0 and d) 7.4 under 100 mW/cm^2 AM 1.5 simulated solar illumination. The leak-in of O_2 into the reactor was estimated based on the measured amount of N_2 and subtracted from the total O_2 amount. Theoretical amounts were calculated from charge passed through the electrodes.

Figure 5.5 Analysis of H₂ and O₂ gas evolution from water splitting by WO₃ photoanodes operated at 1.23 V vs. RHE in 0.1 M KPi buffer at a pH of 1.0, 3.0, 5.0 and 7.4 under 100 mW/cm² AM 1.5 simulated solar illumination and Pt anode control experiments operated at 1 mA/cm² in a 0.1 M KPi buffer of pH 3.0 without (Ctrl 1) and with (Ctrl 2) the saturation with sodium persulfate (Na₂S₂O₈). a) Integrated amounts of H₂ and O₂, b) their faradaic efficiency and c) their ratio.

these measurements are shown in Figure 5.5a after the full reaction times, and in Figure 5.4 and the Appendix (Figure 5.13, Figure 5.16 and Figure 5.19) in a time-resolved fashion. All oxygen amounts were corrected for oxygen leak-in into the reactor. The O₂ leak-in flux was estimated from the parallel leak-in of N₂. The correction factor was calculated from the O₂/N₂ ratio determined in the dark prior to the start of the experiment. The maximum total amounts of gases produced were 4.2 μmol O₂ and 6.3 μmol H₂ at pH 7.4 at a reaction time of 5 h. However, no major trend in O₂ and H₂ production was observed at different pH. The faradaic efficiency across all individual single point measurements (Figure 5.5b)

was $49.4\% \pm 16.5\%$ for O_2 and $46.4\% \pm 8.7\%$ for H_2 with an H_2/O_2 ratio (Figure 5.5c) at the stoichiometric value of 2.0 ± 0.6 over all samples.

In our experiments, a single cell reactor with no physical separation between working and counter electrode was used which allows the back-reaction, *i.e.* oxidation of H_2 at the WO_3 photoanode and reduction of O_2 at the platinum cathode. To quantify these reactions, we have performed two experiments in which we exchanged the WO_3 photoanode by a Pt-covered highly doped silicon wafer anode and performed galvanostatic water splitting at 1 mA/cm^2 in a 0.1 M KPi solution (pH 3.0) without (control 1) and with (control 2) saturated sodium persulfate ($Na_2S_2O_8$). The persulfate anion is reduced to sulfate at 2.05 V vs. NHE (Eq. 5.5) and thus acts as a sacrificial electron acceptor to prevent H_2 production at the cathode.

Figure 5.6 shows the evolved (Figure 5.6a, c) and integrated (Figure 5.6b, d) H_2 and O_2 over time for these controls. Results when no persulfate was added and H_2 and O_2 evolved in parallel in the reactor (Figure 5.6a, b) were found to be similar to the WO_3 photoanode. The yield for O_2 was $27.1 \text{ } \mu\text{mol}$ or 51.4% and for H_2 $53.2 \text{ } \mu\text{mol}$ or 50.5% (Figure 5.5). When H_2 evolution was suppressed by saturation with sodium persulfate, the O_2 yield was $53.2 \text{ } \mu\text{mol}$ or 101.1% , following almost exactly the theoretically calculated values over time (Figure 5.6d). This means that neither in the first control experiment in which no persulfate was added nor in the WO_3 photoanodes tests oxygen was reduced at the Pt counter electrode in the reactor. Instead, the loss of around 50% faradaic efficiency is due to H_2 oxidation. Oxidation of H_2 at the anode reduces both the total detected amount of H_2 and produced O_2 proportionally. With the average detected H_2/O_2 ratio of 2:1 we assume that oxygen evolution and hydrogen evolution would occur with 100% faradaic efficiency when gas cross-over is prohibited by a membrane between the anode and the cathode compartment.

Figure 5.6 Analysis of H₂ and O₂ gas evolution from water splitting by Pt anode control experiments operated at 1 mA/cm² in a 0.1 M KPi buffer of pH 3.0 without (Ctrl 1, a, b) and with (Ctrl 2, c, d) saturation with sodium persulfate (Na₂S₂O₈). a) and c) show the time-resolved evolved amounts and b) and d) the cumulative amounts integrated over time. The leak-in of O₂ into the reactor was estimated based on the measured amount of N₂ and subtracted from the total O₂ amount. Theoretical amounts were calculated from charge passed through the electrodes.

We have chosen to use a KPi buffer based on the publication of Hill *et al.*^[15] who studied the effect of cations and anions and pH of the electrolyte on the stability of WO₃ photoanodes and faradaic efficiencies towards O₂ evolution. Best results in their study were obtained in a Na₂SO₄ (pH 5) and KH₂PO₄ (pH 3) solutions with photocurrent to oxygen conversion efficiencies of 88% and 87% for 1 h of operation. We made the choice in favor of phosphate because sulfate is well known to be oxidized to persulfate (reversed Eq. 5.5) on the WO₃ surface whereas phosphate is more stable.^[13, 14] Nevertheless, Mi *et al.* suggested that phosphate can be oxidized to peroxydiphosphate.^[14] Furthermore, Augustynki *et al.* reported that a significant portion of the photon-generated holes oxidize water only partially (Eq. 5.2) and lead to an accumulation of a few percent H₂O₂ in the

solution and the formation of peroxo species on the surface of WO₃, causing the loss of WO₃ photoactivity during operation.^[13] In order to determine the H₂O₂ concentration in our experiments we have analyzed the electrolyte immediately after reaction by two different methods, *i.e.* the KMnO₄ and the LabAssayTM Glucose method. The permanganate ion is a strong oxidizing agent having a deep purple color and is reduced in strong acidic solutions to colorless Mn²⁺ and water according to Equation 5.6.

The permanganate ion reacts with all reagents which are able to reduce it in solution, including H₂O₂ (Eq. 5.4). However, since this reaction is not specific, we have performed an additional H₂O₂ analysis in parallel with the LabAssayTM Glucose method, originally designed for quantitative determination of glucose in solutions. During enzymatic glucose oxidation, H₂O₂ is developed and further processed by a second enzymatic reaction of a coloring dye and H₂O₂ transformation to a red pigment and water (Eq. 5.7). We used only the second part of the LabAssayTM Glucose kit to determine H₂O₂ specifically.

The amounts of H₂O₂ in electrolyte solution in our reactions were calculated from the UV-Vis absorption decrease at 525 nm in the KMnO₄ method and its increase at 505 nm in the LabAssayTM Glucose method. Figure 5.7a shows measured amounts in comparison to theoretical maximum assuming 100% faradaic efficiency of water oxidation to H₂O₂ and protons (Eq. 5.2). Measured values for H₂O₂ range between -0.26 μmol and 0.23 μmol for the KMnO₄ method and between -0.03 μmol to 0.18 μmol in the LabAssayTM Glucose method. Negative values result when the reference sample which was treated in parallel to the actual sample showed a lower absorption in the KMnO₄ method or a higher absorption in the LabAssayTM Glucose method. We consider the negative values as our experimental error margin. Since positive and negative values fluctuate in the same range, we find that no significant amounts of H₂O₂ were produced during the reaction. However, we neither can confirm nor exclude the appearance of H₂O₂ in very low amounts of a few percent compared to the theoretical maximum.

Also, it is well possible that formed peroxides or peroxo-species attach to the surface and do not migrate into the electrolyte.^[21]

To verify whether WO₃ photoanodes suffer from corrosion we analyzed the tungsten content in the electrolyte by inductively coupled plasma optical emission spectrometry (ICP-OES). Degradation was only found in solution at pH 7.4 for all times of photocatalytic operation and a small amount at pH 5.0 after 5 h of operation (Figure 5.7b). After 5 h of photocatalytic operation of the WO₃ photoanodes in pH 7.4, 0.27 mg tungsten was dissolved into the electrolyte solution. This is about 30% of the total amount of tungsten on the photoanode. The total WO₃ amount on 1.13 cm² electrode area was calculated to be 1.13 mg and thus of tungsten 0.90 mg, while estimating a 50% porosity of the 2.8 μm thick WO₃ layer. These results are consistent with literature indicating WO₃ being thermodynamically stable in acidic solutions at a pH below 4.^[25, 26] SEM images after photocatalytic activity (Figure 5.8, and in Appendix Figure 5.14, Figure 5.17, Figure 5.20) confirm these findings. WO₃ particles showed degradation at pH 7.4, whereas at all other pHs, the particles remained intact. Also, the SEM images show that the WO₃ films adhered well and kept contact to the surface after the photocatalytic tests, and that the underlying ITO layer remained stable.

Figure 5.7 Analysis of a) H₂O₂ by UV-Vis spectroscopy and b) W by ICP-OES in the electrolyte after photocatalytic operation for 0.5 h, 1.0 h, 2.0 h and 5.0 h of WO₃ photoanodes at 1.23 V vs. RHE in 0.1 M KPi buffer at a pH of 1.0, 3.0, 5.0 and 7.4 under 100 mW/cm² AM 1.5 simulated solar illumination.

Figure 5.8 Top-view (a, b, d, e, g, h, j, k) and cross sectional (c, f, i, l) SEM images after 5 h photocatalytic operation of WO_3 photoanodes at 1.23 V vs. RHE in 0.1 M KPi buffer at a pH of 1.0 (a, b, c), 3.0 (d, e, f), 5.0 (g, h, i) and 7.4 (j, k, l) under 100 mW/cm² AM 1.5 simulated solar illumination.

The presence of oxygen vacancies in WO_3 is essential for its usage as a photoanode material. These lattice defects, induced by a small fraction of W^{5+} , are responsible for the n-type character, and increase the electrical conductivity and light absorption.^[5, 6, 27-30] Also, W^{5+} has been reported to improve chemical and photocatalytic long-term stability.^[17, 28, 31] Self-oxidation of W^{5+} to W^{6+} and

Figure 5.9 W 4f XPS spectra of WO₃ photoanodes a) before photocatalytic tests and after 5 h operation in b) pH 1.0, c) pH 3.0 and d) pH 5.0. The dots represent experimental data, the colored areas deconvoluted peaks and the black line is the sum of all deconvoluted areas. The white area underneath the curves is the subtracted Shirley-type background.

thereby a reduction of oxygen vacancies may cause a gradual loss of photocurrent. Analysis of XPS results before and after 5 h photocatalytic performance in KPi solutions of pH 1.0, 3.0 and 5.0 showed changes neither in the overall element spectrum (Figure 5.22, Appendix), nor in the O 1s spectrum (Figure 5.23, Appendix), nor in the W 4f spectrum (Figure 5.9) in comparison to an unused WO₃ photoanode. This indicates that the WO₃ surface structure did not change during reaction and that surface morphology changes are not responsible for the decrease in photocatalytic current density. The deconvolution of the W 4f signal shows two pairs of peaks. The first, well resolved doublet with binding energies of 35.8 eV and 37.9 eV corresponds to W⁶⁺ 4f_{7/2} and 4f_{5/2}, respectively.^[17, 32-34] The second doublet with binding energies of 33.5 eV and 37.5 eV is assigned to W⁵⁺ 4f_{7/2} and 4f_{5/2}, respectively.^[17, 33, 34] Based on the peak

areas in XPS, the photoanodes consisted of $2.2\% \pm 0.1\%$ W^{5+} and $97.8\% \pm 0.1\%$ of W^{6+} . The finding of W^{5+} on the WO_3 surface is in agreement with our Raman results (Figure 5.2b). Also, the XPS data confirm that the WO_3 surface is free of hydrocarbon impurities. Only traces of adventitious carbon were found (Figure 5.22, Appendix).

Furthermore, to investigate whether the photocatalytic deactivation of WO_3 photoanodes over time is permanent or reversible, we have performed tests in which we have run photocatalytic water splitting experiments with two kinds of interruptions. Type 1 interruption was to block the light after 2 h of operation with a shutter and switch off the applied external bias of 1.23 V *vs.* RHE for 1 h, and then continue the photocurrent measurements for another 2 h. Type 2 interruption was to remove the electrolyte from the reactor, rinse the sample and reactor well with high-purity water, gently blow the sample and reactor dry, and let it sit for 13 h or 2 h. Figure 5.10 shows the results in air-saturated 0.1 M KPi solutions of pH 1.0, 3.0 and 5.0. The photoactivity of WO_3 at pH 1.0 dropped by 84% from 0.74 mA/cm² to 0.12 mA/cm² and did not substantially recover in the dark and no applied bias. Also, the photocurrent did not regain after cleaning the sample with high-purity water and drying. At pH 3.0 the photoanode lost 60% of the initial photocurrent, from 0.72 mA/cm² to 0.29 mA/cm², within the first 120 min of operation. However, it recovered to 0.62 mA/cm² after 1 h type 1 interruption, fell below 0.29 mA/cm² after 35 min of operation and dropped to 0.17 mA/cm after 120 min. The photoanode regained to a starting current of 0.56 mA/cm² which was 78% of the initial photocurrent after the first type 2 interruption and then lost photocurrent at a similar rate as before type 2 interruption. The regain of the initial photocurrent after the second type 2 interruption was similar as after the first type 2 interruption but here the photocurrent decay rate was much higher. The photocurrent behavior of WO_3 photoanodes at pH 5.0 was similar to pH 3.0 in the first test. The initial photocurrent of 0.76 mA/cm² dropped by 71% to 0.22 mA/cm² but regained to 0.60 mA/cm² after type 1 interruption. The regains after type 2 interruptions were lower than at pH 3.0 and showed a higher photocurrent loss rate. These observations suggest that the deactivation in pH 1.0, 3.0 and 5.0 is due to a mix

Figure 5.10 Photocurrent regeneration tests of WO₃ photoanodes in 0.1 M KPi buffer at a pH of a) 1.0, b) 3.0 and c) 5.0. In every test the electrode was biased at 1.23 V vs. RHE under 100 mW/cm² AM 1.5 simulated solar illumination during the first and last 120 min of operation. In between these photoactivity tests the electrode was held in the reactor at an open circuit potential in the dark. In between the tests, the reactor was opened and the electrolyte removed. The WO₃ sample was rinsed with high-purity water, gently blow-dried with air and exposed to air for 13 h after test 1 and for 2 h after test 2.

of two parallel processes of which one is reversible and one irreversible by the two types of interruptions. In pH 1.0, the irreversible process dominates whereas in pH 3.0 and pH 5.0 both processes occur in parallel. The irreversible process might be the loss of catalytic centers for water oxidation, potentially induced by surface binding of peroxo species as suggested by Augustynski *et al.*^[13] or by other deactivation processes. The formation of peroxo species is supported by the findings of Augustynski *et al.* that the initial performance of WO₃ photoanodes can be regenerated by steps which are able to destroy tungsten peroxides, such as annealing in oxygen atmosphere, a short reductive current pulse or exposure of

intense UV illumination.^[13] Also, the increasing rate of WO₃ photoanode deactivation from pH 5.0 to pH 3.0 to pH 1.0 correlates well with the stability of peroxides at different pHs, which increases at decreasing pH.^[35, 36] The reversible process is presumably the build-up of a pH gradient between the electrodes during photocatalytic water electrolysis. A pH gradient is more easily built up at higher pHs, explaining the observed occurrence at pH 3.0 and 5.0 compared to pH 1.0.

5.4 Conclusions

In conclusion, we have studied potential factors which lead to the deactivation of WO₃ photoanodes during photocatalytic water splitting in KPi buffer solutions of pH 1.0, 3.0, 5.0 and 7.4. We found that faradaic efficiencies for oxygen evolution were 100% when recombination losses of O₂ and H₂ in the single compartment cell are taken into account. Thus we conclude that no major parallel oxidation reactions, such as the formation of H₂O₂, occur, as confirmed by analysis of the electrolyte composition with different H₂O₂ assays. The lowest photocurrent stabilities over time were observed at pH 1.0, followed by pH 7.4, pH 3.0 and pH 5.0. The photoanodes are chemically instable at pH 7.4 and stable at pH 5.0 only for a few hours. Thus, the optimal pH for WO₃ photoanodes is at around 3. Our study showed no observable change of the surface of the WO₃ photoanode after 5 h of photocatalytic operation in pH 1.0, 3.0 and 5.0. However, as put forward by Augustynski *et al.*, the deactivation may be due to unfavorable formation of surface peroxides on the WO₃ surface. This study provides a basis for further *in situ* studies to fully understand the mechanism of the loss in photocurrent on WO₃ photoanodes and analyze the formation of surface peroxides or other species.

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5.6 References

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5.7 Appendix

Figure 5.11 Photocurrent stability tests of WO₃ photoanodes at 1.23 V vs. RHE in 0.1 M KPi buffer at a pH of 1.0, 3.0, 5.0 and 7.4 under 100 mW/cm² AM 1.5 simulated solar illumination. Measured photocurrents are divided by their maximum for a current loss comparison at different pH.

Figure 5.12 Photocurrent stability tests of WO_3 photoanodes at 1.23 V vs. RHE in 0.1 M KPi buffer at a pH of a) 1.0, b) 3.0, c) 5.0 and d) 7.4 under $100 \text{ mW}/\text{cm}^2$ AM 1.5 simulated solar illumination. H_2 , O_2 and N_2 gases were collected by a constant He purge of $10 \text{ ml}/\text{min}$ through the reactor, separated with a GC and detected with a Pulsed Discharge Detector. The leak-in of O_2 into the reactor was estimated based on the measured amount of N_2 and subtracted from the total O_2 amount. The two vertical axis are aligned in such that the current density represents the theoretical amount of O_2 produced at the photoanode assuming 100% faradaic efficiency. The first minute of the measurement was in dark to illustrate the absence of a dark current.

Figure 5.13 Integrated H₂ and O₂ gas evolution over time of WO₃ photoanodes operated at 1.23 V vs. RHE in 0.1 M KPi buffer at a pH of a) 1.0, b) 3.0, c) 5.0 and d) 7.4 under 100 mW/cm² AM 1.5 simulated solar illumination. The leak-in of O₂ into the reactor was estimated based on the measured amount of N₂ and subtracted from the total O₂ amount. Theoretical amounts were calculated from charge passed through the electrodes. The first minute of the measurement was in dark to illustrate the absence of a dark current.

Figure 5.14 Top-view (a, b, d, e, g, h, j, k) and cross sectional (c, f, i, l) SEM images after 0.55 h photocatalytic operation of WO_3 photoanodes at 1.23 V vs. RHE in 0.1 M KPi buffer at a pH of 1.0 (a, b, c), 3.0 (d, e, f), 5.0 (g, h, i) and 7.4 (j, k, l) under 100 mW/cm² AM 1.5 simulated solar illumination.

Figure 5.15 Photocurrent stability tests of WO₃ photoanodes at 1.23 V vs. RHE in 0.1 M KPi buffer at a pH of a) 1.0, b) 3.0, c) 5.0 and d) 7.4 under 100 mW/cm² AM 1.5 simulated solar illumination. H₂, O₂ and N₂ gases were collected by a constant He purge of 10 ml/min through the reactor, separated with a GC and detected with a Pulsed Discharge Detector. The leak-in of O₂ into the reactor was estimated based on the measured amount of N₂ and subtracted from the total O₂ amount. The two vertical axis are aligned in such that the current density represents the theoretical amount of O₂ produced at the photoanode assuming 100% faradaic efficiency. The first minute of the measurement was in dark to illustrate the absence of a dark current.

Figure 5.16 Integrated H₂ and O₂ gas evolution over time of WO₃ photoanodes operated at 1.23 V *vs.* RHE in 0.1 M KPi buffer at a pH of a) 1.0, b) 3.0, c) 5.0 and d) 7.4 under 100 mW/cm² AM 1.5 simulated solar illumination. The leak-in of O₂ into the reactor was estimated based on the measured amount of N₂ and subtracted from the total O₂ amount. Theoretical amounts were calculated from charge passed through the electrodes. The first minute of the measurement was in dark to illustrate the absence of a dark current.

Figure 5.17 Top-view (a, b, d, e, g, h, j, k) and cross sectional (c, f, i, l) SEM images after 1.0 h photocatalytic operation of WO₃ photoanodes at 1.23 V *vs.* RHE in 0.1 M KPi buffer at a pH of 1.0 (a, b, c), 3.0 (d, e, f), 5.0 (g, h, i) and 7.4 (j, k, l) under 100 mW/cm² AM 1.5 simulated solar illumination.

Figure 5.18 Photocurrent stability tests of WO_3 photoanodes at 1.23 V vs. RHE in 0.1 M KPi buffer at a pH of a) 1.0, b) 3.0, c) 5.0 and d) 7.4 under 100 mW/cm^2 AM 1.5 simulated solar illumination. H_2 , O_2 and N_2 gases were collected by a constant He purge of 10 ml/min through the reactor, separated with a GC and detected with a Pulsed Discharge Detector. The leak-in of O_2 into the reactor was estimated based on the measured amount of N_2 and subtracted from the total O_2 amount. The two vertical axis are aligned in such that the current density represents the theoretical amount of O_2 produced at the photoanode assuming 100% faradaic efficiency. The first minute of the measurement was in dark to illustrate the absence of a dark current.

Figure 5.19 Integrated H₂ and O₂ gas evolution over time of WO₃ photoanodes operated at 1.23 V vs. RHE in 0.1 M KPi buffer at a pH of a) 1.0, b) 3.0, c) 5.0 and d) 7.4 under 100 mW/cm² AM 1.5 simulated solar illumination. The leak-in of O₂ into the reactor was estimated based on the measured amount of N₂ and subtracted from the total O₂ amount. Theoretical amounts were calculated from charge passed through the electrodes. The first minute of the measurement was in dark to illustrate the absence of a dark current.

Figure 5.20 Top-view (a, b, d, e, g, h, j, k) and cross sectional (c, f, i, l) SEM images after 2.0 h photocatalytic operation of WO_3 photoanodes at 1.23 V vs. RHE in 0.1 M KPi buffer at a pH of 1.0 (a, b, c), 3.0 (d, e, f), 5.0 (g, h, i) and 7.4 (j, k, l) under 100 mW/cm² AM 1.5 simulated solar illumination.

Figure 5.21 Electrodeposition of 4 layers WO₃ on ITO coated highly p-type doped silicon from a 0.1 M peroxo-tungstic acid plating solution at 45 °C and applied potentials of -0.6 V and 0.2 V for 60 s each *versus* Ag/AgCl (3 M NaCl) reference electrode. After the deposition of each layer the substrate was rinsed with high-purity water for 2 min, gently blow-dried with an air gun and dried in a preheated oven at 120 °C for 30 min after deposition of layer 1 to 3 to prevent crack formation.

Figure 5.22 XPS survey spectra of WO_3 photoanodes a) before photocatalytic tests and after 5 h operation at b) pH 1.0, c) pH 3.0 and d) pH 5.0.

Figure 5.23 O 1s XPS spectra of WO₃ photoanodes before photocatalytic tests and after 5 h operation at pH 1.0, pH 3.0 and pH 5.0.

Chapter 6

Integration of molybdenum-doped, hydrogen-annealed BiVO₄ on silicon microwires for photocatalytic applications

BiVO₄ is a promising photoanode material for photoelectrochemical water oxidation. However, its short minority-carrier diffusion lengths minimize the allowable thickness of the films, typically below the values required for complete light absorption. In order to increase the amount of deposited material without the limitation of short diffusion length, we have deposited nanoporous molybdenum-doped and hydrogen-annealed H-BiVO_{4-x}:Mo on microwire-structured silicon substrates covered with indium tin oxide (ITO). In this Si-BiVO₄ tandem architecture we aimed to decouple the directions and path lengths of light absorption and charge carrier transport to improve its performance. Mo doping of the BiVO₄ was applied to improve the charge carrier diffusion, while hydrogen annealing targets the same by enhancing the formation of oxygen vacancies. High internal surface area of the nanoporous n-type BiVO₄ is expected to create a high junction area between semiconductor and electrolyte and thus enhance electron and hole separation. Devices with microwires of 4 μm radius, 4 μm to 20 μm spacing, and 5.3 μm to 15.9 μm length were prepared, sputtered with ITO, subsequently covered by BiOI in an electrodeposition process and converted to H-BiVO_{4-x}:Mo. While the optical properties of H-BiVO_{4-x}:Mo were favorable as compared to flat surfaces, photocatalytic tests of these devices showed that flat equivalents of Si substrates outperformed microwire-structured devices in sulfite (SO₃²⁻) oxidation in a KPi buffer solution (pH 7.0). We attribute this to diffusion limitations of redox species in the internal volume of the microwires. This hypothesis is supported by the observation, during the deposition process, of BiOI starting to grow at the bottom of the microwires, and additionally faster growth on microwire-structured arrays with a lower spacing.

6.1 Introduction

Bismuth vanadate (BiVO_4), an n-type semiconductor, is one of the most promising photoanode materials for photoelectrochemical oxidation of water. It is stable in a pH range between 3 and 11,^[1] environmentally benign, widely available, non-toxic, inexpensive and is commonly used in industry as a yellow pigment. The valence band edge of the monoclinic phase is located at 2.8 V vs. NHE^[2] and is thus sufficiently positive to oxidize water at a potential of 1.23 V vs. NHE. The conduction band edge is located at 0.3 V vs. NHE,^[2] which is near the H_2 evolution potential of 0 V vs. NHE, and thus the photocurrent onset potential is relatively low, leading to a high photocurrent generation in the low bias region in comparison to other photoanode materials with a more positive conduction band edge.^[3] The direct bandgap of 2.4 eV to 2.5 eV^[2, 4] allows to absorb up to 11% of the solar spectrum which equals a theoretically maximal photocurrent of 7.5 mA/cm² and a solar to hydrogen efficiency of 9% when illuminated with an AM 1.5 spectrum.^[5] Further efficiency improvement can be achieved by stacking BiVO_4 on a lower band gap absorber, such as silicon.^[6, 7]

However, the BiVO_4 minority-carrier diffusion length of 70 nm^[8] is below the required thickness for total optical light absorption. This means that the layers in BiVO_4 photoanodes cannot be made sufficiently thick to absorb all of the incident photons with energies above 2.5 eV. When the layer becomes too thick, the photogenerated charge carriers will not be able to either reach the electrolyte to perform the oxidation reaction, or the conductive layer to be collected and close the circuit in a photo-electrochemical cell.

Several routes have been described in literature to overcome this drawback. Most of them focus on charge transport improvement by doping with for instance molybdenum,^[9-11] tungsten^[5, 12] or nitrogen,^[13] or by the creation of oxygen vacancies by annealing in hydrogen atmosphere.^[14, 15] Others have created BiVO_4 layers with a high internal surface area. This was achieved by developing a procedure to create nanoporous BiVO_4 from electrodeposited BiOI sheets. This method of preparation suppressed bulk carrier recombination without additional doping.^[3, 16] Furthermore, others have created $\text{WO}_3/\text{BiVO}_4$ core/shell heterostructures which combine the merits of the two semiconductors, *i.e.*, the

excellent charge transport characteristics of WO₃ and the good light absorption capability of BiVO₄.^[17-22]

A further alternative to improve the activity of BiVO₄ photoanodes is to deposit BiVO₄ on structured conductive substrates which provide a high internal surface area such as nano- or microwires. They reduce electron and hole recombination by allowing to keep the BiVO₄ layers thin, providing short minority carrier diffusion lengths and thus reduce electron and hole recombination.^[23] Additionally, these systems have light trapping properties and thus lead to a much higher absorption of incident photons with energies above the semiconductor bandgap.^[24-27]

Many methods have been developed to deposit BiVO₄ on substrates, such as spray pyrolysis,^[28, 29] chemical bath deposition,^[30] chemical vapor deposition,^[31] pulsed laser deposition,^[32] hydrothermal^[33] or direct^[34] and indirect^[3, 16, 35] electrodeposition. However, the method has to be compatible with: (i) deposition on 3-dimensional structures, (ii) introduction of dopants, (iii) a high surface area of nanoporous BiVO₄, and (iv) favorable pricing and scalability.

Herein we integrate nanoporous, molybdenum-doped, and hydrogen-annealed H-BiVO_{4-x}:Mo on p-type silicon flat surfaces and microwire arrays with an intermediate indium tin oxide (ITO) layer using a two-step synthesis procedure developed by Choi *et al.*^[3, 16] First, the electrodeposition of BiOI was studied with a focus on the influence of microwire spacing and length (Section 6.3.1). The BiOI deposition process is triggered by a local pH change which allows to trace back the formation of pH gradients in-between the microwire structures through the observation of BiOI thickness gradients. Then, the transformation to H-BiVO_{4-x}:Mo was evaluated, varying the thickness of H-BiVO_{4-x}:Mo on microwires of variable length and spacing (Section 6.3.2). The results are evaluated on the basis of sulfite oxidation performance during the photo-electrochemical process (Section 6.3.3). Finally, we evaluate the influence of Mo doping and annealing conditions in our preparation procedure (Section 6.3.4) on performance.

6.2 Materials and methods

6.2.1 Fabrication of silicon microwire arrays

Figure 6.1 Schematic illustration of the integration of H-BiVO_{4-x}:Mo on silicon microwires as a photoanode. a) Definition of microwire arrays by standard UV lithography. b) Deep reactive ion etching (DRIE) and removal of photoresist. c) HF etching of silicon oxide and sputtering of aluminum/silicon alloy (99% Al, 1% Si) on the backside and ITO on the frontside. d) Electrochemical deposition of BiOI from a KI, Bi(NO₃)₃ and p-benzoquinone in water/ethanol solution at -0.1 V vs. Ag/AgCl (3 M NaCl). e) Formation of H-BiVO_{4-x}:Mo by dropcasting VO(acac)₂ and Na₂MoO₄ in DMSO, evaporation of DMSO at 100 °C, calcination at 450 °C in air, soaking in 1 M KOH and reduction in a 5% H₂/95% Ar atmosphere at 300 °C for 0.5 h.

Figure 6.1 schematically shows the fabrication process of BiVO_{4-x}:Mo coated silicon microwires. Highly boron-doped, p-type silicon substrates (<100>-oriented, resistivity 0.010 - 0.025 Ωcm, 100 mm diameter, 525 μm thickness, single-side polished, Okmetic Finland) were cleaned by immersion in 100% nitric acid (HNO₃) (2×5 min) and in 69% nitric acid (10 min), followed by quick dump rinsing in de-mineralized (DI) water, immersion in a 1% aqueous hydrofluoric (HF) acid for at least 1 min to remove the formed oxide shell and another quick dump rinsing cycle. After spin-drying the wafers, areas with an array of microwires (specifications: diameter 4 μm, spacing 4 μm - 20 μm, hexagonally stacked, 0.5×0.5 cm² cell size on a specimen of 2×2 cm²) were defined in photoresist (Olin 907-17), and post-baked for 10 min at 120 °C after exposure and development. The photoresist acted as a mask layer during deep reactive ion etching (CF-chemistry, SPTS Pegasus). The height of the wires was determined by the etch duration, which was set to 60 s, 120 s or 180 s, resulting

in microwire lengths of approximately 5.3 μm , 10.6 μm and 15.9 μm . The surface area enhancement factors between projected and effective surface area for a complete and partially microwire structured area is shown in Table 6.1.

Table 6.1 Total surface area enhancement by microwires of 4 μm diameter and sample area enhancement containing 22.1% microwire-structured area during BiOI deposition and 85.7% microwire-structured area during photocurrent measurements. The active area is illustrated inside the black frame in the schematic illustrations. The centered square is a microwire-structured area with a projected surface area of 0.25 cm^2 .

Microwire spacing (μm)	Effective area enhancement factor for 5.3 10.6 15.9 μm long microwires	Effective area enhancement factor during BiOI deposition for 5.3 10.6 15.9 μm long microwires	Effective area enhancement factor during photocurrent measurements for 5.3 10.6 15.9 μm long microwires
4	2.04 3.08 4.12	1.23 1.46 1.69	1.88 2.80 3.73
6	1.67 2.33 3.00	1.15 1.29 1.44	1.55 2.14 2.73
8	1.46 1.93 2.39	1.10 1.20 1.31	1.37 1.78 2.19
10	1.34 1.68 2.02	1.08 1.15 1.23	1.27 1.57 1.87
15	1.18 1.37 1.55	1.04 1.08 1.12	1.13 1.29 1.45
20	1.12 1.23 1.35	1.03 1.05 1.08	1.07 1.17 1.27
Schematic illustration of the active area

6.2.2 Sputtering of indium tin oxide (ITO)

The wafers were treated with oxygen plasma for 20 min followed by C₄F₈ cleaning for 1 min to remove fluorocarbon residues (GIGAbatch 360P), and immersed in 100% nitric acid (HNO₃) (2×5 min) and consecutively in 69% nitric acid (10 min), followed by: a quick dump rinse in DI water to remove any residue from the etching process, immersion in 1% aqueous HF for at least 1 min to remove the silicon oxide shell, washing by quick dump rinsing in DI water, and spin-drying. Subsequently, the backside was sputter-coated with a 1 μm thick aluminum/silicon alloy (99% Al, 1% Si) (Oxford PL 400, 7000 W) to create a

low resistance Ohmic contact. Thereafter, the frontside was coated with ITO in a home-built reactive magnetron sputtering system (TCOater) in direct current (DC) mode, using a 90 wt% In_2O_3 – 10 wt% SnO_2 (99.99%) target of 4.00 inch diameter. A DC power of 100 W was applied. The distance between the target and the substrate was kept at 44 mm, and the substrate was rotated at 5 rpm during the whole deposition process. The reactor chamber was pumped down to a base pressure of 5.0×10^{-7} mbar prior to sputtering, and a mix of 40 sccm Ar and 1 sccm O_2 (99.5%) was introduced as reactive gas and an Ar (99.99%) flow of 20 sccm as sputtering gas. The process pressure was 5.0×10^{-7} mbar and the substrate temperature during deposition was maintained at 20 °C. Before ITO was sputtered on the wafer, pre-sputtering was carried out under the same conditions for 1 min with a shutter covering the substrate. The deposition times were either 5 min or 20 min and the ITO deposition rate varied from 7 nm/min in the center to 6 nm/min at the edge on the horizontal part of the wafer. ITO thicknesses were determined by SEM.

6.2.3 Electrodeposition of BiOI

The electrodeposition procedure of BiOI and the following transformation to BiVO_4 was derived from publications of Choi *et al.*^[3, 16] A 0.4 M potassium iodide (KI) and 0.04 M bismuth(III) nitrate ($\text{Bi}(\text{NO}_3)_3$) solution was prepared by dissolving KI ($\geq 99.0\%$, Sigma-Aldrich) in high-purity water (Millipore, MilliQ, $R = 18.2 \text{ M}\Omega\text{cm}$), adjusting the pH to 1.7 with nitric acid (HNO_3 , 70%, ACS reagent, Sigma-Aldrich) and adding $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ($\geq 98.0\%$, Sigma-Aldrich). To this solution, a solution of 0.23 M p-benzoquinone ($\geq 98\%$, Sigma-Aldrich) in ethanol (99.8%, AA Chemie B.V.) was added in a ratio of 2:5 (ethanol:aqueous) and stirred vigorously for 1 h. The deposition was performed potentiostatically at -0.1 V vs. a Ag/AgCl (3 M NaCl, BioLogic RE-1B) reference electrode in a custom-made Teflon-based reactor with a volume of about 8 ml and a platinum mesh counter electrode. A potentiostat (PAR, VersaStat 3) served as a power source. The active silicon/ITO surface area was 1.13 cm^2 as defined by the O-ring, and the deposition times were 30, 60, 120 or 300 s. This area covered 0.25 cm^2 of the structured, and 0.88 cm^2 of a flat surface (see drawing in Table 6.1). All deposition experiments were performed at room temperature and the reactor was open to the environment. The samples were prepared in two batches

and each sample in each batch was processed consecutively. The data reported in the results paragraph are based on samples from the same batch.

6.2.4 Synthesis of H-BiVO_{4-x}:Mo

A solution (25 μ l) of dimethyl sulfoxide (DMSO, $\geq 99.5\%$, Sigma-Aldrich) containing 0.4 M vanadyl acetylacetonate (VO(acac)₂, 98%, Sigma-Aldrich) with or without 0.004 M sodium molybdate (Na₂MoO₄, $\geq 99\%$, Sigma-Aldrich) was added on top of the BiOI-coated substrate and dried in a preheated drying oven at 100 °C for 60 min. Samples were calcined immediately at 450 °C for 2 h (at a heating rate of 2 °C/min). Afterwards, the excess of vanadium(III) oxide (V₂O₃) was removed by placing 500 μ l of an aqueous (MilliQ) 1 M KOH (99.99%, Sigma-Aldrich) solution on top of the sample for 30 min, rinsing with MilliQ water, and drying with compressed air, and repeating this whole procedure. Subsequently, the samples were annealed in a tube furnace at 300 °C for 0.5 h at a heating rate of 10 °C/min in a 5% H₂/95% Ar atmosphere at a flow of 500 sccm. The microwire-structured samples were prepared in two batches, and all samples in each batch were processed simultaneously. The data reported in the results paragraph are based on samples from the same batch.

6.2.5 Photoelectrochemical measurements

Photoelectrochemical measurements of individual electrodes were performed in a custom-made Teflon-based reactor with a volume of about 8 ml which was open to the environment. Illumination occurred through a quartz glass window and 25 mm electrolyte (front-side illumination), and the incident beam was perpendicular to the specimen surface. A solar simulator (Newport) with a 300 W xenon lamp and an air mass (AM) 1.5 global filter was used as light source. The intensity of the simulated sunlight was adjusted to 1 sun (100 mW/cm²) with a standard reference silicon solar cell. The *J-V* photocurrent data were obtained using a standard three-electrode setup with a platinum mesh counter electrode and a Ag/AgCl (3 M NaCl, BASi MF 2052) reference electrode at room temperature. The reference electrode has a potential ($E_{\text{Ag/AgCl}}^0$) of +0.209 V with respect to the standard hydrogen electrode (SHE), which was confirmed with a new Ag/AgCl (3 M NaCl, BASi MF 2052) master reference electrode before

measurements. All voltages reported were calculated versus the reversible hydrogen electrode (RHE) using the following Equation 6.1:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}}^{\circ} + 0.059 \text{ V} \times \text{pH} + E_{\text{Ag/AgCl}} \quad (\text{Eq. 6.1})$$

An air-saturated 1 M sodium sulfite (Na_2SO_3) in 0.5 M potassium phosphate (KPi) buffer solution with a pH of 7.0 served as the electrolyte. The potential was swept with a scan rate of 10 mV/s from 0 to 2.0 V *vs.* RHE first in dark and then under illumination. A potentiostat (PAR, VersaStat 4) served as a power source. The active surface area was 0.28 cm² as determined by the O-ring. This area covered 0.24 cm² of the structured and 0.04 cm² of flat surface (see drawing in **Table 6.1**). These values were incorporated in the determination of the effective surface area calculation. The samples were prepared in two batches, and all samples in each batch were processed consecutively. The data reported in the results paragraph are based on samples from the same batch.

6.2.6 Scanning electron microscopy (SEM)

High-resolution scanning electron microscopy (HR SEM) images were taken with a FEI Sirion FEG SEM with a Through the Lens Detector (TLD), operated at acceleration voltages of 10 kV. The imaged areas are random, and somewhere around the center of the sample.

6.2.7 X-ray powder diffraction (XRD)

X-ray diffraction patterns were determined with a Bruker D2 PHASER XRD using Cu K α radiation at an acceleration voltage of 30 kV.

6.2.8 Raman spectroscopy

Raman spectra were collected at ambient conditions by using a Bruker SENTERRA Raman Spectrometer equipped with a 532 nm laser and a cooled CCD detector. Measurements were performed at 10 mW laser power intensity and integration times of 2.0 s.

6.3 Results and discussion

6.3.1 Electrodeposition of BiOI

Hexagonally stacked microwires of 5.3, 10.6 and 15.9 μm length, 4 μm diameter and 4, 6, 8, 10, 15 and 20 μm spacing were prepared on areas of $0.5 \times 0.5 \text{ cm}^2$ in the center of $2 \times 2 \text{ cm}^2$ cells on highly boron-doped ($\sim 2 \times 10^{18} \text{ cm}^{-3}$ - $\sim 8 \times 10^{18} \text{ cm}^{-3}$) silicon substrates. High boron doping was chosen because of its high conductivity and thus low series resistance, the possibility to use silicon with p/n junctions of which the surface would be highly p-type doped, and the creation of a low resistance ohmic contact to sputtered ITO. A direct contact between p-type silicon and BiVO₄ has been shown to be favorable in creating a photovoltage of up to 150 mV under 3.5 eV illumination with 0.3 mW/cm^2 intensity.^[36] However, a $\sim 30 \text{ nm}$ intermediate ITO layer was sputtered on top of the (flat and pillared) silicon substrates to prevent the oxidation of the silicon surface which would have increased the electrical resistance between silicon and H-BiVO_{4-x}:Mo. Such an ITO interlayer has been shown to enhance anodic photocurrent densities of WO₃ on p-Si^[37] which can also be expected between p-Si and H-BiVO_{4-x}:Mo.

The first step in H-BiVO_{4-x}:Mo preparation is the electrodeposition of BiOI from a solution of KI, Bi(NO₃)₃ and p-benzoquinone in aqueous ethanol. BiOI deposits in a two-dimensional crystalline morphology of $\sim 20 \text{ nm}$ thin plates with voids between them.^[16] After transformation, this low density structure was shown in the literature to yield high-surface-area nanoporous BiVO₄.^[16] Following the literature procedure, a pH increase near the Si surface is induced by the electrochemical reduction of p-benzoquinone to hydroquinone (Equation 6.2).^[3]

Figure 6.2 Transferred charge densities during electrochemical deposition of BiOI from a solution of KI, $\text{Bi}(\text{NO}_3)_3$ and p-benzoquinone in water/ethanol at -0.1 V vs. Ag/AgCl (3 M NaCl) on flat and pillared p-type doped silicon substrates, the latter with 5.3 μm (a), 10.6 μm (b) and 15.9 μm (c) long hexagonally arranged microwire arrays of 4 μm diameter and various spacing, with ITO sputtered for 5 min. Solid lines are correlated to the projected surface area and dashed lines are recalculated values scaled to the effective surface area of the same sample. The projected sample area was 1.13 cm^2 as defined by the O-ring which contained microwires in a 0.25 cm^2 cell. d) Direct comparison of the effect of microwire spacing on charge density, demonstrating increasing charge density (*per* effective surface area) as a function of decreasing microwire spacing.

To study the influence of microwire length and spacing on pH gradients, and therefore gradients in BiOI deposition quantities, the deposition time was kept constant at 30 s or 120 s. Figure 6.2 shows the charge densities passed during the BiOI growth on 1.13 cm^2 flat, and 0.25 cm^2 structured area containing pillared Si. The curves show the projected surface area (solid lines) and are recalculated to the effective surface area (dashed lines). The values are negative to represent the direction of electron flow towards the working electrode. At all microwire

lengths, the passed charge densities are higher on structured samples than on flat. The charge densities increase with decreasing microwire spacing, and thus with increased surface area. However, the charge density increase is not proportional to the surface area increase, and the disproportionality increases with smaller microwire spacing and longer length. The effective surface area enhancement by microwires is between 1.12 for microwires with a length of 5.3 μm and 20 μm spacing and 4.12 for microwires with a length of 15.9 μm and 4 μm spacing (Table 6.1). During BiOI electrodeposition, 22.1% of the active surface area was microwire-structured and thus the effective surface areas were enhanced by factors between 1.03 to 1.69 compared to the projected surface area.

Figure 6.3 SEM images (45° tilted) of electrodeposited BiOI for 30 s (a, b) and 120 s (c, d) on 15.9 μm long hexagonally arranged p-type doped silicon microwire arrays of 4 μm diameter and 6 μm (a, c) or 15 μm (b, d) spacing, with ITO sputtered for 5 min.

Figure 6.3 shows selected SEM images of microwire arrays with 6 μm and 15 μm spacing and 15.9 μm length after BiOI deposition. SEM images of all samples coated with BiOI are shown in the Appendix (Figure 6.14, 6.15 and 6.16). It can be seen that the BiOI growth is feasible on three-dimensional surfaces and that

the microwire surface is covered completely with BiOI after a deposition time of 120 s (Figure 6.3c, d). However, at deposition times of 30 s, the samples are either completely (Figure 6.3a) or partially covered (Figure 6.3b) with a thin layer of BiOI. BiOI apparently starts to grow gradually from the bottom to the top, and shows the highest growth rate at the lowest microwire spacing.

Several explanations are possible for this phenomenon. The presence of mass transfer limitations within the microwire system appears the most plausible explanation. The conversion of benzoquinone results in the consumption of protons and an increase of pH. The pH increase is locally the highest at the base of the microwire arrays, because there protons and p-benzoquinone are not only consumed by electrochemical conversion on the surface of the pillar, but also on the exposed base. Towards the base, the path length for proton and p-benzoquinone transport from the bulk of the solution above the pillared surface is the largest. Since the area over volume ratio of the Si microwire array increases with decreasing spacing, the pH increase is also favored by a relatively small microwire spacing. A depletion of p-benzoquinone in between the microwires due to diffusion-limited mass transport explains the disproportionality of charge density of effective surface areas during BiOI deposition. Other reported results strengthen this hypothesis. In Chapter 4, which is based on our publication on spatioselective electrochemical and photoelectrochemical functionalization of silicon microwires with axial p/n junctions,^[38] we have observed an inversed gradient of electrodeposited Pt particles from a solution containing H_2PtCl_6 on an array of microwires with 7 μm length, 4 μm diameter and 2 μm spacing. There, the deposited Pt particle density was higher at the bottom than the top. We have tentatively attributed this to a diffusion limitation of the precursor in between the microwire arrays and have verified this with a control experiment in which we performed the deposition under the same conditions on microwire arrays of 16 μm spacing. We have found optically significantly less inhomogeneity. Shaner *et al.* have electrodeposited WO_3 from a tungstic peroxy-acid solution on ITO-coated silicon microwires of 40 μm o 70 μm length, ~ 2 μm diameter and 4 μm spacing in a square lattice.^[39] Also they have found a gradient in WO_3 thickness over the microwire length for which the WO_3 thickness decreased from

the top to the bottom due to a quicker depletion of the peroxo-tungstic acid at the bottom compared to the top.

We exclude that a voltage drop along the microwires causes the gradient in BiOI during its deposition. Accounting for the highest wafer resistivity of 0.025 Ωcm , 15.9 μm length and 4 μm diameter of the microwire and a highest current density during BiOI deposition of 3 mA/cm^2 , the maximal potential drop is 1.1×10^{-7} V.

Another potential cause for the area disproportionality in charge density during BiOI deposition and its inhomogeneous growth, is that the sputtered ITO layer is too thin and does not cover the sides of the microwires completely. Using our recipe, a ~ 30 nm film formed on a flat substrate during 5 min sputtering. However, if ITO is truly inhomogeneously distributed at the microwire sides, then we would expect BiOI growth to be similar on the bottom between the microwires and on the microwire tops, which is not evident. Nevertheless, we have sputtered a fourfold amount of ITO (20 min sputtering time, ~ 120 nm thickness on a flat substrate) on the samples in a second batch of production of microwires. We have constructed microwire arrays with spacings of 6 to 15 μm , kept the microwire length constant at 10.6 μm , and deposited BiOI for 30 to 300 s. Figure 6.4 shows the charge densities passed during the BiOI growth on these samples which had an active surface area of 1.13 cm^2 including a 0.25 cm^2 structured area. The flat samples were prepared two times of which one was further transferred to BiVO_{4-x}:Mo and one used for analysis of the deposited thickness (Figure 6.6).

Also with a thicker ITO layer, BiOI deposited well on microwire-structured surfaces (Figure 6.5). However, more charge passes through the system when thicker ITO layers are sputtered (Figure 6.6). We speculate that this is due to a lower resistance of thicker ITO, which might originate from a different relative oxygen content in ITO or a higher crystallinity. Note that a less pronounced trend in effect of smaller microwire spacing on increasing charge density of Figure 6.2 is observed in Figure 6.4, while a wider spread in absolute values of charge density was obtained when comparing variable BiOI deposition times. A direct control experiment in Figure 6.4 in which we deposited BiOI for 120 s on microwires with an ITO coating sputtered for 5 min or 20 min confirmed this.

Thus, some effect of ITO uniformity, besides the advocated mass transfer limitation, cannot be excluded.

Figure 6.4 Cumulative transferred charge densities during electrochemical deposition of BiOI on 10.6 μm silicon microwire arrays with ITO sputtered for 5 min (d) or 20 min (a, b, c, e). Solid lines represent projected surface area and dashed lines effective surface area; f) shows a direct comparison of the effect of microwire spacing on transferred charge density. The value for flat is the average of both total cumulative charge densities.

Figure 6.5 SEM images (45° tilted) of electrodeposited BiOI for 30 s (a, b), 60 s (c, d), 120 s (e, f) and 300 s (g, h) on 10.6 μm long hexagonally arranged p-type doped silicon microwire arrays of 4 μm diameter and spacings of 6 μm (a, c, e, g) and 10 μm (b, d, f, h), with ITO sputtered for 20 min.

Figure 6.6 Cumulative transferred charge densities (a, b), 45° tilted (c-g) and cross sectional (h-l) SEM images of BiOI electrochemically deposited from a solution of KI, $\text{Bi}(\text{NO}_3)_3$ and p-benzoquinone in water/ethanol at -0.1 V vs. Ag/AgCl (3 M NaCl) on flat p-type doped silicon with ITO sputtered for 5 min (a dotted line, b circle, f, k) and 20 min (a solid lines, b squares, c, d, e, g, h, l, j, l). The projected sample area was 1.13 cm² as defined by the O-ring.

On flat Si substrates, the BiOI growth rate appeared linear over the passed charge density between a deposition time of 30 s and 120 s (Figure 6.6). At a higher deposition time of 300 s, the BiOI thickness decreased. This is due to a decreasing current density over time, evident from Figure 6.6a, which becomes too low to sustain a significant pH gradient between substrate surface and bulk solution. BiOI starts to re-dissolve back into solution when the pH becomes too low at the surface.

6.3.2 Transformation of BiOI into H-BiVO_{4-x}:Mo

Figure 6.7 SEM images (45° tilted) of H-BiVO_{4-x}:Mo prepared from BiOI electrodeposited for 30 s (a, b) and 120 s (c, d) on 15.9 μm long hexagonally arranged p-type doped silicon microwire arrays of 4 μm diameter and 6 μm (a, c) or 15 μm (b, d) spacing with ITO sputtered for 5 min.

The transformation of BiOI into H-BiVO_{4-x}:Mo was performed by dropcasting a DMSO solution with vanadyl acetylacetonate (VO(acac)₂) and sodium molybdate (Na₂MoO₄) in a ratio of 100:1, evaporating the DMSO at 100 °C in a drying oven, calcining at 450 °C, removing the excess of vanadium and molybdenum by soaking in a 1 M KOH solution, and annealing in a reducing H₂/N₂ (1/20) atmosphere. Figure 6.7 shows selected SEM images of microwire arrays with spacings of 6 and 15 μm and a length of 15.9 μm, sputtered with ITO for 5 min and coated with H-BiVO_{4-x}:Mo after BiOI deposition times of 30 s and 120 s. SEM images of all prepared samples of 5.3, 10.6 and 15.9 μm length and 4, 6, 8, 10, 15 and 20 μm spacing are shown in the Appendix (Figure 6.17, 6.18 and 6.19). The H-BiVO_{4-x}:Mo coating was nanoporous and covered the three-dimensional microwire surfaces when BiOI was deposited for 120 s, but showed defects in the form of cracks (Figure 6.7c, d). These defects are attributed

Figure 6.8 45° tilted SEM images of BiVO_{4-x}:Mo prepared from BiOI electrodeposited for 30 s (a, b), 60 s (c, d), 120 s (e, f) and 300 s (g, h) on 10.6 μm long hexagonally arranged p-type doped silicon microwire arrays of 4 μm diameter and 6 μm (a, c, e, g), or 10 μm (b, d, f, h) spacing with ITO sputtered for 20 min.

to crystallization during the DMSO evaporation process. Microwires on which BiOI was deposited for only 30 s and thus were not completely covered, were also incompletely covered with H-BiVO_{4-x}:Mo (Figure 6.7a, b). Similar results were achieved when H-BiVO_{4-x}:Mo was prepared on microwires sputtered with ITO for 20 min and BiOI deposition times were 30 s, 60 s, 120 s and 300 s (Figure 6.8). Also here, a complete H-BiVO_{4-x}:Mo coating was obtained at BiOI deposition times greater than 30 s.

6.3.3 Photoelectrochemical characterization

Photocurrent measurements were performed by linear potential sweeps from 0 to 2.0 V *vs.* RHE at a scan rate of 10 mV/s, first in dark and then under simulated AM 1.5 solar illumination. The 0.5 M potassium phosphate (KPi) buffer solution with a pH of 7.0 contained 1 M sodium sulfite (Na₂SO₃) as a sacrificial hole acceptor. The intrinsic catalytic water oxidation activity of BiVO₄ is relatively poor whereas sulfite oxidation is kinetically fast and also thermodynamically more favorable than the oxidation of water.^[34, 40, 41] Thus, the addition of a hole scavenger allows the investigation of the photoelectrochemical properties of BiVO₄ without the necessity of a water oxidation catalyst.^[16, 42] The resulting photoactivities of H-BiVO_{4-x}:Mo, prepared from BiOI electrodeposited for 120 s, on microwire arrays of various lengths and spacings and BiOI deposited between 30 s and 300 s on microwires of 10.6 μm length and various spacings are shown in Figure 6.9 and Figure 6.10, respectively. Linear sweeps are presented in a potential range from 0 to 1.6 V *vs.* RHE. Two samples in Figure 6.9, *i.e.* microwire arrays with a 15 μm spacing and 10.6 μm length and with a 8 μm spacing and 15.9 μm length, did not follow the photocurrent trends of the other samples. These samples are considered as outliers, and one of these samples was reproduced in Figure 6.10 and did not show the outlying behavior. For a better comparison, photocurrents at 0.5 and 1.1 V *vs.* RHE have been plotted as a function of microwire spacing (Figure 6.9d, e and Figure 6.11). The choice of photocurrent comparisons at 0.5 V and 1.1 V is arbitrary and serves only to represent a low and a high bias region. The sulfite photooxidation onset potential occurred at ~0.35 V *vs.* RHE and the dark current onset potential at ~1.10 V *vs.* RHE. In the low bias region at 0.5 V *vs.* RHE microwire samples

Figure 6.9 a-c) Linear potential sweeps (10 mV/s) of H-BiVO_{4-x}:Mo (120 s BiOI deposition) on Si microwires with sputtered ITO (5 min) in a solution of 1 M Na₂SO₃ in 0.5 M KPi buffer (pH 7.0) and current density comparison at 0.5 V (d) and 1.1 (e) over microwire spacing. Solid lines represent projected and dashed lines effective surface area.

Figure 6.10 Linear potential sweeps (10 mV/s) of $\text{H-BiVO}_{4-x}\text{:Mo}$ (120 s BiOI deposition) on flat (a) and Si microwires of 10.6 μm length and 6-15 μm (b-e) spacing with sputtered ITO (20 min (various colors), 5 min (blue)) in a solution of 1 M Na_2SO_3 in 0.5 M KPi buffer (pH 7.0). Solid lines represent projected and dashed lines effective surface area.

Figure 6.11 Photocurrent densities vs. BiOI deposition time as a function of microwire spacing at 0.5 V (a) and 1.1 V (b) for projected (filled symbols, solid lines) and effective (empty symbols, dashed lines) sample areas of H-BiVO_{4-x}:Mo-coated Si microwire arrays of 10.6 μm length with sputtered ITO (20 min (squares), 5 min (circles)). Data is obtained from linear potential sweeps presented in Figure 6.10.

outperformed (Figure 6.9) or slightly underperformed (Figure 6.10 and Figure 6.11) compared to flat samples, while in the high bias region at 1.1 V vs. RHE, H-BiVO_{4-x}:Mo on flat samples outperformed all microwire-structured samples. Several reasons are plausible for this behavior and are addressed in below, *i.e.* (i) limited mass transfer of the redox species in between the microwires, (ii) sub-optimal light absorption, (iii) over-proportional increase in surface recombination of electrons and holes on the microwire-enhanced surface of H-BiVO_{4-x}:Mo, (iv) inhomogeneous distribution of the sputtered ITO layer on the microwire sites and thus lack of electrical connection of H-BiVO_{4-x}:Mo to the silicon substrate, and (v) the H-BiVO_{4-x}:Mo thickness is closer to the optimum on flat than on microwire-structured samples.

Mass transfer effects

Photocurrents of microwire-structured samples increased steeply between the onset potential at ~0.35 and ~0.70 V vs. RHE and then leveled off until ~1.30 V vs. RHE. This might be due to two reasons: (i) mass transfer limitations of redox species in the internal volume of the microwire array, or (ii) insufficient light absorption and thus depletion of available photoinduced holes in the valence band of H-BiVO_{4-x}:Mo. We used a scan rate of 10 mV/s in our linear potential sweeps, resulting in a pass time of ~3.5 s between the photocurrent onset and the

beginning of the photocurrent leveling off in which SO₃²⁻ ions at the electrode surface can deplete. This is in line with our observations and discussions on the electrochemical BiOI deposition and with literature reports. For instance, Xiang *et al.* studied the mass transport of 50 mM/5.0 mM cobaltocenium⁺/cobaltocene⁰ redox species in CH₃CN – 1.0 M LiClO₄ electrolyte in between p-type microwire arrays of 3 μm diameter, ~100 μm length, and 4 μm spacing in a square lattice.^[43] They found that fill factors were low and that the obtainable photocurrent densities were limited to 17.6 mA/cm² even under high illumination intensities due to mass transport limitations of the redox species within the internal volume of the silicon microwire arrays.^[43] Their simulations with COMSOL Multiphysics showed that the solution-phase reagent concentration decreased to zero over the lower ~70% of the wire length relative to the bulk concentration above the microwire, implying that more than two thirds of the microwire length only contributed to light absorption but not to the redox process.^[43, 44] Vijselaar *et al.* decoupled light absorption and catalytic activity of silicon microwires with radial p/n junctions, 4 μm diameter, 40 μm length and various spacings by depositing a proton reduction catalyst spatioselectively on the microwire tops and achieved similar efficiencies in photoelectrochemical and photoelectrical measurements.^[45] Their results strengthen our hypothesis of diffusion limitation of redox species in the internal volume of the microwire array, since in the cited study light trapping properties of the microwire structure were utilized without suffering from mass transfer inside the microwire array because of the placement of the catalyst at the top only.

Light absorption properties

Various studies have proven that structuring the silicon surface with microwires enhances the photovoltaic performance due to enhanced light absorption and a greater junction area.^[25, 46] For instance, Elbersen *et al.* have studied the effects of microwire length on photovoltaic activity of silicon microwires with radial p/n junctions and a spacing of 2 μm and found that all tested microwires with a length between 10 μm and 60 μm outperformed flat equivalents under perpendicularly oriented illumination.^[47] However, Boettcher *et al.* prepared similarly sized microwire arrays with a radial n⁺/p junction, deposited platinum on the tops and tested them for photocatalytic hydrogen evolution.^[48] They found that the

efficiencies of silicon microwire photocathodes were 5.8% and that of planar control samples 9.6%. In another publication Boettcher *et al.* tested energy conversion efficiencies of p-type microwires for the reduction of methyl viologen (MV^{2+}).^[49] They observed energy conversion efficiencies of 3.6% for structured and 12.9% for flat substrates. The authors argue that this is due to minimized optical absorption of the perpendicularly oriented illumination beam to the Si microwire arrays. By tilting the substrate, the external quantum yield increased from ~0.2 to close to 0.7 at 60°. Also others have observed similar angle-dependent photocatalytic behavior on microwires.^[50] Visselaar *et al.* found that photovoltaic current densities of silicon microwires with a radial p/n junction increase with increasing microwire spacing.^[45] Our results show predominantly the same trend (Figure 6.9) which indicates that underperformance of devices with a low microwire spacing might be due to limitations in light absorption. This is supported by the study of Chakthranont *et al.* who published a similar concept as discussed in this chapter, after completion of our study, and obtained higher photocurrents in sulfite oxidation on microwire-structured samples than on flat equivalents.^[51] These authors used silicon nanowires instead of microwires, tin oxide (SnO_2) instead of indium tin oxide as the interlayer between Si and $BiVO_4$, prepared $BiVO_4$ by spray coating, used W instead of Mo doping and also annealed their devices in a H_2 atmosphere. The biggest difference between their and our study was the dimensions of the silicon structures, *i.e.* Chakthranont *et al.* used so-called black silicon which shows a very high light absorption and is composed of needle-shaped (tapered) nanowires, in their case ~3 μm length, ~200 nm average diameter and ~300 nm spacing. We assume that the microwires in our system do absorb more light than flat equivalents as proven by Elbersen *et al.*^[46, 47] and Kelzenberg *et al.*^[25] but believe that mass transfer overcompensates this effect and leads to an overall underperformance of the microwire structures compared to flat samples. In contrast, the positive light trapping effect of microwires overcompensated the negative diffusion effect in the system reported by Chakthranont *et al.* as these authors used smaller microwire dimensions leading to a significantly shorter ion diffusion path length.

Surface recombination

$BiVO_4$ suffers from surface recombination of photogenerated charges which limit

the photocurrent of bare BiVO₄ in photocatalytic water oxidation.^[52] Zachäus *et al.* showed that the role of deposited CoPi on spray-deposited BiVO₄ films is mainly the passivation of the surface and thus suppression of surface recombination and not the improvement of charge transfer kinetics.^[52] An increase of the surface area in our microwire systems would also increase the amount of H-BiVO_{4-x}:Mo recombination centers and may lower the overall photoactivity in comparison to flat samples. However, due to the addition of sulfite as a hole scavenger to the solution, the loss of holes by surface recombination at the BiVO₄-electrolyte interface is negligible^[42] and thus we do not expect surface recombination making a significant difference in photoactivity between flat and structured samples in our experiments. In parallel, also the interface areas between H-BiVO_{4-x}:Mo/ITO and ITO/p-Si increase with increasing surface area. It is theoretically conceivable that these interfaces were defect-rich and led to an increase in electron and hole recombination. From our experiments, no judgement is possible whether these interfaces limit the performance of microwire structured devices.

ITO layer thickness

As discussed in the BiOI deposition section above, the ITO layer thickness on the microwires might have been too thin or the grown H-BiVO_{4-x}:Mo layers might have been closer to the optimal range on the flat samples than on the microwires. Linear potential sweeps in Figure 6.10 and the comparison of photoactivities at 0.5 V and 1.1 V vs. RHE in Figure 6.11 show that the underperformance of microwire-structured samples in comparison to flat samples is not due to ITO and H-BiVO_{4-x}:Mo layer thicknesses since the flat samples also show a better performance than the microwire-structured samples for thicker ITO and H-BiVO_{4-x}:Mo layers.

H-BiVO_{4-x}:Mo layer thickness

The photocurrents of H-BiVO_{4-x}:Mo (Figure 6.6) on flat substrates and on microwire arrays with a high microwire spacing correlate well with BiOI and thus H-BiVO_{4-x}:Mo thickness which was found to be thickest at a BiOI deposition time of 120 s (Figure 6.11). In contrast, microwire-structured samples with a low spacing showed the highest photocurrents at the highest BiOI deposition time

(300 s). At a deposition time of 30 s, microwire-structured samples showed higher photocurrents than flat samples. Regarding our findings that BiOI layer growth is fastest at the smallest microwire spacing, it is likely that H-BiVO_{4-x}:Mo layers became too thick and out of the optimal range on samples with small microwire spacing and long deposition time. Consequently, the layers were closer to the optimal range at the short (30 s) deposition time, explaining the better performance.

6.3.4. Influence of Mo doping and H₂ annealing

To dope BiVO₄ deposited on silicon microwires, 1% Mo relative to V was added to the DMSO solution during transformation of BiOI to BiVO₄:Mo. Subsequently, BiVO₄:Mo was annealed in a 5% H₂/95% Ar atmosphere at 300 °C for 0.5 h. To study the effects of Mo addition and hydrogen annealing, reference samples were prepared in which the transformation of BiOI to BiVO₄ was performed without Mo addition and in which BiVO₄:Mo was not annealed in hydrogen atmosphere. X-ray diffractometry (XRD) and Raman spectroscopy revealed that nanoporous doped and undoped BiVO₄ is highly crystalline and of purely the monoclinic scheelite phase (Figure 6.12).^[53, 54] No detectable diffraction peak shifts were observed in the XRD due to Mo doping or annealing in hydrogen atmosphere which is in agreement with earlier reports.^[11, 14, 15, 40, 55] The Raman spectra show characteristic VO₄ tetrahedron vibrational modes of the monoclinic BiVO₄ at around 211, 328, 367, 712 and 826 cm⁻¹. The major band at 826 cm⁻¹ represents the A_g mode of the symmetric V-O stretching.^[53] A shift of this vibrational mode to lower frequency of 822 cm⁻¹ and the appearance of an additional peak at 876 cm⁻¹ confirmed the Mo doping in BiVO₄ in these samples. The redshift of the A_g mode frequency in BiVO₄:Mo and H-BiVO_{4-x}:Mo is interpreted as an increase of the bond lengths in the tetrahedrons by a substitution of Mo for V, and the peak at 876 cm⁻¹ is due to Mo-O-Mo stretching.^[56, 57] The exact doping level of Mo in our experiments is not known but it is assumed to be below 6.0%. Mo doping levels higher than 6.0% should lead to a noticeable change in the XRD pattern due to a structural change from monoclinic to tetragonal phase or precipitation of V₂O₅.^[40, 42, 58] Chen *et al.* tested 1% to 5.5% Mo-doped BiVO₄, prepared by reactive co-sputtering, and found that at all doping levels the material performed better than undoped BiVO₄ in the photocatalytic

sulfite oxidation.^[40] In their study, the sample with 3.4% Mo doping showed the best photocatalytic performance. Park *et al.* have prepared BiVO₄:Mo with doping levels of 1%, 3% and 6% via a different electrochemical route.^[42] They also found that all doped materials showed higher photocurrents than undoped BiVO₄ in the sulfite oxidation. Also here, the sample with a 3% doping level showed the best performance.^[42]

Figure 6.12 a) XRD patterns and b) Raman spectra of BiVO₄, BiVO₄:Mo and H-BiVO_{4-x}:Mo on flat highly p-type-doped Si coated with ITO.

The annealing of BiVO₄:Mo in a 5% H₂/95% Ar atmosphere was performed according to the publication of Gan *et al.*^[14] These authors prepared BiVO₄ via the same route as used in this chapter and compared hydrogen-annealed and unannealed samples. They found that the photocurrent density of H-BiVO_{4-x} in a solution of 1 M sodium sulfite in 0.1 M borate buffer at pH 9 is substantially higher than that of BiVO₄. They attribute this to an increase in oxygen vacancies and introduction of hydrogen impurities through hydrogenation. These oxygen vacancies improve photoelectrochemical performance by improving the electrical conductivity which increases the charge transfer and collection in H-BiVO_{4-x}. The process shifts the Fermi level position towards the conduction band, thus facilitating charge separation at the semiconductor/electrolyte interface. Moreover, these oxygen vacancies and hydrogen impurities act as shallow donors, which create a new level in the band gap and enhance the charge transfer at the interface between BiVO₄ and fluorine-doped tin oxide (FTO).^[14]

Figure 6.13 Linear potential sweeps at a scan rate of 10 mV/s for BiVO₄, BiVO₄:Mo and H-BiVO_{4-x}:Mo obtained from BiOI deposited for 30 s (a), 60 s (b), 120 s (c) and 300 s (d) on flat p-type silicon in a solution of 1 M sodium sulfite (Na₂SO₃) and 0.5 M potassium phosphate (KPi) buffer with a pH of 7.0 under simulated AM 1.5 solar illumination.

Cooper *et al.* in contrast argue that the improvement of photocurrent of post-synthetically annealed BiVO₄ in 100% hydrogen atmosphere is not due to the introduction of oxygen vacancies but rather to incorporation of hydrogen donors.^[15] The authors found that annealing in H₂ at temperatures up to 290 °C led to near-complete elimination of majority carrier transport limitations.^[15] In our photocurrent measurements of BiVO₄, BiVO₄:Mo and H-BiVO_{4-x}:Mo prepared from BiOI deposited for 30 to 300 s (Figure 6.13) we have observed a slight improvement due to Mo doping and hydrogen annealing only at a BiOI deposition time of 60 s. At BiOI deposition times of 120 s and 300 s, undoped, unannealed BiVO₄ showed the highest photocurrents, followed by BiVO₄:Mo and then H-BiVO_{4-x}:Mo. The reason for the decrease in photocurrent due to Mo

doping and hydrogen annealing in these samples, contrary to a positive effect of these procedures reported in the literature^[40, 42], is not known. We assume that this is, in the case of Mo doping, due to a different preparation procedure, *i.e.* reactive co-sputtering, and a different electrodeposition route, in comparison to literature.^[40, 42] As for the hydrogen annealing, the used temperature in the present study might have been too high. While the applied temperature of 300 °C is below the value of 320 °C reported by Cooper *et al.* to induce lower photocurrents of BiVO₄ when annealed in pure hydrogen atmosphere due to the formation of metallic species by reduction of BiVO₄,^[15] Gan *et al.* have reported the optimum to be at 250 °C in a 5% H₂/95% Ar atmosphere. At higher temperatures, Gan *et al.* suppose that trap states in the BiVO₄ band gap are introduced by the occurrence of defects.^[14]

6.4. Conclusions

In conclusion, molybdenum-doped and hydrogen-annealed H-BiVO_{4-x}:Mo in different thicknesses was successfully deposited on ITO-coated, highly doped p-type silicon flat surfaces and microwire arrays of 4 µm diameter, 4 µm to 20 µm spacing and 5.3 µm to 15.9 µm length. At the same time, we encountered several unexpected effects that hampered the efficiency of our devices.

The influence of Mo doping and hydrogen annealing in combination with different preparation methods needs to be further investigated as they decreased the photocatalytic performance of our H-BiVO_{4-x}:Mo films, which is contrary to literature. Yet, leaving out Mo doping and hydrogen annealing during the preparation may have further increased the observed difference in photocatalytic performance between flat and microwire-structured devices by amplifying the mass transfer phenomena.

Observed photocurrents for the oxidation of sodium sulfite (Na₂SO₃) on microwire-structured samples were mainly lower than on flat equivalents. We have excluded various hypotheses to explain the differences in photo-electrochemical performance, and our results support the hypothesis that ion diffusion in the internal volume of the microwires overcompensates the positive effect of higher light absorption and H-BiVO_{4-x}:Mo mass loading compared to

flat equivalents, thus limiting the performance of our microwire-structured devices. This is supported by the findings that during potential sweeps from low to high bias region, microwire-structured devices outperformed flat equivalents in the low bias region and strongly underperformed in the high bias region, since the low bias region is tested before SO_3^{2-} ions could be depleted. When water is oxidized on the microwire-structured anodes instead of sulfite, oxygen and protons evolve which have an effect on mass transport. Protons have a much higher diffusion rate than sulfite ions, and oxygen production could introduce convection. However, the observation of a thickness gradient in BiOI deposition, which is triggered by a local pH change, showed that either proton or p-benzoquinone diffusion is limited in our microwire system. The light beam was oriented perpendicularly to the samples in the photoelectrochemical experiments, which does not lead to optimal light trapping of the system. To learn more about the influence of light absorption, ion diffusion inside the microwire system and their relative contributions to the overall photocatalytic activity, tests at various tilt angles, different potential scan speeds and chronoamperometry measurements are needed.

In the development of substrates for photocatalysts with the aim to enhance surface area and to create a tandem device for solar water splitting, our results showed unintentionally the limits of (silicon) microwire dimension, structure and architecture. Whereas surface structuring has presumably a positive effect, ion diffusion inside the microwire array has a negative effect on the overall photocatalytic performance. As recent results of Chakthranont *et al.*^[51] have shown, the use of silicon nanowires can increase the photocatalytic performance of BiVO_4 . However, optimization of silicon wire length, spacing and diameter is needed to obtain maximal photocatalytic device activity.

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6.7 Appendix

Figure 6.14 45° tilted SEM images of electrodeposited BiOI for 30 s (a-f) and 120 s (g-l) on 5.3 μm long hexagonally arranged p-type doped silicon microwire arrays of 4 μm diameter and 4 μm (a, g), 6 μm (b, h), 8 μm (c, i), 10 μm (d, j), 15 μm (e, k) or 20 μm (f, l) spacing with ITO sputtered for 5 min.

Figure 6.15 45° tilted SEM images of electrodeposited BiOI for 30 s (a-f) and 120 s (g-l) on 10.6 μm long hexagonally arranged p-type doped silicon microwire arrays of 4 μm diameter and 4 μm (a, g), 6 μm (b, h), 8 μm (c, i), 10 μm (d, j), 15 μm (e, k) or 20 μm (f, l) spacing with ITO sputtered for 5 min.

Figure 6.16 45° tilted SEM images of electrodeposited BiOI for 30 s (a-f) and 120 s (g-l) on 15.9 μm long hexagonally arranged p-type doped silicon microwire arrays of 4 μm diameter and 4 μm (a, g), 6 μm (b, h), 8 μm (c, i), 10 μm (d, j), 15 μm (e, k) or 20 μm (f, l) spacing with ITO sputtered for 5 min.

Figure 6.17 45° tilted SEM images of $\text{H-BiVO}_{4-x}\text{:Mo}$ prepared from BiOI electrodeposited for 30 s (a-f) and 120 s (g-l) on 5.3 μm long hexagonally arranged p-type doped silicon microwire arrays of 4 μm diameter and 4 μm (a, g), 6 μm (b, h), 8 μm (c, i), 10 μm (d, j), 15 μm (e, k) or 20 μm (f, l) spacing with ITO sputtered for 5 min.

Figure 6.18 45° tilted SEM images of $\text{H-BiVO}_{4-x}\text{:Mo}$ prepared from BiOI electrodeposited for 30 s (a-f) and 120 s (g-l) on 10.6 μm long hexagonally arranged p-type doped silicon microwire arrays of 4 μm diameter and 4 μm (a, g), 6 μm (b, h), 8 μm (c, i), 10 μm (d, j), 15 μm (e, k) or 20 μm (f, l) spacing with ITO sputtered for 5 min.

Figure 6.19 45° tilted SEM images of H-BiVO_{4-x}:Mo prepared from BiOI electrodeposited for 30 s (a-f) and 120 s (g-l) on 15.9 μm long hexagonally arranged p-type doped silicon microwire arrays of 4 μm diameter and 4 μm (a, g), 6 μm (b, h), 8 μm (c, i), 10 μm (d, j), 15 μm (e, k) or 20 μm (f, l) spacing with ITO sputtered for 5 min.

Chapter 7

Summary and perspective

The transition from a fossil fuel-dependent society towards the use of renewable energies is desirable to reduce pollution, CO₂ emission and thus slow down global warming. So far, the focus has been on electricity production from sustainable sources, such as photovoltaics and wind power plants. However, their energy input is fluctuating and does not meet the demand. Whereas short term intermittencies in electricity, under or overproduction, are potentially balanced with pumped hydro storage systems or batteries, solutions for energy storage to deal with long term intermittencies, such as summer and winter cycles, are needed. One of the proposed solutions is to generate hydrogen from water with the energy from the sunlight. This hydrogen could be used as a fuel itself or converted further to hydrocarbons. By replacing the current hydrogen demand, of which around 96% is produced from fossil fuels, would reduce the total yearly emission of CO₂ by about 2% or 685 million metric tons.

The research described in this thesis has focused on the development of photoelectrochemical devices for solar-driven hydrogen generation from water splitting. For this purpose, silicon was used as a base material as it is nontoxic, abundant, easily available and is being produced in high purity and quantity in industry. Electrochemistry was utilized as the coating and functionalization technique as it provides a versatile range in usable materials and the ability to control the morphology of deposited materials during the deposition process, the possibility to coat structured substrates conformally, a good electrical contact between substrate and deposited material, and compatibility with ambient conditions and scalability.

In Chapters 3 and 5, a metal and a semiconductor, *i.e.* platinum (Pt) and tungsten oxide (WO₃), were electrodeposited on flat ITO-coated p-type silicon. Chapter 3 has reported how Pt particle size and density can be controlled and

tuned to the nano range by the addition of H_2O_2 to the electrolyte solution. This is important for the construction of a hydrogen-generating photocathode and allows to cover the p-Si surface by high density Pt particles. At the same time, the method allows to reduce the deposited mass of the precious and expensive metal and to optimize the photocathode for light absorption and hydrogen evolution properties. The Pt particle density was increased 18.5 times by addition of an optimized quantity of 81 mM H_2O_2 to the electrolyte solution, while simultaneously decreasing the particle diameter from 302 to 60 nm at a passed charge density of 20 mC/cm^2 . At higher H_2O_2 concentrations it was observed that the deposited mass decreased upon increasing charge density which we attribute to cathodic dissolution caused by formed hydroxyl radicals. In Chapter 5, a photoanode was created with a WO_3 top coating, and its deactivation was studied over time in a phosphate buffer at various pH. WO_3 is a promising, inexpensive, and environmentally benign photoanode material for the oxidation of water but loses its activity after minutes to hours of operation in a photo electrochemical cell. Understanding the deactivation processes is essential in the fabrication of a long-lived device. During device operation, the evolved gases H_2 and O_2 were measured with high time and concentration resolution. It was found that the rate of deactivation was strongest in a solution of pH 1.0, followed by pH 7.4, pH 3.0 and pH 5.0. At pH 7.4 the photocathode was unstable and dissolved into solution whereas at other pH values the deactivation might be caused by peroxo-bound species on the WO_3 surface, although significant amounts of H_2O_2 were not detected in the electrolyte.

In Chapters 4 and 6, microwire-structured silicon substrates were used. These architectures have improved light-trapping properties and provide a high internal surface area, whereby a higher fraction of the incident light is absorbed, current densities at the surface are decreased during photoelectrochemical operation, and a higher loading of semiconductors becomes possible without increasing its thickness. Chapter 4 has shown a novel method to deposit two different materials, *i.e.* silver (Ag) and platinum (Pt), spatioselectively on the microwire top and bottom sections, respectively without any masking steps. This significantly improves the fabrication of devices which require two different deposits, potentially oxidation and reduction catalysts. For this, an

axial p/n junction was created with a top n-Si part and its diode behavior was utilized. The metals were cathodically deposited, and the presence or absence of light steered the deposition. In Chapter 6, p-type silicon microwires with an ITO layer were coated with molybdenum-doped and hydrogen-annealed bismuth vanadate (H-BiVO_{4-x}) to study its effect on photocatalytic performance. The performance was evaluated by studying the oxidation of the hole scavenger sulfite to sulfate. H-BiVO_{4-x} thickness, microwire length (5.3 to 15.9 μm) and spacing (4 to 20 μm) were varied to optimize the device performance and compare it to flat substrates. It was found that microwires of these geometries did not improve photocatalytic performance, which we attribute to diffusion limitation of redox species in the internal volume of the microwires.

In conclusion, the research on flat substrates in Chapters 3 and 5 on control of Pt particle size and density and WO_3 deactivation contributes to the materials development for photocatalytic water splitting. The results from Chapter 3 provide synthetic means for optimizing silicon-based photocathodes for hydrogen evolution. These results may be further extended to other semiconductor types and also for other applications, as Pt is used as a catalyst in many chemical reactions. Moreover, the understanding of Pt corrosion processes in the presence of H_2O_2 may be of use in the development of more stable and long-lived (photo)catalysts. The deactivation of WO_3 during photocatalytic water oxidation is still not fully understood and needs further *in situ* surface studies to make this material viable for practical devices, by for instance tailored surface modification or passivation with protective (mono)layers which do not absorb a significant portion of the incident light.

The research described in Chapters 4 and 6 on spatioselective functionalization and H-BiVO_{4-x} coating contributes to efforts on the utilization and functionalization of microwire-structured silicon. The method presented in Chapter 4 opens up opportunities to create devices that have value also outside of the area of photocatalysis, as micro- to nanowires are used in various applications, such as electronics, sensors, and photonics. The results from Chapter 6 have shown that the microwire dimensions, structure and architecture commonly used in literature may not be suitable for photocatalysis. A very recent study on a similar construction but with the usage of black silicon with

shorter wire length, did show slight photocatalytic improvements in comparison to flat substrates. Here, more research is needed on the optimization of silicon wire length, spacing and diameter.

Considering that Fujishima and Honda described the first photocatalytic water splitting on a semiconductor electrode almost five decades ago, the field is still in an early stage of development and many challenges remain. Besides the materials development which was tackled in this thesis, the engineering of a device design which includes gas collection and component arrangement is under debate. Furthermore, the vast majority of the experiments reported in the literature so far have been performed under controlled lab conditions, and it is not yet clear how temperature changes, physical impact from wind, rain and hail, day/night and summer/winter cycles will impact the performance and durability of the devices. Especially freezing temperatures might be a hurdle and exclude photocatalytic hydrogen production at many areas on the planet. Also, commonly overlooked is the fact that hydrogen would be evolved on a large surface area which makes the sealing of the device difficult as hydrogen is the lightest molecule and diffuses through many materials. All these points raise doubts whether photocatalytic water splitting will ever see the light of the day on a large scale that is relevant for solving the energy problem. Nevertheless, past research was and further research is needed as generation and storage of sustainable energy is one of the key challenges of this century and all viable approaches need to be explored.

Hoofdstuk 7

Samenvatting en perspectief

De overgang van een samenleving die afhankelijk is van fossiele brandstoffen, naar één die gebruik maakt van duurzame energie, is wenselijk om CO₂-emissies, en daarmee de opwarming van het klimaat, tegen te gaan. Tot nu toe heeft de nadruk gelegen op de productie van elektriciteit uit duurzame bronnen, zoals fotonvoltaïsche panelen en windmolens. De energieproductie daarvan schommelt echter en voldoet meestal niet aan de vraag. Onderbrekingen in de productie van elektriciteit op de korte termijn, kunnen mogelijkwerwijs opgevangen worden door waterkrachtaccumulatie of batterijen, maar energieopslag is ook nodig voor de langere termijn om zo seizoensfluctuaties te compenseren. Eén van de voorgestelde oplossingen voor lange-termijnfluctuaties, is om waterstof te maken uit water, met energie uit zonlicht. Deze waterstof kan zelf als brandstof of energiebron gebruikt worden, of omgezet worden naar koolwaterstoffen. Momenteel wordt 96% van alle waterstof vanuit fossiele brandstoffen gemaakt. Daarom zou de CO₂-uitstoot jaarlijks met 2%, of 685 miljoen ton, verminderd kunnen worden indien deze waterstof met behulp van duurzame energie uit water wordt gevormd.

Het onderzoek dat in dit proefschrift is beschreven, is gericht op de ontwikkeling van foto-elektrochemische systemen voor de vorming van waterstof uit water. Als basismateriaal is silicium gebruikt omdat het niet giftig is, maar wel ruimschoots beschikbaar en makkelijk te verkrijgen, en al in grote hoeveelheden en hoge zuiverheid geproduceerd wordt in de halfgeleiderindustrie. Elektrochemie is toegepast om coatings en functionaliteiten toe te voegen. Deze techniek biedt diverse opties, zoals een brede materiaalkeuze, controle over de morfologie van de gedeponeerde materialen, de mogelijkheid om gestructureerde oppervlaktes gelijkmatig te bedekken, een goed elektrisch contact tussen

substraat en het gedeponeerde materiaal, normale procesomstandigheden en opschaalbaarheid.

In de hoofdstukken 3 en 5 zijn een metaal en een halfgeleider, te weten platina (Pt) en wolframoxide (WO_3), door middel van elektrodepositie aangebracht op p-gedoteerd silicium, dat voorzien was van een laag ITO (indium-gedoteerd tin-oxide). Hoofdstuk 3 beschrijft hoe de grootte en dichtheid van Pt-deeltjes kan worden gecontroleerd en dat de grootte een functie is van de hoeveelheid H_2O_2 die wordt toegevoegd aan het elektrolyt. Dit is belangrijk voor de constructie van een fotokathode die waterstof genereert en maakt het mogelijk het silicium met een hoge dichtheid aan Pt-deeltjes te bedekken. Tegelijkertijd staat deze methode ook toe om de totale gedeponeerde massa van dit dure en kostbare metaal te verminderen, en de lichtabsorptie en waterstofgeneratie van de kathode te optimaliseren. De dichtheid van de Pt-deeltjes werd 18.5-voud verhoogd door de optimale hoeveelheid H_2O_2 toe te voegen aan het elektrolyt, en daarmee werd ook de diameter van de deeltjes teruggebracht van 302 naar 60 nm bij een ladingsdichtheid van 20 mC/cm^2 . Bij hogere concentraties H_2O_2 werd geconstateerd dat de gedeponeerde massa verminderde bij toenemende ladingsdichtheid; dit werd toegeschreven aan de vorming van hydroxylradicalen.

In hoofdstuk 5 werd een fotoanode gemaakt met een WO_3 -coating, en de deactivering van de elektrode werd bestudeerd in een fosfaatbuffer bij verschillende pH. WO_3 is een veelbelovend, goedkoop, en milieuvriendelijk fotoanodemateriaal voor wateroxidatie, maar verliest haar activiteit na verloop van tijd in een fotoelektrochemische cel. Begrip van het deactiveringsproces is essentieel om een systeem met een lange levensduur te kunnen maken. De gevormde gassen, H_2 en O_2 , werden in bedrijf gemeten met goede tijds- en concentratieresolutie. Het bleek dat de deactivering het snelst plaatsvond in een oplossing van pH 10, gevolgd door pH 7.4, dan pH 3.0 en het langzaamst bij pH 5.0. Bij pH 7.4 was de fotoanode niet stabiel, en loste op; bij de ander pH-waardes zou de deactivering veroorzaakt kunnen worden door peroxo-gebonden moleculen op het WO_3 -oppervlak, hoewel geen significante hoeveelheden H_2O_2 in het elektrolyt werden gevonden.

In hoofdstukken 4 en 6 werden siliciumsubstraten met micropilaren gebruikt. De architectuur hiervan zorgt voor een verbeterde lichtinvang en een groot intern oppervlak, waardoor een grotere fractie van het invallende licht geabsorbeerd kan worden, en efficiënter gebruik van halfgeleiders mogelijk is zonder de dikte ervan te vergroten. Hoofdstuk 4 laat een nieuwe methode zien om twee verschillende materialen te deponeren, te weten zilver (Ag) en platina (Pt), respectievelijk op de onder- en bovenkant van de pilaren, zonder gebruik van enig masker. Dit is een significante verbetering van het productieproces van elektroden die twee verschillende functies nodig hebben, zoals bv. katalysatoren die oxidatie en reductie kunnen bewerkstelligen. Hiertoe werd een axiale pn-overgang gemaakt, waarvan de bovenkant n-gedoteerd silicium is. De metalen werden kathodisch gedeponerd, en de aan- of afwezigheid van licht bepaalde de plaats van depositie.

In hoofdstuk 6 werden p-gedoteerde, silicium-micropilaren bedekt met ITO, en vervolgens met bismutvanadaat (H-BiVO_{4-x}). Bismutvanadaat werd vervolgens gedoteerd met molybdeen en behandeld in waterstofatmosfeer, om het effect hiervan op de fotokatalytische prestatie te bestuderen. Evaluatie van de fotokatalytische activiteit werd uitgevoerd met de oxidatie van sulfiet naar sulfaat en de reductie van protonen naar waterstof. De dikte, lengte (5.3 tot 15.9 μm) en tussenruimte (4 tot 20 μm) van de micropilaren voorzien van H-BiVO_{4-x} werden gevarieerd, om de prestatie van de elektrode te optimaliseren en te vergelijken met één met een vlakke geometrie. De micropilaarstructuur bleek de fotokatalytische prestatie niet te verbeteren, hetgeen toegeschreven kan worden aan de beperkte diffusie van redoxmoleculen in de ruimte tussen de micropilaren.

Concluderend heeft het onderzoek op vlakke substraten beschreven in hoofdstukken 3 en 5 bijgedragen aan de ontwikkeling van materialen voor het fotokatalytisch splitsen van water. De resultaten van hoofdstuk 3 bieden een synthesesmethode om fotokathodes, gebaseerd op silicium, te optimaliseren voor waterstofproductie. Deze resultaten kunnen nog verder uitgebreid worden naar andere soorten halfgeleiders alsook andere toepassingen, aangezien Pt wordt gebruikt in vele chemische reacties. Bovendien is het begrip met betrekking tot de corrosie van Pt in de aanwezigheid van H_2O_2 cruciaal voor de ontwikkeling

van stabiele (foto)katalysatoren met een lange levensduur. De deactivering van WO_3 wordt nog altijd niet volledig begrepen en behoeft verder *in-situ* onderzoek om praktisch gebruik van dit materiaal rendabel te maken, bijvoorbeeld door specifieke structuren op het oppervlak aan te brengen, of door het te beschermen met (mono)lagen van een ander materiaal, zonder daarbij een significante hoeveelheid licht te absorberen.

Het onderzoek beschreven in hoofdstukken 4 en 6, over plaatsgebonden depositie en de H-BiVO_{4-x} -film, draagt bij aan beter begrip van de functionalisatie en de toepassing van silicium met micro-pilaren. De methode uit hoofdstuk 4 is ook toepasbaar voor de fabricage van systemen buiten de fotokatalyse, aangezien micropilaren gebruikt worden in vele toepassingen, zoals elektronica, sensoren, en fotonische systemen. De resultaten van hoofdstuk 6 tonen aan dat de dimensies, structuur en architectuur van veelgebruikte micropilaren misschien niet geschikt is voor fotokatalyse. Een recente studie, die een vergelijkbare constructie beschrijft die gemaakt is van zwart silicium met korte micropilaren, laat echter wel een bescheiden verbetering van de fotokatalyse zien in vergelijking met een vlakke geometrie. Meer onderzoek is nodig om de lengte, tussenruimte en diameter van de micropilaren te optimaliseren.

Aangezien Fujishima en Honda pas 50 jaar geleden voor het eerst fotokatalytisch water wisten te splitsen op een halfgeleidende electrode, is het veld momenteel nog in een pril stadium van ontwikkeling en er zijn dan ook nog veel aspecten die moeten worden onderzocht. Naast het ontwikkelen van materialen, zoals in dit proefschrift is beschreven, is het ontwikkelen van een apparaat, compleet met gasopvang en de organisatie van de verschillende onderdelen, noodzakelijk. Bovendien zijn verreweg de meeste experimenten in gecontroleerde laboratoriumomstandigheden gedaan, en het is nog niet duidelijk hoe variaties in temperatuur, de fysieke invloed van wind, regen en hagel, en dag/nacht- en seizoens-cycli de prestatie en levensduur van dit soort apparaten zullen beïnvloeden. Met name temperaturen onder het vriespunt kunnen een struikelblok vormen en de toepassing van deze apparaten verhinderen. Een ander onderbelicht feit is dat waterstof op een groot oppervlak gegenereerd zal worden, waardoor het afsluiten van het apparaat een uitdaging zal worden: waterstof is het lichtste molecuul en diffundeert door vele materialen heen. Al deze punten leiden tot

twijfel over de haalbaarheid van het fotokatalytisch splitsen van water, ook omdat een benadering van het rendement op een grote schaal nodig is om een relevante bijdrage te leveren aan het oplossen van het energieprobleem. Desalniettemin was, is en blijft onderzoek noodzakelijk, aangezien de productie en opslag van energie één van de grootste vraagstukken van deze eeuw is, en alle mogelijke benaderingen uitgeprobeerd moeten worden.

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Alexander, April 2018

About the author

Alexander Milbrat studied Bachelor and Master Chemical Engineering at Münster University of Applied Sciences (Germany) with the specialization in Applied Chemistry. He received his Bachelor of Science in October 2010 after a 6-month exchange at Juniata College (USA) where he did an internship and performed the research for his Bachelor thesis. During this time, he worked on the preparation and characterization of bis-diazomethylketones as chelate ligands under the supervision of Prof. Richard R. Hark (Juniata College) and Prof. Hermann Büttner (Münster University of Applied Sciences).

Alexander received his Master of Science in December 2012. He focused in his Master assignment on the preparation of silicon nanowires for photocatalytic applications. The project was carried out at the University of Twente (The Netherlands) in the Photocatalytic Synthesis (PCS) and Molecular Nanofabrication (MnF) groups under the supervision of Prof. Guido Mul, Prof. Jurriaan Huskens (both University of Twente) and Prof. Thomas Jüstel (Münster University of Applied Sciences).

Apart from his study, Alexander also worked as a Research Assistant in the Tailored Optical Materials (TOM) group at Münster University of Applied

Sciences between November 2009 and February 2012 where he researched novel afterglow phosphors.

Between April 2011 and April 2012, Alexander was an elected member of the faculty council Chemical Engineering at Münster University of Applied Sciences. During this time, he represented over 500 Chemical Engineering students together with three other students in the council.

Since January 2013, Alexander has been working as a Ph.D. candidate under the supervision of Prof. Guido Mul (PCS) and Prof. Jurriaan Huskens (MnF) at the University of Twente. The results of this research are described in this thesis.