

ENABLING SOLAR ENERGY TO FUEL CONVERSION ON SILICON-BASED NANOMATERIAL CATALYSTS

AHMED FARID HALIMA

أحمد فرید حلیمة



School of Chemistry
Faculty of Science
Monash University
Clayton, Victoria, Australia

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Ahmed Farid Halima, *MSc, BSc.Ed.*

Enabling Solar Energy to Fuel Conversion on Silicon-based Nanomaterial Catalysts

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Research Supervisors:

Prof. Douglas R MacFarlane

Dr. Xinyi Zhang

Green Chemical Futures

13 Rainforest Walk,

Monash University

Clayton, Melbourne

VIC 3800 Australia



O MY LORD!
INCREASE ME IN
KNOWLEDGE.

[20:114]

THE QURAN

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The inclusion of co-authors reflects the fact that the work came from active collaboration between researchers and acknowledges input into team-based research. In the case of Chapter 2 and Chapter 4 of this thesis, my contribution to the work involved the following:

Thesis Chapter	Publication Title	Status	Candidate contribution	Co-author contribution
Chapter 2	Boron-Doped Diamond (BDD) Coatings Protect Underlying Silicon in Aqueous Acidic Media—Application to the Hydrogen Evolution Reaction	Published	Concept, Experimental Design, Data collection and analyses Manuscript preparation Primary author 85%	Prof. Douglas R MacFarlane Concept, Manuscript preparation 10% Dr. Usman A Rana Concept 5%
Chapter 4	Metal-Free Black Silicon for Solar-powered Hydrogen Generation	Published	Concept, Experimental Design, Data collection and analyses Manuscript preparation Primary author 85%	Prof. Douglas R MacFarlane Concept, Manuscript preparation 10% Dr. Xinyi Zhang Concept 5%

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In regards to experimental work presented in this dissertation, I solely conducted all experiments unless otherwise stated. Appropriate assistance was offered due to restrictions/training on using these facilities, mainly from the following experts:

- Massimo Raveggi for assistance with inductively coupled plasma mass spectroscopy (ICP-MS) experiments at the school of Earth, Atmosphere and Environment, Monash University.
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VII

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This thesis received language editing by Katherine Nairn. Scientific editing and opinion has not been provided.

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ABSTRACT

Silicon plays an important role in the electronics industry, solar cells, and a wide-range of other applications, due to its abundance and excellent semiconducting attributes. In recent decades, the functionality of silicon, as the photovoltaic component in solar energy to chemical-fuel conversion, has been investigated meticulously; its use has been inhibited in prototype photoelectrochemical devices by its severe deterioration, with spontaneous oxide formation taking place in aqueous electrolytes. In some cases, the corrosion is worsened upon stimulation by light. These limitations in silicon are a significant drawback, and to enable silicon-based materials in solar to fuel applications the interface of silicon requires considerable development to include nanostructuring and inclusion of co-catalysts/ The physical and chemical attributes of a range of developed silicon-based interfaces are described herein, especially in regards to their performance and stability in the hydrogen evolution reaction of solar water splitting.

For the first time, monolithic protective coatings designed from inert and robust diamond interfaces and incorporated on silicon electrode ensembles are developed to improve the stability and improve kinetics of redox reactions on silicon. The thin-layer diamond interfaces having high-conductivity from boron doping, optical transparency as well as uniform topology on super-flat silicon are used in this work and functionalised with platinum nanoparticles, which are regarded as excellent proton-reduction catalysts. These cathodes are subjected to a series of electrochemical tests during proton reduction under relatively harsh conditions, to assess the performance of the developed cathodes. The results show remarkable performance for proton reduction, with onset at -0.26 V vs. RHE for the silicon/diamond interfaces, and identical to bulk platinum electrodes when functionalised with nanoparticulate platinum. In addition, this performance is improved for the silicon/diamond interface even after exposure to such harsh conditions for up to 280 hours.

To develop silicon exhibiting improved redox kinetics in solar-to-fuel conversion, the morphology of the underlying Si is further developed to incorporate nanostructures producing a material known as black-Si. The objective is to investigate the capabilities of nanostructured black silicon interfaces for the hydrogen evolution reaction, through photoelectrochemical characterisation. For this purpose, silicon surface modification is achieved via metal-assisted chemical etching, based on a mechanistic study established to understand the influences of metals and oxidant compositions of the fluoride-based etchants. The metals involved in assisting the etching process include gold, silver, palladium or copper salts which undergo nucleation and growth, before the silicon interface is subjected to a chemical etchant. The remnant metal-dendrites are removed via metal recycling chemical techniques to obtain pristine, and completely metal-free silicon nanostructures. A range of nanostructured silicon materials are investigated as metal-free photocathodes for the HER, or functionalised with catalysts such as platinum, palladium or copper. This investigation involved materials characterisation of the interface morphology,

photovoltaic attributes, as well as light-absorption and luminescence of a variety of silicon nanostructures.

For the metal-free ensembles, the catalytic activity and solar-to-hydrogen conversion efficiencies are analysed; they are explained in relation to the different influences on the nanostructuring process. In regards to durability tests, the pristine black silicon sustains long-term operation for several hundred hours of continuous hydrogen evolution (> 250 hours) as well as tolerating the harsh electrochemical conditions for more than a hundred days of exposure. It is shown that this high performance is primarily due to advantageous physico-chemical properties and the vast geometry of these interfaces, in that they offer significant photoelectrochemical area, which contribute to the overall performance. The generation of catalytically-active sites formed by the surface modifications, produces enhanced current-voltage features, as compared to planar counterparts of the same electrode size. It is demonstrated that these excellent attributes of nanostructured silicon interfaces can also be used as supports for catalysts to facilitate other solar-to-fuel conversion reactions, such as in carbon dioxide reduction.

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This work is dedicated to you.

Ahmed Farid Halima

THESIS NAVIGATOR

Chapter 1

This introductory chapter lays out the background and fundamental physico-chemical attributes of silicon materials, and their role in the development of sustainable energy devices, based on solar energy to chemical fuel conversion. Motivated by the global drive to clean up our act with the environment, this literature synopsis outlines the different challenges facing energy materials, and presents an overview of the desirable properties required for developing devices based on earth-abundant catalysts, that could play a significant role in the hydrogen economy.

In this context, the fundamental concepts and importance of using silicon materials as promising photoelectrode platforms are assessed, based on their suitability for solar energy conversion. The literature review will be brief, considering that each of the subsequent chapters is composed of a peer-reviewed publication, and hence contains a relevant literature review. This chapter concludes with the main research objectives that motivate this research investigation.

Chapter 2

The status of planar silicon materials and their role in solar energy conversion, has been severely influenced by their susceptibility to spontaneous interfacial corrosion, rendering them unstable in typical electrochemical environments. This chapter investigates the mechanisms involved in silicon corrosion, and sheds the light on the literature efforts involved in resolving the stability problem, which involve the implementation of protective coatings. Most of the literature reports were only partially successful in achieving this, due to the inevitable compromise of the electrode efficiency, associated with utilising a range of multi-layered coating materials, which also exhibited electrical insulating properties.

For this purpose, robust diamond coatings were obtained on silicon electrodes and tested for their performance and electrochemical activity under relatively harsh experimental conditions. The pin-free, micrometre-thin, and highly conductive diamond coatings demonstrate significantly enhanced performance and inherent stability over the course of experimental durations of up to 280 hours, under constant exposure to acidic electrolytes, which are considered rapidly corrosive to pristine silicon.

In addition to these enhancements, the devised silicon/diamond electrode assembly shows improved hydrogen catalysis after long-term operation. It also provides an excellent platform for functionalising noble-metal platinum nanoparticles which further enhance hydrogen evolution, all whilst preserving the underlying bulk silicon materials. The paper “*Boron-doped diamond (BDD) coatings protect underlying silicon in aqueous acidic media-application to the hydrogen evolution reaction*” was published in *Electrochimica Acta*. in 2014.

Chapter 3

In this era of nanomaterials, a new approach is under the spotlight towards enhancing silicon materials for energy applications. Intricate nanostructures manifest a range of superior physico-chemical nanoscopic properties, allowing nanomaterials to interact with photoelectrochemical phenomena in novel interfacing paradigms, as compared with their conventional bulk counterparts. These properties extend beyond the light enhancement in highly photo-absorbing black silicon nanostructures, to include a higher electrochemically active surface area, and introduce a contribution from quantum effects, such as luminescence from crystallographic defect features.

These attributes significantly impact the performance of Si nanomaterials at the interface between light and redox chemistry on a device scale. Especially beneficial for scalability, a simple, cost-effective and efficient method in achieving silicon nanomaterials, is highly sought-after. The mechanism of metal-assisted electroless chemical etching, is investigated for developing a variety of silicon nanowires with tuneable morphologies, all regulated by the composition of a chemical etching solution. In this context, the chapter presents experimental methods related to the advanced nanofabrication, and materials characterisation methods for the purpose of understanding the physico-chemical properties of black silicon nanostructures.

Chapter 4

Driving solar hydrogen evolution using pristine black silicon photocathodes, and without the use of any co-catalysts, for up to 250 hours of continuous operation involving the charge transfer of $1.61 \times 10^4 \text{ C.cm}^{-2}$, and under overpotentials as low as -0.2 V vs. RHE , has not been demonstrated before, especially without the aid of stabilising materials and electrolytes. The results of photoelectrochemical performance and stability testing of metal-free black silicon photoelectrodes demonstrated this successfully, for pristine silicon nanowires. For this purpose, the complete recycling of metal residues from metal-assisted etching, is also achieved, as evident from spectroscopic characterisation of the processed substrates.

My paper "*Metal-Free Black Silicon for Solar-powered Hydrogen Generation*" was published in *Electrochimica Acta*. in 2017. The published electronic supplementary information is also attached. Additional characterisation for the bSi photocathodes was further conducted after the results were published, and includes: the influence of the geometric surface area of black silicon nanostructures on their photoelectrochemical performance, solar-to-hydrogen efficiency, as well as analysis of their electrocatalytic activity using Tafel-like analysis, towards solar water splitting.

Chapter 5

The nanostructured photocathodes investigated in Chapter 4, are further studied here for hydrogen photogeneration, assisted with co-catalyst metal nanoparticles. Several metal deposition techniques are considered to generate platinum, palladium and copper catalyst nanostructures, to establish a mechanistic morphological and photoelectrochemical study. Especially for copper, the

electrochemical redox potential does not match silicon energetics, making it difficult to nucleate copper structures on black silicon.

The work in this chapter encompasses: exploring the routes of metal deposition via electroless, electrochemical, and photoelectrochemical methods, understanding the mechanisms for copper nucleation from buffered salts and fluoride containing chemical solutions, as well as comparing their morphology and composition.

Chapter 6

This chapter outlines the conclusions drawn from this research investigation, and the proposed future work, based on the experimental findings.

All indexes including list of figures, tables, equations and all substrates used in this study are collated together in the end of the thesis.

PUBLICATIONS

“Metal-free black Silicon for solar-powered hydrogen generation”

A. F. Halima, X. Zhang and D. R. MacFarlane,

Electrochimica Acta, 2017, 235, 453-462.

doi: 10.1016/j.electacta.2017.03.086.

**“Boron-doped diamond (BDD) coatings protect underlying Silicon in aqueous acidic media
- Application to the hydrogen evolution reaction”**

A. F. Halima, U. A. Rana and D. R. MacFarlane,

Electrochimica Acta, 2014, 115, 639-643.

doi:10.1016/j.electacta.2013.10.185.

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LIST OF ABBREVIATIONS

bSi	Black silicon
BDD	Boron doped diamond
CL	Cathodoluminescence
CVD	Chemical vapour deposition
CA	Chronoamperometry
E_{CB}	Conduction band energy level
J	Current density
CV	Cyclic voltammogram/voltammetry
DRIE	Dry reactive ion etching
A_{eff}	Effective electrochemical interface surface area
ECD	Electrochemical deposition
E_g	Band gap energy
$E_{Ag/AgCl}$	Electrochemical potential <i>vs.</i> Ag/AgCl
E_{RHE}	Electrochemical potential <i>vs.</i> RHE
ED	Electroless deposition
e^-	Electron
GSA/A_{geom}	Geometrical electrochemical interface surface area
h^+	Hole
$E(H^+/H_2)$	Hydrogen evolution potential
HER	Hydrogen evolution reaction
J_{Lim}	Limiting current density
LSV	Linear sweep voltammogram/voltammetry
M	Metal
MaCE	Metal-assisted chemical etching
OCP	Open circuit potential
OHR	Oxidation half-reaction
φ^{ox}	Oxidation potential
$E(H_2O/O_2)$	Oxygen evolution potential
OER	Oxygen evolution reaction
p -Si	p -type Silicon
PEC	Photoelectrochemical
PED	Photoelectrodeposition
V_{Lim}	Potential at limiting current density, also saturation potential
A^+/A	Redox couple
RHR	Reduction half-reaction
φ^{red}	Reduction potential
RHE	Reversible hydrogen electrode
SC	Semiconductor

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SiNW	Silicon nanowire
STH	Solar-to-hydrogen
SHE	Standard hydrogen electrode
E°	Standard potential
SA	Surface area
A_{2D}	Two-dimensional planar surface area
E_{VB}	Valence band energy level

1.1 Introduction

Sustainable energy pathways are needed to reduce our carbon foot-print and environmental impact.^[1] The constant rise of greenhouse gas emissions is leading to detrimental phenomena such as ongoing global warming and increasing severity of natural disasters. It is well established that the rising global CO₂ concentration in the atmosphere (*cf.* Figure 1) is the primary driving cause of global warming.^[2] An urgent need to locate alternative benign energy resources is now evident.^[3]

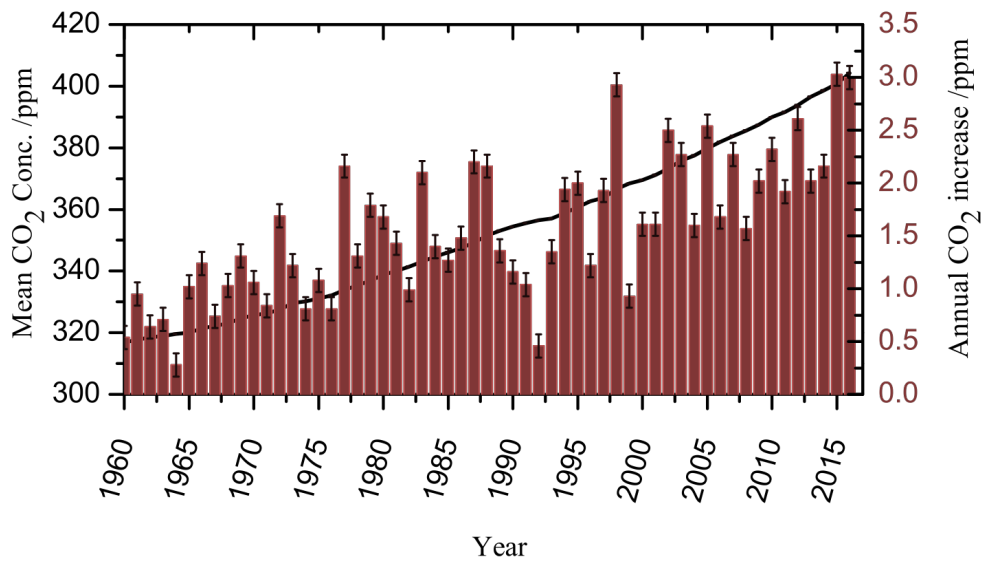


Figure 1 Demonstrates the alarming increasing trends of CO₂ concentrations in the atmosphere during the past 50 years (left axis) and the corresponding annual increase in ppm per annum. Data collected by The Global Monitoring Division of NOAA, Mauna Loa, Hawaii.^[4]

Hydrogen as fuel provides a high energy-density of 33.3 kWh.kg⁻¹ from combustion (*cf.* Equation 1), as compared with fossil fuel combustion. Besides, hydrogen burns more efficiently, due to its excellent physico-chemical properties.^[5] In addition to its thermal energy, hydrogen can also be used to produce electrical energy, through reaction with oxygen in a fuel cell.^[6] In both cases, water is the only byproduct of the process. In a hydrogen-based economy, hydrogen makes up the carrier medium to store and deliver energy to meet global requirements. This end-to-end process comprises three major components,^[2] *viz.* fuel generation, storage, and electricity

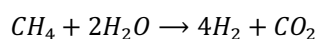
generation from a hydrogen fuel cell, as illustrated in Figure 2. While all three components of this process are needed for a fully implemented hydrogen economy, achieving sustainable production is the main obstacle to a reliable hydrogen economy.^[7]

Equation 1: Hydrogen combustion to produce water, an exothermic reaction with a very large enthalpy, is important for energy provision in a green hydrogen economy.



A major proportion of the hydrogen currently used in these technologies originates from steam reformation, by using natural gas as the feed-stock (*cf.* Equation 2 below).^[8,9] However, the trends to greener approaches are better served by using abundant solar energy and water to drive the generation of hydrogen by water electrolysis, to achieve a sustainable approach without detrimental environmental impact.^[6]

Equation 2: Industrial hydrogen production relies on methane reformation using natural gas as feed-stock. This process produces CO₂ as a byproduct, making it an unsustainable of a hydrogen-based economy.



Hydrogen generation via water electrolysis is typically performed in an electrolyser device containing electrodes that catalyse then water splitting reaction. Hence, they are already used in the industry, powered directly from the energy grid; however, this is an unsustainable approach considering the continual burning of fossil fuels to supply the energy grid. Instead of supplying electrical energy to split water in an electrolyser, and for a greener approach, renewable sunlight can be harvested and converted directly into chemical energy in PEC solar water splitting cells.

Hydrogen-powered technologies are indeed becoming reality. For instance, the famous train company ALSTOM released the world's first hydrogen-powered train "Coradia iLint", and this is scheduled to run in 2018.^[10] The vehicles were tested at speeds exceeding 140 km.h⁻¹. The trains are run by hydrogen which is produced entirely as a byproduct of industrial processes, however the company intends to develop a more sustainable approach in the future. Many other examples where hydrogen energy utilization has been implemented industrially are well-discussed in the literature.^[5]

The state-of-the-art in renewable energy production encompasses solar energy to chemical energy conversion in photoelectrochemical (PEC) cells to generate important fuels *viz*; water splitting to hydrogen,^[6,9,11–14] CO₂ reduction to hydrocarbons,^[15–18] or N₂ reduction to ammonia.^[19,20] Solar-to-fuel conversion is in fact now a reality, as the hydrogen economy continues

to roll out in society.^[9,21] In world news today, green energy is frequently emerging for industrial, transport, residential and personal technologies.^[5]

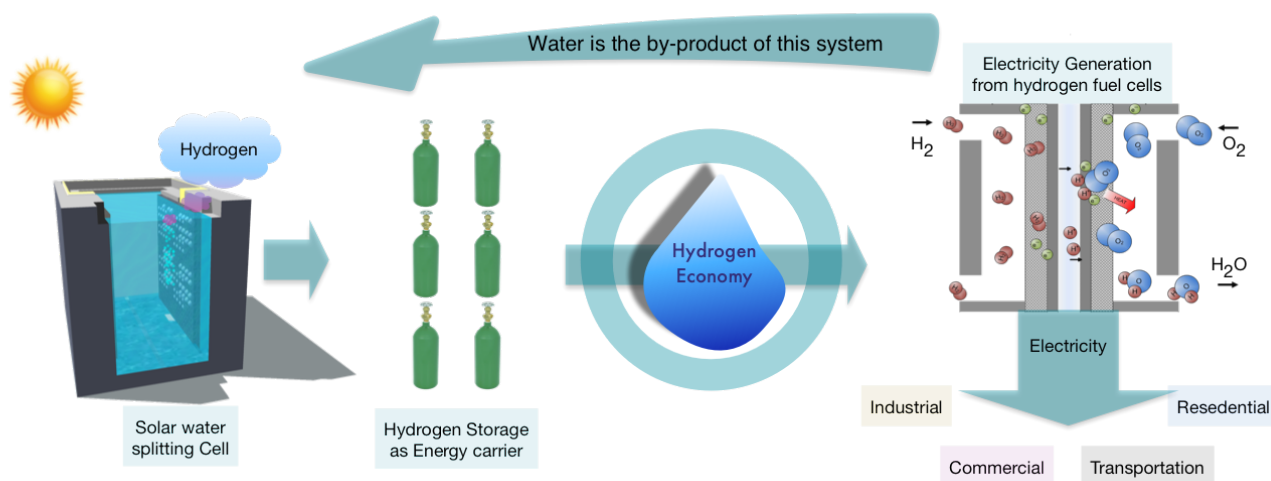


Figure 2 Illustration of the end-to-end processes that makes up a fully implemented hydrogen economy. Hydrogen produced in solar water splitting cells, can be regarded as an energy carrier. When combined with oxygen in a hydrogen fuel cell, electricity can be produced. The hydrogen economy aims to supply industrial, residential and transport units with their local fuel stations to facilitate energy where needed, cutting costs of distribution.

This approach to greener energy pathways mimics natural energy systems in plants which are based on carbohydrates. Photosynthesis is nature's own way of producing fuel in an efficient manner in plants, using solar energy. In this process, the Chlorophyll pigment utilises photons to convert CO_2 and water into carbohydrates and oxygen.^[22] In this manner, artificial photosynthesis attempts to mimic this natural process to achieve solar-to-fuel conversion. Conversion of solar energy is attractive, given the immense amounts of solar radiation incident on the earth's surface. In fact, accessing a portion of the 10^4 TW of renewable solar radiation that is readily available onto earth's surface in an hour, is sufficient to supply humanity's needs with "free" energy for an entire year.^[3] Hence, hydrogen generated from solar-assisted electrolysis of water has great potential as a sustainable fuel, produced from a renewable resource.

1.2 Photoelectrochemical Processes, Materials and the Energy Challenge

It has been four decades since Fujishima and Honda^[23] first demonstrated solar-assisted water splitting at semiconductor electrodes. Since then, scientists have focused on evaluating new photoelectrode assemblies that are suitable for the anodic/cathodic processes involved in solar water splitting. A wide-range of materials have been studied and reported for their performance and stability in solar-to-hydrogen (STH) conversion in PEC cells. These materials have been categorised, based on their cell configurations, into monolithic and multicomponent assemblies, which are capable of either solely or collectively performing the function of a PEC cell.^[6]

Semiconductor materials are capable of harvesting light energy in the form of photogenerated charge carriers, electron-hole pairs, hence they can be used as the functional component of a solar water splitting cell. The overall process of H_2 generation in a PEC cell involves three key steps: photoexcitation of semiconductor to populate the conductance band with electrons, charge separation and migration to respective electrode/electrolyte interface, and utilising these charges for catalysis of redox reactions at the interface to form the necessary chemical fuel products that store energy within their bonds. Therefore, components that exhibit excellent photovoltaic and catalytic properties are required in order to drive this process in a holistic manner.

There are many factors which inevitably reduce the efficiency of a PEC cell.^[11,22,24] The requirements and limiting efficiencies for any solar conversion system have been reviewed previously by Archer and Bolton.^[24] In theory, efficiency limitations are imposed by the nature of semiconductor materials, concerning their band gaps and charge excitation processes. The bandgap energy (E_g) is calculated from the wavelength λ_g of the red absorption edge, according to $E_g = hc/\lambda_g$. The ratio of successful charge supply to the electrode interface to the incident illumination intensity, is taken into consideration when calculating the solar conversion efficiency for a particular semiconductor. Consequently, the following factors comprise the primary contributing causes to efficiency losses:

- All incident photons whose wavelength is higher than that of the bandgap wavelength $\lambda > \lambda_g$ corresponding to $E < E_g$, cannot be absorbed by the semiconductor, and hence are considered an energy loss in this process.
- Photons incident with a narrower wavelength, $\lambda < \lambda_g$ (ie., energy $E > E_g$) are absorbed by the semiconductor. However, a proportion energy in excess of E_g is eventually lost by the system in the form of heat. Despite the capability of mitigating these losses by devising cell componentry that can capture heat energy such as in thermocells, alas, these losses are not utilised in charge conversion, hence reduce the overall efficiency of the material.
- An illuminated semiconductor exhibits an interfacial chemical potential as a result of the photogenerated charges, which is dependent on their steady-state concentrations. This chemical potential assists in driving redox conversion at the electrolyte interface. In order for optimum power output, there needs to exist a significant concentration of these charges partaking in the conversion process. However, a small amount of photoexcited charges undergo radiative processes leading to spontaneous emissions, which contribute a small loss to the overall efficiency.
- After the charge pairs are separated, they may recombine due to electron-hole interaction, before migrating to the interface. For semiconductors, this is the majority of the losses in solar-to-chemical conversion.

The band gap data of several common semiconductors used for water splitting are presented in Figure 3, with reference to the standard potentials associated with the water splitting reactions (*cf.* Equation 5 for the half-reactions) and redox potentials (ϕ^{red}/ϕ^{ox}) of the semiconductor interface. The most prominent semiconductor for use in the hydrogen evolution reaction (HER), in terms of the energy band width and positioning around the redox reaction, is Silicon (Si), whose

$E_g = 1.1$ eV. At this low energy gap, a significant proportion of the solar spectrum can be absorbed and converted into the necessary charges required for solar water splitting, hence making Si desirable for hydrogen production.

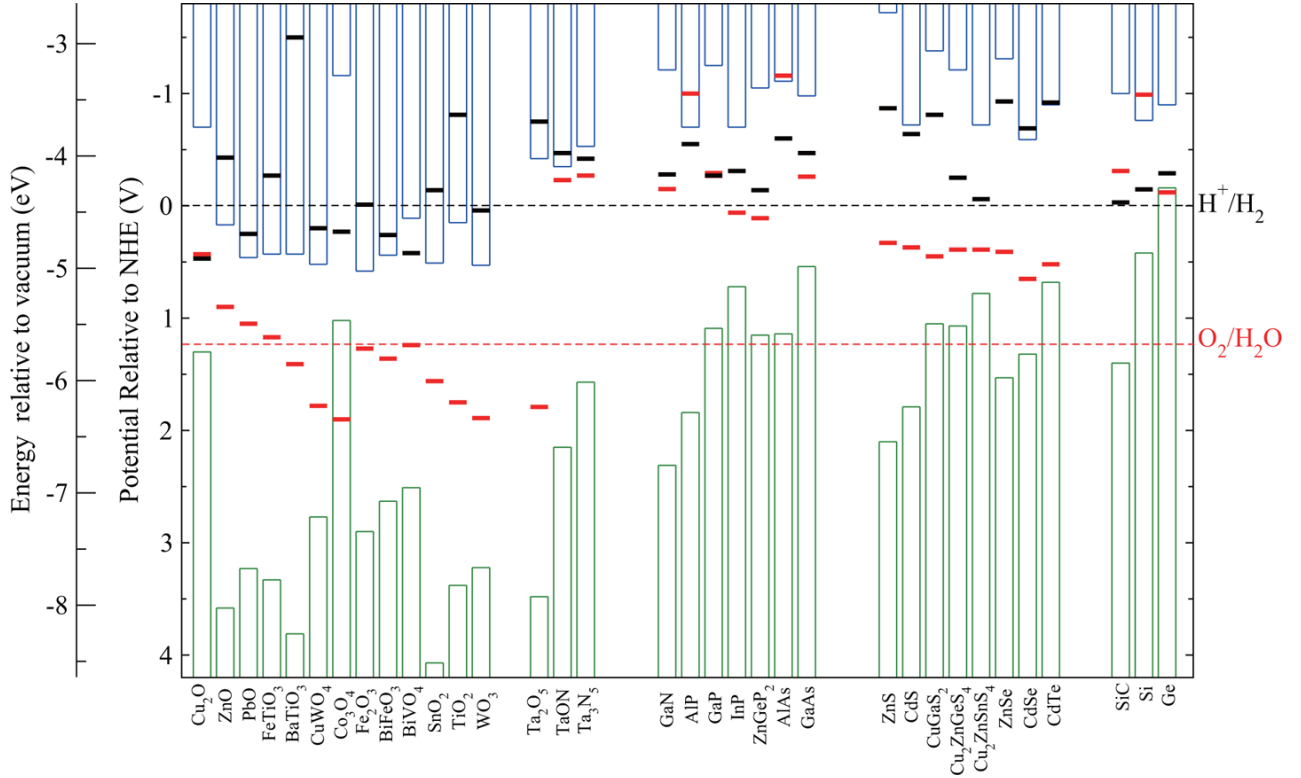


Figure 3 Comparison of a variety of semiconductor band gaps with respect to the standard potentials of water splitting reactions; HER: $E(\text{H}^+/\text{H}_2)$, OER: $E(\text{O}_2/\text{H}_2\text{O})$, relative to the normal hydrogen electrode (NHE). The material's oxidation potential, Φ^{ox} (red bars) and reduction potential, Φ^{red} (black bars) for each of the semiconductors are also displayed. Reprinted with permission from Chen et al.^[25] Copyright ©2012 American Chemical Society.

For Si, the band gap value corresponds to a threshold wavelength of $\lambda_g = 1127$ nm. According to mathematical integration of the global power density of the solar irradiance of AM 1.5G (*cf.* Figure 4) short of 1127 nm; the photovoltaic interface of Si allows for absorption of approximately 81% of the solar spectrum. The inevitable energy losses because of the band gap photon absorption of Si, without taking into consideration any other losses, contributes at least 18% of the solar spectrum because these photons cannot be absorbed and hence will not result in photogenerated charge carriers.

Additionally, there are thermodynamic losses that are brought about because of the significant proportion of ground states present in the system, even during excitation.^[11] For this reason, the open-circuit potential V_{OCP} of Si is always short of 1.1 eV (experimental $V_{\text{OCP}} \leq 0.8$ V) due to these losses. Under operating experimental conditions, an ideal maximum solar energy to chemical energy conversion efficiency of $\sim 30\%$ is achievable under 1 Sun irradiation (equivalent to a power of $100 \text{ mW}\cdot\text{cm}^{-2}$), according to the Landsberg thermodynamic calculations.^[26,27]

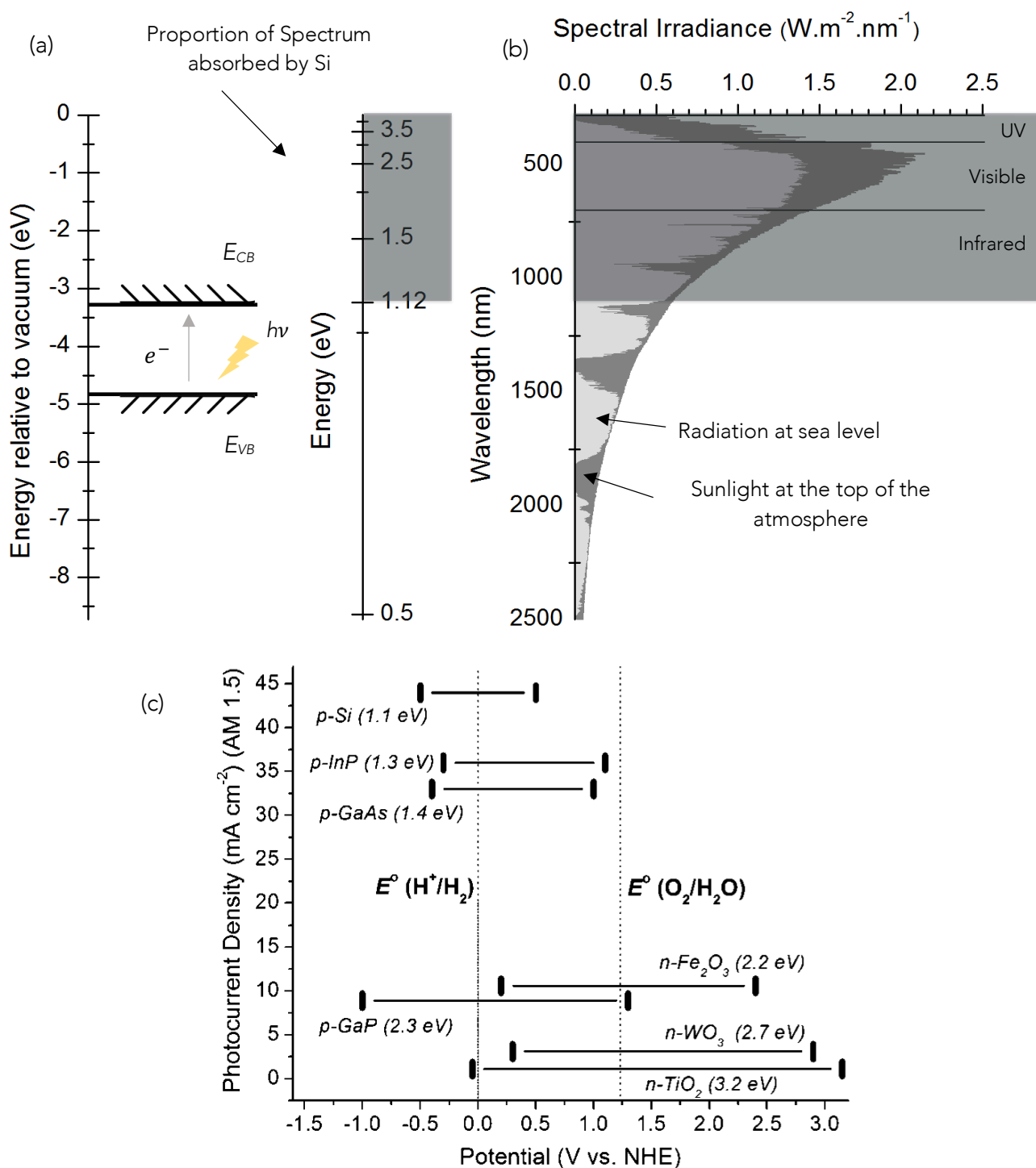


Figure 4

(a) E_g of Si.^[25] (b) The solar irradiance at the top of the atmosphere and at sea level, specific for Air Mass (AM) 1.5 standard. The shaded regions indicate the proportion of energies that can be absorbed by Si due to E_g . Data obtained from U.S. Department of Energy (DOE). (c) The potential *vs.* NHE and the maximum theoretical photocurrent density achievable for a range of semiconductors, with respect to the HER and OER. The band gap energies are denoted in parentheses. Figure adapted with permission from Walter et al.^[6] © 2010 American Chemical Society.

Despite the limited maximum efficiency due to energy losses, Si provides a large photocurrent density in chemical conversion, when compared with other common semiconductor

materials (*cf.* Figure 4(c)) This high performance from Si is advantageous to the wide application of Si in photovoltaic devices, and therefore, make it attractive for use as an HER photocathode.

Despite the limited maximum efficiency due to energy losses, Si provides a large photocurrent density in chemical conversion, when compared with other common semiconductor materials (*cf.* Figure 4(c)) This high performance from Si is advantageous to the wide application of Si in photovoltaic devices, and therefore, make it attractive for use as an HER photocathode.

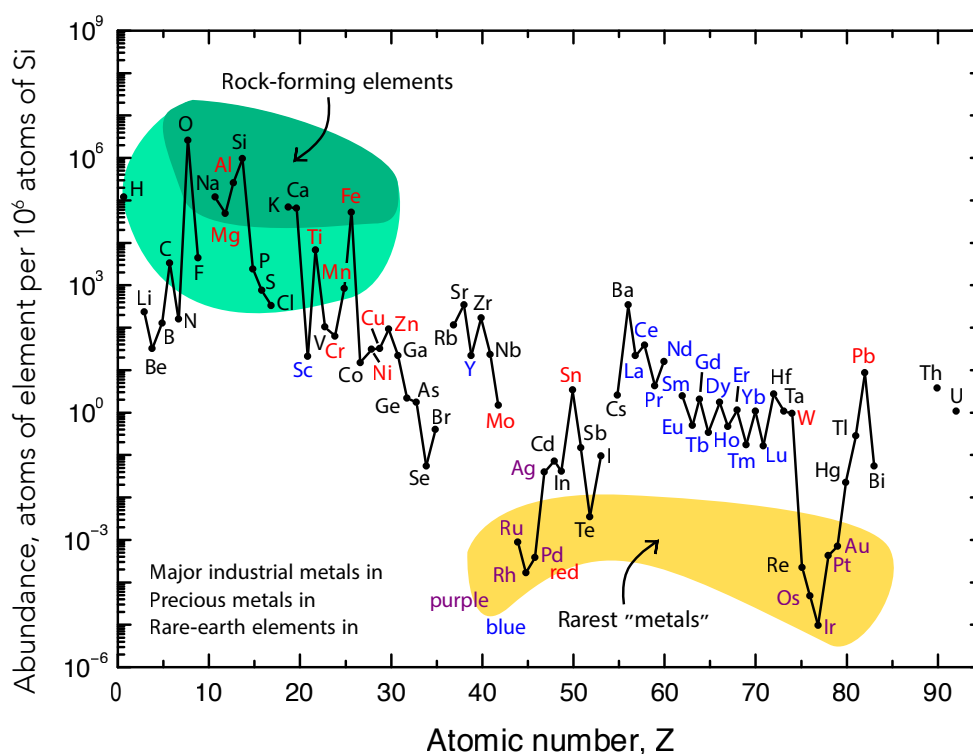


Figure 5 Relative abundance of earth's crust elements, plot *vs.* their atomic number, per every million Si atoms. The data shows the scarcity of the majority of the efficient HER catalysts: Pt, Pd, Ru, Au, Ag, etc. Image credit: USGS.

In fact, Si is the most studied material in the field of semiconductor electrochemistry.^[28] This is probably due to its vast abundance in the earth's crust, being the second most abundant element and most abundant solid material (*cf.* Figure 5 for elements abundance in ratio of that for Si). Hence working with Si at large scale is viable as a cost-effective and sustainable approach. For this reason, a large variety of Si wafers and devices can be obtained off-the-shelf worldwide, given the Si manufacturing processes are well developed, as discussed in very great detail in literature publications.^[28–33]

However, the electrocatalytic activity of the interface is a downside. Si exhibits sluggish kinetics towards catalysis for a range of solvated redox species. This is primarily attributed to weak interaction kinetics of the surface Si atoms towards ion absorption/desorption. In a PEC where Si is positioned as the photocathode, it amounts to additional overpotentials required to overcome

the low catalytic activity of the interface.^[28] Considering the limitations imposed by Si photoelectrode efficiency; the energy losses, and sluggish catalytic activity, a sensible approach to the rectification of these issues is to assemble electrodes using surface-functionalised catalysts that can contribute with enhancing the catalytic efficiency of the photocathode.^[28] Typically, metal particles are functionalised on the interface via a range of advanced materials fabrication techniques, such as electrochemical deposition (ECD) or photoelectrochemical deposition (PED).^[34,35]

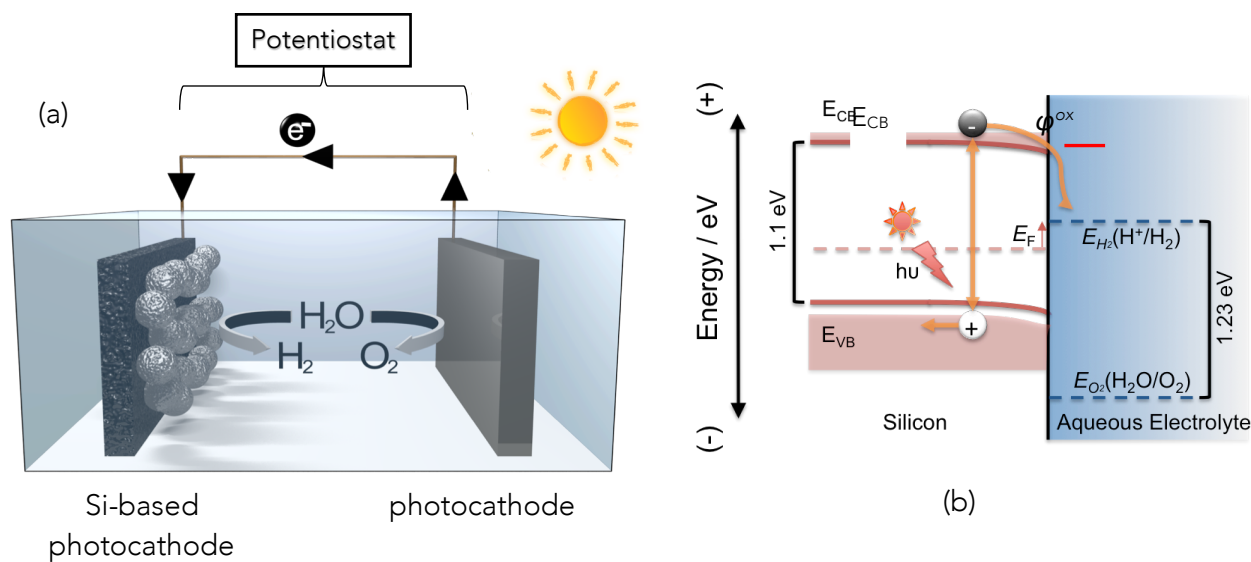


Figure 6 Schematic illustrations for (a) a typical PEC water splitting cell consisting of a photocathode/anode electrodes to catalyse HER/OER, respectively. This system can operate standalone if the experimental photovoltage accumulates in excess of 1.23 V, or otherwise externally-biased by potentiostat to provide the overpotential required in water splitting (Figure design courtesy of Dr. Mathias Wiechen). (b) the Si photocathode harvests light energy ($h\nu$) for photogeneration of the electron-hole pairs that are necessary for redox conversion at the electrolyte interface; in this case, acidic aqueous solution. For Si, the corrosion potential (oxidation) of the surface atoms lies above the OER potential, $E(H_2O/O_2)$, hence is an inevitable process.

Platinum has been a prominent catalyst which promotes the HER, due to its excellent kinetics towards proton reduction.^[6,36,37] For this reason, it has been widely incorporated as a co-catalyst to enhance Si photocathodes.^[38–41] The catalytic activity that Pt nanoparticles add to Si is demonstrated in detail in Chapter 2 and Chapter 5 of this thesis. Given the high costs associated with the use of Pt^[42] and its scarcity (*cf.* Figure 5), there is a vast research drive to solve the “Pt Challenge” by: a) Investigating alternative electrocatalysts that mimic the performance of Pt.^[12,28,43–47] b) reducing the Pt loading using monolayers or metal traces such as nanocatalysts and discontinuous layers.^[36,40,41,48]

Metal particles can be functionalised onto electrode interfaces via ECD methods from metal salt solutions in an electroplating cell. This process can also be performed under illumination, using PED, for metal-particle functionalisation on a semiconductor, such as the case with Si.

Alternatively, electroless deposition (ED) can be used if the ions from the metal salt can spontaneously reduce on the surface of the substrate; which can also be performed under illumination, if the electrochemical redox potential of the metal system is well positioned with respect to the Si band gap. These techniques can be effectively tuned to achieve a variety of nanocatalyst structures and layers. The mechanisms for metal nanocatalyst functionalisation are further investigated throughout this thesis and are especially detailed in Chapter 5.

1.3 Si Nanomaterials as Photoelectrode Platforms

An emerging trend in fabricating efficient photocathodes is via surface modification of the Si interface, in an aim to integrate nanotechnology for enhancing solar water splitting mechanisms. In nanomaterials, the physical properties and phenomena taking place in the nanoscale allow the interactions of light, chemicals and materials to be redefined subject to the nanoscopic dimensions and features of these nanomaterials. There are many phenomena to expand on, and the advantages of using Si in the nanoscale include, but are not limited to, the enhancement of the PEC-active interface and its morphology,^[28,49,50] development of the electrolyte interfacing energetics and kinetics by incorporating nanoscopic features and boundaries,^[51–54] improving light absorption and scattering capabilities,^[55–58] as well as being able to tune the physical properties of bulk materials such as electrical conductivity,^[59] and individual band gaps,^[60] by varying the feature dimensions.

There are two possible approaches that can be employed in materials nanofabrication: the “bottom-up” synthesis from raw materials and precursors, and “top-down” modification of bulk structures.^[61] There are advantages for using either approach, while the current perspective for using Si materials favours the top-down approach for assembling PEC electrodes, due to the wide availability of Si wafers that can be cheaply procured off-the-shelf, and that these materials exhibit highly-uniform crystallographic topographies. Furthermore, nanostructuring such platforms by top-down atomic removal and pitting methods yield imperfect surfaces with significant defects whilst preserving the crystallographic traits of the original material.^[61] These defects and nanoscopic features serve as electrochemically-active sites which are beneficial in catalysing redox reactions. Hence it is vital to study these mechanisms by developing a range of nanostructures by tuning the fabrication parameters accordingly.

In fact, the preparation of bulk semiconductors for PEC applications involves doping by chemical impurities, such as boron (B) in *p*-type Si and phosphorus (P) in *n*-type, which results in a large amount of crystallographic defects in the material. This is generally performed to enhance the conductivity in bulk semiconductors, which are otherwise nonconductive in pristine composition. Doping is also beneficial for enhanced optical absorption, increasing the minority carrier diffusion length, and in some cases improving the catalytic activity of the interface.^[28,62] However, this could result in adverse effects such as providing recombination pathways for photogenerated charges, such as through bulk defects, or limited photovoltage due to acquiring quasimetallic attributes leading to a reduced band gap.^[29] In practice, the photoconversion efficiency of semiconductors depends on the surface and bulk defects, which are influenced by chemical treatment. The formation of surface states and their properties are altered based on the physical interaction of these defects with the photogenerated charges, often attributed to quantum-mechanic effects due to quantum confinement or recombination processes. Because of the size enlargement and enhanced light scattering effects, nanostructured Si is characterised with a visually

black appearance, hence the terminology black Si (bSi) is used. The degree of light scattering in nanostructured Si highly depends on the features geometries. Since the photoexcitation of charges and their separation occurs at the nanoscale, nanomaterial interfaces can tolerate much higher proportion of surface and bulk defects, as compared to planar structures, before energy conversion efficiency is compromised.^[63]

Si nanostructures can be obtained using a combination of surface patterning and physical etching methods such as photolithography accompanied dry reactive ion etching (DRIE),^[28,64–66] or chemically, using metal-assisted electroless chemical etching (MaCE) for both purposes.^[31,67–69] In MaCE, the type of metal used for surface patterning plays a key role in the overall fabrication process, giving rise to a range of nanostructural morphologies, such as nanoporous, wall-like, pyramidal, or nanowire structures.^[31] The choice of metal allows for achieving a desirable nanostructured interface.

This common and easy approach utilises spontaneous nucleation and growth of metal nanoparticles onto the Si surface via galvanic interactions. The patterned surfaces are then subjected to chemical etchants of adequate compositions, optimised by varying their concentrations, in order to modify the Si surface and etch down into the bulk. In this process, the metal plays a primary role in the etching process due to the physico-chemical interactions involved between Si, M and etching chemicals. This cost-effective approach only requires immersion of Si substrates in appropriate solutions containing the desired metal-salt and fluoride etchant. The mechanisms involved in MaCE are described in detail in Chapter 3 and Chapter 4, including characterisation of the produced black Si.

Equation 3: A redox system involving electron transfer. A/A^+ denotes the redox couple at equilibrium. E is the reaction potential *vs.* the standard hydrogen electrode (SHE) at which the reduction can take place. The hydrogen evolution reaction (HER) has an absolute energy of 4.44 eV relative to vacuum, which corresponds to an electrochemical potential of 0 V *vs.* SHE



1.4 Fundamentals of Water Photoelectrolysis

The state-of-the-art in alternative energy research promotes electrical to chemical energy conversion. In this section, fundamentals of solar water splitting are discussed in brief detail. For a rather comprehensive detail, the reader is referred to dedicated textbooks in this field, such as “*Photoelectrochemical Hydrogen Production*” by Krol and Gratzel,^[70] or “*Electrochemical Methods*” by Bard and Faulkner.^[71]

A typical redox reaction involves the exchange of electrons spontaneously (galvanic), or driven by an external power supply (*cf.* Equation 3) depending on the energetics of the reaction.

The redox couples of all elements/molecules are compared in the electrochemical series at standard conditions (1 M, 25°C, 1 atmos. pressure) based on the standard potentials (E°), with respect to the standard hydrogen electrode (SHE).^[5,21,37] The reaction potentials can be calculated using the Nernst equation (*cf.* Equation 5), which takes into account various solution outside of standard conditions.^[72]

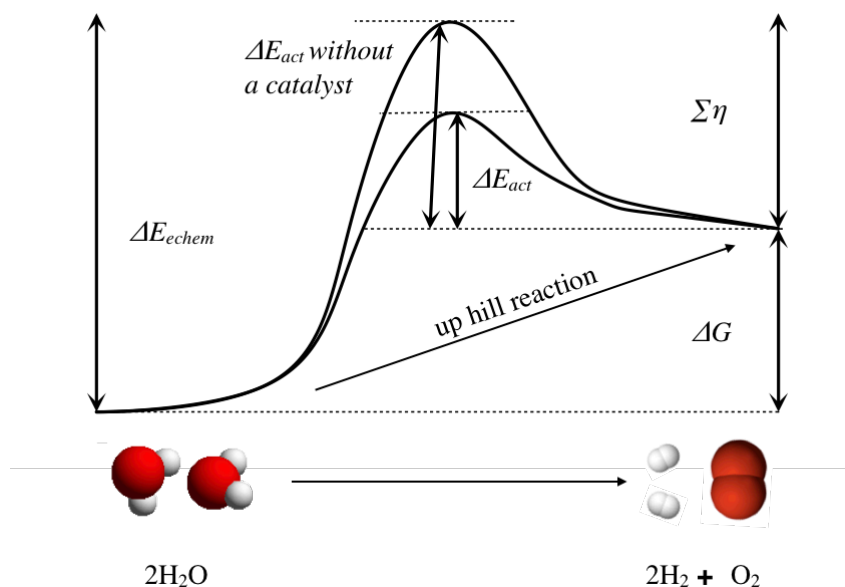


Figure 7 Schematic illustration of the uphill energetics involved in water electrolysis. For a catalyst to facilitate this reaction, a total electrochemical energy (ΔE_{chem}), involving the Gibbs free energy (ΔG) and the sum of overpotentials ($\Sigma\eta$) accrued due to limitations from materials and experimental conditions such as mass transport and overcoming the activation barrier for the reaction intermediates, must be provided.

Redox reactions occur spontaneously if the reduction half-reaction (RHR) potential (φ^{red}) is more positive than that (φ^{ox}) for the oxidation half-reaction (OHR), hence the oxidising agent draws electrons from the reductant. Such is the case, for example, in the corrosion of metals (Fe for example) or semiconductors (such as Si) from exposure to oxidants. The oxidation reaction is inevitable under some conditions, hence drives materials corrosion by forming an oxide layer on the interface. One can drive a specific electrochemical reaction by applying an external potential to the system, using a potentiostat, or by driving photovoltages generated from illumination of semiconductors, or by applying both a voltage and photovoltage simultaneously. The chemical splitting of water involves the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER),^[6,11] as described in Equation 5.

Water splitting is difficult to achieve because it is an energetically uphill reaction that requires a driving force (*cf.* Figure 7). The Gibbs free energy required for the splitting of one water molecule into its components (H_2 and $\frac{1}{2}O_2$) under standard conditions is $\Delta G^\circ = 237.2 \text{ kJ.mol}^{-1}$ (*cf.* Equation 4).^[73] This value represents the minimum amount of work required to proceed with the reaction. It is calculated from the difference between enthalpy (ΔH) and the entropy (ΔS)

changes in water splitting, as shown in Equation 4. This indicates that the reaction will not proceed if no external energy is applied. As previously mentioned, this energy can be supplied either by a potentiostat or by generating a photovoltage.^[9,74]

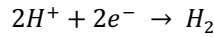
Equation 4: The Gibbs free energy associated with splitting of a water molecule at standard conditions is the difference in enthalpy and entropy changes of the system. The electrochemical standard potential is the free energy divided by the factor nF , where n is the number of electrons transferred in the reaction (in this case 2 per mole of H_2O) and F is the Faraday constant ($96\,500\text{ C.mol}^{-1}$).

$$\Delta G^\circ = \Delta H - T\Delta S = 237.2\text{ kJ.mol}^{-1}$$

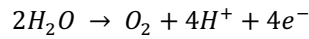
$$E^\circ = -\frac{\Delta G^\circ}{nF} = -1.23\text{ V}$$

Theoretically, an electrochemical potential of -1.23 V is required by an water electrolysis cell at standard conditions, according to Equation 4 and Equation 5. This is the potential difference required when both the HER/OER were to proceed at the cathode/anode of an electrochemical cell. When the process is solar-driven, the photovoltage supplied by the photoelectrodes provides this potential difference, or contributes to it.

Equation 5: The redox reactions involved in water electrolysis. The hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER) both require applied potentials to proceed. The value of E depends on electrolyte pH and concentrations. The standard potential values in parentheses (0 V , 1.23 V) are described in the electrochemical series for standard conditions (1 M , 25°C , 1 atmos. pressure).



$$E(H^+/H_2) = [(E^\circ = 0\text{ V}) - (0.059\text{ V}) \times pH] \text{ vs. SHE}$$



$$E(H_2O/O_2) = [(E^\circ = 1.23\text{ V}) - (0.059\text{ V}) \times pH] \text{ vs. SHE}$$

In practice, this electrochemical potential difference will not be sufficient in yielding hydrogen gas at the cathode of an electrochemical cell. This is because an additional “overpotential” is required to overcome the reaction activation barrier, overcome interfacial sluggish kinetics, compensate for catalytic inactivity, the inevitable energy losses accumulating on semiconductors under illumination, or ohmic losses in driving the cell (wiring, electrolyte, and connections).^[6,75] Furthermore, some proportion of this energy is consumed in the process of charge transfer between semiconductor/electrode materials and electrolyte components.^[76] A great deal of energy can also

be consumed in the degradation of the interface, especially in Si, by the formation of an insulating oxide layer,^[77] which results in poor electrode performance and hence leading to further overpotential increase. The collective of energy losses drives the effective experimental potential difference higher, from 1.23 V up to anywhere in the range 1.6 V - 2.4 V, to overcome the numerous limitations.^[6,75]

Since the kinetics of the HER process are critical for the use of hydrogen as fuel. In order to facilitate the HER efficiently, catalysts can be utilised for driving electrochemical reduction with lower overpotentials due to their excellent catalytic activity. Therefore, proton reduction is catalysed efficiently when the onset potential (V_{os}) of the cathodic conversion is facilitated as closely as possible to the standard potential indicated in the electrochemical series, i.e. 0 V *vs.* RHE (*cf.* Equation 5). Furthermore, several electrode design factors can facilitate the conversion process by enhancing the interfacial characteristics. Both of these streams resemble the core focus of this research investigation.

1.5 Research Objectives

The overall aim of this research is to develop Si photocathode platforms for solar-assisted hydrogen generation. In doing so, the mechanistic understanding of the physico-chemical properties of pristine Si interface and co-catalysts, need to be established, for bulk and nanomaterials structures. In order to better facilitate solar water splitting, this thesis included the following objectives:

- 1 | The stability of semiconductor Si is of great concern, due to its inevitable corrosion. Therefore, the performance of assemblies based on an underlying Si platform, supporting a protective coating and an efficient HER catalyst, needs to be established by investigating hydrogen production under harsh electrochemical conditions.
- 2 | Si nanomaterials can offer beneficial performance based on literature reports. Therefore, the fabrication methods of bSi nanostructures that are applicable to photocathode interfaces, need to be investigated by using cost-effective and safe approaches for large-scale feasibility. The morphology of these structures and their nanoscopic properties need to be characterised to expand on the effects that originate from nanoscale modifications towards energy conversion devices.
- 3 | The performance and prolonged stability of pristine bSi are not fully established in the literature, especially during operation for facilitating the HER in PEC cells for extended periods of time. Furthermore, the effect of the geometrical aspects of the nanostructured interface and its activity and efficiency for STH conversion need to be studied in detail.
- 4 | The incorporation of nanosized metal-catalysts can result in significant enhancement of the performance on nanostructured photoelectrode. Some catalysts such as Pd- and Cu-based nanoparticles, are not only desirable for HER, but also a range of other applications including potential use in CO₂ reduction in PEC cells. Furthermore, the modified Si interface can host a wide-range of these catalysts and also interfacial junctions, such as surface inversion, which allows for improving the energetics on the interface. In this case, common HER catalysts, such as Pt and Pd need to be functionalised in order to study the effect of surface inversion for core-shell *p-n* bSi nanowires used in catalyst-mediated STH conversion. For this purpose, an in-depth investigation

of the fabrication parameters is required to fully understand metal-patterning on bSi nanostructures via a range of metal deposition techniques.

- 5 | Essentially, bridging nanoscale materials with solar-to-fuel conversion, is anticipated to reveal vital traits for enhanced performance, durability and scalability towards sustainable energy applications. Such advanced materials fabrication techniques are promising for enhancing the kinetics of the Si especially when combined with surface catalysts and illumination. Hence, a mechanistic study is sought-after, for understanding the role of these materials in as PEC photoelectrodes, to drive solar-to-chemical fuel conversion. The objective of this study is to focus on testing these photocathode platforms and catalysts for the hydrogen generation aspect of solar water splitting.

Monash University

Specific Declaration for Chapter 2

Declaration by candidate

In the case of sections 2.4 and 2.5, the nature and extent of my contribution to the published work was the following:

Paper title	Extent of contribution (%)
Boron-doped diamond (BDD) coatings protect underlying silicon in aqueous acidic media - Application to the hydrogen evolution reaction.	Concept, Experimental Design, Data collection and analyses Manuscript preparation Primary author 85%

The undersigned hereby certify that the above declaration correctly reflects the nature and extent of the candidate's and co-authors' contributions to this work.

Candidate:

Signature:

Print Name:

Date:

Main Supervisor:

Signature:

Print Name:

Date:

Secondary Supervisor:

Signature:

Print Name:

Date:

CHAPTER 2 WATER ELECTROLYSIS ON SI BASED CATHODES

2.1 Chapter Overview

The following chapter encompasses a paper titled “Boron-doped diamond (BDD) coatings protect underlying silicon in aqueous acidic media - Application to the hydrogen evolution reaction” published in *Electrochimica Acta* in 2014. This chapter investigates protective diamond coatings for the prevention of corrosion on Si cathodes. The study involved electrochemical testing of a variety of substrates, to evaluate the performance of the cathode half-cell in a water electrolysis cell.

Conductive diamond can be cheaply synthesized in microwave plasma reactors, and potentially offers electrochemical attributes in addition to its chemical inertness and robust morphology. Therefore, it is hypothesized that conductive diamond films grown on the surface of Si can stabilise the underlying electrode from corrosion in aqueous media.

The effects of harsh electrochemical conditions during the HER on *p*-Si|BDD assemblies are examined in aqueous media. A series of cathodic scans were performed using linear sweep voltammetry (LSV) for an electrochemical cell containing highly-acidic electrolyte. The performance of these cathodes are studied during short and long term potentiostatic experiments, under conditions chosen to maximise corrosion. The published results have shown that BDD coatings enhance the stability and performance of the cathode assembly to facilitate the HER. Furthermore, Pt nanoparticles were functionalised onto BDD for enhanced catalysis; where the BDD was used as a catalyst support platform. Further detailed studies of HER nanocatalysts are presented in Chapter 5 of this thesis.

2.2 Background

2.2.1 Mechanism of Si corrosion

Extensive reviews on the physico-chemical properties of Si and SiO₂ are widely available, such as “*Electrochemistry of Silicon and its Oxide*” by X G Zhang,^[29] where immense detail on the relevant electrochemical properties of Si and the science of its corrosion are discussed in great detail.

Corrosion in semiconductors is the spontaneous oxidation of the interface atoms as a result of chemical interaction with an electrolyte medium. The oxidation reaction of silicon involves the formation of Si-O bonds, oxidation of Si⁰ to Si⁺⁴ and the transfer of the valence electrons of Si (4e⁻) in an overall reaction depicted in Equation 6.^[29] The oxidation of Si can be facilitated by the consumption of holes, which are considered the majority carriers in *p*-type Si, or the minority

carriers in *n*-type Si. Hence generation of holes in *n*-type Si is required to proceed with oxidation, either by illumination or external applied potential, while for *p*-type Si, the oxidation process proceeds spontaneously under appropriate chemical environments, regardless of illumination. To incorporate semiconductor Si interfaces for stable solar water splitting, under illumination, corrosive electrolytes and perhaps anodic currents, this issue must be resolved.

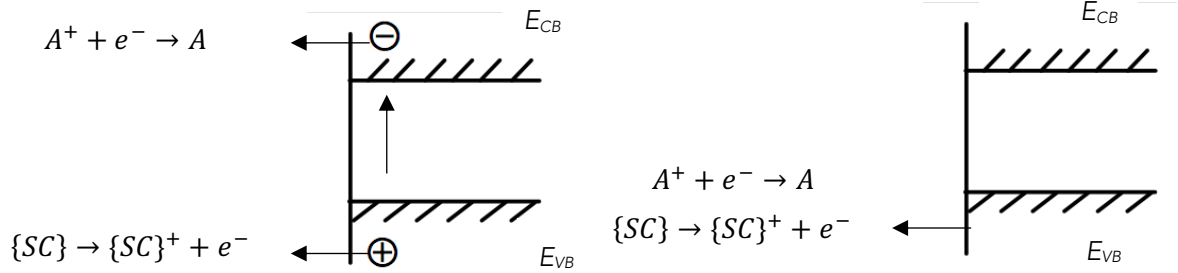


Figure 8 Corrosion pathways in semiconductor (SC) Si can occur via two pathways, depending on illumination conditions. In light (left), photogenerated holes proceed for Si oxidation via the valence band, while a reduction current from the conduction band balances this reaction by conversion of a redox couple A^+/A . On the other hand, in dark (right), the reduction reaction facilitates oxidation of the surface atoms by an oxidant drawing electrons from the silicon for the provision of holes, hence both reactions proceed via charge transfer from the valence band. When connected to a cell terminal, a constant cathodic potential is required in order to prevent the corrosion process, otherwise it can proceed even under no externally-applied bias, due to the Si/SiO₂ redox chemical stability. This corrosion process renders the surface of Si electrochemically-inactive due to the insulating SiO₂ layer formed at the Si/electrolyte interface.

The mechanism of corrosion on semiconductors is distinct from that on metals, where all charge carriers, i.e. holes (h^+) of the valence band (E_{VB}) and electrons (e^-) of the conduction band (E_{CB}), partake in the oxidation process.^[78] In a semiconductor, the surface species, $\{SC\}$ oxidise to $\{SC\}^+$ in two different ways, as illustrated in Figure 8. For *p*-Si under dark conditions, oxidation reaction can initiate, from valence electrons participating in the reduction of solvated species, hence the $\{SC\}/\{SC\}^+$ process is facilitated from the holes provided in this process. Another mechanism involves corrosion initiated from photogenerated holes in the valence band. The rate of the reaction in the second mechanism is influenced by the illumination parameters, and material type. For instance, illumination influences the kinetics of the oxidation process because it determines the population of photogenerated carriers.^[29]

Recently, Chen et al.^[25] compiled the redox potentials for a range of semiconductors at aqueous interfaces, along with the band gap alignment, as derived from experimental electrolysis data. In the $\{SC\}/\{SC\}^+$ redox conversion process, the reduction (oxidation) potential, denoted φ^{red} (φ^{ox}) for the photocathode (photoanode) is determined based on the Gibbs free energy or band edge alignment calculations. It was found that, the semiconductor was inherently stable from oxidation ($\{SC\} \rightarrow \{SC\}^+ + e^-$) if the φ^{ox} lies lower than the standard potential for OER; $E(H_2O/O_2)$ or lower than E_{VB} of the semiconductor. This in turn, works in the favor of the semiconductor

where corrosion is prevented; the hole transfer is not energetically feasible. The $\varphi^{red}/\varphi^{ox}$ values for a range of common semiconductors are adapted from their works and displayed in Figure 3.

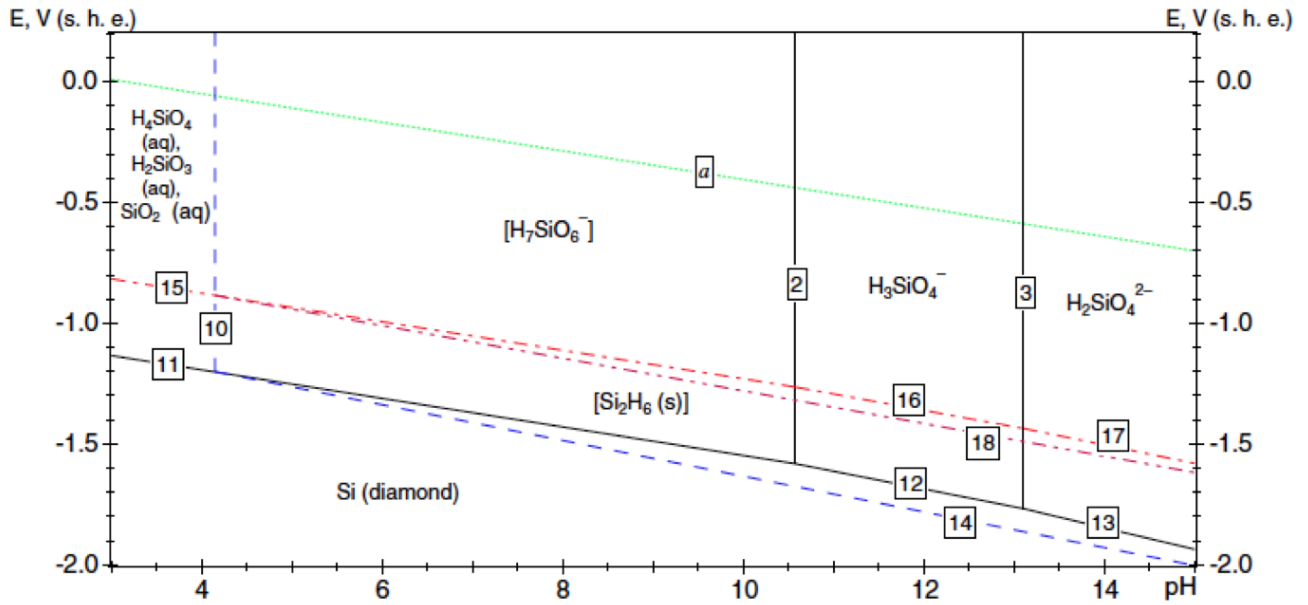


Figure 9 The Pourbaix diagram of Si and solvated redox couples. Image adapted with permission from The Revised Pourbaix Diagram for Silicon, Pavel Anatolyevich,^[79] © SpringerLink 2014.

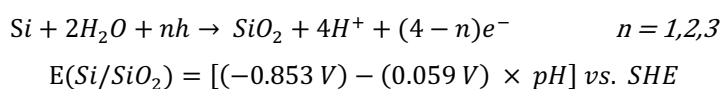
2.2.2 Silicon oxide as a natural protective Interface

The feasibility of Si materials for PEC applications was addressed previously in Chapter 1. In brief, Si interfaces facilitate the HER because the standard potential for HER lies between E_{VB} and E_{CB} , as shown in Figure 3 and Figure 6. However, Si is extremely susceptible to corrosion in aqueous media due to the positioning of φ^{ox} at higher potential with respect to the $E(H_2O/O_2)$, such that oxidation of surface atoms occurs through hole consumption from E_{VB} . This process is generated spontaneously because the oxidation reaction “costs” negative energy, hence the interfacing atoms decompose even in dark conditions.^[25,29]

Growth of the oxide layer proceeds on Si surface, until reaching a certain thickness, after which, the oxidation process is slowed down, or comes to a halt, due to the band edges of the oxide layer. At this stage, the Si valence band holes are blocked from migrating to the oxide layer due to the lower position of the oxide layer valence band. In some way, this process results in material stability, kinetically, while only allowing electron transfer from the conduction band towards the electrode/electrolyte interface. This process is possibly advantageous for energy conversion efficiency because it mitigates oxide formation from the photogenerated charges, besides reducing electron-hole recombinations. However, the dielectric nature of this oxide may impinge on electron mobility towards the surface, hence limiting the HER reaction rate. This layer hence contributes with a resistance, which significantly adds to the sluggish kinetics for water electrolysis at the interface, which is investigated later in this chapter.

The corrosion thermodynamics on Si follow the Pourbaix stability relations illustrated in Figure 9.^[79,80] The chemical stability of Si/SiO₂ is outlined in Equation 6, which is onset at –0.853 V *vs.* SHE. This means that, when no external bias is applied, the surface will undergo spontaneous corrosion. Alternatively, the electrode can be protected from any oxidation processes when cathodically-biased. Hence, electron-transfer to the electrolyte is better facilitated by the position of the band edges.

Equation 6: The redox reactions involved in the spontaneous corrosion of Si at an aqueous interface under corrosive conditions satisfy the stability conditions outlined in the Si Pourbaix diagram in Figure 9.



In the case of highly doped *p*-type Si photocathodes, they can be used to drive the HER, as long as anodic currents are not driven and exposure to corrosive electrolytes does not occur.^[25,28,29] Nevertheless, Si wafers exhibit corrosion naturally, even under exposure to form an oxide layer, 1-2 nm thick when exposed to aqueous interface or up to 20 Å when exposed to air for several days.^[29] Exposing the surface to corrosive conditions result in the increase of the thickness and rate of the oxide layer formation. This phenomenon severely hinders the electrochemical activity at the interface.

The oxide layer can be removed using etchants composed of fluoride ions; the kinetics and mechanisms of such etching processes are well-studied in the literature,^[29] this method will be implemented in investigating Si surface modification, in Chapter 3. However, in terms of utilising these materials in prototype devices, the frequent removal of the oxide layer can pose as a difficulty, especially that the interface corrodes rapidly enough to prevent long-term functionality in a PEC device. It is crucial that the corrosion problem is rectified before the feasible use of Si photocathodes in PEC devices.

2.2.3 Passivation layers and their requirements

One approach to tackling the stability problem is to incorporate corrosion-resistant coatings of light-transparent, highly-stable and conductive materials onto Si, or other desirable semiconductors, to yield robust photoelectrode assemblies. Protecting Si against corrosion has been at the core of a substantial amount of theoretical and experimental work for many years.^[9,39,81–93] Attempts to stabilise Si have involved several approaches, most notably surface functionalisation by organic coatings,^[94–97] metal-based coatings,^[29,98–100] thin oxide coatings,^[29,101] wide band gap semiconductors,^[102–106] or mitigating it using appropriately selected alternative electrolytes.^[107–109] While some of these methods have been successful in passivation of the Si interface, their use is accompanied by a compromise of the catalytic efficiency in exchange for long-term stability in

driving the required redox conversion, considering that most of these successful interfaces exhibited insulating properties or sluggish catalytic activity for proton reduction.

In designing electrode multilayers, it is important to select materials that can offer beneficial functionalities in addition to their passivating properties. This has been previously explored for passivation coatings that also possessed antireflective properties.^[110–113] Alternatively, careful material selection which comprises functional layers that enhance the catalytic activity and stability of the photoelectrode ensembles, can also be implemented.^[101–103,114,115] For instance, Chen *et al.*^[82] developed a multi-layered electrode assembly combining SiO₂ as passivating thin-layer, TiO₂ as a UV-range photoabsorber as well as Ir (and IrOx) as an electrocatalyst for driving the OER. Similar assemblies have also been devised for the photocathode half-cell using combinations of oxide films and catalysts.^[28] The downside of this approach is that the performance is greatly affected by the morphology of these coatings and their inherently-low electrical conductivity. Hence obtaining intermediate thickness to allow electrocatalysis while preventing corrosion is mandatory. Furthermore, the design costs and fabrication experiments are relatively time-consuming because additional components, such as ohmic-contacts, need to be devised in order to compensate for the limited charge-transfer.

Ideally, protective coatings should be designed to satisfy the following requirements: inhibit corrosion from aqueous species while facilitating charge migration, allow transmission of light to the underlying Si electrode to generate the electron/hole pairs, exhibit excellent electrocatalytic activity, and consume low-cost, abundant materials as well as the capability of fabrication via feasible experimental means, in order for device scalability and sustainability. It is therefore essential to design coatings that provide pin-free, uniform layers, are robust, and can facilitate the catalytic conversion of solvated species by providing an active electrochemical interface. Most importantly, these protective coatings are required to facilitate this at no compromise to the performance of the underlying Si electrode, such as by preventing interfacial resistance build-up in the process.

2.2.4 Diamond coatings as inert electrochemical interfaces

Diamond is considered one of the hardest materials known.^[116] It is transparent, and due to naturally formed nitrogen vacancy centres, it exhibits a range of optical emissions. Proposing the usage of diamond as an electronic material for electrochemical devices surprises many, as it is commonly known as an insulator. However, highly-advanced materials fabrication techniques allow scientists to synthesize diamond films which are tuned to exhibit a variety of desirable attributes, such as high conductivity, as elaborated in this section.^[116–118]

Synthetic diamond is fabricated using microwave-plasma chemical vapour deposition (CVD), which allows for the epitaxial growth of thin films, with a variety of tunable properties. Semiconductor or quasi-metallic attributes can be obtained through doping with impurities (such as Nitrogen or Boron), hence leading to the formation of inter-band states capable of electron occupancy, which can be beneficial for use in PEC devices. This also allows the interface to exhibit ultra-high conductivity due to the nature of bonding in the grain boundaries, which is highly-influenced by the dopant concentration.

Conductive diamond is typically grown in Ar-rich plasmas containing 1% of Methane (CH_4) and 1% Hydrogen (H_2) and 98% Ar.^[119] The desirable properties can be achieved by tuning the ratio of H_2/CH_4 precursors, plasma temperature and chamber pressure. This results in highly conductive coatings that are capable of charge transfer even in dark conditions. It has been shown that boron-doped diamond (BDD) films can exhibit resistivities as low as 10^{-3} ohm.cm, for highly-doped samples containing 10^{21} B atoms per cm^3 .^[120,121]

In synthetic form, amorphous films may have quasi-metallic or semiconductor-like attributes, which can be useful for a variety of electrochemical applications.^[120–122] Showing a dielectric morphology in undoped form, it exhibits properties of a super-wide band gap material ($E_g = 5.5$ eV) when its moderately doped and metallic attributes at ultra-high doping, as described above. Furthermore, diamond exhibits chemical inertness to harsh environments due to the inherent stability of its C-C bonding and pin-hole free morphology due to its uniform nucleation/growth mechanisms.^[119,123]

Epitaxially-grown diamond exhibits one unusual property concerning their energetics; when the interface is chemically treated to obtain hydrogen terminated surfaces, the conduction-band edge lies more positively (-0.8 -1.3 eV) than the vacuum level, hence acquires the semiconductor with a negative electron affinity.^[124,125] Consequently, electrons excited into the conduction band by $E > 5.5$ eV radiation, can readily diffuse the surface and be emitted at the interface of an electrolyte with no or little energy barrier,^[124,125] hence diamond can be used as a solid-state electron source. This attribute is most advantageous for light-assisted cathode use of diamond, and therefore has been previously exploited as a source of solvated electrons for the reduction of chemical fuels such as N_2 to NH_3 ,^[126] or CO_2 to CO .^[127]

Diamond interfaces also combines robustness with unique optical attributes that originate from its natural contamination with impurities, or derived transparency.^[116] For instance, the optical transparency of highly conductive diamond films measured on quartz or through PEC tests on Si, suggested that it is at least 70% transparent to incident illumination.^[118] The absorbed proportion of incident light contributes with high-energy (UV) excitations depending on the energetic properties and type of synthesized diamond. Luo *et al.*^[119] investigated the use of conductive diamond in photochemical (PC) and PEC applications, motivated by its transparency to a wide range of the solar spectrum. In addition, it has also been used as antireflective coatings for solar cell devices.^[128]

The electrochemistry of diamond has been studied previously in numerous reports.^[121,129–131] These studies are in agreement that the significant electrochemical and semiconducting attributes in diamond, are related to the nature of the grain-boundaries which surrounding the crystalline diamond growth. The grain-boundaries are comprised of sp^2 -hybridised carbon, due to doping with different impurities and concentrations. It is understood that the grain-boundaries at an electrolyte interface act as electrochemically-active sites, and promote charge transfer to facilitate redox conversion. In fact, the conductivity attributes of nanocrystalline diamond interfaces are also related to the grain-boundaries, where the inter-grain crystalline structures do not exhibit conductivity, although may possess inter-band dopant energy states, which are beneficial for the semiconductor use of diamond. Admittedly, most research efforts in utilising BDD for electrochemical applications have optimised the interface for wide potential windows, high

capacitance or insulating properties for application in biomedical or wastewater treatment devices.^[132–134] Therefore, investigating BDD interfaces for enhanced catalytic activity towards the HER process is a new direction for implementing these materials as multi-functional protective coatings.

Furthermore, diamond has not yet been used to stabilise long-term electrolysis in a Si-based assembly (or any similar protective coating in a PEC cell). Hence it is necessary to investigate its suitability in a HER cell with typical electrolytes. Proton reduction mechanisms are much more feasible in acidic electrolyte conditions,^[6] which are typically corrosive to Si interfaces. Therefore, to lay the grounds for a functional electrode based on planar Si and coated with a uniform BDD diamond layer, this study investigates the electrode's performance and durability for STH conversion, undergoing relatively harsh electrochemical parameters.

2.3 Experimental Parameters

The following section presents experimental analyses and results for a range of planar Si-based cathodes, in publication form. The electrochemical testing was conducted in dark conditions, dedicated to testing the Si stability. Therefore, ultra-low resistivity Si wafers were selected because they demonstrate two key characteristics for this purpose: that this high level of doping renders the electrodes highly conductive due to quasimetallic attributes, and hence better charge transfer across the interface in dark,^[29] and that the Si surface corrosion rate is significantly increased for ultrahigh B-doping in *p*-type Si.^[135] A list of the specifications of the Si wafers used and their classes is included in Table 13 (*cf.* Index of Samples).

The stabilisation by diamond coatings was tested under severe electrochemical conditions. The uncoated Si (*p*-type, class B) and BDD-coated Si (*p*-type, class A) cathodes were subjected to linear sweep voltammetry (LSV) scans in 1 M H₂SO₄. They undergo continuous cycling and long-term electrolyte exposure. Their performance was compared, and their morphology was characterised using scanning electron microscopy (SEM), before and after the stability tests. The electrocatalytic performance of surface-functionalised Pt particles was also investigated. The performance of the *p*-Si|BDD|Pt towards the HER was studied during 280 h of continuous exposure to the acidic media.

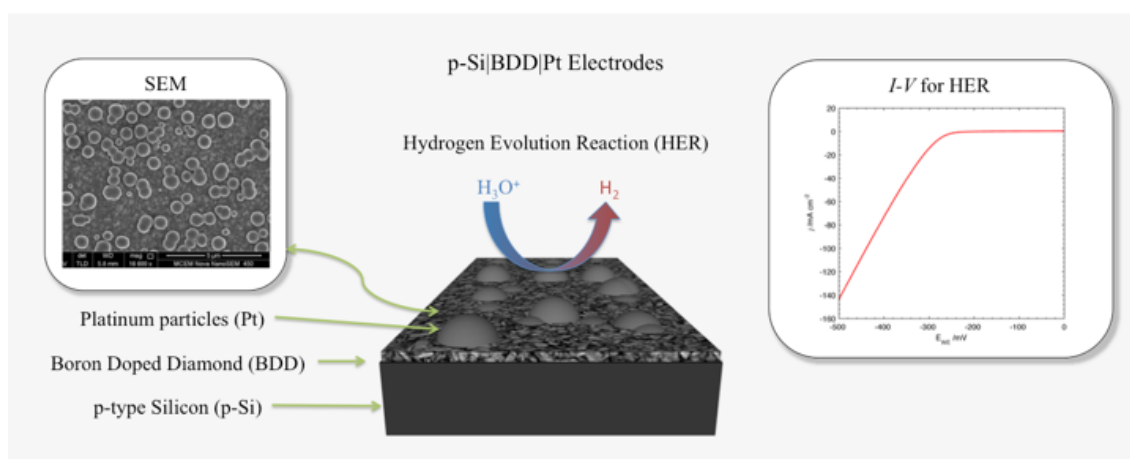


Figure 10 Graphical abstract to accompany published article presented in section 2.4

- 2.4 Published Article:
Boron-Doped Diamond (BDD) Coatings Protect Underlying
Silicon in Aqueous Acidic Media - Application to the Hydrogen
Evolution Reaction.



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Boron-Doped Diamond (BDD) Coatings Protect Underlying Silicon in Aqueous Acidic Media–Application to the Hydrogen Evolution Reaction

A.F. Halima^a, U.A. Rana^b, D.R. MacFarlane^{a,*}^a Australian Centre for Electromaterials Science School of Chemistry, Monash University, Clayton, Victoria 3800, Australia^b Sustainable Energy Technologies (SET) Center, College of Engineering, King Saud University, P.O. Box 800, Riyadh 11421, Kingdom of Saudi Arabia

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ABSTRACT

Silicon has potential application as a functional semiconductor electrode in proposed solar water splitting cells. It is abundant and has excellent photovoltaic attributes, however it is extremely susceptible to corrosion, even in the dark, resulting in the formation of an electrochemically passive oxide upon interaction with aqueous media. This work investigates the potential for conductive, inert and transparent boron doped diamond (BDD) coatings to protect p-type Silicon (p-Si). The stability and electrochemical performance of p-Si and p-Si|BDD were investigated using voltammetric techniques in 1 M H₂SO₄, before and after long-term exposure to the acidic medium (up to 280 hours) under no applied potential bias. Unprotected Si degraded very rapidly whilst BDD was shown to protect the underlying Si, as evident from *I*-*V* curves that indicated no increased resistance across the Si-diamond interface. Furthermore, BDD supported facile proton reduction at significantly lower onset potential for the hydrogen evolution reaction (up to -500 mV vs. SCE) compared with bare Si cathode (-850 mV vs. SCE). The activity of the BDD electrode/electrolyte interface was further improved by coating with platinum catalyst particles, to produce a p-Si|BDD|Pt structure, which reduced the HER onset to nearly zero overpotential. Tafel analysis indicated that desirable electrochemical activity and stability were achieved for p-Si|BDD|Pt, making this a promising electrode for application in water splitting cells.

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1. Introduction

In photoelectrochemical cells (PECs), solar energy is harvested by a semiconductor electrode and converted to electron-hole pairs that can provide sufficient energy to split water into its components at an electrolyte interface [1]. Ideally, functional electrode materials for solar water splitting cells harvest a significant proportion of the solar spectrum, support rapid charge transfer across the electrode/electrolyte interface, are highly stable in long-term operation in common aqueous electrolytes, and are produced from abundant elements with low-fabrication costs for large-scale applications [2,3]. Silicon thus appears suitable as a photo-electrode in PECs, having desirable photovoltaic properties while being abundant and easy to fabricate [2,4], and has been used in such devices to drive the hydrogen (HER) or oxygen (OER) evolution reactions [5]. Passivation of the silicon, however, reduces the performance through corrosion and dissolution of the silicon electrode, making pure silicon an impractical photo-electrode in aqueous systems [6].

The kinetics and rate of SiO₂ formation have been studied in detail in the literature, and shown to be dependent on applied potential, pH, composition of the electrolyte, and light intensity [6].

Protecting Si against passivation has been at the core of a substantial amount of theoretical and experimental work for many years [2,7]. Attempts at stabilising silicon have involved several approaches, most notably surface functionalization by organic materials [7–11], metal and metal derivative coatings [2,12–19], and nanometre thick SiO₂ coatings [20,21]. While these methods do improve the performance of silicon as a photo-electrode, passivation still occurs and the cell performance deteriorates. The most promising approach used an oxide coating [21], though conductivity of the oxide is inherently low and stability was only tested for a 24 hour period. Study on this system is continuing, observing the effects of coating thickness on overpotential of water oxidation [22].

Ideally, a coating for protecting Si in PECs will inhibit corrosive aqueous species while allowing electron transport. It will also allow transmission of light to the Si electrode to generate the electron/hole pair. The coating should also be a good electrocatalyst, as the electrochemistry occurs on the coating surface, rather than on the underlying Si. Diamond has been used as a coating to protect Si

* Corresponding author. Tel.: +

E-mail address:

D.R. MacFarlane).

in other contexts and in the current work we have examined diamond's ability to protect Si in acidic media in the context of the HER.

Diamond is well-studied in the literature due to significant advances in gas phase chemical vapour deposition technique, low-cost fabrication and facile optimization to produce desirable attributes [23]. Si represents one of the most common substrates for diamond film studies, due to similarities in structural properties of both materials [23]. Diamond acquires metal-like conductivity when doped with high concentrations of boron, and is an ideal electrode material due to its chemical inertness and corrosion resistance [23,24]. It can also be optimized for light transparency, and has been used as an optically transparent electrode [25]. Diamond can also serve as a substrate electrode to exploit the catalytic properties of nanoparticle materials, such as platinum (Pt) [24,26,27] whereby Pt coated diamond has been used as an electrocatalyst assembly in the methanol oxidation reaction [26]. However, to the authors' knowledge, diamond has not been utilized as a protective coating for Si in the context of HER.

In this work, we report on the performance of three different electrodes with respect to the HER under acidic conditions; p-type silicon (p-Si), boron doped diamond on p-Si (p-Si|BDD) and an assembly of p-Si|BDD with platinum nanoparticles as an electrocatalyst (p-Si|BDD|Pt). This initial report will focus on each electrode's performance, without exposure to light, for prolonged periods (>200 h) in a highly acidic environment to explore the protective nature of the diamond coating on Si.

2. Experimental

2.1. Electrode preparation

The Si substrates used for all electrodes were highly doped metal-like p-Si, due to rapid oxide formation kinetics on degenerate Si [28], thus highly suitable for the destructive testing involved. This type of Si represents a worst case scenario in terms of its instability with respect to passivation and therefore offers a useful basis for rapid corrosion testing.

Single crystalline Si wafers (p-Si, 0.003–0.007 ohm.cm, SSP, 0.5 mm thick, 0.5 cm² area, (111) orientation), were obtained from University Wafer Inc. Preparation of the electrodes involved native oxide removal, where electrodes were etched in a still solution of 10 wt% hydrofluoric acid (HF) in deionised water (DI) for 60 s, then washed with distilled water for 10 s and rapidly dried by nitrogen gas flow.

The p-Si|BDD electrodes were obtained from FRAUNHOFER USA. These consisted of a highly uniform BDD coating (2 µm thickness, concentration of boron to carbon ratio >6000 ppm - >10²¹ cm⁻³ in solid phase, resistivity 0.06 ohm.cm) on Si (p-type, <0.002 ohm.cm, 1 mm thick, 0.5 cm² area) that was pre-etched by HF for removal of the native oxide layer. The p-Si|BDD electrodes were obtained with a thin gold backing layer in order to protect the underlying Si layer from corrosion during storage and handling.

2.2. Electrochemical measurements

All electrochemical measurements were carried out using a multi-channel PAR VMP2Z potentiostat with a standard three-electrode configuration. All potentials were referenced to an Envirosensors E8090 saturated calomel electrode (SCE) and voltammetry sweeps were obtained at a scan rate of 50 mV.s⁻¹.

Electrochemical experiments were conducted in a three-component custom-built Teflon cell consisting of a base, electrolyte chamber and a non-sealing cell cap. The base component consists of a copper plate designed to hold the working electrode (WE) in place. Ohmic contact between the WE backside and the copper plate was

made using a thin layer of indium/gallium alloy. The WE was held in place and a working area of 20.2 mm² was defined using an o-ring secured to the base of the electrolyte chamber. The cell cap holds the reference electrode (RE) and the counter electrode (CE) in place. The CE consisted of a coiled platinum wire, separated from the working electrode by a glass frit containing 1 M H₂SO₄. The WE compartment was regularly inspected against any electrolyte leakage or short-circuiting after all experiments were concluded. The cell was operated in a Faradaic cage under normal atmospheric, room temperature, and dark conditions in all experiments. The HER onset potential is defined in a practical way as the potential at current density $j = -0.2 \text{ mA.cm}^{-2}$.

2.3. Long-term storage of electrodes

Electrodes were stored in acidic aqueous solution of 1 M H₂SO₄ in dark without applied potential bias. The p-Si and p-Si|BDD electrodes were stored for 200 h, whilst the p-Si|BDD|Pt electrode was stored for 280 h. After storage, all electrodes were briefly washed in a mixture of acetone/ethanol/DI water. All diamond electrodes were electrochemically activated following the procedure from Girard et al. [29], before and after electrochemical measurements. The activation process was repeated several times, successively until reproducible *I-V* curves were obtained.

2.4. Platinization of BDD electrodes

The method used for electrodeposition of platinum onto the BDD surface, is similar to that discussed by Sine et al. [30]. Electrodeposition of Pt was performed by applying a single potential step on the diamond electrode surface in a 2 mM H₂PtCl₆ in 1 M HClO₄ solution, which was deaerated for 1 hour and sonicated for several minutes. For deposition, the electrode was held at equilibrium potential (1000 mV vs. SCE for 30 s) followed by a potential step of 50 mV.s⁻¹ where platinic ions are reduced (-100 mV), and held there for 60 s to allow a sufficient amount of nanoparticles to deposit on the surface of the electrode (SEM micrograph in Fig. 1(a)). SEM was carried out on FEI Nova NanoSEM 450 Field Emission Microscope.

3. Results and discussion

3.1. Electrochemistry of p-Si, p-Si|BDD and p-Si|BDD|Pt

3.1.1. Activation of BDD electrodes

Current versus potential (*I-V*) curves obtained from linear sweeps on the p-Si|BDD electrode to cathodic HER potentials, are shown in Fig. 2 to demonstrate the significance of activation on the electrolytic activity of BDD. The HER onset potential before activation was observed at -800 mV, similar to that reported by Gerger et al. [31], where the BDD electrode showed an onset potential slightly more negative under similar conditions. The performance of the electrode improves after activation, where the HER potential shifts 300 mV in the positive direction at the same current density.

3.1.2. HER on p-Si|BDD|Pt

The *I-V* curve of the p-Si|BDD|Pt (SEM shown in Fig. 1), prepared as discussed in section 2.4, is compared in Fig. 3 with that of a solid Pt electrode for reference. Both curves show HER onset potential at -240 mV and overlap at higher cathodic potentials, which illustrates the similar catalytic activity of the assembly to solid Pt. These results show that this assembly could also potentially be used in other applications as an alternative to high-cost solid Pt electrodes. Several studies in the literature have investigated the catalytic properties of electrodeposited catalysts on assemblies similar to our p-Si|BDD|Pt [24,26,30]. However, the nature of

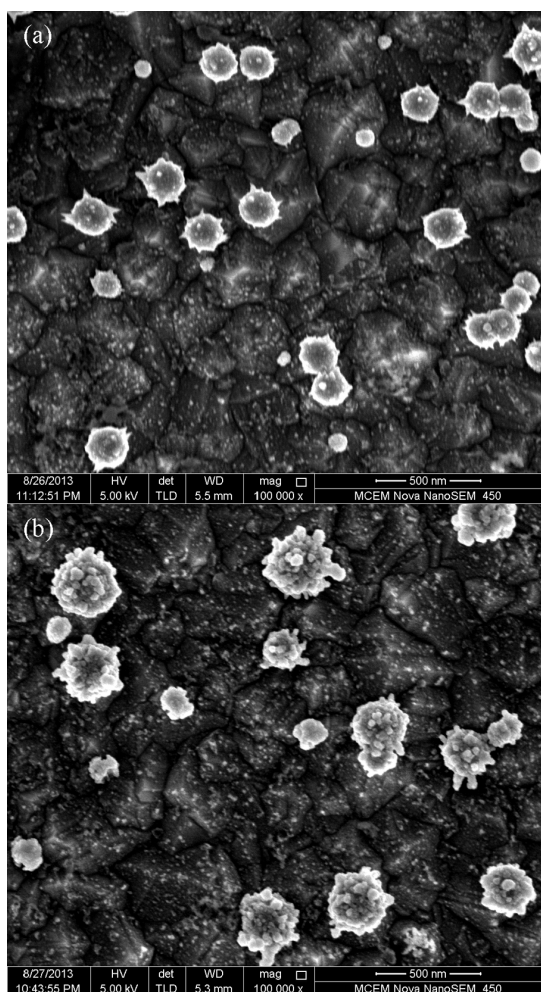


Fig. 1. SEM micrographs for p-Si|BDD|Pt electrodes; (a) freshly prepared and (b) after 200 h of storage and 1000 cycles, prepared by electrodeposition with a single potential step from 1000 to -100 mV at $50 \text{ mV}\cdot\text{s}^{-1}$ in N_2 -saturated $2 \text{ mM H}_2\text{PtCl}_6$ in 1 M HClO_4 solution.

Si-diamond interface was not discussed in all applications, and the stability of the assembly was not investigated for HER.

3.2. Long-term stability of the electrodes

3.2.1. p-Si

I-V curves of the etched p-Si electrode were measured by LSV between the open circuit potential (E_{OCP}) and -1500 mV vs. SCE, before storage (solid line), and after storage (dotted line), are shown in Fig. 4. As expected, the performance of the electrode deteriorated significantly after storage. A third LSV curve obtained after the electrode was etched for 60 s in HF media demonstrates improved activity for the HER. This implies that the electrode was corroded by the formation of an oxide layer during storage, which is removed in the presence of HF. The increased activity after etching the electrode as compared to the initial reference curve is likely due to the increase in the roughness of the surface as caused by excessive etching by HF [6].

3.2.2. p-Si|BDD

Long-term stability of the p-Si|BDD electrode was tested in a similar manner to the p-Si electrode. *I-V* curves of the activated

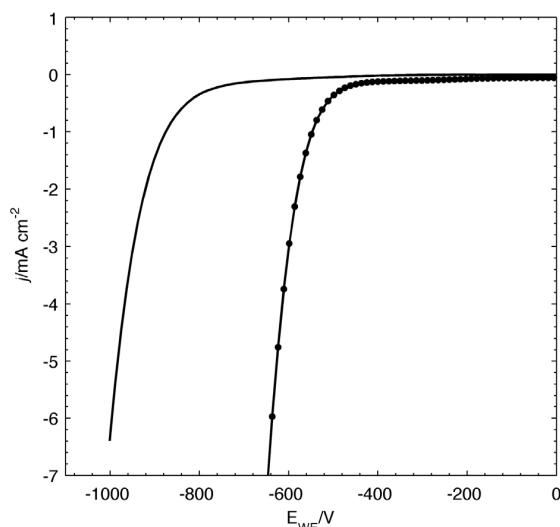


Fig. 2. Current-potentials curves illustrating the effect of diamond activation on the electrocatalytic activity of the p-Si|BDD electrode; before activation (solid line) and after activation (dotted line). Activation carried out by applying double-step galvanostatic pulses of +100 mA and -100 mA several times until reproducible results were achieved, scan rate: $50 \text{ mV}\cdot\text{s}^{-1}$ vs. SCE in $1 \text{ M H}_2\text{SO}_4$.

p-Si|BDD electrode before storage (solid line), and after storage (dotted line), are shown in Fig. 5; the HER onset potentials are -500 mV and -400 mV respectively. The activity of p-Si|BDD does not appear to be deteriorated by this exposure to acidic aqueous media—in fact the performance of the electrode is enhanced, as illustrated by a positive shift of $\sim 100 \text{ mV}$ in the HER onset potential, probably due to further activation of the electrode. These results also confirm that the morphology of the diamond, in particular the grain boundary structure [32–34], is stable, there being no evidence of deterioration of the electrode under these conditions.

3.2.3. p-Si|BDD|Pt assembly

Stability tests were conducted on the p-Si|BDD|Pt by two methods; long-term aqueous acidic medium exposure (280 h), and

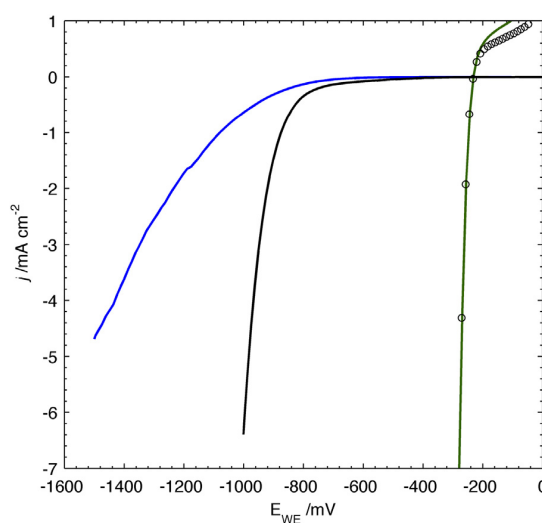


Fig. 3. Current-potential curves for freshly prepared p-Si (blue), p-Si|BDD (black), p-Si|BDD|Pt (green), and a solid Pt electrode (circles). The *I-V* curve of solid platinum electrode overlaps with that of the p-Si|BDD|Pt assembly. Scan rate: $50 \text{ mV}\cdot\text{s}^{-1}$ vs. SCE in $1 \text{ M H}_2\text{SO}_4$.

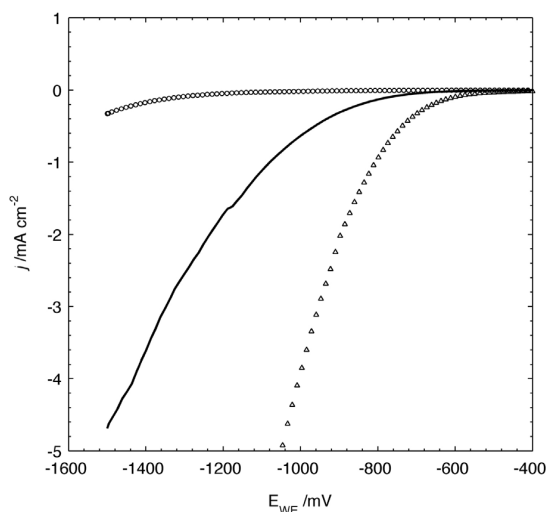


Fig. 4. LSV of p-Si electrodes before (solid line) and after 200 h storage (dotted line) in 1 M H_2SO_4 and after 60 s of HF etching (triangles). Scan rate: 50 mV s^{-1} between 0 mV and -1500 mV vs. SCE in 1 M H_2SO_4 .

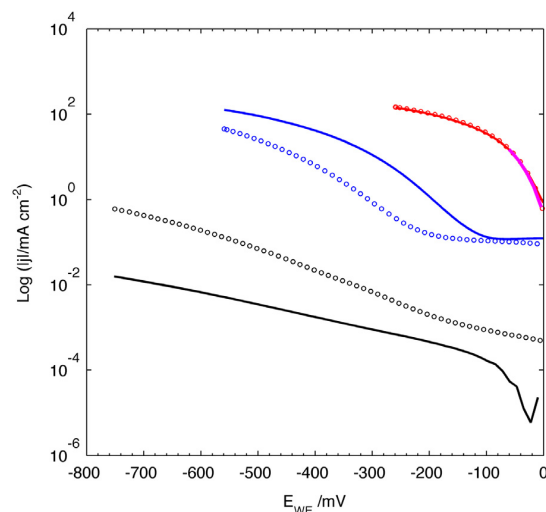


Fig. 6. Semilog Tafel plots of all electrodes; p-Si (black), p-Si|BDD (blue), and p-Si|BDD|Pt (red), before (dotted lines), and after storage (solid lines), compared to a solid Pt electrode (magenta). Scan rate 50 mV s^{-1} in 1 M H_2SO_4 .

continuous cycling in 1 M H_2SO_4 between 0 mV and -400 mV. The two p-Si|BDD|Pt electrodes were prepared as discussed in section 2.4. After-storage the I - V curve of p-Si|BDD|Pt was found to be identical to that before storage (as shown in Fig. 3), giving the HER onset potential at -240 mV. This indicates that the platinum coating on the diamond electrode was stable under these conditions.

A second electrode was cycled 1000 times between E_{OC} and -400 mV (where HER activity is initially $j < -10 \text{ mA cm}^{-2}$). The first cycle, as shown in Supplementary Information (Fig. S1), reproduced the p-Si|BDD|Pt curve shown in Fig. 3. After 1000 cycles and an activation sweep the curve was not significantly altered (Fig. S1). Montilla et al. [26], characterized Pt stability on their BDD based methanol oxidation electrode, (Pt deposited under slightly different conditions to this work). They observed an instability of the Pt coating due to detachment of a significant fraction of the nanoparticles (65% as reported from cyclic voltammogram electrical charge calculations), and considerably decreased currents. It

seems likely that this detachment of Pt was due to the continuous cycling to the OER potential. In our work, cycling the electrode to positive potentials was avoided and good stability therefore observed.

3.3. Tafel analysis

Fig. 6 shows the i - V data in a Tafel plot format. The overpotentials have been calculated with respect to the theoretical HER overpotential (0 mV vs. SHE) under these conditions. The p-Si shows an irreversible decrease in slope after storage, due to the formation of the oxide layer. Moreover, the open circuit potential shifts negatively due to the corrosion reaction. All of the diamond stabilised electrodes displayed significantly higher activity than p-Si as can be seen from the upward shift and steeper slopes in the linear regions in Fig. 3.

As before, the results for p-Si|BDD|Pt and solid platinum electrodes overlap; the curves show significant activity as indicated by a higher exchange current at zero overpotential, and a steeper slope in the linear region. This confirms the high electrocatalytic performance of the Pt particles in the acidic aqueous electrolyte and the formation of a low-resistance contact between the BDD and Pt. In all cases, a mass transport limit seems to be emerging at around 200 mA cm^{-2} . Any increase in resistance at the interface between the p-Si and the BDD due to the growth of an oxide layer would appear as an additional resistance in these plots and the reproducibility of the p-Si|BDD|Pt results indicates that this is not occurring.

4. Summary and Conclusion

Si is a very desirable material for photoelectrochemical applications, but its extreme instability in common aqueous electrolytes, mainly due to oxide formation, is a major obstacle for its use. In this work, the performance and durability of an electrode assembly consisting of p-Si protected with a boron doped diamond coating has been investigated under strong acidic conditions. Highly conductive, corrosion-resistant BDD coatings showed excellent stability after up to 280 h exposure to acidic aqueous media. Unprotected Si degraded very rapidly under the same conditions. Furthermore, a p-Si|BDD|Pt assembly showed good durability and

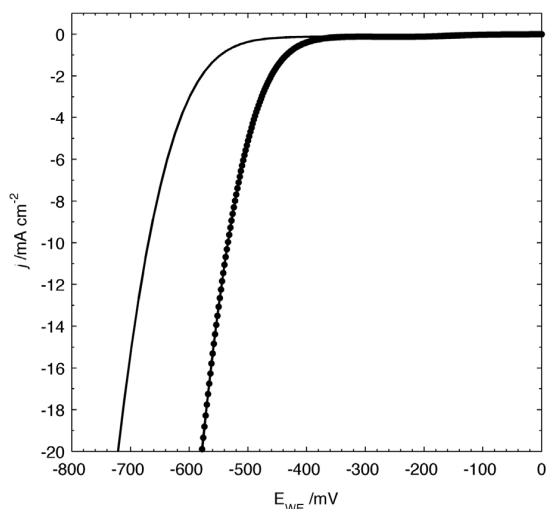


Fig. 5. LSV of activated p-Si|BDD electrode scanned before (solid line), and after 200 h storage (dotted line). Scan rate: 50 mV s^{-1} vs. SCE in 1 M H_2SO_4 .

similar electrocatalytic characteristics to solid Pt. These results also suggest that diamond could be used to protect other semiconductors against corrosion in electrochemical applications. Further research is underway to investigate the efficiency of p-Si|BDD|Pt electrode assembly in solar water splitting cells.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.electacta.2013.10.185>.

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2.5 Supplementary Information for Section 2.4

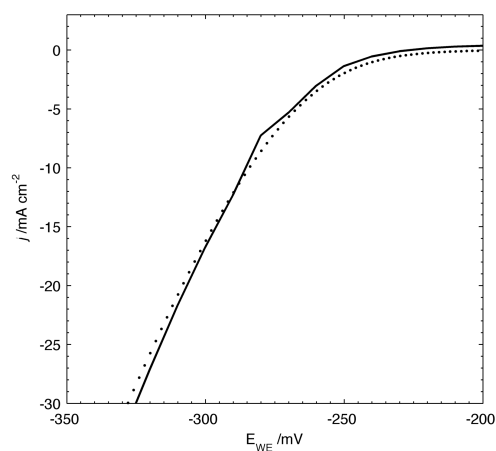


Figure 11 LSV scans of a p-Si|BDD|Pt electrode before (solid line) and after (dotted line) 1000 cycles in 1 M H₂SO₄. scan rate: 50 mV.s⁻¹ vs. SCE

2.6 BDD Characterisation

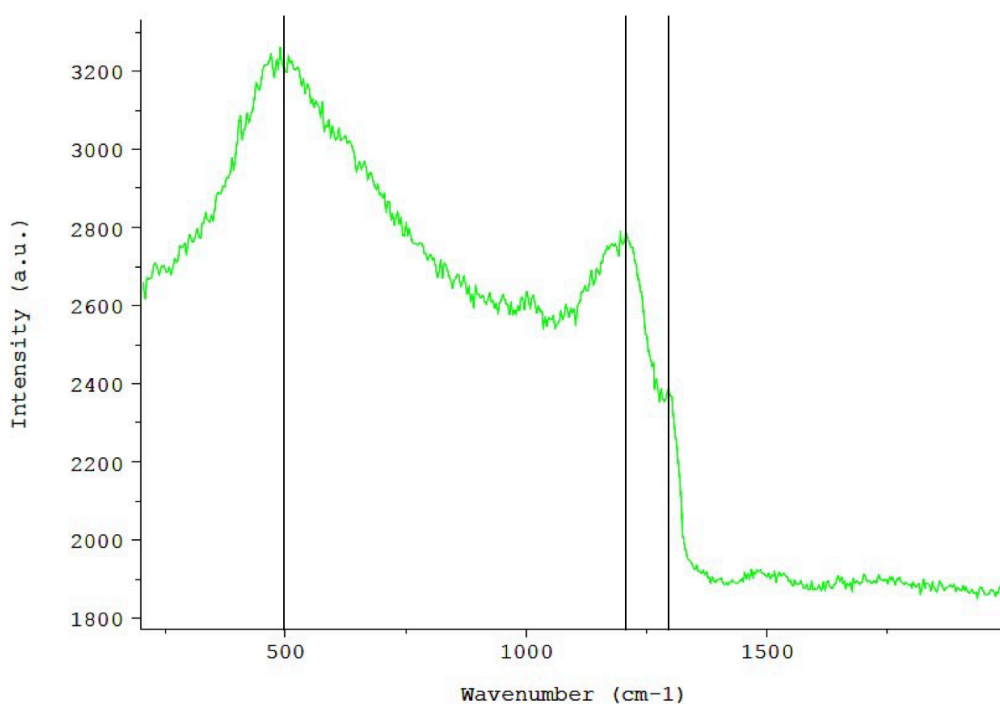


Figure 12 Raman spectrum indicating the phonon excitation bands in highly boron-doped diamond, The peak at $\sim 1301 \text{ cm}^{-1}$ is characteristic for diamond (sp^3 carbon) while the broad bands at 1226 cm^{-1} and $\sim 500 \text{ cm}^{-1}$ are characteristic of the locally disordered structures induced by the heavy boron doping.^[136–138] Data provided by FRAUNHOFER USA

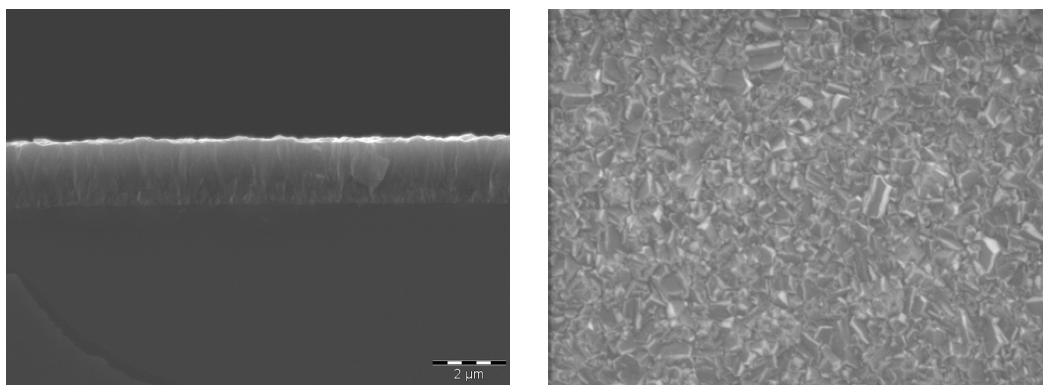


Figure 13 Cross section (left) and aerial (right) SEM images for as-deposited BDD on Si substrates, fabricated and imaged by FRAUNHOFER USA.

2.7 Tafel Analysis

The gradients of the $\log|j|$ *vs.* overpotential graph (*cf.* Figure 6, section 2.4, p. 45), are linear for an activation-controlled reaction and are defined as the Tafel slopes. The Tafel regions were used to extract slopes from all LSV data so that trends in electrocatalytic activity of the different interfaces can be compared. There are seven calculated slopes in total, including that for a reference platinum bulk wire, listed in Table 1.

The data in Table 1 demonstrate several key features:

- The *p*-Si substrate has a Tafel slope value of 192 mV.dec^{-1} which is in agreement with that reported for *p*-type Si materials in dark or under illumination conditions, and therefore is characteristic of the catalytic activity of Si interfaces in driving the HER process.^[29] The increase in the slope after exposure is likely related to severe deterioration by the formation of an interfacial oxide layer on the surface. Hence, a larger overpotential per current density decade is observed, which implies further limitation of the supply of electrons to the interface.
- The electrode performance of the BDD-coated substrates shows a lower slope for the same reaction, and decreases further over long-term testing of the electrode. This behaviour is characteristic of an electrode that improves with cycling, as this is indicative of the enhanced charge transfer across the $2 \mu\text{m}$ -thick BDD coating upon interface activation and catalytic activity for electrochemical processes.
- The performance of Pt catalyst in *p*-Si|BDD|Pt shows a very similar Tafel slope value to that for pure bulk platinum electrodes. With a difference of only 3 mV.dec^{-1} (assuming experimental error is of the same order of magnitude), these values are therefore practically the same. Thus despite the relatively lower performance shown by *p*-Si and interface of the BDD coating solely, the *p*-Si|BDD|Pt performance with the submicron-sized catalyst particles is competitive as compared to that of solid Pt electrode. This excellent performance demonstrates that the developed electrodes practically replace Pt under these conditions, with only a minor difference over the course of the long-term testing, of an additional 8 mV.dec^{-1} . This can be attributed to minor losses of catalyst

particle size or amount at the interface, and are less likely to be indicative of electrode deterioration given that diamond has shown inertness under such electrochemical conditions.

Table 1: Tafel slopes for all p-Si, p-Si|BDD, and p-Si|BDD|Pt measured in aqueous acidic media before and after 200 h of exposure.

Sample name and condition	Tafel Slope (mV.dec ⁻¹)
p-Si before long term exposure	192
p-Si after exposure	341
Pt wire	27
p-Si BDD before long term exposure	112
p-Si BDD after long term exposure	94
p-Si BDD Pt before long term exposure	30
p-Si BDD Pt after long term exposure	38

3.1 Chapter Overview

This chapter begins with a discussion of the advantages and use of Si-based nanomaterials for PEC applications. Section 3.3 discusses approaches to fabrication of black Si, section 3.4 reviews in detail the MaCE method and the several factors that affect this process including the effect of the etchant compositions and type of metals used. A variation of this was developed in this work and described in section 3.5 and 3.6. Section 3.7 presents optical characterisations for the produced Si nanostructures.

3.2 Nanomaterials - The Energy Perspective

Chemical energy production involves catalysis of redox species at the interface of electromaterials to yield gaseous fuel products. This requires the availability of active sites on the electrode interface to facilitate the conversion of solvated redox species. Si is an abundant semiconductor material whose excellent photovoltaic attributes make it an attractive candidate for sustainable solar to chemical fuel conversion. However, its sluggish interfacial kinetics requires improvement. Previously in Chapter 2, Si-based planar photocathodes assembled from readily available Si wafers were investigated for hydrogen generation in conjunction with nanoparticle Pt catalysts. The results implied that the topology of electrode materials can be tailored to enhance photocathode efficiency and stability by employing nanomaterials.

While surface modification and texturing of Si is well-founded in the science of materials processing and manufacturing, it was mainly used to implement Si materials in integrated circuits as well as large-scale photovoltaic solar cells. A major advantage of such a widely-used material is its commercial availability for industrial and research purposes. Many applications have gained from exploiting the superiorly uniform and flat interface that arises from the uniform crystallographic properties of Si wafers. For instance, the fabrication process of diamond coatings, which were implemented previously in Chapter 2, requires such Si interface characteristics, as they are key for precursor nucleation, uniform topology, epitaxial growth mode, as well as the electronic properties of the grown diamond.^[139]

Despite Si generating interest in photovoltaics, it was only recently incorporated in PEC devices. However, due its poor stability, significant efforts were instead devoted towards other semiconductors and catalysts which exhibited better durability during long-term performance. The photovoltaic properties, abundance, and ready availability of Si make it worth reassessing the materials fabrication aspect of photoelectrodes. Could developing nanoscale structures and interface modifications allow Si to fulfil its promise in solar-to-fuel applications?

Certainly, many recent efforts have focused on addressing this question, considering that Si nanomaterials exhibit exceptional attributes, which are desirable for many technologies and devices within biomedical,^[140–142] optoelectronic,^[55,56,143,144] energy,^[53,54,92,145–151] as well as other applications. These nanostructured interfaces may encompass the same chemistry as planar materials; however, their geometrical morphology and nanoscale design render them properties different from those of their bulk counterparts, hence they interact with PEC phenomena in novel characteristics and are influenced by their feature size.

Several reports focused on investigating the beneficial photocurrent and photovoltage capacity of Si, which are tailored by nanoscale modifications, including interfacial features such as nanoporous, pyramidal, cylindrical or wire-like platforms.^[28,31,72,152,153] Nomenclature of these materials depends on their morphology, for instance nanoporous Si is referred to as NP, and the wire morphologies are referred to SiNW. Consequently, because the nanostructured Si appears deep black in colour as seen by the naked eye, the terminology black Si (bSi) is generally used for describing the textured range. Assembling PEC devices from nanomaterial platforms and catalysts has therefore recently emerged in the literature, particularly with the potential use of Si for gaseous fuel products for anodic (e.g. OER),^[81,108] or cathodic schemes (e.g. HER, Nitrogen reduction, CO₂ reduction to hydrocarbon fuels).^[28,92,93,154–156]

3.3 Black Si Nanofabrication

In this chapter, the nanofabrication of bSi materials via etching, and their subsequent characterization is investigated. Fluoride etching is most effective of the processes that are typically employed for surface modification and design of nanostructured bSi interfaces. A range of etching parameters were evaluated to closely assess the factors that directly influence the nanostructuring process, and their subsequent chemical, physical and optical properties. The aim was to obtain adequate assemblies including pristine Si composition for solar-to-fuel conversion devices. Furthermore, a range of spectroscopic and microscopic techniques were used to establish a holistic understanding of the bSi-based materials produced.

Some characterisation techniques are included in the next chapter, such as XRD, which is used to compare substrates based on the degree of crystallinity/amorphous nature of the interface, or high accuracy quantitative/qualitative composition analysis of the substrates using inductively coupled plasma - mass spectroscopy (ICP-MS).

3.3.1 Design Approaches

There are several well-developed approaches that can be used to achieve Si nanostructuring, and are classified into either “bottom-up” or “top-down” approaches, as discussed previously in Chapter 1. For instance, deposition of uniform Si nanostructures, or selective deposition can be achieved using vapour-liquid-solid growth (VLS), which is an example of the bottom-up fabrication of Si nanostructures.^[157–159] In this method, Si ions can be deposited from plasma at an activated interface, to yield 3D structures of varying morphologies.^[31]

Generally, for the top-down approach, nanostructuring of Si requires the etching (removal) of individual surface atoms by chemical reaction. Fluoride is used as the main reagent for the chemical removal of Si due to its vigorous reaction with SiO₂. Therefore, in this approach,

chemical oxidation of the surface Si atoms is a key step. While the techniques that utilise this phenomenon may vary, they include two prominent methods: dry reactive ion etching (DRIE), or wet metal-assisted electroless chemical etching (MaCE). Both of these methods require feedstock of Si wafers and pre-/post-treatments to ensure that desirable etching is achieved. These two methods are the most commonly used in the literature, with dedicated reviews and reports published previously.^[31,64,65,68,160–175]

DRIE can be employed to achieve high aspect-ratio etching while offering advanced and specific nanostructure-profile control such as smooth surfaces.^[65,165] DRIE is a time-consuming process because it requires dedicated instrumentation and adequate facilities. DRIE uses an inductive plasma source which targets surface ions to yield etch-rates in excess of 10 $\mu\text{m}/\text{min}$. Etching directionalities may be either isotropic or anisotropic, and can be controlled by tuning relevant parameters and plasma constituents. Therefore, this technique offers a *top-down* approach for highly uniform nanostructures from flat Si wafers.

On the other hand, solvated fluoride-based wet etching methods offer *top-down* etching with good control over a number of nanostructuring parameters. The simplicity offered by the chemical approach is advantageous, and therefore, this approach is used here for surface modification of Si. This chapter outlines some of the important factors which influence the nanostructuring process and also characterises some of the resultant structures and their properties.

3.3.2 Metal Assisted Electroless Chemical Etching (MaCE)

Chemical etching offers controllable fabrication of a range of Si nanostructures, including a variety of geometries as a result of anisotropic etching depending on the lattice morphology of the Si wafer used. In this mode of etching, Si wafers are immersed in etchant solutions for a prescribed period of time. MaCE has attracted increasing attention over the past several years for a number of reasons. Firstly, it offers a simple approach to nanostructuring, as well as a low-cost avenue which is capable of processing large batches. This is useful considering other techniques require highly specialised instruments or expensive facilities, to yield only a small batch size. Secondly, MaCE provides the capability to control various parameters (e.g. uniformity, length, diameter and orientation) of the nanostructures by tuning the fabrication parameters, such as chemical compositions, concentrations, and immersion time. Thirdly, this technique allows fabrication of epitaxial nanowires without the use of templates, such as that required by VLS, by using metals to pattern the interface. Therefore, MaCE results in a range of nanowire direction which is governed by the crystallographic orientation (anisotropic) of the Si wafer. Besides, the crystalline quality of MaCE etched Si, is relatively high, hence is advantageous for obtaining well-defined nanostructures. Fourthly, the nanostructures etched using this technique can exhibit several profiles depending on the assisting metal used, allowing the control over the resulting structure shape and density. Finally, this method can also be adapted to deposit metal nanoparticles such as Pt, Pd, Au, Ag, and Cu, which are known to be highly active for solar-to-fuel conversion, which will be employed in Chapter 5.

Therefore, MaCE has become increasingly important for Si processing due to its experimental advantages.^[31] The exact mechanism involved in the metal-assisted etching of Si is

currently controversial, due to the complex nature of the interface. Also, the method has only recently been implemented for developing silicon for catalysis.

The first account of MaCE was reported in 1997 by Dimova *et al.*^[176] to fabricate porous Si with the assistance of a sealing aluminium (Al) layer in a solution composed of HF, HNO₃ and H₂O. This was later developed in 2000 by Li *et al.*^[177], who established a method for the catalysed etching of Si in a mixture containing HF and H₂O₂ when a thin layer of noble metal (e.g. Au, Pt) was sputtered on the surface of Si, leading to the nanostructuring effect by creating straight-down pores into the bulk of the material, hence resulting in columnar structures. This etching method has since been further developed to fabricate Si-based nanostructures with various features and sizes, as will be demonstrated throughout the literature survey and experiments studied throughout this chapter.

A simple description of a typical MaCE procedure is illustrated in Figure 14. Generally, a Si wafer is initially coated with a layer of a chosen metal, by wafer immersion in a mixture of the desired metal salt in a solution of fluoride ions and an oxidizing agent. The oxidant's role is to drive the Si oxidation to produce SiO₂. The general chemical oxidation of Si to form SiO₂ and its chemical stability has been described previously for aqueous solutions in Equation 6. The Si oxidation and dissolution mechanisms in HF-containing aqueous solutions varies slightly from fluoride-free solutions, as discussed in detail in this chapter.

This oxide vigorously reacts with the present fluoride ions, resulting in etching of the Si interface. However, the Si atoms beneath the metal coating encounter etching at a rate much faster than that for Si without the metal layer. The faster etching rate results in the metal particle sinking through the Si bulk and generating pores. These sinking particles continually “dig” into the bulk due to the highly active region at the Si/M interface. This process lasts for a certain duration of time, and can be terminated when pores reach a desirable length, where the structures adjacent to the pores form the nanostructures.

Therefore, the type of metal-particle is paramount for an end product of nanostructured Si with desirable morphology. The metal coverage is the primary driving parameter of this method which dictates the resultant nanostructure morphology. The formed metal coating morphology vary widely and are influenced by metal type, coating method and pre-treatment conditions. Additional NP-Si maybe obtained in the bulk or regions of the nanostructures around the metal particle, under appropriate experimental conditions.^[31] Therefore, this tool is a powerful method for the design of intricate Si nanostructures by scalable and low-cost means. This section aims to deliver experimental and theoretical clarification of the factors that affect the etching of Si with regards to the parameters used for the development of SiNW.

3.4 Factors Affecting MaCE

3.4.1 Si pre-treatment methods

3.4.1.1 Contaminations and surface cleaning

There are several crucial parameters for obtaining a uniform and high quality of etching. The surface of Si wafer comprises atoms with unsaturated bonds or dangling bonds. These atoms

are rather unstable and tend to undergo oxidation. The dangling bonds are those responsible for the naturally-formed protective layer, through reaction with oxygen in air, depending on the water vapour content.^[29] While these oxidations take place over a prolonged period of time, the oxide layer may not be as uniform as desired to achieve uniform etching.

In terms of preparing the interface prior to etching, the chemical termination is therefore a key step in order to proceed with the necessary steps that are typically involved in MaCE. Hence, wafer pre-treatments is important in this regards, and careful washing/degreasing is used in order to achieve uniform processing across the interface. The typically-used surface cleaning for industrial manufacture of Si-based devices, began with a procedure called “RCA cleaning”. Originally developed by Kern and Puotinen in 1970,^[178] and later reviewed by Kern in 1980,^[179] it is still widely used for the cleaning and preparation of Si wafers. This process involves the immersion of as-obtained Si wafers in a heated solution (80 °C) consisting of H₂O₂ (30%) and H₂SO₄ mixed in a ratio of 1:3 *v/v*%, for a period of 20 min. This solution is called “piranha” because it is effective for the removal of any organic contaminants because of the oxidizing strength of the hydrogen peroxide.

This treatment also forms a surface oxide on the Si, and removes any metal contaminants from the surface (such as Au, Ag, Cu, Ni, Cd, Co, Cr). These metal contaminants are undesirable because they affect the etching of Si, as will be discussed later in this section. The wafers are then washed thoroughly with deionised water (DI) after using piranha, and dried with a N₂ stream for a clean and clear surface, ready for further processing. Essentially, this treatment achieves a thicker oxide layer than that grown naturally.

Following the RCA clean, the wafer is now oxide-coated with a thick layer, since this process ensures a uniform layer is formed, as compared with that naturally grown on the surface. This oxide layer needs to be removed again by etching to expose a uniform surface and enable subsequent steps, which requires direct charge transfer between Si/M ions in solution. Etching can be carried out using a variety of chemical solutions. A solution mixture containing fluoride ions can be used for the successful removal of the oxide layer, as will be discussed further in following sections.

3.4.1.2 Si-H termination

In addition to oxide termination, the surface can be terminated by several other functional groups, such as hydrogen. For the present experiments involving preparing Si wafers for etching, hydrogen termination is preferred for several reasons:

- From an electrochemical perspective, the hydrogen termination (Si-H) of dangling bonds can occur under all potentials below the oxidation potential,^[29,179,180] irrespective of pH of the solution.^[181] Hydrogen termination is bound to occur for Si immersed in all fluoride-containing solutions. This takes place provided a minimum concentration is used. For HF, this is as low as 10 ppm in water, while for NH₄F it is a 10% concentration. This limits the formation of the oxide,^[182] by ensuring a faster rate of oxide dissociation than oxide formation, according to Equation 7 and Equation 8. For NH₄HF₂ however, the surface reactions are essentially

independent from the concentration. One of the advantages of difluoride is that it buffers the pH and the solvated fluoride, allowing a constant range of pH = 3.2 – 4, according to Equation 9.

- When preparing the surface of the Si for uniform etching, a pre-etch step in NH_4HF_2 is adequate to perform the surface termination. Only a short time (< 1 min) is required for the complete termination of a Si surface.
- The process of Si-H bond formation occurs without significant dissociation or exchange current. This indicates that a minimal loss of material and hence retaining a relatively flat, uniform interface is involved.^[173,183–185] If the interface is used after this treatment to support a cathodic treatment and as long as an anodic current is absent throughout, the interface remains H-terminated, until oxidation/corrosion starts to take place on the surface.
- Oxide growth on Si-H terminated and passivated surfaces is characterised by slow kinetics. The inevitable oxidation process occurs in two stages, where a slow initial growth is attributed to the breakage of the H-termination, and is followed by faster growth which increases exponentially in rate.^[29,186,187] The initial slow oxidation kinetics are favourable for preparing the photocathodes stably and consistently for experimental testing purposes.

Equation 7: The chemical stability of Si in the presence of fluoride ions at pH < 7. This redox equilibrium is established in moderate acidic solutions (between pH = 2 and 3.75) for $[\text{F}^-] = 0.01 \text{ M}$.^[29]



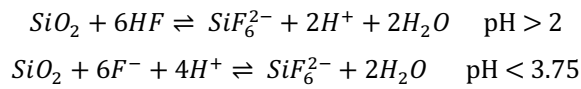
3.4.2 Chemical stability of fluoride intermediates and selection of suitable fluoride media

It is reported that in the presence of 1 M fluoride ions, Si dissolution is possible as dominated by the soluble Si-hexafluoride (SiF_6^{2-}), in acidic conditions (pH < 7), according to the chemical stability of Si species.^[29] For instance, at lower concentrations such as $[\text{F}^-] = 10^{-2} \text{ M}$, the dissolution of the hexafluoride species is bound between pH = 2 and pH = 3.75, as per Equation 7. SiO_2 undergoes etching similarly, reacting with both of the fluoride species in ionised, F^- , and non-ionised form, HF, leading to different chemical equilibrium based on the pH conditions. The stability reactions for $\text{SiF}_6^{2-}/\text{SiO}_2$ at the two pH boundaries (pH = 2 and pH = 3.75) are illustrated in Equation 8. Accordingly, the formation of SiF_6^{2-} involves the reaction between SiO_2 and HF, at pH = 2 boundary, or with F^- at the pH = 3.75 boundary. Meanwhile between these boundaries, the chemical stability of the SiF_6^{2-} makes it exist in its dissolved form. Other stable fluorosilicates may also be present, including SiF_6^{2-} , SiF_3^- , SiF_5^{2-} . In these conditions, SiF_6^{2-} is the most dominant due to their reported values of their ionisation constants being relatively higher than the other species.^[29]

Only a very small portion of HF is ionised to F^- and HF_2^- . The chemical equilibrium of the different ionisations are described in Equation 9. Using HF in its liquid form is not particularly

a practical way of obtaining an etching agent containing fluoride. The experimental handling of HF liquids is very hazardous due to the high electronegativity of the fluoride, which attacks metals vigorously, and poses dangers if it comes into contact with the human body. Fluoride can scavenge all calcium and magnesium it encounters, and therefore extreme care is necessary when dealing with chemical derivatives of fluoride. HF presents this danger due to its liquid form, which makes it more likely to be spilt and therefore increases the risk of exposure.

Equation 8: The chemical dissolution of SiO_2 in the presence of fluoride ions at $\text{pH} = 2$ and $\text{pH} = 3.75$ for $[\text{F}^-] = 10^{-2} \text{ M}$, leads to the formation of fluorosilicates SiF_6^{2-} . Therefore, the stability of the $\text{SiF}_6^{2-}/\text{SiO}_2$ interface is determined by the first equation at the lower pH boundary, and by the second equation at the higher boundary.^[29]



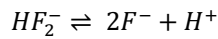
For this reason, the use of HF for experiments at Monash University facilities is controlled and prohibited. Alternatively, fluoride-containing salts can be utilised, such as ammonium hydrogen difluoride (NH_4HF_2), which involves different chemical stability conditions in terms of its ionisation into free fluoride ions. The ionisation of NH_4HF_2 is quite dependent on the constituents of the solution mixture, due to its buffering attributes, which can be directly controlled by varying the acidity of the mixture. In highly acidic conditions, such as those implemented here, and according to Le Chatelier's principle, the fluoride dissolution is relatively weakened by the high proton concentration in the solution.

Ammonium-based salts are often also used to prepare buffered fluoride solutions for the etching of Si and its derivatives. The equilibrium reactions for a system of NH_4HF_2 are described in Equation 9. The stability conditions show that the formation of the fluoride derivatives is dependent on the pH of the system. Such buffering properties are advantageous to regulate the etchant conditions throughout etching. There are only few published reports on the use of NH_4HF_2 for nanostructured Si fabrication.^[172,188,189] For instance, Tomita *et al.*^[189] studied the surface properties of difluoride-etched nanostructures in detail; however, they employed Si(111) wafers, and obtained highly irregular surfaces without columnar structures. On the other hand, Brahiti *et al.*^[172] compared several metals for assisting etching using NH_4HF_2 on a similar grade Si, and showed that highly ordered nanostructures can be fabricated from Ag-, Au-, Pd-, or Pt-assisted etching, however, porosity was accompanied in some cases. Matsui *et al.*^[188] further studied Pd-assisted etching parameters and their influence on the resulting morphology and optical properties, demonstrating the wide-range of bSi materials that can be produced using this method.

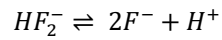
Sim *et al.*^[190] reported on a mechanistic study which investigated “Nanostructural dependence of hydrogen production in silicon photocathodes”, on a range of SiNW prepared from etching in AgNO_3/HF and without the use of an oxidant, over several durations ranging from 10 mins to 480 mins. The resulting SiNW materials in this study showed slow etch rates to achieve the nanostructures, where a nanowire length of $8 \mu\text{m}$ required up to 200 min of continuous

etching, and this method did not yield definitive nanostructures below 120 mins of etch time. Despite these drawbacks, the SiNW were used to establish a mechanistic study for the STH conversion on their interfaces, where facile H_2 production was shown. Because the etching parameters are relevant to this chapter, the performance of these materials in PEC testing is further discussed in Chapter 4.

Equation 9: The chemical stability in an NH_4HF_2 aqueous system. Its buffering characteristic is advantageous considering the solubility of the difluoride $[HF_2^-]$ with its derivatives over the pH of the system. This advantage sets the acidity buffering to a constant, moderate acidic pH (3.2 - 4) in a wide range of concentrations.^[29,191,192]



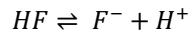
$$K_a = 6.31 \times 10^{-10}$$



$$\log [F^-]^2 / [HF_2^-] = -3.85 + pH$$



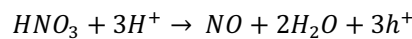
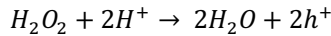
$$\log [HF_2^-] / [HF]^2 = -2.51 + pH$$



$$\log [F^-] / [HF] = -3.18 + pH$$

Ammonium fluoride NH_4F can be used to manufacture NH_4HF_2 .^[193] It was used by other groups because it has been shown to have similar effects to its difluoride derivative, except for exhibiting a higher pH in solution, and a lower ionisation constant for the formation of active fluoride.^[29] Megouda *et al.*,^[163] for example, conducted a short study on its use for etching both *p*-type and *n*-type Si wafers, and showed successful etching, although, reported relatively short nanostructures were obtained from this method. The objective behind this work is to establish a mechanistic study on the use and influence of etchant compositions involving the difluoride. Using the difluoride is anticipated to enhance the mechanism of nanostructure formation in Si, through facilitating a uniform concentration of intermediates at the interface, and due to the kinetics derived from its buffering properties.

Equation 10: Common oxidants that are used for MaCE, and their aqueous reactions provide the holes necessary for the oxidation of Si, in a key step involved in etching.^[194,195]



3.4.3 Influence of metal and oxidant components in the etchant

A MaCE etchant usually consists of three components; the fluoride-based solution, an oxidant and a metal (M). As discussed, the fluoride compound is the primary Si etchant. The other

two components; the metal and the oxidant, facilitate the etching in order to produce specific types of etching. This can be achieved by selecting the type of chemical and mixture ratios.^[31]

3.4.3.1 Role of the oxidant in Si etching

Understanding the exact mechanism involved in the SiO_2 formation and etching for Si nanostructuring, has varied amongst previous reports.^[31,67,163,194,196,197] Common oxidants used in this process include, but not limited to, H_2O_2 or HNO_3 . The redox reaction potential for H_2O_2 lies more positively compared with that of HNO_3 and the valence band of Si. Therefore H_2O_2 reduction is capable of injecting holes deep into the valence band of Si, independent of the Si wafer doping specifications (*cf.* Equation 10 for the ionisation of both oxidants). The strong oxidizing strength leads to rapid Si oxidation, according to the conditions outlined before in Equation 6, forming an SiO_2 coating.^[177,198,199] This process was found to occur over the entire Si interface regardless of the coated metal particles, because holes can be injected directly at the surface of Si and do not require the metal particle to do so. Hence in an etching system composed of fluoride/oxidant media, etching should still take place. However, this etching occurs at a very slow rate, due to the sluggish kinetics of the Si interface towards the adsorption of solvated oxidant species, as outlined previously. Nevertheless, the fluoride media vigorously react with the oxide layer, and therefore, does not contribute to the slow etching kinetics.^[31]

3.4.3.2 Role of the metal particles and deposition techniques

The role of metal particles, when coated or deposited onto the planar Si surface, is to drive the etching process towards the substrate bulk, anisotropically. The presence of the metal particle results in activity variation on the surface of Si. The Si/M interface underlying the metal particle exhibits significant activity compared to the surroundings. This is because the charge transfer through this interface is therefore much more feasible than that at the Si/electrolyte interface. Therefore, the metal particle here acts as a microscopic electrode, at which electrolyte redox reactions can occur at the surface (refer to the mechanism of charge transfer illustrated in Figure 14).^[31,194]

In this process, the SiO_2 layer interfacing with the metal particle undergoes faster etching due to the rapid transfer of charges, and fluoride in the vicinity. While, the Si/electrolyte interface can either undergo slow etching, or as discussed before, porous etching, but not resulting in definitive features. However, due to the vigorous interaction at the Si/M boundary, surface roughness may be introduced, resulting in nanoscale features on the sidewalls. Therefore, as desired the metal particle acts as form of “drill” which etches straight pores, and gives rise to nanostructures with geometries that depends on the size or adjacent spaces between metal particles. These variations are a characteristic of the metal type used to assist the etching process.

It has been reported that the oxidants also undergo reduction at the metal interface, producing a large concentration of holes, which oxidise the underlying Si (*cf.* Equation 10 and Figure 14).^[31,168,194,200] Hence, etching can still occur on regions without the metal coverage (metal-free regions), which in turn contributes to shaping the etched nanostructures, resulting in thin nanostructure tips. From this perspective, it is anticipated that the resultant nanostructures are thinner in the case of etching with H_2O_2 , as compared with HNO_3 , or any other weaker oxidant.

The metal acts as a “charge sink” because of the enhanced kinetics for charge transfer as compared with the Si interface. Hence, the metal particle acts as a microscopic cathode which catalyses the oxidant reduction on its surface. The produced holes are transferred to the underlying Si/M interface in exchange for the electrons generated from Si oxidation (*cf.* Equation 6). This results in a faster-rate oxidation process than that where the metal particle is not present. Hence, it is necessary that the substrate is coated with the metal particles in order to induce fast-rate etching. This can be beneficial in obtaining bSi nanostructures within short durations of several tens of minutes.

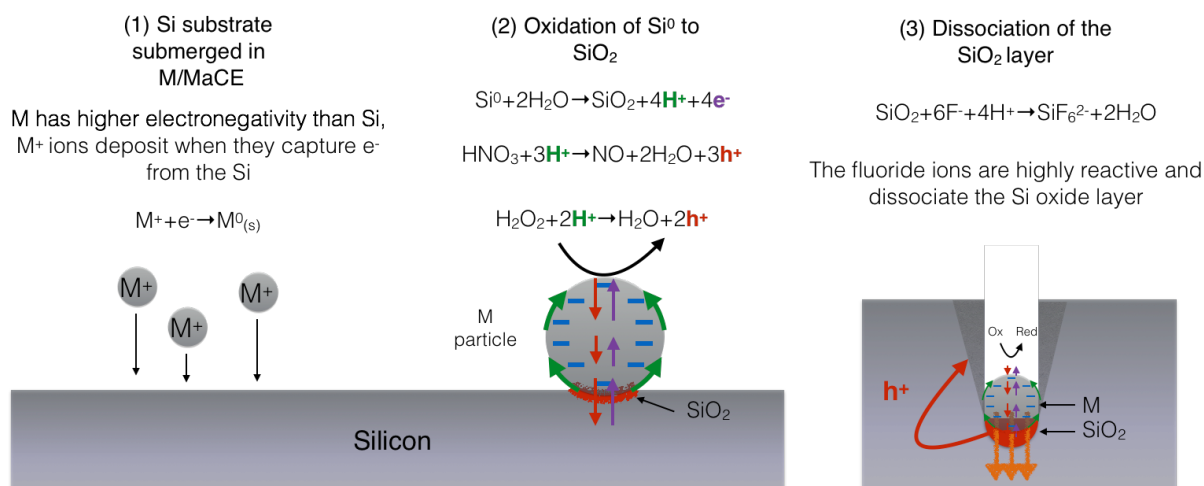


Figure 14 Illustration of MaCE of silicon: (a) etching is initiated by electroless deposition of M onto the surface due to the electronegativity of the metal, (b) Si oxidation step occurs rapidly due to the activity of the metal particle and the oxidants (H_2O_2 , HNO_3), and catalysed by the metal nanoparticle, (c) in the presence of the NH_4HF_2 etchant, SiO_2 forming is rapidly converted to soluble SiF_6^{2-} , this results in the formation of vertically aligned nanostructures.

The morphology of the particle may vary during etching, depending on the electrochemical potentials of the metal/oxidant. When the underlying oxide layer is etched away, the metal particle, or a proportion of it, undergoes oxidation due to the mechanism of a local galvanic cell. Hence, the metal particle sinks to establish a new M/Si bond by the reduction of the metal ions. A step-by-step illustration of how MaCE possibly takes place can be visualised in Figure 14. In this manner, Si nanowires are created when their adjacent pits increase in depth due to the metal particles.

In metal-assisted etching, Ag, Au, Pt and Pd are among the most commonly used noble metals.^[31,198] They can be deposited on the Si surface by several methods including sputtering,^[201] thermal evaporation,^[195] or electrochemical deposition (ECD).^[31] The functionalised metals are patterned in a manner to allow thin and non-uniform coating because uniform metal coatings are known to prevent the etching of nanostructures. This is because they limit the penetration of fluoride species through to the underlying Si atoms.^[194] Electrochemical deposition (ECD) of metal particles is the simplest approach for obtaining surface-dispersed metal particles on Si. There are common electrochemical methods which can be used to yield a range of metal particle

morphologies.^[145,202–205] In addition, metal deposited under illumination can be performed via PED.^[206] These methods can be combined with interfacing templates, such as by using anodic aluminium oxide (AAO) membranes as templates,^[31] which have been shown to yield custom etched Si structures.

ECD also includes electroless deposition (ED) of metal particles from solution. This process is a typical galvanic process which was previously reviewed by Ogata *et al.*,^[35] and the mechanism will be further discussed in Chapter 5. Briefly, ED proceeds for metals that exhibit a redox potential positive to the valence band edge of Si. The solvated ions can spontaneously reduce on Si via charge exchange, as illustrated in Figure 14. Metal coating can also be performed in an oxidant-containing fluoride solution. This allows the deposition process to occur at much faster rates, and exhibit metal growth in various dendrite-like forms. In addition, this results in the formation of pits in the Si interface, because this method is simultaneously, a MaCE process.

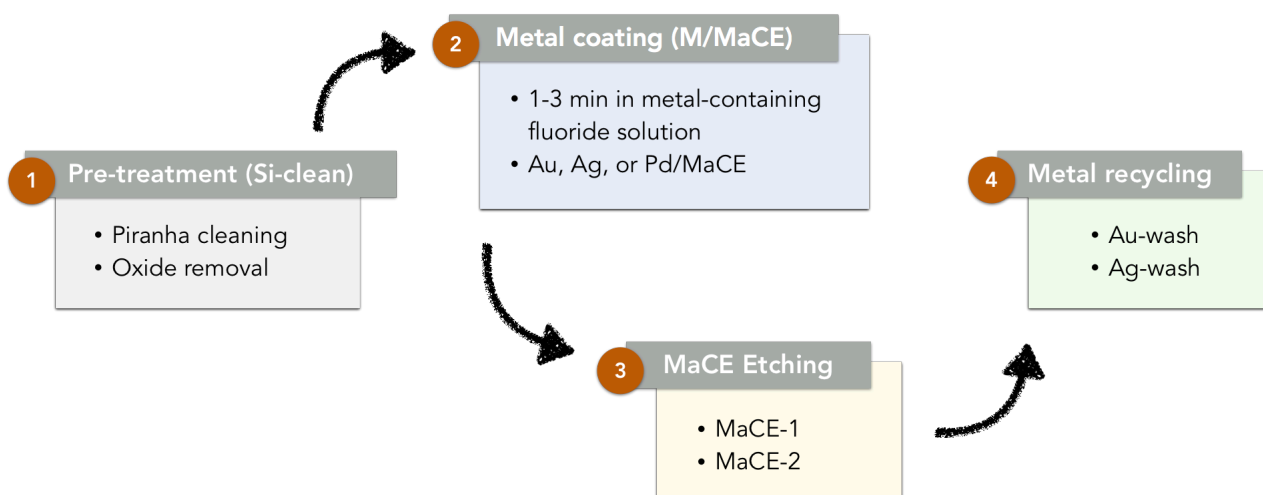


Figure 15 Schematic illustration of all the steps involved in surface modification of Si via metal-assisted chemical etching (MaCE). Information on the etching compositions of each step and its purpose is outlined in Table 3. Steps 2 and 3 are usually combined to simultaneously perform metal coating and etching. However, resolving these two steps allows for better control over the amount of metal deposited and other etching parameters.

The choice of metal for deposition is dependent on its redox potential such that spontaneous reduction occurs at the interface of Si. The reduction potential should be more positive than the valence band edge of Si, otherwise the metal deposition would require to be driven by an external source.^[31] Metal ions with suitable redox potentials include Pt^{4+} , Au^{3+} , Ag^+ , Pd^{2+} and Fe^{3+} .^[31,168,188] The sidewall morphologies were shown to depend on the metal type and deposition method. It was reported that some metals resulted in porous structures, and therefore produced conical-like nanostructures due to the continuous etching of the sidewalls.^[31,197] However, the porous structure formation was more pronounced for Pt, but not for Au or Ag assisted MaCE under the same conditions. On the other hand, the structures produced from Au, Ag, or Pd/MaCE take the form of nanowires of varying structural morphologies.

Table 2: List of etchant mixtures prepared for MaCE etching of nanostructured Si and the electroless coating of Si wafers with noble metals.

Solution		Chemical composition		Purpose
1. Si-clean	Piranha	H ₂ O ₂ (35% conc. in water) : H ₂ SO ₄ (1:3) <i>v/v%</i>		– Cleaning from organic contaminants and metal traces/impurities, – To introduce a preconditioning oxide layer to Si wafers as a protective coating against contamination and in preparation for etching.
1. MaCE	MaCE-1	H ₂ O ₂ 0.4 M	(NH ₄)HF ₂ 2.4 M	– For Si oxide layer cleaning and removal of alkali metal contaminants. – For termination of Si wafers with hydrogen to obtain Si-H interfaces. – Used for etching of Si nanostructures of metal-coated wafers.
	MaCE-2	H ₂ O ₂ 1 M	(NH ₄)HF ₂ 2.4 M	
2. M/MaCE	Au/MaCE	Au/MaCE-1	NH ₃ (1 M)	– Metal (Au, Ag, Cu, or Pd) electroless deposition onto Si via galvanic displacement of Si atoms with Metal ions. Different morphologies of metal dendrites grow on the surface depending on the type of metal used. (Cu deposition to be used later in Chapter 5) – Also used as metal-assisted etchant for longer immersion durations to produce nanostructural features with a range of morphological characteristics based on several factors investigated in this chapter.
		Au/MaCE-2	+	
	Ag/MaCE		(NH ₄)HF ₂ (1 M)	
	Cu/MaCE		+	
	Pd/MaCE		HNO ₃ (1.89 M)	
3. M-wash	Au-wash		25 g/L of I ₂ + 100 g/L KI in H ₂ O	Used for recycling remnant metal dendrites One day's immersion is sufficient for complete metal removal.
	Ag-wash		HCl : HNO ₃ : H ₂ O (1:1:1) v/v%	

3.5 Experimental Methods

A range of chemical solutions were prepared for the purpose of Si wafer cleaning (Si-clean), metal deposition (M/MaCE), etching (MaCE-1 or 2), and metal dendrite-removal (M-wash) in order to obtain pristine nanostructured bSi interfaces. All the chemical solutions used, their compositions, and purposes, are listed in Table 2. The fluoride media used in etchants were composed of NH_4HF_2 , due to reasons outlined previously in section 3.4. The etchants composed of various concentrations of the metal salt, oxidant and NH_4HF_2 . These variations were tested for several etching durations in order to properly establish a mechanistic study of the different factors that affect the overall nanostructuring process. Initially, the Si wafers are washed using de-ionised (DI) water, acetone, ethanol and isopropanol, for the purpose of general cleaning. In preparation of the wafer surface, removal of contaminants (Si-clean) was performed. This included immersion in two solutions namely: piranha cleaner composed of H_2O_2 (35% conc. in water) : H_2SO_4 (1:3) v/v%, followed by oxide removal and H-termination using MaCE-1, whose composition is described below.

The metal-plating solutions (M/MaCE) comprised mixtures of NH_3 (1 M), NH_4HF_2 (1 M) HNO_3 (1.89 M) as the oxidant, and the desired metal salt ($\text{HAuCl}_3 \cdot 3\text{H}_2\text{O}$, AgNO_3 , or PdCl_2) in different concentrations. HNO_3 was selected due to a moderate oxidation strength as compared with H_2O_2 . The etching solution, MaCE-1 and MaCE-2 were prepared from H_2O_2 : NH_4HF_2 with mixing ratios of 0.4 M : 2.4 M and 1 M : 2.4 M, respectively. For the final step of metal-dendrite removal, two solutions were prepared (M-wash):: Au dendrite removal (Au-wash) composed of 25 g/L of I_2 + 100 g/L KI in H_2O , and Ag dendrite removal (Ag-wash) composed of HCl : HNO_3 : H_2O (1:1:1) v/v%. This step was not performed for the substrates prepared using Pd/MaCE. Si wafers of different *p*- and *n*-type specifications were purchased from University Wafer (*cf.* Table 13 for a list of the wafer classes). The wafers were processed as whole. For each step of the surface preparation and etching, the relevant solution was poured in a petri-dish and the wafers were handled using a size-specific teflon wafer holder, which allowed moving the wafers across solutions safely. It is important to mention that the surface of Si showed hydrophobic properties after dipping in fluoride-containing solutions, hence cross-contamination was minimal.

An illustration of all etching steps is demonstrated in Figure 15. Initially, surface cleaning was conducted in piranha clean for 20 mins at 80 °C, then the wafers were allowed to cool to room temperature before washing in DI water, acetone and isopropanol, followed by drying with N_2 stream. This was followed by the complete removal of oxide layer in MaCE-1 for 1-3 mins. Each wafer was then introduced to the appropriate M/MaCE solution for metal coating for 1-3 mins. The metal-coated wafers were then placed in MaCE-1 or MaCE-2 for etching in ambient room temperature and light conditions for different durations of 10, 20, 30, 40, or 60 mins. The etched wafers were then placed in M-wash accordingly, then stored overnight in order to allow for maximal metal-removal. After processing, the wafers were washed by copious amounts of DI water, and stored in DI water for later testing. In the case of Ag/MaCE, the metal coating and etching was performed in the same solution using one-step etching. For Au/MaCE, the metal coating and etching steps were carried out separately, this allowed for additional control over the amount of metal deposited.

The prepared substrates were imaged using SEM technique. The range of bSi substrates that were obtained are listed in Table 14 together with their fabrication parameters and respective figures that illustrate their characterisation methods.

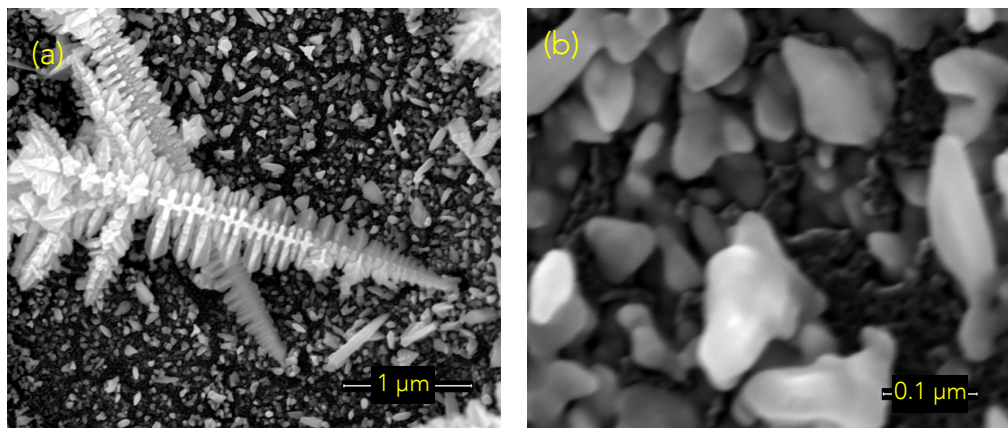


Figure 16 Aerial SEM micrographs of p-Si|Au after Au coating by 1 min immersion in Au/MaCE-2 which contains 0.02 M of HAuCl_4 . The morphology of the coating shows three different types of gold growth: dispersed nanoparticles, micro-sized particles, and fern-like growth.

3.6 Morphology of Produced bSi Nanostructures

A range of bSi nanostructures were produced by MaCE etching. The variation in the morphologies and characteristics of the produced features are a result of using different etchant compositions and concentrations. This was performed with the aim of obtaining a variety of bSi photocathodes to understand the influence on the morphology of the nanostructures obtained. These substrates are later implemented in PEC experiments in Chapter 4 and Chapter 5. The results for the etched substrates are discussed here for Au and Pd/MaCE while those for Ag/MaCE are included in the publication presented in Chapter 4.

In the case of Au deposition, the metal growth exhibits several different structures; dispersed nanoparticles, micro-sized particles, and dendrite-like growth. This variation in growth can be attributed to the nucleation mechanisms of Au on the Si surface in the presence of fluoride and the oxidant. This growth is commonly observed for Au electroless deposition under such conditions.^[207] On the other hand, Ag particles deposit in sphere-like morphologies for a variety of etchant compositions, as shown in previous reports.^[208] Furthermore, Yae *et al.*^[209] compared the resulting metal particle depositions for Au and Ag on Si and found that Ag particles exhibit significantly larger sizes and spherical shapes.

During Si oxidation and subsequent etching, the metal particles undergo continuous redox conversion to establish new galvanic sites in order for appropriate charge transfer to occur. This process is spontaneous for the metal because its redox potential is more positive than that for Si, as described before. When the underlying SiO_2 is etched, the Si/M contact is reestablished, by reduction of the metal on new Si interface. The particle morphology changes in the process. This is evident by morphology variation of the Au particles before etching (*cf.* p-Si|Au in Figure 16) and

after 20 mins etching in MaCE-1 (*cf.* bSi-4 in Figure 18). It is evident that the average size of particles is significantly reduced, besides the shape change, where the formations showed agglomeration of capsule-like Au particles. This suggests that they undergo continuous dissolution throughout the etching process. This also suggests that their catalytic activity during etching was dependent on the activity of specific facets, and hence affected their shapes, which has also been suggested previously by other groups.^[31,197]

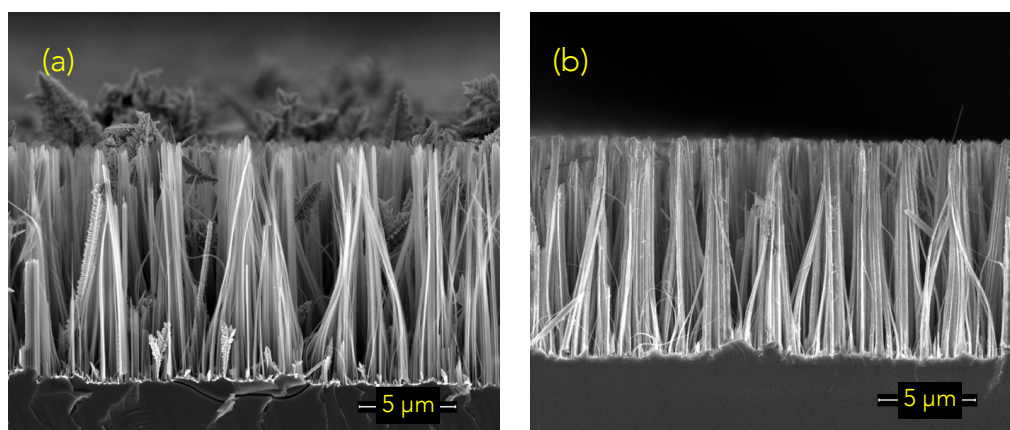


Figure 17 Cross-sectional SEM images of bSi-4 (a) before, and (b) after the complete removal of the Au dendrites using Au-wash which is comprised of I_2/KI in H_2O solution (*cf.* Table 2). The substrate was fabricated by Au-coating in Au/MaCE-2 for 3 min followed by etching in MaCE-1 for 20 mins. This has resulted in nanowires of $\sim 10.8 \mu m$ in length.

Si wafer types (*p* or *n*) were etched by Au or Pd/MaCE for comparison. The nanostructures obtained from Au/MaCE showed relatively uniform density of nanowires across the interface of *p*-bSi as shown for bSi-4 in Figure 17, and resulted in nanowires $\sim 10.8 \mu m$ in length. On the other hand, the same etching parameters on *n*-bSi (*cf.* bSi-17 in Figure 19), have resulted in less uniform nanostructures of needle-like wires with variable heights ranging between a few microns up to $11.9 \mu m$ in lengths. This variation indicates contribution from fluoride and oxidant towards the etching of sidewalls in the case of *n*-Si. The lengthier structures produced on *n*-bSi also indicate that etching on *p*-Si occurs at a slower rate, under the same conditions and time (20 mins in this case). This is in agreement with Zhang *et al.*,^[160] who showed that *p*-type Si (7-13 ohm.cm) etched slower than *n*-type of the same specifications, resulting in shorter nanowires.

In regards to Au- and Pd-assisted etching on *n*-type Si, Pd/MaCE resulted in relatively ordered structures as compared with Au/MaCE. The SEM images for bSi-17, etched by Au/MaCE, and *n*-bSi|Pd, etched by Pd/MaCE, are shown in Figure 19 and Figure 20, respectively. The notable difference is that the nanostructures heights in the case of *n*-bSi|Pd were longer ($13.5 \mu m$) as compared with bSi-17 ($< 11.9 \mu m$). Furthermore, the nanowire thicknesses were more uniform in *n*-bSi|Pd, while needle-like formations were prominent in the case of bSi-17.

One interesting feature in the metal particles is that Pd and Au metal particles show different shapes, while both maintaining similar sizes at the bottom of the pits. The Pd particles showed flat-facets while the Au ones showed capsule-like structures. These results indicate that the

Pd nanoparticles induce faster etching rates in *n*-Si, hence deeper etching has been observed here. This supports findings by Yae *et al.*^[210] for the high catalytic activity of Pd particles in Si etching using oxidant-free etchants. The uniform nanowires in the case of Pd/MaCE are most likely due to the interaction of the Pd nanoparticles with the sidewalls during the etching process. Brahiti *et al.*^[172] reported that the Pd particles were partially oxidized to form Pd⁺ ions during etching, these ions may undergo reduction on the sidewall profile of the nanowires, resulting in uniform lateral etching, and they do so more prominently than Au or Ag metals.

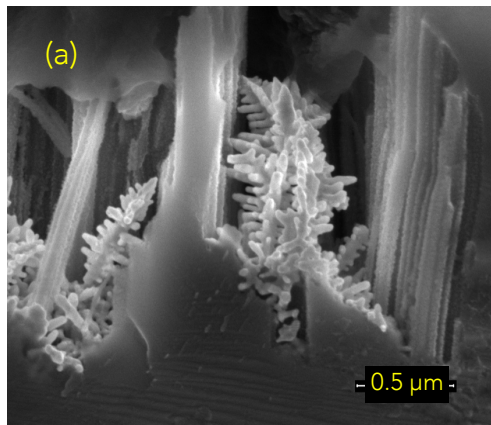


Figure 18 High magnification cross-sectional SEM for bSi-4 showing the morphology of the metal particles after the etching was completed, a general decrease in size and shape can be noted.

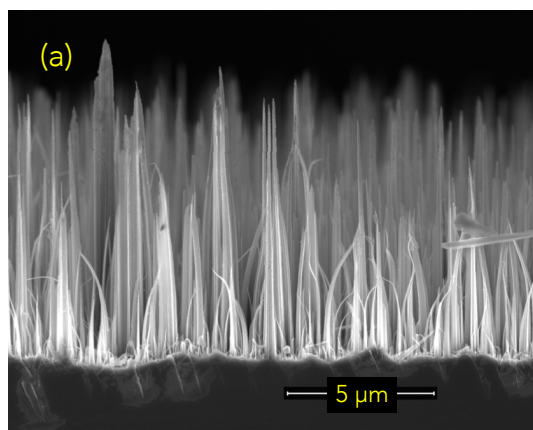


Figure 19 SEM micrograph of bSi-17 (*n*-type, class E) prepared by Au-coating in Au/MaCE-2 for 3 mins followed by etching in MaCE-1 for 20 mins. This has resulted in nanowires of < 11.9 μm in lengths.

The effect of varying the oxidant concentration is investigated for Au/MaCE by using 0.4 M and 1 M of H₂O₂, and for Ag/MaCE by using 1 M HNO₃ and has therefore resulted in different morphologies. The nanostructure tips were observed to be tapered in some cases, and, in other cases, broad and flat-ended. Lower oxidant concentrations resulted in thinner structures, this trend is also observed for Au/MaCE. The broad features were seen to match the same pore-width for low

oxidant concentration, indicating limited Si etching has occurred directly from the fluoride media. The tapered structures were likely produced by fluoride etching of Si, due to the high oxidant concentration used. This is observed when the oxidant concentration was decreased from 1 M (MaCE-2) to 0.4 M of H_2O_2 (MaCE-1). This phenomenon can be clearly noted on the SEM images for samples bSi-(1-8) displayed in section 0, where the nanostructure tips show wire-like morphologies when MaCE-1 was used and needle-like tips when MaCE-2 was used.

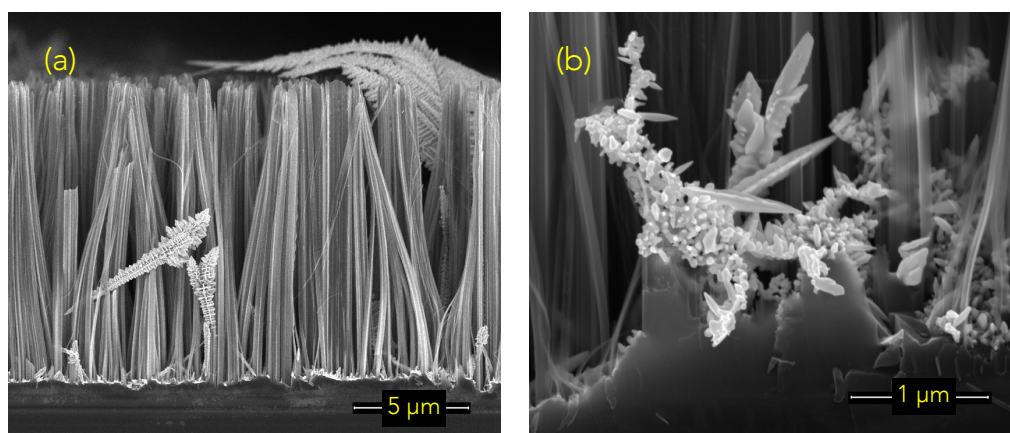


Figure 20 Cross-sectional SEM images for n-bSi|Pd (*n*-type Si, Class E) prepared by Pd-coating in Pd/MaCE for 3 mins followed by etching in MaCE-1 for 20 mins. This has resulted in nanowires of $\sim 13.5 \mu\text{m}$ in length.

In regards to the diffusion of the dissolved species from the etching sites, such as fluorosilicates, several theories have been formulated to explain the mechanism of mass transfer, depending on the type of metal and its morphology.^[31,211–215] One model suggests that the dissolved species at the reaction site, are transferred laterally alongside the walls of the metal and the sidewalls of the produced Si nanostructures.^[31,211,212] Other models suggest that such mass transfer occurs by the diffusion of the Si atoms through the metal particles.^[213–215] Although, this explanation is not yet experimentally proven, due to the difficulty of observing the mechanism of etching *in situ*, there is evidence that the pore bottom is filled.

3.7 Optical Characterisation of bSi Nanowires

Through measuring luminescence, a morphology-specific emission fingerprint is obtained indicating the contributing nanoscale features to these phenomena, is key to understanding the morphology and interactions of materials to illumination. In this section, the optical properties of bSi are assessed with respect to their reflectance/absorbance to incident light in the UV-vis range and their luminescence analysed with Cathodoluminescence (CL) spectroscopy. The objective of this study is to essentially understand how much of incident light will the bSi absorb, and investigate what the absorbed spectra undergo within the material, in order to build a holistic understanding of the interaction of bSi with light, considering the intended use of bSi in PEC devices.

3.7.1 UV/Vis/NIR spectroscopy

3.7.1.1 Reflectance on photovoltaic materials

The factors that result in energy losses in semiconductors have been previously described in Chapter 1. There are additional energy losses that are incurred from the absorption capability of the material for incident light. The energy loss due to the incident light being reflected instead of being absorbed and converted to photogenerated charge carriers, affects the overall efficiency of the material as a photoabsorber. Reflection highly depends on the composition and morphology of the interface. It can occur due to the crystalline structure of the photoactive nanostructures.

Equation 11: The reflectance $R(\lambda)$ (or $R\%$, simplified to R in this work) is also known as the reflection coefficient, and is calculated in percentage from the reflected luminous flux of light $L(\lambda)$, or Luminance, divided by the incident flux $E(\lambda)$, or illuminance. It is usually measured as a function of wavelength (λ), is unit-less and is expressed in percentage: This is calculated according to the equation:

$$R(\lambda) = \frac{L(\lambda)}{E(\lambda)}.$$

The experimental testing of reflection requires that incident and reflected light rays from a surface are coplanar and possess the same angle value. However, bSi nanostructures exhibit 3D structures, and hence testing their reflectance requires recollection of all reflected light with various reflection angles. Accordingly, two different techniques are used to characterize reflection properties for a substrate: (i) Specular reflection is applied for smooth, planar, or perfectly flat surfaces, where the reflected rays from the surface are all parallel to each other, giving a highly defined image of the source, like mirrors. Such is the case when measuring the reflectance of planar *p*-Si substrates. (ii) Diffuse reflection concerns any rough, nanostructured, or microcrystalline interfaces. In this case, the reflected rays' direction highly depends on the shape of the surface features, resulting in loss of image definition due to multiple scattering effects. This method is suitable for measuring the reflectance of bSi nanowires, where light encounters significant scattering due to the nanostructures.

3.7.1.2 Experimental methods

The diffuse reflection of bSi materials; bSi-(5,8) and that of unmodified *p*-Si were measured and compared using a UV/Vis/NIR spectrophotometer (Lambda 950 – Perkin Elmer) equipped with a 150 mm integrator sphere; a hollow spherical chamber where all reflected rays from the substrate bounce back at its wall until it they reach the light detector. The experimental parameters used were similar to those used by Sim *et al.*^[190] Briefly, the spectrophotometer's detector was set to diffuse reflectance mode ($R\%$), the wavelength range scanned from 2300 to

280 nm with a 600 min^{-1} scan rate. Each sample was attached with a transparent PVC film to a sampler holder which lies inside the integrator sphere chamber.

A blank measurement using only an empty auto sampler in the chamber was set before starting the study. The wrap was also measured separately to avoid any interference in our interpretation, only a small change of background with the apparition of a broad peak was observed at 1712 nm. For a better clarity, this peak was removed from the spectra shown in this work.

3.7.1.3 Reflectance results and interpretation

Diffuse reflectance spectra results for *p*-Si and bSi-(5,8) are shown in Figure 21. The three substrates reflected all of the incident light ($R = 100\%$) in the infrared region; 1200 – 2300 nm ($1.03 - 0.54 \text{ eV}$), due to the intrinsic Si band gap energy situated at 1.1 eV. In the 380 – 1200 nm ($3.26 - 1.03 \text{ eV}$) range the three substrates show different reflectance, due to the variation of their interfacial features. The unmodified *p*-Si surface shows the highest reflectance of all three, with a plateau at $R = 65\%$ reflectance, this is a known characteristic of perfectly flat *p*-Si interfaces, that are treated with a surface polish when manufactured (these wafers were purchased with a single-side polish – SSP). In regards to the surface-modified bSi reflectance in this range, sample bSi-8 demonstrates intermediate reflectance, showing a plateau close to $R = 40\%$, while sample bSi-5 reflects the least proportion of light, showing a plateau close to $R = 10\%$.

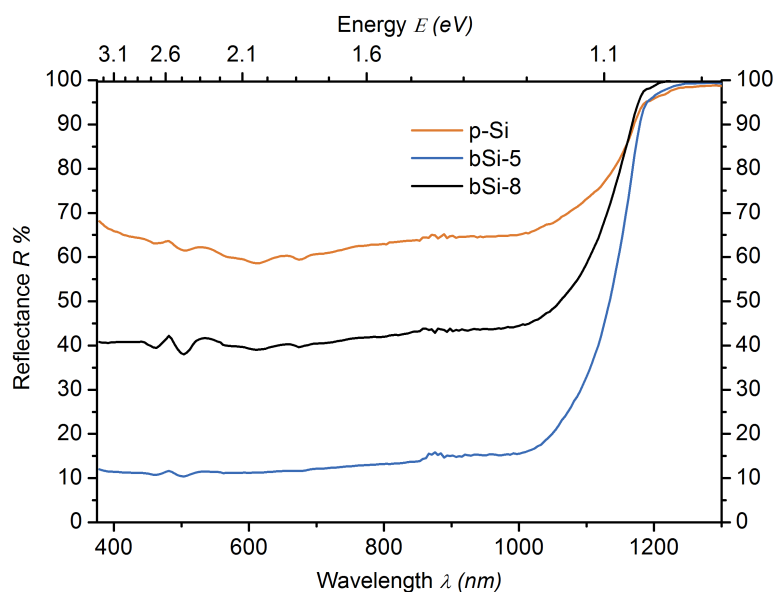


Figure 21 Diffuse reflectance spectra from unmodified *p*-Si and samples bSi-(5,8) photocathodes plot against the wavelength and energy scales.

Such a minimal loss of incident light in this wavelength region demonstrated by the bSi samples is highly advantageous, especially for solar irradiance on the nanostructures (cf. Figure 4 for solar irradiance spectrum AM 1.5). From these results, it is evident that the nanostructuring of

bSi offers interfaces with beneficial anti-reflectance properties, without the requirement of highly-specialised antireflection coatings.^[57] In regards to post-absorption processes that occur in bSi nanostructures; their luminescence, is studied in detail in the following section, for the same range of spectral wavelengths.

The amount of light reflected from the surface is dependent on the topology, considering the preparation steps for both bSi-5 and bSi-8 were different. Both substrates differ in their second etch-step duration in MaCE-2; 10 mins for bSi-5 and 40 mins for bSi-8. Their SEM images in Figure 29(i,l), show that the nanostructures in bSi-5 are more uniform, dense and average $6.4 \mu\text{m}$ in length, than those for bSi-8, which are non-uniform, $30 - 45 \mu\text{m}$ in length, and exhibited a non-dense morphology due to the severe etching of the nanostructure due to the highly concentrated etchant and long duration.

In this manner, it can be explained that the reflectance of bSi-5 was lowest because the diffuse-reflected rays undergo consecutive absorption upon reflection, to yield maximal absorption. This is attributed to the highly dense nanostructure topology. Similarly, in the case of bSi-8, the demonstrated moderate reflectance was likely due to lower secondary absorption of reflected rays because of the lower density of the nanostructures.

Table 3: Cathodoluminescence imaging parameters on NOVA SEM microscope.

Parameter	Spectrum image	Photomultiplier tube (PMT image)
Accelerating voltage	10 keV	
Spot size	5	6.5
Microscope mode	Immersion mode	
Working distance	5.1 mm	
Aperture	50 μm	
Specimen current	2 nA	10 nA

3.7.2 Cathodoluminescence spectroscopy

Planar Si materials typically show very poor infrared (energy $> E_g = 1.12 \text{ eV}$) luminescence due to their narrow and intrinsic indirect band gap.^[216,217] Essentially, this makes them attractive for solar energy devices because this low luminescence implies that only a small proportion of the photogenerated charge pairs undergo recombination. However, the introduction of surface states due to impurities leads to Si lattice deformation through oxidation. This results in the formation of oxygen deficiency centres (ODC) originating from various silicon oxide (SiO_x) nanostructures. The interface morphology hence becomes defect-rich. In this case, incident light contributes to some quantum phenomena due to existing defects. Quantum wells have been reported in a variety of shapes and morphology, and they provide local sites for the confinement of excitons.^[218] The

quantum confinement effect in black silicon is not covered in this study, hence for detailed information on defect types in varying Si morphologies, the reader is advised to refer to specific reports.^[217,219,220]

The luminescence properties of nanostructured bSi can be investigated using CL in an SEM equipped with an appropriate detector. This type of spectroscopy and imaging exhibits two main advantages: the high-energy electron probe used in imaging causes excitations even in insulator materials such as SiO₂, while the high spatial resolution of the technique allows mapping of the interface at the nanoscale.^[218] For this reason, CL spectroscopy has been applied to several morphologies of Si and its oxide including planar bulk substrates,^[221,222] microstructures achieved by laser ablation,^[223,224] and DRIE.^[225] However, the literature lacks detailed investigations on the morphological attributes of bSi achieved via MaCE fabrication.

3.7.2.1 Experimental parameters and data analyses

SEM-CL spectroscopy and imaging were carried out with a FEI Nova NanoSEM 450 FEGSEM instrument equipped with a Delmic SPARC CL system, and an Andor Shamrock 303i spectrometer, with iVac spectral camera. The substrates were subjected to an accelerating voltage of 10 keV. Other spectral and imaging parameters are listed in Table 3. Wide-area spectral surveys were collected for the black Si nanostructures via the photomultiplier tube image (PMT). Selected area CL surveys were collected from aerial and cross-sectional views of the Si bulk and nanostructures.

Equation 12: Mathematical data manipulation steps to obtain spectral energy data $f(E)$ from the measured spectral wavelength data, adjusted for the instrument spectral response and Jacobian transformation in order to properly conduct quantitative analysis to scale in the energy domain.^[226]

$$f(\lambda) = \frac{\text{measured spectrum}}{\text{spectral response}}$$

$$E = \frac{hc}{\lambda}, \quad f(E) = f(\lambda) \frac{d\lambda}{dE} = f(\lambda) \frac{d}{dE} \left(\frac{hc}{E} \right) = -f(\lambda) \cdot \frac{hc}{E^2}$$

The peaks in the measured CL spectra were deconvoluted by fitting to Gaussian line shapes using a MatlabTM program (Fitting software and assistance provided by Ari Mayevsky, School of Chemistry, Monash University, Australia). Data manipulation involved normalising the spectral wavelength measurements over the spectral response of the instrument according to Equation 12 and truncating 15% of the edge data due to low instrument response efficiency. The same equation also demonstrates the mathematical steps involved in the spectral conversion of the data recorded in wavelength units, to the energy domain. This conversion is required because $E_{i+1} - E_i = hc \left(\frac{1}{\lambda_{i+1}} - \frac{1}{\lambda_i} \right)$, hence the signal values are scaled by a factor of $\frac{-hc}{E^2}$.^[226]

Once data adjustments were performed, peak fitting was carried out to locate the individual contributing energy distributions. Although, conventional methods reported in the

literature involve the Gaussian fitting of spectral wavelength data, the method implemented here is recommended for analysing luminescence in energy units, according to a study reported by Mooney *et al.*^[226] This adjustment allows the direct comparison of energies and their spectral profiles across a profile or several spectra. Selected spectral wavelengths of the original CL measurements are attached in the supplementary information of this chapter (*cf.* section 3.9). The energy analysis was then used to compile signal intensity false-colour maps (SIFCM), which reflect the energy signal at each pixel scaled for the global contributions from all scanned pixels in the substrate towards this energy.

3.7.2.2 Results and understanding energy emissions

Most Si/SiO_x structures result in red/orange energy emissions, due to the clustering effects and aggregate surface defects including ODC's. Some emissions in the UV range in the spectra are evidence of the presence of very small features under ~ 1.4 nm.^[227] The CL data displayed in Figure 22 and Figure 24 show the resolved Gaussian fits compiled into energy-specific SIFCM images, together with polychromatic CL and SEM images of the substrate. A range of visible emissions can be observed, centred around 1.26 eV, 1.51 eV, 1.76 eV, 2 eV, 2.3 eV and 2.7 eV. The peak centre locations are shifted slightly in the aerial view CL analysis for the same substrate. All peaks correspond to several luminescent centres characteristic of the bulk Si and the bSi nanowires. UV peaks around 3 eV were only observed for a few pixels on the scan region, with low counts; hence this peak centre was not used in peak fitting.

There are low-energy emissions in the range 1.25 - 1.5 eV (992 nm - 827 nm) are commonly observed for Si-based nanostructures. High-intensity, low-energy emissions on bSi-18, centred at 1.26 eV (984 nm) and 1.51 eV (821 nm). Considering their low energy, and that they are located higher than the band gap luminescent energy at 1.1 eV, it is likely that these emissions are from luminescent centres in Si clusters with nanoscopic or microscopic sizes, and therefore exhibit individual energy band gaps. It has been shown by means of theoretical and experimental analysis that the energetics of nanoscale features induced in Si, including quantum dots, nanowires (NW) and nanoparticles, are highly dependent on the size of these features.^[227-230] The band gap increases with decreasing size of these nanoscopic features. For instance, Sanders *et al.*^[227] modelled the optical luminescence of free-standing SiNW based on a quantum model and reported the inverse energy dependence of luminescence energy on feature size, as shown in Figure 23. Accordingly, the range of emissions from 1.25 - 1.5 eV corresponds to feature sizes of $\sim 3 - 3.8$ nm.

According to their respective SIFCM plots, the majority of the pixels contributing towards this energy centre originate from the SiNW core, as demonstrated by the intense red region in the image. The emissions for these two peaks are different in the case of thinner nanowires; the signal intensity reduces indicating that this signal is morphology-dependent. Finally, the emissions from Si regions underlying the nanostructures also contribute towards this energy centre, down to a depth of ~ 3 μ m from the pore bottom. Beyond this depth, low signal intensities were observed, which fade to minimal counts at the Si bulk. This distance-dependence indicates that defect-rich Si phases are introduced and influenced by MaCE etching, and that these phases extend to a limited depth into the Si bulk, depending on the etching conditions. This is consistent with findings in the literature.^[31]

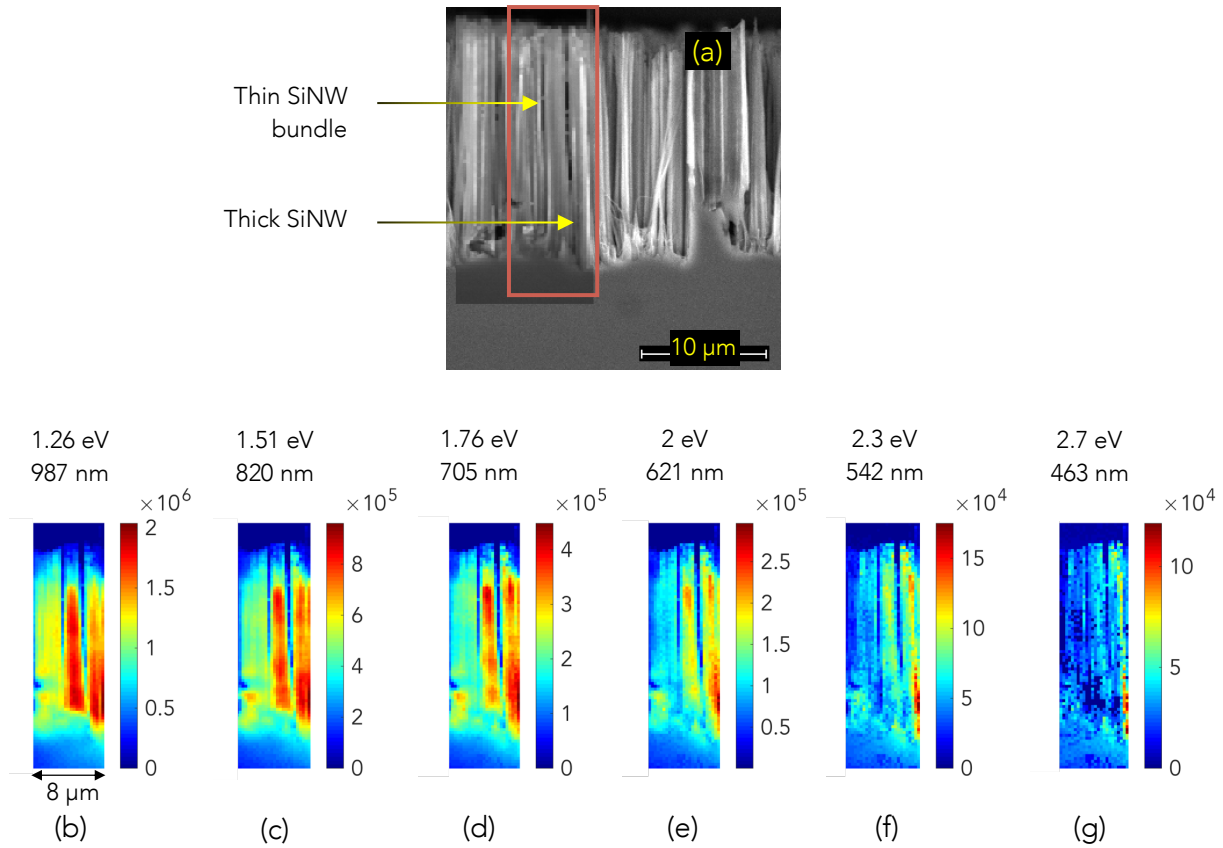


Figure 22 Display of CL analysis on the cross-sectional view of bSi-18 nanowires. (a) PMT image, (b-g) signal intensity false-colour maps (SIFCM) for the pixel contribution of the substrate features towards each energy. The nanowire features include two thicker nanowires, $\sim 1.75 \mu\text{m}$ thickness (RHS of SIFCM) and three thinner nanowires, 800 nm thickness (LHS of SIFCM).

The MaCE process used for fabrication of the standing nanowires, influences the morphology of the interface quite significantly. The fluoride species and oxidizing agent play a role in deforming the crystal lattice structure at the interface. This gives rise to a variably rough surface, with a range of microscopic features from standing NW, down to sub-nanometre roughness. Hence, transitions in these surface features yield emissions in the red wavelengths.^[230] This explains the strong 1.26 eV and 1.51 eV luminescence from the cross-sectional spectroscopy (1.25 eV and 1.5 eV for aerial view) originating from the thicker nanowires, because of the predominant composition of Si in the core. On the other hand, SiO_2 dominates the thinner nanowires,^[31,162,177,231] hence contributing lesser luminescence in this region due to the absence of nanoscale bulk Si clusters. This is also in agreement with the low degree of luminescence (low counts) contributed from pixels at the very tip of the nanowires.

Another red wavelength emission observed from the nanowires at 1.76 eV has been attributed to the presence of nanocrystalline Si clusters at the interface of SiO_2 clusters.^[225,232] At this energy, emissions start to appear from the smaller nanostructures in the aerial SIFCM images, while moderate and high intensities occur in the cross-sections in patches of thick nanowires, indicating a larger contribution from the thicker nanowires. In contrast, the thin nanowires demonstrate lower, uniform luminescence at this particular energy. This is evidence that the

concentration of features in the nanowires is nanowire dependent, which is understood to be related to the chemical interaction during etching. Similar emission was reported for nanostructured SiNW obtained by DRIE.^[225] In addition, amorphous SiOx has demonstrated the same emission, which was associated with the formation of Si nanocrystals during annealing treatments, which is known to result in an increase in the Si cluster size, and reduce the SiOx centres.^[233] It was also explained that the luminescence in this case was related to the phase segregation of Si from the SiOx features, which are likely predominant from oxidation during etching. Therefore in the current study, the luminescence intensity are higher in the core region of the thicker nanowires indicate that they are likely to exhibit an intact Si core, and a SiOx shell.

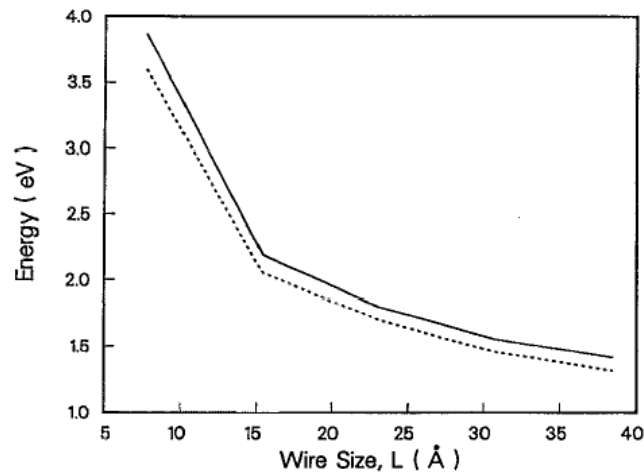


Figure 23 Dependence of energy gap (solid curve) and luminescent transition energies (dashed curve) on the lengths for free-standing Si quantum wires (L) determined by theoretical quantum modelling at 300 K conditions. These wires are significantly smaller than observed in the current study, although they indicate the effect of feature size on the individual band gap energy. Image credit: Sanders *et al.*^[227] reprinted with permissions AIP Publishing LLC© 1992.

For the 2 eV visible emission in the red region of the spectrum, a common peak overlap was observed in the peak fitting. Because the peak centres are relatively close in their values (1.96 and 2 eV), the peak fitting was only conducted for one central peak at 2 eV. The reason for their close energy emissions is possibly due to emissions in neighbouring states. Several groups reported this multiple peak overlap which contributes to this emission. Lin *et al.*^[234] and Wang *et al.*^[235] have reported similar features in CL analysis on SiNW prepared by DRIE, and photoluminescence measured on Ag/MaCE etched SiNW, respectively. Emissions in this range have thus been attributed to two primary components. The red contribution was related to localised excitons at Si/SiO₂ interfaces, and the infrared is contributed by electron excitation through intersystem crossing in single-triplet state transitions (which is explained in ref^[236] for emissions from nanoscale features in the form of wires).^[234–236]

The luminescence at 2.2 - 2.3 eV, is attributed to Si clustering related to a Si-Si centre, E_{σ} , which essentially comprises an unpaired charge delocalised over five Si atoms.^[233] These centres originate from the presence of Si nanoclusters in the amorphous SiO₂ region.^[221,237] Nishikawa *et*

al.^[221] has observed this emission on amorphous Si oxide films that were prepared by CVD, and attributed it very small nanoclusters. Other groups have attributed emission at 2.2 - 2.3 eV to SiOx defects.^[224] This difference may simply reflect the co-existence of SiOx defects and neighbouring Si-Si clusters. Similarly, a visible emission at 2.24 eV, attributed to nonstoichiometric SiOx self-trapped excitons has been also reported by Fabbri *et al.*^[223] on microstructured Si achieved by laser ablation, and amorphous SiO₂ films.^[221]

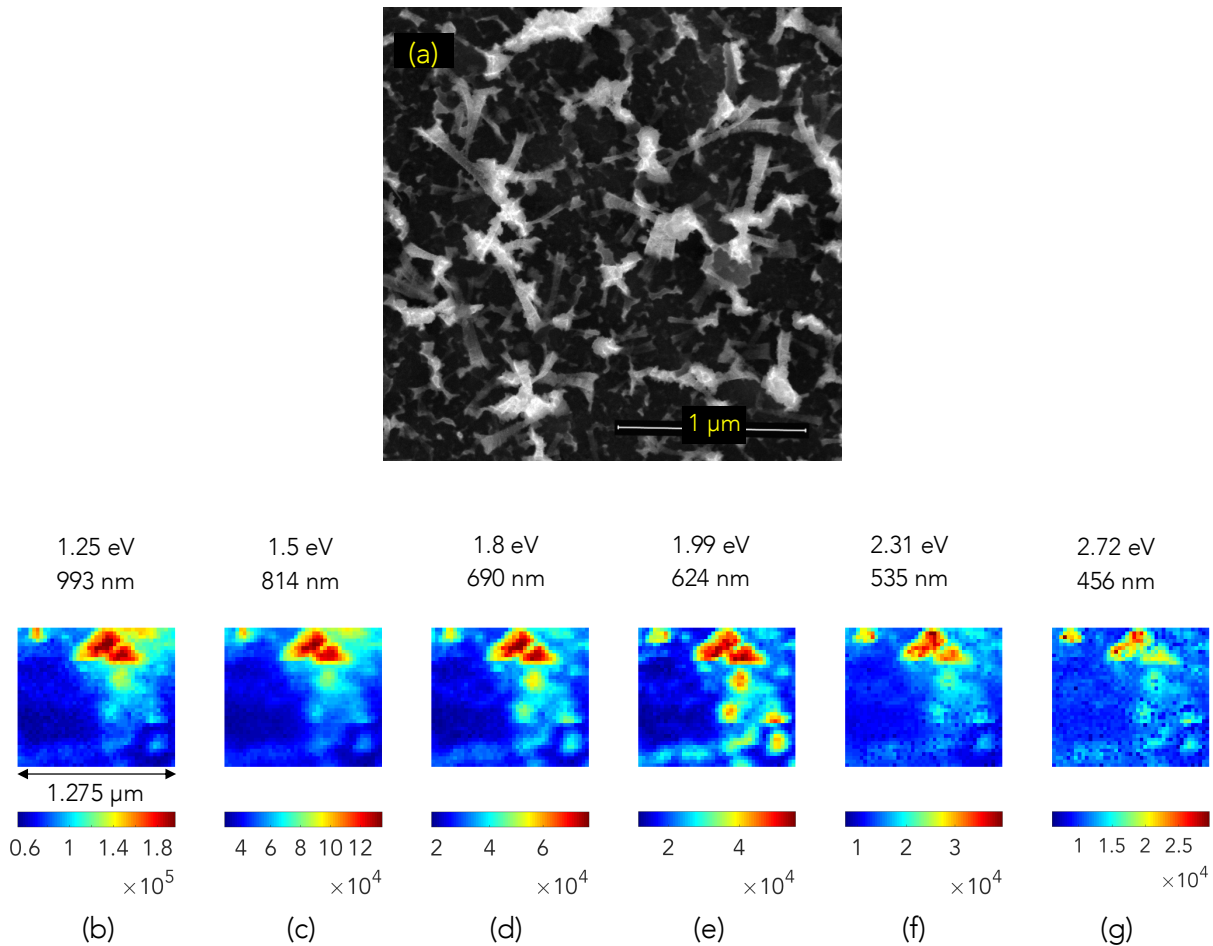


Figure 24 Display of CL analysis for the aerial view of bSi-18 nanowires. (a) SEM image (PMT image not displayed) and (b-g) signal intensity false-colour maps for the pixel contribution of the substrate features towards each energy.

The visible broad band emission centred around 2.77 eV is characteristic of the intrinsic charge pair recombination of amorphous SiOx structures, attributed to existing silicon-oxygen deficiency centres.^[223,238,239] The emission is commonly observed for a variety of Si morphologies, and is a benchmark of the native oxide that develops upon oxidation of Si-Si atoms. It also may arise from coordinated Si-Si defects that are pre-existing in the substrate.

A possible cause for the formation of a large proportion of ODCs is hole-injection from the oxidant into the Si lattice during the etching process. The interfacing Si atoms oxidize and are therefore vigorously etched by the fluoride media. While hole injection in the underlying bulk

lattice structures results in the formation of various ODCs, which are observed in CL analysis. These centres vary in their feature size and hence give rise to a number of observed visible emissions. Furthermore, because the oxidant influences the rate of hole-injection, changing the oxidant concentration is anticipated to affect the luminescence intensity and centre distribution on the nanostructure surface and cores. Therefore, the variation in intensities in the SIFCM images is a result of different geometries of the nanostructures. This change is also based on the solution distribution subject to diffusion-limited mass transfer of the solvated species in the inter-wire pores.

The Si-H_x termination is invisible in a CL spectrum because Si-H_x readily degrades from the accelerated voltage, which is in the order of keV. Therefore, a hydrogen plasma pretreatment renders SiO_x defects non-luminescent, due to stabilising all ODC centres.^[219,240] For instance, Cullis *et al.*^[241] investigated the optical and luminescence properties of porous Si and found that the CL spectra post H₂ plasma termination showed in a relatively flat and broad emission with diminished intensity, suggesting that the CL peaks are quenched due to the hydrogen termination. This implies that the observed CL spectral lines in the current study are characteristic of mostly Si-Si and ODC defect sites at the interface of the modified bSi.

3.8 Conclusions and Results Summary

In this chapter, the chemical fabrication of Si nanostructures (bSi) was achieved by metal-assisted chemical etching (MaCE). The assisting metals used were Au, Ag, or Pd. Specific control of the resulting bSi interface morphology was achieved by tuning the etchants' compositions. A range of bSi wafers of different types (*p*- and *n*-type) were fabricated by etching for 10, 20, 30, 40, or 60 minutes in ammonium difluoride (NH₄HF₂)-based etchants, containing oxidants (H₂O₂ or HNO₃) of varying concentrations. The metals were incorporated as metal salts (HAuCl₄, AgNO₃ or PdCl₂) either during a pre-etching metal deposition step in two-step etching (conducted for Au and Pd), or during etching, in one-step etching (conducted for Ag). In this manner, Si nanostructures were produced with varying areal densities, shapes and dimensions. The produced nanostructures ranged from ~ 0.3 μm to more than 35 μm depending on their etching time.

The physical properties were investigated by electron microscopy, the interface morphology and compositions, using spectroscopic techniques to examine and quantify the surface reflectance and luminescence properties. The reflectance was significantly decreased in the case of bSi as compared with planar Si, where a reflectance just above 10% was observed. The absorbed portion induced excitons in the existing defects, hence exhibit surface and bulk defects. The luminescence patterns from nanoscopic SiO_x structures show characteristic emissions in the visible and IR wavelength range, based on SEM microscopy and the cathodoluminescence spectroscopy technique.

3.9 Supplementary Information

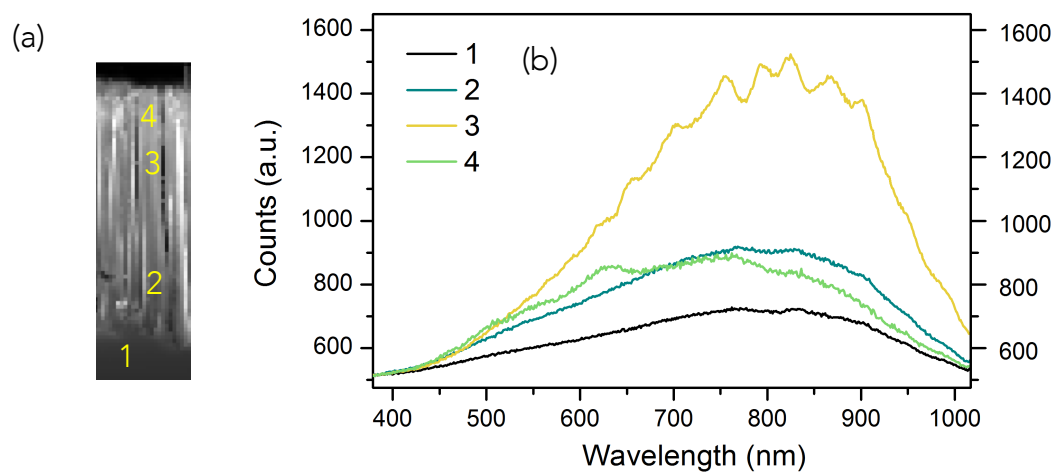


Figure 25 Cross-sectional SEM micrograph and CL profile for bSi-18. The wavelength spectral profiles for spots 1-4 on the SEM image are displayed in the graph.

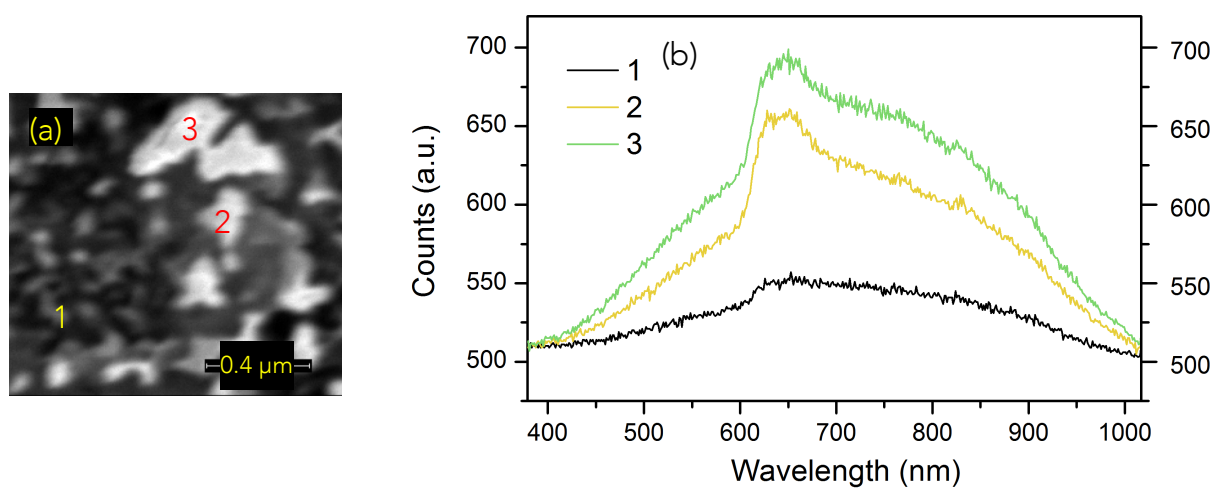


Figure 26 Aerial SEM and CL analysis of bSi-18. The wavelength spectral profiles for spots 1-3 on the SEM image are displayed in the graph.

4.1 Chapter Overview

In recent years, the scope for nanomaterials development to facilitate important solar-to-fuel conversion has been successful in prompting abundant silicon as an excellent substrate due to its suitability for hydrogen generation. Especially, *p*-type Si is a promising material for the H₂-generating photocathode of a water-splitting PEC system.^[28] As pointed out in previous chapters, the energy band-gap of Si is thermodynamically suited to the HER, because it straddles the standard potential of the redox reaction.^[6] However, due to its indirect bandgap, in order for planar Si-based devices to be efficient, the Si photocathode must be highly pure, because impurities add to the inefficiency of a photo-absorber material (*cf.* section 1.2 before). In contrast, surface modified nanostructuring of Si is one pathway to increase the light-absorbing surface facets or areal density of the effective interface. In addition, nanostructuring enhances charge carrier diffusion in the Si material, by reducing the diffusion length required for the transfer of minority photogenerated carriers, through Si material. This nanostructuring allows highly-doped Si to be used instead of planar surfaces, or high purity intrinsic Si, because highly-doped Si is more conductive, hence it is better candidate for a photocathode.

The nanostructured bSi absorbs a greater proportion of incident light than does planar Si, as shown previously in Chapter 3. This is attributed to the light-scattering characteristics of the black Si morphology, where reflected light is absorbed in a secondary manner provided internal reflections take place within nanostructures. Therefore, this phenomenon renders the material visually deep black in colour, depending on the areal density of the nanostructures. Typically for planar Si, the interface forms an oxide by spontaneous corrosion under these conditions.^[29] This layer is of a dielectric nature, hence it acts as charge resistance and reduces the kinetics of redox conversion on the interface. According to Figure 4 which is presented in Chapter 2 (p.45), shows the performance of planar Si interfaces without a protective coating is heavily diminished by the formation of the oxide layer. Therefore, it is important to explore the impact of nanomaterial Si photocathodes, without the influence of added catalysts or protective interfaces, on the challenging Si corrosion problem.

The objective of this chapter is to discuss thorough PEC characterisations on various bSi nanostructures which were developed previously in Chapter 3. The first part of this chapter consists of a paper titled “*Metal-free black silicon for solar powered hydrogen generation*”, published in *Electrochimica Acta* in 2017. In summary; the chemical fabrication of nanostructured black Si nanomaterials involves the use of hazardous hydrofluoric acid, or costly DRIE techniques. Herein a metal-free black Si material was developed via a fast and cost-effective method that is consistent

with scalability requirements in a greener hydrogen based economy. There is much interest in black Si due to its enhanced PEC attributes in comparison to its planar counterparts. This includes the vast interface available for light absorption arising from exceptional light trapping and scattering capabilities, together with its significant electrochemical interface. The result, as demonstrated in this work is an ability to generate hydrogen at close to the maximal theoretical limit. Furthermore, the long-term stability in hydrogen generation is demonstrated during at least 250 hours in a prototype hydrogen cell.

The second part of this chapter presents further performance and stability characterisation, which was performed on the bSi photocathodes after the paper was published.

The effect of the etchant composition on the structure and morphology of black Si impacts the PEC performance and photocathode durability. The chemical fabrication, optical characteristics and morphological attributes of bSi were previously discussed in Chapter 3. The mechanism of etching is also summarised in this paper. The electroless fabrication of bSi involves “assisting” metals such as Au or Ag. To investigate the catalytic activity of pristine Si nanostructures, all metal dendrites must be removed. A chemical “metal recycling” method was used for this purpose, and the resulting pristine bSi electrodes were verified to be completely metal-free using spectroscopic characterisation.

The kinetics of the HER at the surface of pristine bSi nanostructures are not fully understood in regards to their electrochemical interface. The nanostructural projections span the surface of the photocathode, allowing them to protrude in the electrolyte. The available active electrochemical surface area that contributes effectively to the catalysis of redox-solvated species, is significantly larger for nanostructured black Si photocathodes than for their planar counterparts, and thus will have an effect on the performance.

In PEC characterisation, electrochemical techniques such as cyclic voltammetry (CV), linear sweep voltammetry (LSV) and chronoamperometry (CA) were used to study the catalytic performance of substrates in the presence and absence of 1 sun illumination (100 mW.cm^{-2}). This was performed in acidic aqueous electrolyte (1 M H_2SO_4 , $\text{pH} = 0$) against a frit-separated Pt counter electrode. The etching parameters were varied to investigate their effect on the overall HER performance of the photocathodes. Furthermore, the solar-to-hydrogen conversion efficiency, catalytic activity and Tafel analysis of the photocathodes are studied and discussed in the extended supplementary information in section 4.4.

4.2 Published Paper: Boron-Doped Diamond (BDD) Coatings
Protect Underlying Silicon in Aqueous Acidic Media -
Application to the Hydrogen Evolution Reaction.

Black silicon nanostructures for HER

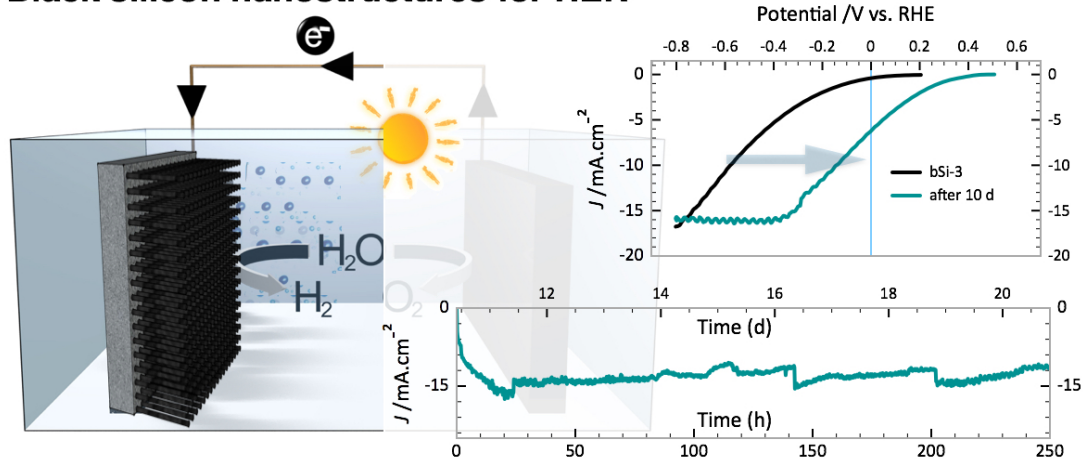


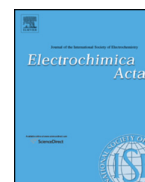
Figure 27

Graphical abstract to accompany published article presented in section 4.2.



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Metal-Free Black Silicon for Solar-powered Hydrogen Generation

Ahmed F. Halima^a, Xinyi Zhang^a, Douglas R. MacFarlane^{a,b,*}^a School of Chemistry, Monash University, Clayton, Victoria 3800, Australia^b ARC Centre of Excellence for Electromaterials Science, Australia

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ABSTRACT

Nanostructured black Si materials prepared by metal-assisted wet chemical etching (MaCE) using HF to drive the nanostructuring, have emerged as excellent light-harvesting materials for solar water splitting. Recently, their remarkable solar-to-hydrogen conversion capability was attributed to their surface oxidation mechanism. However, the same mechanism inhibits the interfacial kinetics within hours, and therefore they are deemed not suitable for a fully-functional hydrogen generating cell. Herein, we investigate the performance and interfacial kinetics of solar-to-hydrogen fuel conversion on black Si photocathodes that, for the first time, are free of any metal catalysts. We developed a near 100% metal-free Si interface by a HF-free etching approach. Systematic analysis and optimization of the nanostructure morphology and photoelectrochemical procedures supported continuous photoelectrochemical hydrogen generation for ~250 h, involving $-1.18 \times 10^4 \text{ C.cm}^{-2}$ of charge transfer at overpotentials as low as -0.2 V vs. RHE. We find that this high-performance of bSi makes it attractive as a green solar-to-hydrogen platform.

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1. INTRODUCTION

Silicon (Si) materials have been at the forefront of photovoltaic technologies due to their abundance in nature and suitable semiconductor attributes. They have been utilized for solar-powered cells due to their band gap ($\sim 1.1 \text{ eV}$) which allows for absorption of a wider window of the solar spectrum, compared to many other semiconductors. In recent years, significant research exploited Si to facilitate direct solar-to-fuel production, including hydrogen which serves as a promising alternative to fossil fuels [1]. These efforts are hampered due to poor redox kinetics at the Si interface [2], suppressed light absorption due to highly reflective surfaces [1], and predominantly due to the presence of its inevitable insulating oxide [1], rendering the material an unsuitable platform to host solar-to-fuel conversion in a fully-functional (PEC) device. A range of modifications have been developed to overcome such limitations, namely the use of noble metal catalysts [3,4], and surface protective coatings [5,6]. These approaches are useful for enhancing the catalytic activity of the photocathode and allow for enhanced stability during prolonged operation, however

they often compromise one another, or are disadvantageous due to being costly and time consuming for scalability [1,5].

Nanomaterials have emerged as superior PEC interfaces in comparison with their planar counterparts, because they offer vast interfaces often accompanied with significant light scattering capabilities. Si surfaces can be processed into 3D nanostructures via well-developed methods including metal assisted electroless chemical etching (MaCE) [7], dry reactive ion etching [8] or epitaxial growth via chemical vapor deposition [9]. MaCE etching is of particular interest as a simple method of spontaneous chemical reaction to achieve nanostructuring. This method relies on spontaneous displacement of surface Si atoms by an oxidant metal ion (such as Au [10] or Ag [11]) in solution. In the presence of a strong oxidant (such as H_2O_2), etching in fluoride media drives vertical pitting into the Si (100) bulk (as illustrated in Fig. 1). Wet etched Si showed two orders of magnitude higher energy conversion efficiencies than those on layers epitaxially grown via vapor deposition [12]. By controlling the chemical parameters in etching, several types of 3D structures can be achieved including nanoporous surfaces [13] and highly ordered nanowire structures (SiNW), referred to as black Si (bSi) [14]. The interface is apparently black due to the absorption of majority of incident photons across the visible spectrum [10,11]. Furthermore, bSi absorbs a wider range of UV wavelengths compared to planar Si (pSi). The

* Corresponding author. Tel.: +613 9905 4540; fax: +613 9905 4597.
E-mail address: douglas.macfarlane@monash.edu (D.R. MacFarlane).

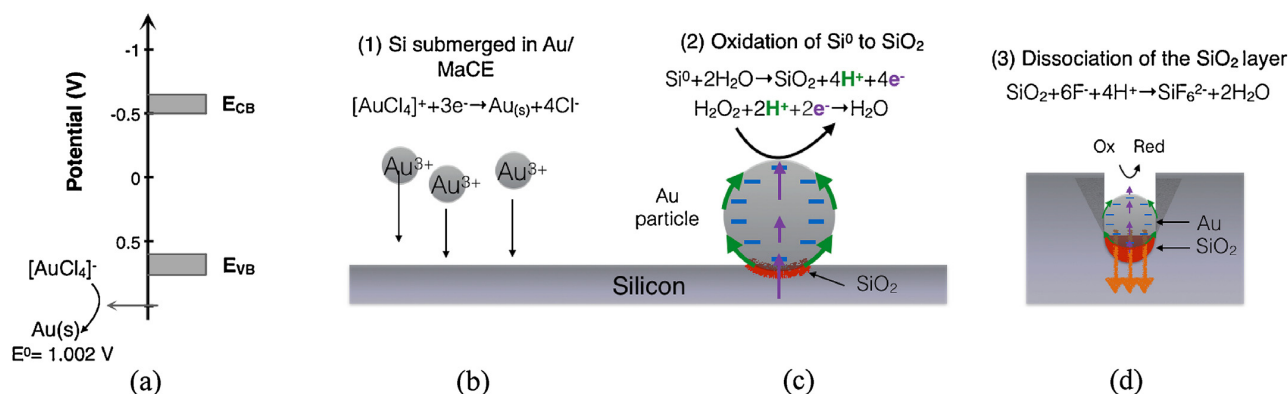


Fig. 1. Illustration of Metal (Au) Assisted electroless Chemical Etching (MaCE) of silicon. (a) $[AuCl_4]^-$ redox potential position with respect to the band positions in Si. (b) MaCE etching is initiated by Au being electrolessly deposited onto the surface due to the electronegativity of the metal, (c) Si is further rapidly oxidized by the action of the oxidant, catalysed by the metal nanoparticle, (d) in the presence of the NH_4HF_2 etchant, SiO_2 forming is rapidly converted to soluble SiF_6^{2-} , this results in the formation of vertically aligned nanostructures.

nanostructuring offers a vast active interface [7], hence they have emerged for applications in drug delivery [15], biosensor devices [16–18], batteries [19], and solar cells [20]. The use of bSi nanostructures has recently emerged for solar-to-fuel conversion. For instance, Ali et al. [21] demonstrated the capabilities of nitrogen reduction using bSi photocathodes. In addition, O'Brien et al. [22] demonstrated viable gas-phase conversion of carbon dioxide to methane using Ru loaded bSi nanostructures.

The PEC performance and stability of nanoporous Si for the hydrogen evolution reaction (HER) has been studied by several groups. Oh et al. [10] demonstrated enhanced catalysis on nanoporous Si containing a high percentage of Au catalyst, with sufficient photocurrents over 5 minutes of continuous operation. Another study by Zhao et al. [13] studied nanoporous Si with a buried Pt nanoparticle layer upon a secondary etch, reported significant enhancement in the HER overpotential due to a positive flat-band potential shift caused by surface oxidation. Initially, the authors observed degradation within 24 h of continuous operation in 0.5 M H_2SO_4 , and claimed to mitigate this issue following a secondary etch that resulted in further positive shift in flat-band potential and a reduced charge transfer resistance across the interface. The authors proposed this leads to stability of at least two months of photocathode air exposure with no performance decrease, until recently Aguiar et al. [23] showed otherwise, that the performance undergoes considerable deterioration within a 100 h operation with more than 95% of photocurrent loss within the first 48 h. Therefore, one may conclude that an interfacial oxide is inevitable for the nanostructures as well as planar Si, as per the Pourbaix diagram [24]. However, for the nanostructures, the oxide interface adds to the performance of the photocathodes until a limiting behavior is observed and the performance significantly deteriorates thereafter.

On the other hand, highly ordered, high-aspect ratio black Si (bSi) offers great advantages for redox conversion due to the vast PEC interface of the nanostructures. Furthermore, the nanostructures offer enhanced photon absorption and light trapping [25], as well as carrier collection capabilities [26]. A study by Sim et al. [11] investigated the nanostructural dependence of hydrogen conversion based on a range of Ag-assisted MaCE etched bSi and the use of these nanostructures loaded with Pt as photocathodes. However, the long term performance of these structures is currently unknown.

Si nanostructures are usually loaded with metal catalysts. Especially for solar water splitting, surface functionalized catalysts are required to aid interfacial catalysis. For instance, this is commonly achieved via electrodeposition of nanoparticles from solution, such as Au [10], Pt [13], Ni/Ni-Mo [27], or MoS_2 [28]. The use of these metals can pose costly challenges in large-scale applications. However, little work has been done on bSi without the use of metals as the catalytic interface in solar-to-hydrogen (STH) conversion.

In the present work, we demonstrate the use of metal-free bSi as photocathodes to drive the HER reaction of solar water splitting, without the use of any catalyst. For this purpose, we have developed a HF-free fabrication method using a two-step MaCE etching to drive effective nanostructuring towards a green and cost-effective approach. We investigate the nanostructural properties of the bSi and their effect on the overall PEC performance for STH conversion under operative and excessive conditions, to probe the optimum PEC conditions that allow for maximal stability. Our findings show that these platforms are breakthrough for PEC Si-based devices, especially for an environmentally benign pathway.

2. Experimental Methods

2.1. Black Si Nanofabrication

Silicon wafers of p-type solar grade, [100] orientation, 500 μm thickness, 1–10 $\Omega \cdot cm$ resistivity with a single side polished, were purchased from University Wafer. The wafers are initially degreased in acetone, ethanol and isopropanol, then rinsed with deionised water (DI) and dried with N_2 for a thorough clean. Si wafers Surface oxidation and cleaning from organic contaminants were carried out in piranha ($H_2O_2:H_2SO_4 = 1:3 v/v \%$) solution at 80° for 20 minutes followed by a thorough DI water rinse, ready for processing.

Table S1 in ESI presents a summary for the chemical compositions of all solutions used for cleaning and etching of bSi, and the steps involved in the etching process for all samples bSi-(1-8). Fabrication was carried out via Au metal-assisted chemical etching (referred to as Au-MaCE in this paper). In total, 8 samples were fabricated through two-step etching, firstly to obtain an Au coating followed by bSi etching in an Au-free etchant, which has shown improved photocathode features and properties,

as concluded from our work. In this study, the Au coating time, etchant concentrations and the etching time are all compared.

All etching was carried out at room temperature in dark conditions in a ventilated fume hood due to the effect of illumination on etching [7]. After Etching, all samples were dipped in acid bath to wash off any metal dendrites formed during etching, and stored in DI water until further use.

2.2. Photoelectrochemical characterisation

All electrochemical measurements were preceded with a 60 s etch in MaCE-1 for removal of an oxide layer if any. Working bSi electrodes bSi-(1,2,6,8) were tested in a standard 3-component photoelectrochemical cell fitted with quartz window, a platinum wire acting counter electrode, and an Ag/AgCl reference electrode, all connected to GAMRY potentiostat. Ohmic contact was established between the WE and a backing copper plate using Indium/Gallium eutectic alloy. The WE surface area was defined using O-ring. Photo/electrochemical experiments were all conducted in 1 M H_2SO_4 . Measurements were collected in dark (ambient laboratory) conditions or under illumination of a 150 W Oriel Xe lamp from Newspec, which was calibrated for solar irradiance ($100 \text{ mW} \cdot \text{cm}^{-2}$) using Suncore solar cell chip and corrected from electrolyte interference.

All photocathodes were stabilised before testing, via an activation process of potentiostatic HER at -1.3 V vs. RHE for 1 min. All j -V data were recorded in 2 cycles and the final cycle reported for statistical stability. Voltages were recorded versus the reversible hydrogen electrode (vs. RHE) unless otherwise stated. The RHE scale offsets $+0.197 \text{ V}$ from a continuously calibrated Ag/AgCl reference used for all measurements and was located easily at the blue y -axis in all j -V graphs.

2.3. Materials characterisation

Scanning electron microscopy; of, planar and cross sections of the samples were collected, and their elemental compositions analysed using energy-dispersive X-ray spectroscopy on a Nova FEI and Bruker respectively, at the Monash centre for electron microscopy (MCEM).

X-ray diffraction spectroscopy; patterns were conducted on bSi-3 sample as well as pSi (as purchased) to determine the crystallinity structure for the substrates and elemental composition at the surface. Spectra were measured on Phillips instrument using $\text{Cu K}\alpha$ radiation by scanning from 20° to 80° (2θ) at a scan rate of 2° min^{-1} .

Inductively coupled plasma mass spectrometry (ICP-MS) The gold content of two Au-etched samples bSi-(3,4) was analysed by using an Optimass 9500 ICP-MS instrument. Substrates were crushed into fine powder using mortar and pestle, and completely dissolved. This was followed by evaporation of silicon tetrafluoride in fume hood. The samples were then diluted and measured against a standard gold solution to inspect for gold residues. The limitation of measurement sensitivity on the instrument is less than 1 ppb(Au); for analysis 0.0288 g and 0.0378 g of Si of bSi-(3,4) dissolved in 50.7 g and 50.8 g of solution, respectively.

3. Results and Discussion

3.1. 3D nanofabrication of bSi photocathodes

Metal-free bSi photocathodes have been fabricated with varying morphologies in order to investigate the effects of nanostructuring on STH conversion. Several in-depth literature reports have been dedicated to understanding how wet etching takes place on Si [7]. In brief, and as illustrated in Fig. 1, the

electroless etching is initiated through the deposition of the metal onto the Si surface due to the formation of a self-assembled local microscopic electrochemical cell, where the metal ion is reduced and the underlying Si undergoes oxidation to form SiO_2 by action of an oxidant, H_2O_2 . In the presence of HF, repetitive etching of the underlying oxide layer leads to sinking of the metal particle and hence drives vertical pitting in (100) Si structures. After the etching the metal components are all recycled by dissolving in an acidified solution, as demonstrated from composition characterization discussed later in this paper. In this work, we use ammonium difluoride $(\text{NH}_4)\text{HF}_2$ as a safer substitute for HF in order to create a scalable pathway. The redox reactions contributing to MaCE are elaborated in the ESI, together with all the experimental methods.

3.1.1. Influence of assisting metal on the MaCE Si nanostructures.

The most frequently used metals for Si wet etching are Ag, Au and Pt due to their redox potential with respect to the valence band positioning of Si [7]. Applying the metal particles to the Si interface can be achieved by several methods including sputtering and electrodeposition, while it can also be achieved electrolessly [7]. The metal assists the etching process spontaneously due to its electronegativity, injecting holes deep into the Si valence band with strengths $\text{Pt} > \text{Au} > \text{Ag}$ in decreasing order. Pt is highly vigorous and has been reported to produce complex etching mechanisms including the formation of helical and non-uniform structures [7]. In this work, 11 samples were fabricated all together: bSi-(1-8) using Au/MaCE, and bSi-(9-11) using Ag/MaCE, with the fabrication steps and etching compositions and parameters tabulated in Tables S1 and S2 of ESI, respectively. We have only conducted SEM analysis on our Ag/MaCE prepared materials for comparison.

The metal ions play two main roles, the local oxidant as well as the etching catalyst. In the former, the charge exchange kinetics are much better at the metal interface than that for Si. In the latter, it increases the etching rate to the underlying Si atoms by orders of magnitude [7]. Successive metal particle deposition onto Si occurs preferentially on defect sites, hence leading to etching in different directions. This does not seem to occur in the case of Ag, however it is more pronounced with metals that induce vigorous etching. For this purpose, we have developed a two-step etching method, similar to that used for coating degenerate Si wafers [15] with these metals due to their high redox potential compared with Si.

The two-step method has been employed for Au/MaCE because it allowed better control over the fabrication process, as compared with the one-step etching commonly used in the literature. The first step achieves a gold coating. This step is the same as the initiating process for Ag/MaCE where Ag dendrites form on the Si surface [7], the only difference is that substrates are etched simultaneously. The following electroless chemical etching process is then carried out in an etchant containing $(\text{NH}_4)\text{HF}_2$ and various concentrations of H_2O_2 . Thus the metal particles in this two-step method act as the catalysts to etch the underlying Si, without deforming the nanostructures, for moderate H_2O_2 concentrations.

Straight pores are formed when either Ag or Au are used, and are vertical for Si with crystal orientation (100), as shown in Fig. 2, as well as in Fig. S3 and Fig. S4 of the ESI [7,29]. The deposited metal particles provide the nucleation sites for successive deposition to form agglomerated metal clusters, which become the active catalyst particles. The irregular-shaped pitting at the base of the nanostructures is evidence for this. The variation in etchant parameters such as the metal type and its concentration give rise to variations in the resulting nanostructure morphologies.

Using 0.02 M concentration, Au electroless deposition on Si grows as nano “ferns” on the surface of the Si substrate, refer to Fig. S2a,b for SEM and EDX analysis, while Ag forms dendrite-like

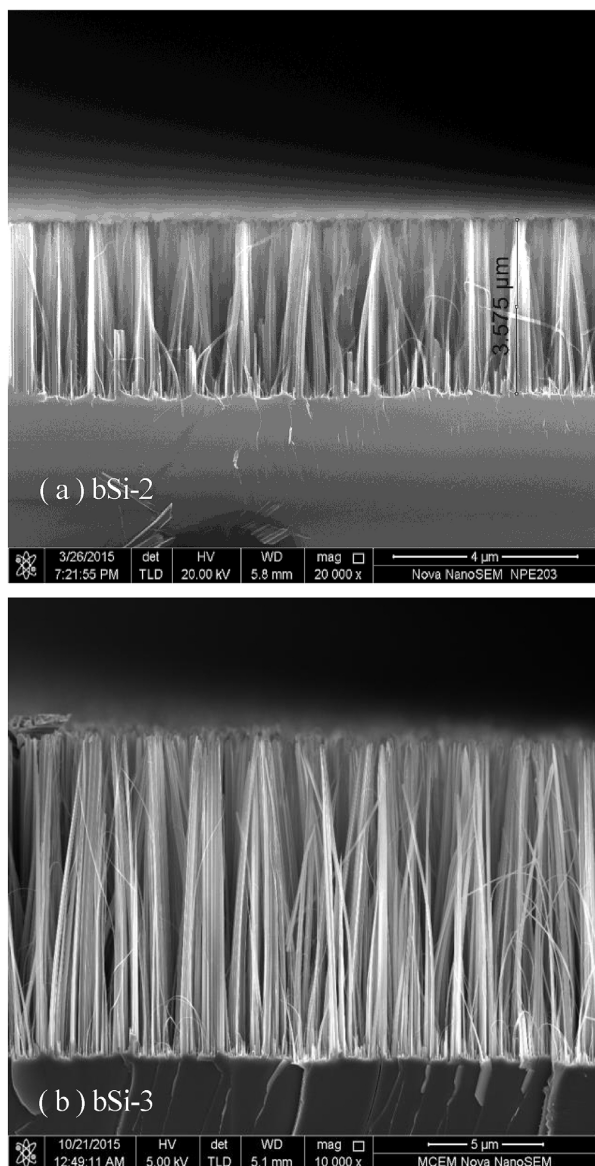


Fig. 2. Cross sectional SEM micrographs of metal-free black Si (bSi) photocathodes. Both micrographs were taken after all etching (20 min) and gold removal was complete. Samples bSi-2 (a), bSi-3 (b) were etched for 20 min each in an aged and freshly prepared etchants containing 0.4 M H_2O_2 /2.4 M $(\text{NH}_4)\text{HF}_2$ respectively, showing the effect of oxidant strength on the height of nanostructures obtained.

structures [7]. The size of the metal cluster deposited on the interface is also influenced by the composition of the etchant and the metal concentration, which we will address later. The morphology of the etched structures assisted by Au and Ag is visualized in the SEM micrographs in Fig. S2 and Fig. S4 respectively. Considering the same etching time and metal concentration are used (20 mins, 0.02 M) in bSi-4,6,10, the higher activity of Au is demonstrated by the significant etching depth as compared with Ag. This is attributed to the more positive reduction potential of Au compared to Ag.

From the SEM cross-sections, the average pore widths are about 75 nm for the Ag-assisted substrates bSi-9,10,11, while the Au-

assisted nanostructures were $\sim 75\text{--}125$ nm. Furthermore, closer analysis shows the possibility of formation of spherical metal particles along with irregular agglomerates that give rise to a range of pore widths. The distance between deposited Au clusters governs the density of the nanostructures. For uniformly deposited layers, the etching therefore gives rise to densely packed nanostructures.

Previous studies have shown that for the gold assisted etching method, vertical pores were created with the same depth regardless of the cluster size, and in some cases, slightly slanted patches indicating rotational force on the particle due to uneven distribution of holes [29]. Results in Fig. S2 also showed that gold assisted etching leads to the formation of highly uniform topologies. The nanowire morphology is consistent across the etched layer, and a flat topology is realized, resulting in a highly ordered nanostructure platform.

3.1.2. Effect of metal concentration in etchant

The coating thickness and roughness depends on the metal ion concentration in the etching solution, and is also influenced by the duration of this coating step. Our ability to control the amount of metal coating in the initial fabrication step has allowed us to study this dependence (refer to Table S1 for all parameters investigated). For this purpose, bSi-3 was coated in 0.01 M HAuCl_4 solution, while bSi-(1,2,4-8) were all coated in a solution containing 0.02 M HAuCl_4 for comparison. The coating time was varied from 1 min such as in bSi-(1,5-8) to 3 min for bSi-(2-4).

A nanostructure length trend can be observed from the SEM images in Fig. S2; for the same coating solution concentration, an increased coating time leads to shorter length such as between bSi-(1,2), which were coated for 1 and 3 min in 0.02 M HAuCl_4 respectively. We attribute this to the effect from a denser metal coating hindering the exposure of the Si interface to the etchant, hence shorter effective etching is observed. On the other hand, and for the same coating time, the increase in concentration of HAuCl_4 from 0.01 M in bSi-3 to 0.02 M in bSi-4 also leads to a decrease in the nanostructure length. This can be attributed to suppressed successive metal deposition from the former solution, and therefore, less etching occurs at the nanostructure tips, leading to longer nanostructures.

3.1.3. Influence of the oxidant on the nanostructure morphology

The second etching step, or for the remaining duration in one-step etching, the coated substrate is dipped in the NH_4HF_2 /oxidant solution. Au-assisted etching commonly uses H_2O_2 as the oxidant, where the concentration highly affects the rate of etching as well as the morphology of the produced nanostructures [7]. In some cases, the direction of etching is governed by the concentration of active oxidant.

The age of the solution plays an important role on the final morphology, as shown from samples bSi-2 and bSi-4 of nanowire lengths of 3.5 μm and 12 μm observed after 20 min etching in aged solution (2 weeks) or a freshly prepared solution stored at 5 °C, respectively. The oxidant plays an important role in etching and determines the rate, and morphology of the etched structures, as anticipated from the results. This faster rate of etching associated with the oxidizing strength of the etchant was further studied; for instance, bSi-(1,2) acquire the shape of thick and cylindrical nanostructures with height of 3.6 and 3.5 μm, respectively. The increase in oxidizing strength of the solution in bSi-(3,4) leads to nanostructures thinner in diameter.

In bSi-(5-8), the peroxide concentration in the etching solution increases from 0.4 M to 1 M. In comparison with the samples prepared with lower peroxide concentrations, the results show much taller nanostructures of height 6.3 μm, 18.5 μm, 31 μm and

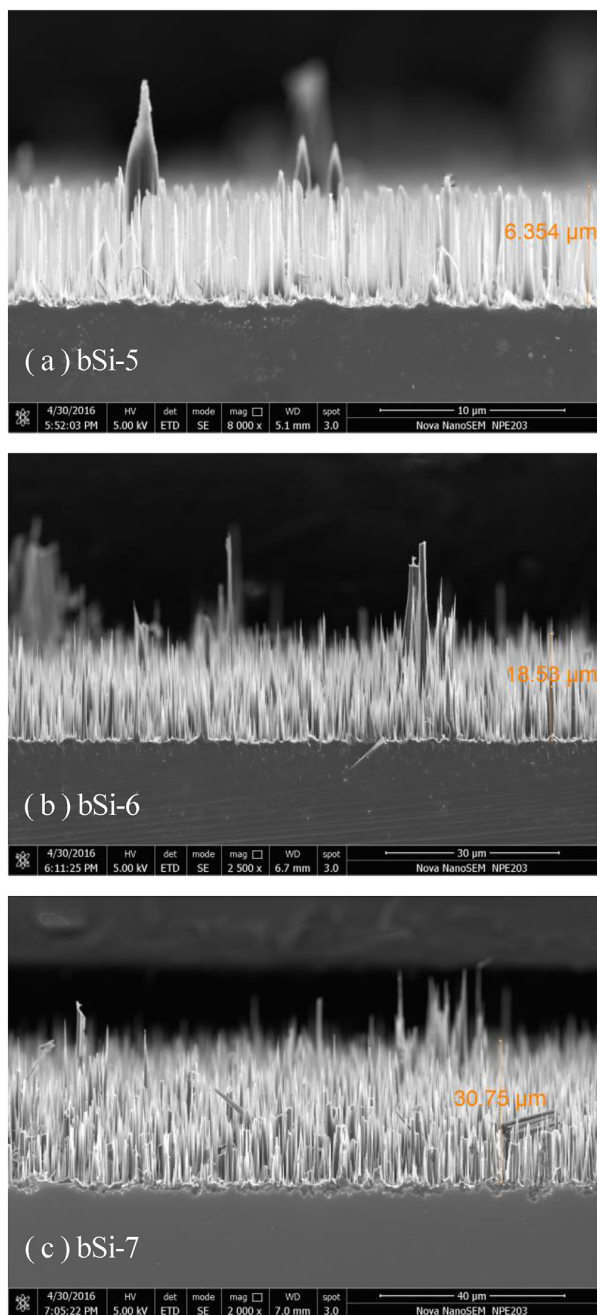


Fig. 3. Cross-sectional SEM micrographs of bSi showing nanostructural length dependence on the etching time. (a) bSi-5, (b) bSi-6, and (c) bSi-7, etched for 10, 20, and 30 min in 1 M H_2O_2 /2.4 M $(\text{NH}_4)\text{HF}_2$ (second etching step) after a uniform gold coating was applied for 1 min in 0.02 M AuCl_4 solution (see Table S1 for more details). The nanostructure heights are 6.4 μm , 18.5 μm and 30.8 μm respectively.

45 μm , respectively. The nanostructures show tapered needle-like structures with more separation.

The SEM images for bSi-(5–8) (presented in Fig. 3 and Fig. S2 show irregular protrusions that are almost twice as tall as the rest of the platform. This has not been well presented in the literature; where major focus has been dedicated to nano-porous/wire/wall structures with a flat topology [7,10,13,30–32]. It is clear that lengthier protrusions scattered around these samples were the

initial depth from etching, however, due to the strength of the etchant, and they continue to etch throughout the nanostructuring stage, even for times as low as 10 mins. This demonstrates that the etchants allow for rapid etching in only very short time. In bSi-8, the majority of nanostructures have an approximate length of 30 μm , due to repetitive etching of the nanostructures, suggesting side-wall etching when the oxidant concentration is high.

3.1.4. Influence of etching time on the nanostructure morphology

The duration of etching in the second step allows for direct control over the lengths of the nanostructures, as desired. We have investigated this dependence in samples bSi-(5–8) where etching was carried out for 10, 20, 30 and 40 mins. A linear height trend is noticed with etching duration, as can be seen in Fig. S4. In a previously reported systematic study [11], the etching rates for up to 500 min of etching were shown to follow an S-shaped dependence rather than linear. For this reason, it has been suggested that bSi etching conforms with a kinetics of nucleation and growth model [33]. In comparison with the Ag/MaCE method reported by Sim et al. [11], our etching method achieves much faster etching rates due to the use of Au/MaCE. For instance, we can achieve nanostructures >6 μm in times as short as 10 mins, which is in some cases, more than 10 times faster.

Several theories have been developed to describe MaCE on Si, however, the formation mechanism at the microscopic scale is still the subject of debate [7,34–37]. Based on our experimental evidence, the metal ions exhibit a more positive reducing potential than Si (refer to Fig. 1), hence spontaneous electron exchange leads to deposition of the gold particles. Si atoms are simultaneously oxidized and dissolved due to vigorous etching by F^- to form solvated fluorosilicates (the redox reactions are illustrated in ESI). The etching rate below the metal particle is several orders of magnitudes higher than along the walls, due to the kinetics of charge transfer at the Si/Au interface, as well as the distribution of holes in the Si around the sinking gold particle [38]. Indeed, the distribution of the metal clusters governs the overall shape of the nanostructures. Furthermore, other parameters have been shown to influence etching rate; briefly a) the rate and depth of hole injection from the assisting metal, b) the concentration of peroxide and fluoride species not only increases the etching rate but also affects the morphology of nanostructures, c) etching rate is dependent on the etching duration. Other factors that influence the morphology of the nanostructures are the type and orientation of Si substrate, illumination and temperature [7,39].

3.2. Formation of metal-free bSi nanostructures

The metal particles remnant from etching can be removed in an acid bath in order to obtain metal-free nanostructures. For Ag-assisted etching, the acid baths typically consist of HCl/HNO_3 acid mixtures [11,40]. It was suspected that unwashed Ag particles that remained at the interface played a catalytic role when Ag/MaCE prepared bSi was used as an electrode [11]. However, spectral analysis has proven that the acid bath treatment is sufficient to replace all Ag-Si dangling bonds with oxygen [41], hence the metal components are successfully removed.

For Au-assisted etching, the photocathodes contain Au dendrites remaining at the interface (as shown in Fig. S2a,b). In order to obtain completely metal-free bSi, and in order to recycle the metal for reuse in the etching process, the photocathodes were given a final treatment in a solution consisting of 25 g/L of I_2 + 100 g/L KI in H_2O . This method is adapted from previous work by Oh et al. [10] In our work, the chemical composition of the photocathodes was investigated after an overnight treatment in the bath.

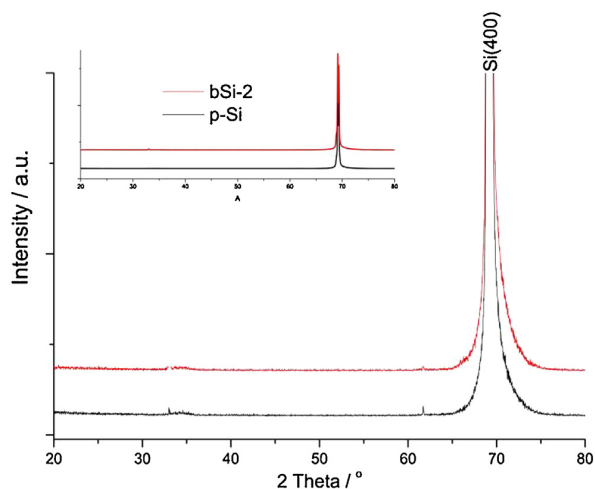


Fig. 4. XRD diffraction patterns measured on black silicon after Au-assisted etching. Inset shows full spectrum. (red) pSi untreated substrates show a distinctive peak for its (100) crystal orientation before $2\theta = 70^\circ$. After etching, gold residues were not found within the detection layer from the absence of their characteristic peaks in bSi-2 (red) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

X-ray diffraction (XRD) patterns were collected to determine the crystallinity of bSi-2, as well as an untreated pSi substrate for reference; the XRD patterns are shown in Fig. 4. A strong peak visible at $2\theta = 69.05^\circ$ is characteristic of the Si (100) crystal orientation of the nanostructures. For bSi-2, the absence of peaks at 38.21° , 44.41° , 64.61° and 77.61° indicate lack of Au (111), (200), (220), and (311) gold cubic metallic clusters, unless their presence is beyond the detection limit of this XRD experiment, or where the crystallinity of the gold is too poor for detection.

For more complete analysis, samples bSi-(3,4) were characterised by ICP-MS after dissolution of the substrate and evaporating all silicon tetrafluoride. The results were very promising, both samples showed no Au peaks above the baseline (lower limits of detection were 1.76×10^{-6} g(Au) per g(Si) for bSi-(3) and 1.34×10^{-6} g(Au) per g(Si) for bSi-4). No other trace impurities were detected in the MS. These results show that an overnight bath treatment is sufficient to achieve an effectively metal-free photocathode via complete removal of the gold components from the nanostructures.

3.3. bSi for Solar-to-Hydrogen conversion

3.3.1. Influence of illumination intensity

Oxide-free bSi surfaces were ensured with a preceding 60 s etch in the etching solution (MaCE-1) prior to electrochemical testing. Firstly, the photocurrent density *versus* the potential polarization was investigated as a function of illumination intensity in the range of $50 - 150 \text{ mW.cm}^{-2}$ (equivalent to 0.5, 1.5 sun respectively). Linear sweep voltammetry (LSV) curves presented in Fig. S7 were collected on test samples in the early lifetime of the photocathode. The y-axis was normalized to reflect unity of the limiting photocurrent density (J_{Lim}) obtained from 1 sun illumination, thus to pronounce the influence of illumination intensity independent of the photocathode performance.

The limiting photocurrent density (J_{Lim}) and the saturation potential (V_{Lim}) correspond to where the photocurrent plateaus, relating to the maximum rate of H_2 evolution possible as the potential sweeps negatively. For this experiment, V_{Lim} is noted at approx. -0.58 V vs RHE . When the light intensity is increased, more photogenerated electrons are available to partake in HER conversion at the interface. This leads to an increase in the photocurrent density without altering the value of V_{Lim} . Hence it appears that J_{Lim} is a determined by illumination intensity, rather than due to enhancement in the redox kinetics. These results are consistent with previous work of Sim et al. [11] (Fig. S6b in ESI). It is worthwhile noting that the polarization curves feature continuous

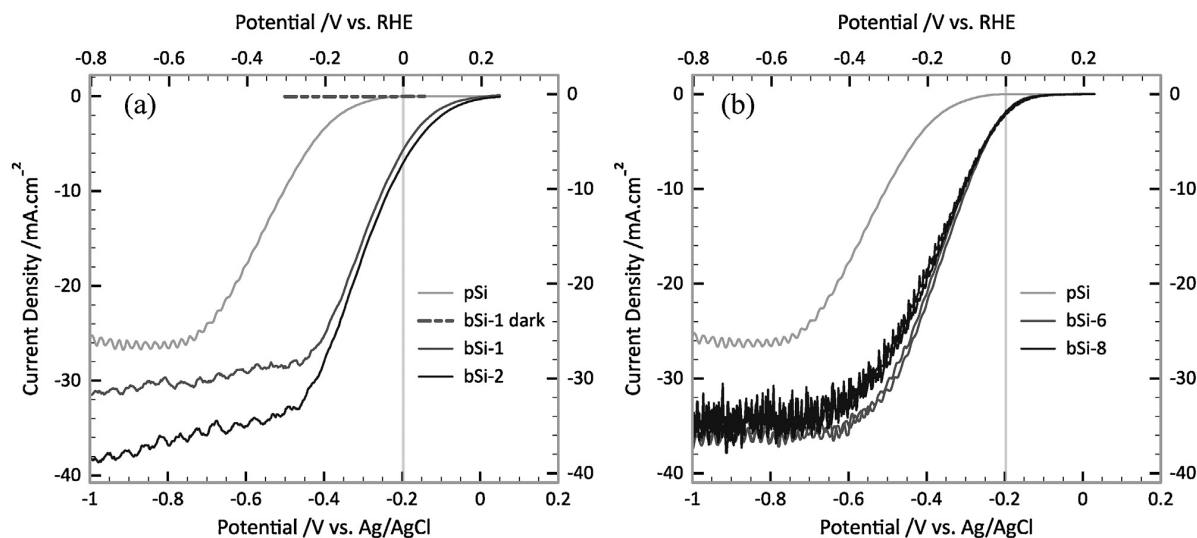


Fig. 5. j-V polarisation for light-driven hydrogen evolution reaction (HER) performed on metal-free bSi-(1,2,6,8) compared with planar untreated pSi performance under the same conditions. Planar pSi photoelectrodes (grey) compared for bSi-(1,2) (a) with bSi-1 in dark (dashed blue) and bSi-(6,8) (b), recorded under 1.5 AM solar simulated illumination. Vigorous H_2 evolution causes fluctuations in the photocurrent near the limit HER conversion rate of each photocathode. Scan rate 50 mV/s in $1 \text{ M H}_2\text{SO}_4$ (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

Table 1
Photoelectrochemical performance of p-type Si planar and nanostructured photocathodes.

Sample	bSi length (μm)	$V_{\text{OS Dark}}$ (V)	$V_{\text{OS Light}}$ (V)	j at $E^\circ(\text{H}^+/\text{H}_2)$ (mA cm^{-2})	Avg. limiting photocurrent (J_{Lim}) (mA cm^{-2})	Saturation Potential (V_{Lim}) (V)
pSi	0	0	0	−0.01	−26	−0.55
bSi-1	3.6	0.07	0.21	−5.7	−30	−0.25
bSi-2	3.5	0.12	0.25	−7.1	−36	−0.25
bSi-6	18.5	0.16	0.19	−1.9	−36	−0.25
bSi-8	30–45	0.14	0.19	−2	−34	−0.25

fluctuations near J_{Lim} due to vigorous hydrogen evolution at the surface of the electrode.

For all photocathodes prepared from the two-step Au/MaCE process, stabilization was achieved by cycling between -1 V vs. RHE and $+0.1\text{ V}$ vs. the open circuit potential (V_{ocp}) after the cell was left to reach equilibrium with the interfacing electrolyte ($1\text{ M H}_2\text{SO}_4$, $\text{pH}=0$) for less than one minute. Fig. 5 compares the photoelectrochemical current density versus the working potential for bSi-(1,2,6,8) and the untreated pSi photocathode (key features are summarized in Table 1).

3.3.2. Dark and solar-driven electrolysis at metal-free bSi

In dark conditions, the performance curves of all untreated pSi and bSi overlap with that for bSi-1 due to their inherently low current densities near the thermodynamic HER potential (Fig. S5). The poor proton reduction kinetics are due to the conduction band (E_{CB}) of Si not being sufficiently occupied by minority carriers (electrons in this case) without the aid of an external bias in dark conditions. A photovoltage effect, which is demonstrated by an anodic potential shift for a given current density facilitated by solar illumination, is seen for all polarization curves, regardless of their nanostructure morphology. This anodic enhancement allows for a higher conversion rate at any given potential cathodic of $E^\circ(\text{H}^+/\text{H}_2)$ of 0 V vs. RHE. Especially at this potential, bSi-(1,2) yield photocurrent density of -5.7 and -7.1 mA cm^{-2} respectively, where noble metal catalysts such as Pt usually begin to reduce protons efficiently [42–44], and compared to its planar pSi which shows as low photocurrent density of -0.01 mA cm^{-2} (cf. Table 1).

3.3.3. Role of nanostructures for photoelectrocatalysis

In order to understand the influence of nanostructuring on the kinetics of the reaction, we have investigated the polarisation dependence of bSi-4 photocathodes throughout the duration of their testing before and after etching the oxide layer. Results in Fig. 6 show that the performance of bSi photocathode is better when an oxide layer is present, as evident from the increase in potential and decrease of catalytic activity for the photocathode after oxide removal. This effect was also observed in previous studies [13], however resulted in hinderance to HER conversion only after the first 48 h of operation, resulting in $>95\%$ deterioration to the photocurrent density [23]. In this study, we carefully investigate the long term performance of our photocathode nanostructures in order to avoid the negative effect of the oxide layer on interfacial redox kinetics, as later discussed in this paper.

A nanostructure reduces the overpotential due to the significant increase of electrochemical surface area. This results in a shift of the j - V polarization curve positively from that for the planar photocathode without affecting its shape. Oh et al. [10] introduced a factor; A_{eff} , which describes the area of an electrode above its projected area. Although their work was conducted on nanoporous Si, the same explanation was employed by Sim et al. [11] to describe the shifts in overpotential observed for photocathodes etched up to 500 mins using Ag-assisted MaCE, to yield nanostructured wires of bSi. A trend was reported where the length of nanostructures increased the positive shift of the potentials, until a limit point is reached, beyond which the reduction in potential is compromised with other competing negative effects arising in the excessive depth of the nanostructures.

In this study, we have varied the nanostructural area with two different nanowire densities; bSi-(1,2) exhibit densely packed structures, while bSi-(6,8) show more widely separated nanowires. Several observations can be seen; the anodic potential shift to the polarization curves from pSi in Fig. 5, the increase of the 0 V vs. RHE photocurrent and the lower saturation potential V_{Lim} in Table 1. The PEC enhancement is larger for bSi-(1,2) indicating that the nanostructures lead to better HER kinetics facilitating a lower overpotential, and an increased photocurrent density for a given overpotential.

The overall J_{Lim} recorded on our samples is also function of the nanostructure morphology. Photocathodes bSi-(1,2,6,8) are of heights about 3.6 , 3.5 , 18.5 and $>30\text{ }\mu\text{m}$ respectively (refer to Fig. S2). The maximum H_2 production rate, which relates to the limiting photocurrent density J_{Lim} , is compared in Fig. 5. A significant increase of J_{Lim} was observed from -26 mA cm^{-2} in the case of planar pSi to -30 , -36 , -36 and -34 mA cm^{-2} for bSi-(1,2,6,8), respectively (refer to Table 1). Considering that orthogonal solar illumination of 1 sun (equivalent to 1.5 AM) provides $2.7 \times 10^{17}\text{ photons cm}^{-2}$ [45], the maximum theoretical photocurrent density acquired from a single junction Si of $\sim 1.1\text{ eV}$ band gap is -43 mA cm^{-2} [46], while photocurrents in the range 20 – 30 mA cm^{-2} are reported from other experimental reports for planar Si [1,46]. Thus it is clear that our bSi structures increase absorption

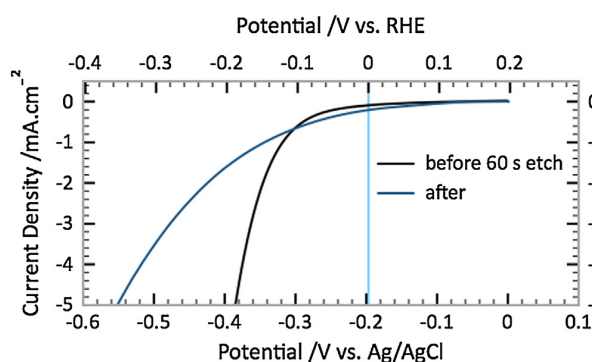


Fig. 6. Effect of the oxide layer on the performance of nanostructured bSi photocathode performance for hydrogen evolution. Polarisation curves for bSi-4 before (black) and after (blue) a 60 s oxide etch demonstrates the positive role of the oxidation on nanostructures contrary to its effect for the planar photocathode (cf. Fig. S6 of ESI). The etching was carried out in a MaCE-1 solution (H_2O_2 (0.4 M); $(\text{NH}_4)\text{HF}_2$ (2.4 M)) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

and therefore the photocurrent. This has also been demonstrated by Garnett et al. [25] who measured the path length of photons in nanostructural Si (fabricated using reactive ion etching), and reported extraordinary light-trapping where the path length of incident solar radiation was enhanced by a factor of 75, well beyond the randomized scattering limit (~ 25) without the use of any antireflection additives. Further enhancements can also originate from sub-band excitations [11].

According to Sim et al. [11] the photocurrent density increases with the increase of the nanostructural heights, up to a limit before the trend is reversed, as observed here. It has been shown that excessive height of the nanostructures leads to the introduction of surface traps and defect sites [11], and an increase in surface charge recombination due to an enlarged depletion region in a lengthier nanowire [10,25,47]. This phenomenon is pronounced in bSi-(1,2) where an increase in length leads to a decrease in the H_2 conversion rate. Our photocathode performance lies beyond the maximal height J_{Lim} enhancement limit, confirming the inverse proportionality.

3.3.4. Durability of bSi photocathodes

The performance of bSi-3 was exploited in a long term experiment that spanned ~ 16 weeks under PEC operating conditions. During this period, potentiostatic Chronoamperometry

(CA) was recorded for a total duration of 450 h with total amount of $-1.61 \times 10^4 C \cdot cm^{-2}$ of charge generated at -0.2 V vs. RHE in 1 M H_2SO_4 under illumination. Meanwhile, potentiodynamic scans were recorded intermittently for the freshly prepared

photocathode, after 1, 10 and 19 days of testing as shown in Fig. 7a. We believe that this is the longest comprehensive test conducted on nanostructured bSi photocathodes under operational conditions.

The photocurrent increased during the initial 24 h period until a steady conversion rate was achieved. This reflects a j -V polarization with 470 mV positive shift requiring lower overpotential to drive the same rate of HER conversion and no loss of J_{Lim} . While further CA for nine days facilitated a stable photocurrent, as shown in Fig. 7b for the first 190 h of the experiment (cf. Fig. S8 for full scan). The fluctuation in data are attributed to vigorous hydrogen evolution and when the electrolyte was replaced. The polarization scan after ten days showed first signs of PEC deterioration, with an ~ 50 mV increase in overpotential and a decrease in the limiting current of up to $4 mA \cdot cm^{-2}$ as at -0.8 V vs. RHE. The performance of the photocathode slowly degraded after ~ 250 h of continuous HER after a total charge transfer of $-1.18 \times 10^4 C \cdot cm^{-2}$. After 450 h, the yield photocurrent was recorded to be $-1.79 mA \cdot cm^{-2}$ which matches the magnitude of the freshly prepared photocathode. The final polarization curve shows slightly lower catalytic activity than that before the experiment.

These results can be explained by the inevitable growth of an interfacial oxide layer. However, its effect is remarkably different from that on pristine Si (cf. Fig. S6 of ESI). Previously, we have shown in Fig. 6 that lifting off the oxide layer has a negative influence on the j -V polarization. The oxidized nanostructured Si facilitate HER more efficiently due to achieving a compromise between the cathodic protection and catalytic activity of the photocathode, until the oxidized layer finally requires removal, after the 450 h to retain the interface. This result is significantly more stable than the recently reported black nanoporous Si (containing Pt catalyst) which underwent up to 95% loss of photocurrent within the first 48 h, illuminated at 0 V vs. RHE under similar conditions [23]. We attribute the higher stability of our photocathodes to the morphology of the nanostructures, being more dense provides a better interface for the reaction. In contrast, bSi-6 whose morphology is less densely packed nanostructures, was tested similarly at -0.5 V vs. RHE, and showed $>50\%$ decrease in current in the first 15 hours before stabilizing for the rest of the experiment (cf. Fig. S9 of ESI).

There was no evidence of visible degradation to the photocathodes after testing, however interface characterization is underway in order to investigate the nature of the interface. Nevertheless, this is an important observation given that it is achieved without the use of any surface catalysts, antireflection coatings or multi layered junctions.

4. Conclusion

For the first time, we have fabricated and systematically investigated metal-free (validated by ICPMS) black silicon nanostructures for STH conversion. We developed a facile wet etching method for the fabrication of metal-free black silicon nanostructures via a combination of HF-free and fast etching approaches using NH_4HF_2 as an alternative. PEC measurements have shown that silicon nanostructures exhibit excellent activities under solar illumination comparable to the performance of metal-catalyst incorporated photocathodes reported by other groups. The high performance is demonstrated to be due to significantly enhanced light scattering and vast electrochemically active surface area. In addition, the absence of metal catalysts demonstrates the capabilities of the silicon nanostructures, and their durability. This

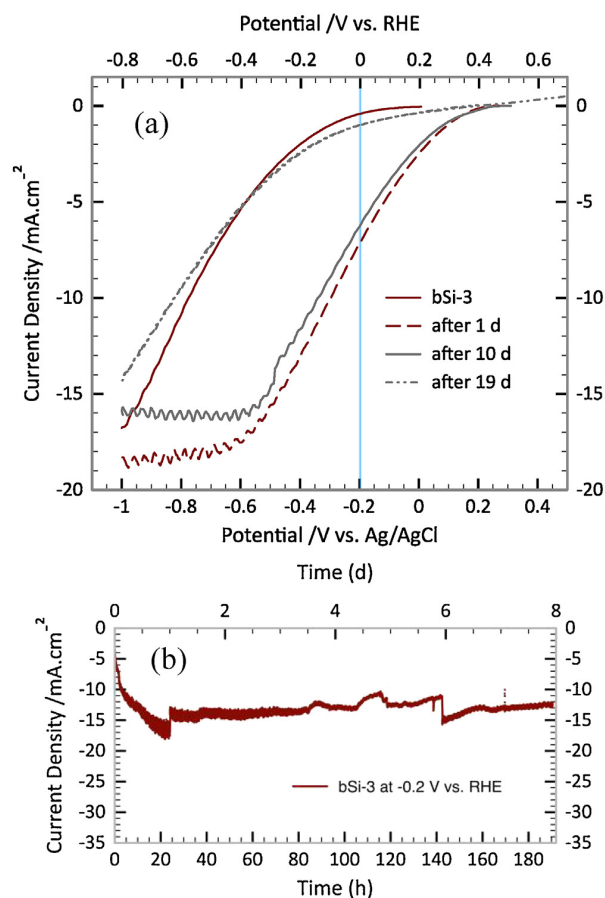


Fig. 7. The performance of bSi-3 during 190 h of long-term HER conversion. a) j -V polarization curves before and after the long term testing. b) long term stability studies conducted over the first 190 h at -0.2 V vs. RHE in 1 M H_2SO_4 .

results in a maximal photocurrent yield, closer to the theoretical limit achievable for Si under these conditions than has been observed previously. The HER performance was found to be stable during 250 h of continuous operation, in conditions otherwise highly corrosive. This cost-effective, environmentally benign process and excellent performance make this metal-free black silicon photocathode an excellent candidate for photoelectrochemical devices.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.electacta.2017.03.086>.

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4.3 Supplementary Information for Section 4.2

4.3.1 Black Si Photocathodes

4.3.1.1 Gold-assisted wet chemical etching (Au/MaCE)

Table 4 Summary of all etchants, samples and the etching steps for black Si photocathodes.

Sample	bSi-1	bSi-2	bSi-3	bSi-4	bSi-5	bSi-6	bSi-7	bSi-8
Cleaning								
MaCE-1 H ₂ O ₂ (0.4 M) : (NH ₄)HF ₂ (2.4 M)	3 min							
Metal-coating (first step)								
Au/MaCE-1 NH ₃ : (NH ₄)HF ₂ : HNO ₃ : HAuCl ₃ .3H ₂ O 1 M : 1 M : 1.89 M : 0.01 M			3 min					
Au/MaCE-2 NH ₃ : (NH ₄)HF ₂ : HNO ₃ : HAuCl ₃ .3H ₂ O 1 M : 1 M : 1.89 M : 0.02 M	1 min	3 min		3 min	1 min	1 min	1 min	1 min
Etching (second step)								
MaCE-1 H ₂ O ₂ (0.4 M) : (NH ₄)HF ₂ (2.4 M)	20 min							
	Aged etchant	Fresh etchant, stored at 5°C						
MaCE-2 H ₂ O ₂ (1 M) : (NH ₄)HF ₂ (2.4 M)					10 min	20 min	30 min	40 min
Metal removal/recycling								
Au-wash 25 g/L of I ₂ + 100 g/L KI in H ₂ O	Overnight							

4.3.1.2 Silver-assisted wet chemical etching

Table 5 Summary of all etchants, samples and the etching steps for black Si photocathodes.

Sample	bSi-9	bSi-10	bSi-11
Cleaning/oxide removal			
MaCE-1 H ₂ O ₂ (0.4 M) : (NH ₄)HF ₂ (2.4 M)	3 min		
Etching			
Ag/MaCE NH ₃ : (NH ₄)HF ₂ : HNO ₃ : AgNO ₃ 1 M : 1 M : 1.89 M : 0.02 M	10 min	20 min	30 min
Metal removal/recycling			
Ag-wash HCl : HNO ₃ : H ₂ O (1:1:1) v/v%	Overnight		

4.3.2 Metal-assisted electroless Chemical Etching (MaCE)

The redox reactions involved in electroless etching assisted by a metal particle follows the model of a microscopic electrochemical cell formed at the Si interface.^[29,31,149,190,195,242] The partaking redox species for the different etchants used are as follows;

– Gold-assisted wet chemical etching

Electroless Gold deposition from aqueous HAuCl₄:

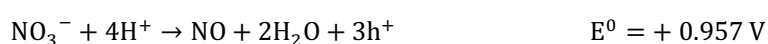


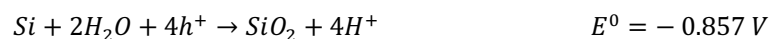
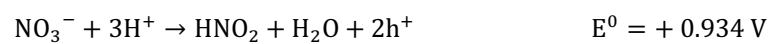
Hole injection into Si:



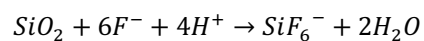
– Silver-assisted wet chemical etching

Electroless Silver deposition from aqueous AgNO₃, hole injection into the Si:





- Silicon oxidation and dissociation



At low pH values, the stability of SiO_2 is determined by:

4.3.3 Morphological Properties

4.3.3.1 Gold-assisted wet chemical etching (Au/MaCE)

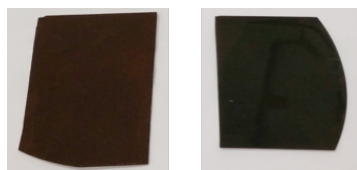
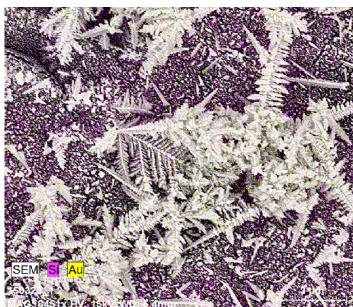
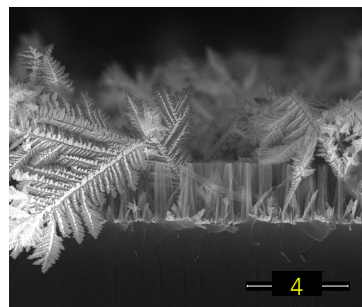


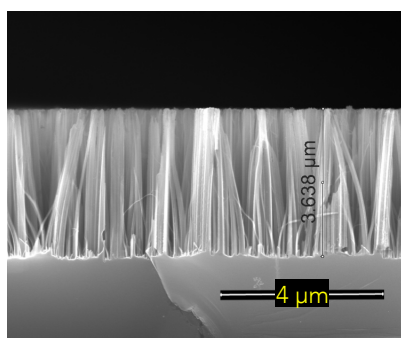
Figure 28 Black Si substrates. Left: Au/MaCE etched before (dark maroon colour), and right: after removal of Au metal dendrites in Au-wash (black).



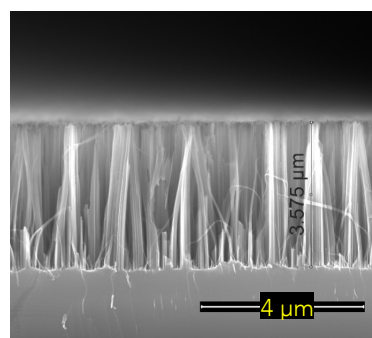
(a) bSi-2 top view after first etching step 3 min in Au/MaCE-2



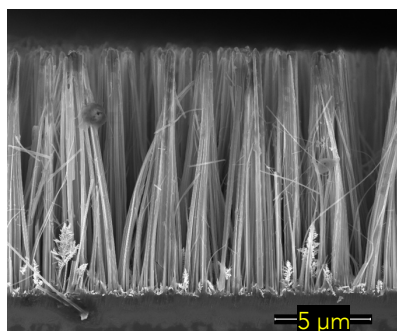
(b) bSi-2 cross section after second etching step 3 min in Au/MaCE-2 + 20 min in MaCE-1



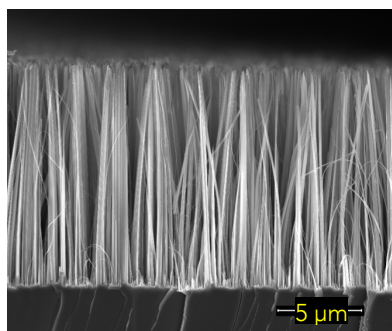
(c) bSi-1 after gold recycling
1 min in Au/MaCE-2 + 20 min in aged MaCE-1,
 $L=3.6 \mu\text{m}$



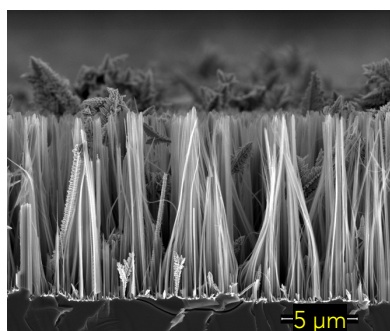
(d) bSi-2 after gold recycling
3 min in Au/MaCE-2 + 20 min in aged MaCE-1,
 $L=3.5 \mu\text{m}$



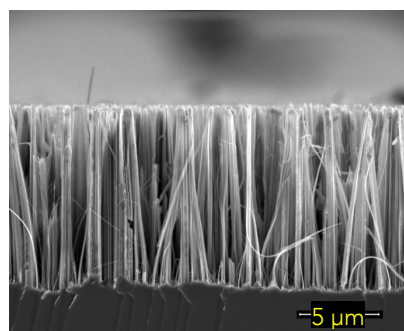
(e) bSi-3 after second etching step 3 min in Au/MaCE-1 + 20 min in fresh MaCE-1



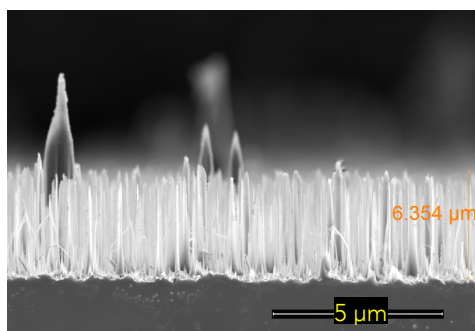
(f) bSi-3 after gold recycling, $L=12.5\ \mu\text{m}$



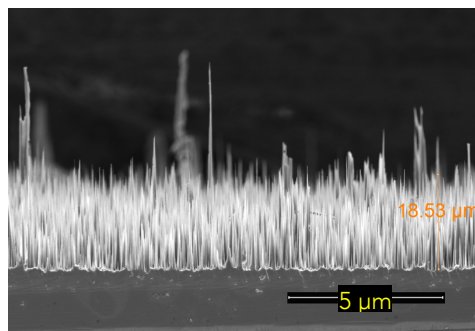
(g) bSi-4 after second etching step 3 min in Au/MaCE-2 + 20 min in fresh MaCE-1



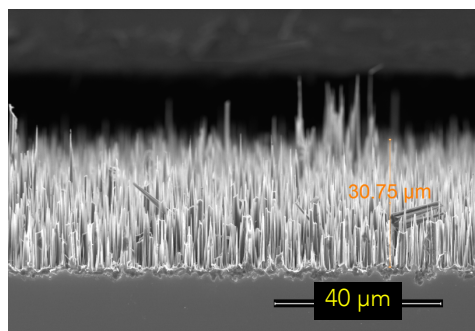
(h) bSi-4 after gold recycling, $L=12\ \mu\text{m}$



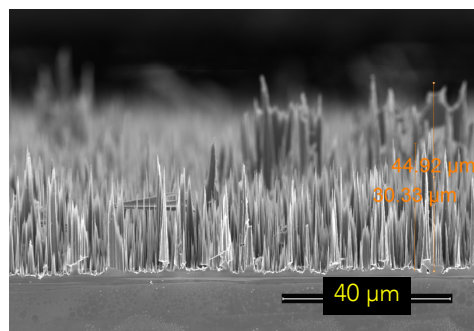
(i) bSi-5 after second etching step 1 min in Au/MaCE-2 + 10 min in fresh MaCE-2, $L=6.4\ \mu\text{m}$



(j) bSi-6 after second etching step 1 min in Au/MaCE-2 + 20 min in fresh MaCE-2, $L=18.5\ \mu\text{m}$



(k) bSi-7 after second etching step 1 min in Au/MaCE-2 + 30 min in fresh MaCE-2, $L=30.8\ \mu\text{m}$



(l) bSi-8 after second etching step 1 min in Au/MaCE-2 + 40 min in fresh MaCE-2, $L=30 - 45\ \mu\text{m}$

Figure 29 SEM micrographs of all Au-assisted MaCE fabricated photocathodes, bSi-(1-8) at different fabrication stages. All fabrication steps are outlined below each micrograph.

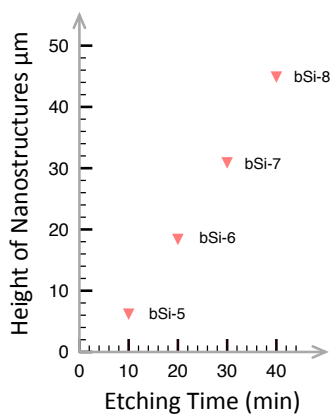
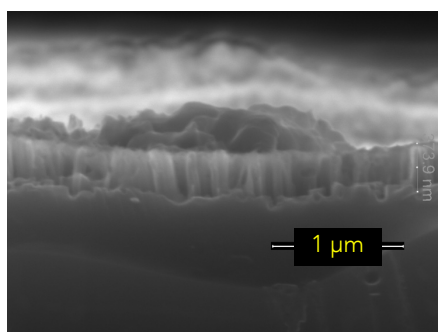
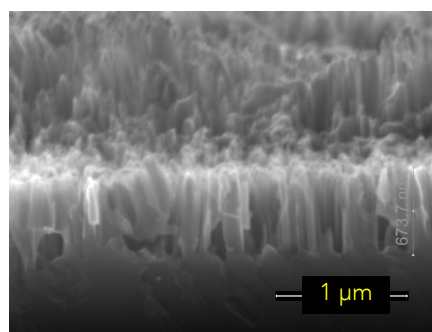


Figure 30 Figure shows the height of nanostructures fabricated by Au/MaCE as a function of etching time in MaCE-2 for bSi-(5-8).

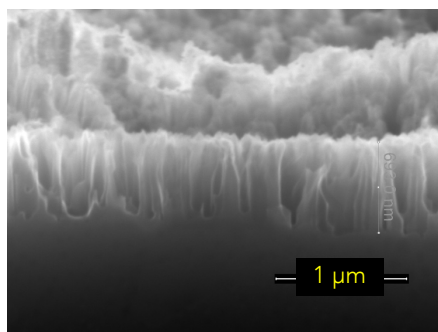
4.3.3.2 Silver-assisted wet chemical etching (Ag/MaCE)



(a) bSi-9 after Ag recycling 10 min in Ag/MaCE, $L=0.37 \mu\text{m}$



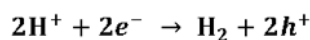
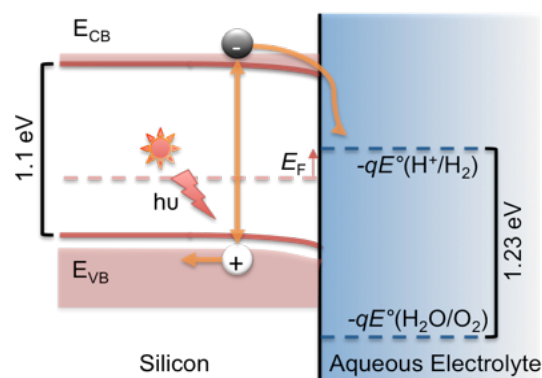
(b) bSi-10 after Ag recycling 20 min in Ag/MaCE, $L=0.67 \mu\text{m}$



(c) bSi-11 after Ag recycling 30 min in Ag/MaCE, $L=0.69 \mu\text{m}$

Figure 31 SEM micrographs of all Ag-assisted MaCE fabricated photocathodes, bSi-(9-11) at different fabrication stages. All fabrication steps are outlined below each micrograph.

4.3.4 Photoelectrochemical studies

4.3.4.1 Photoelectrochemistry on planar *p*-Si

$$E_{\text{H}_2} = [(0\text{V}) - (0.059\text{V})\text{pH}] \text{ vs. SHE at } 298^\circ\text{K}$$

Figure 32

Schematic illustration of Si energetics at an aqueous interface for the HER reaction in solar water splitting. Band gap energetics for *p*-type Si under illumination illustrating redox kinetics for solvated proton species. The system is in a state of chemical equilibrium with the interfacial half reactions for the hydrogen evolution reaction (HER) involved in water splitting. E_{H_2} represents the standard electrochemical redox potentials for the reactions at standard conditions.

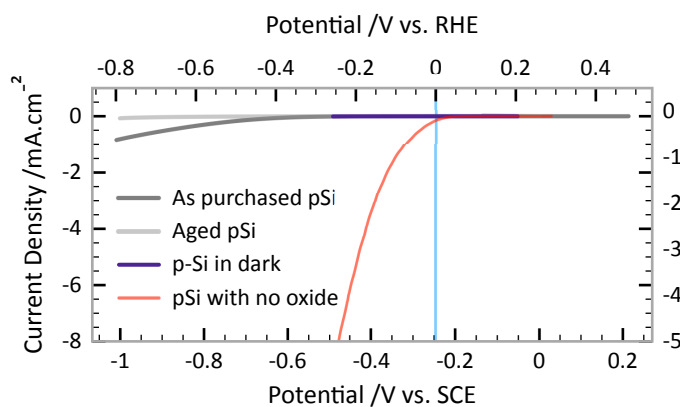


Figure 33

J-*V* data from LSV measurements on untreated *p*-Si photocathodes under illumination. *J*-*V* dependence showing the sluggish kinetics of proton reduction. (black) curve is measured from as-purchased *p*-Si photocathode containing a SiO₂ coating, (grey) after 5 CV scans and, (red) curve after a 60 second treatment in MaCE-17% to remove the oxide layer. The photocathode shows the same behaviour when cycling is repeated. Scan rate 50mV/s in 1 M H₂SO₄.

4.3.5 Photocurrents as a function of solar intensity

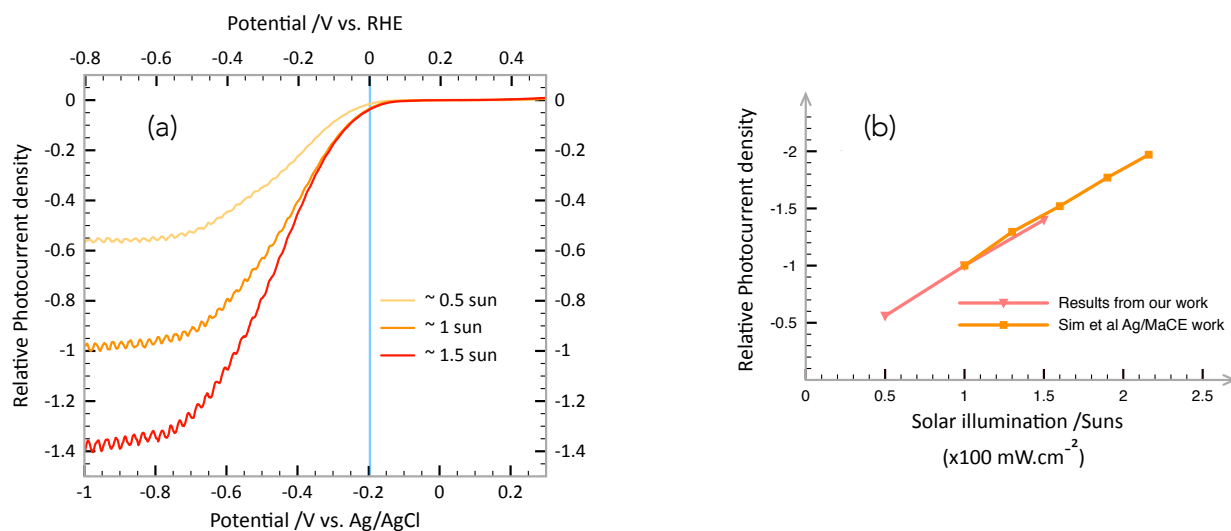


Figure 34 *J-V* data for a test sample used to demonstrate the effect of varying the solar illumination intensities on bSi-4. A proof-of-concept test shows that the limiting photocurrent for the black Si photocathodes is dependent on the incident photon density. a) demonstrates a photocurrent increase brought by increase in lamp power in 0.5 sun increments. b) comparing results from our work with previous work conducted by Sim et al.⁶ on Ag-assisted MaCE bSi. The photocurrents are normalized to reflect the relative photocurrent density from their one sun illumination in order to solely demonstrate the dependence on light intensity rather than performance. Scan rate 50mV/s in 1 M H₂SO₄.

4.3.6 Long term stability

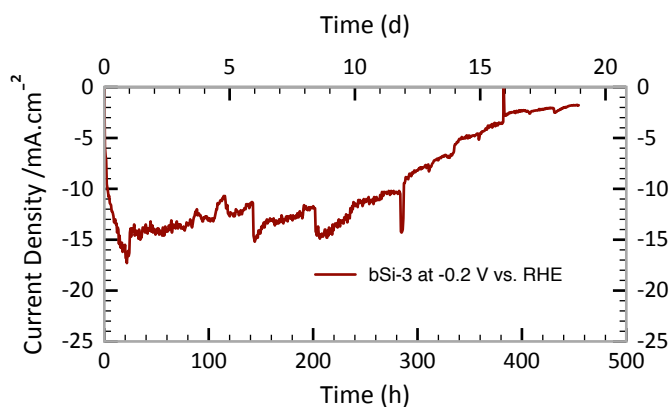


Figure 35 Potentiostatic test for bSi-3 over 450 h (~19 d) of continuous HER evolution at -0.2 V *vs.* RHE for a total charge transfer of -1.61×10^4 C.cm⁻² in 1 M H₂SO₄.

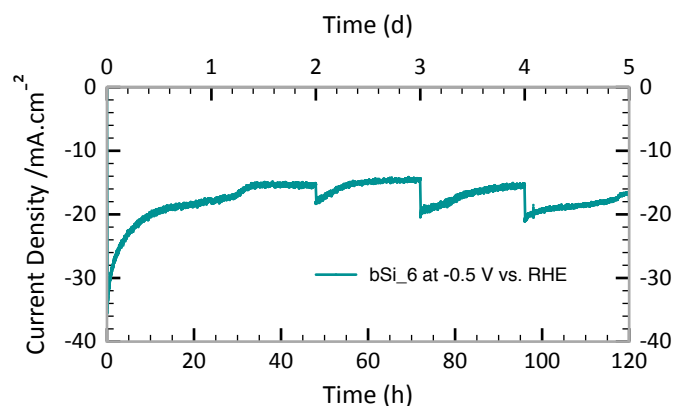


Figure 36 Potentiostatic test for bSi-6 over 120 h (~5 d) of continuous HER evolution at -0.5 V *vs.* RHE in 1 M H₂SO₄

4.4 Further Characterisation of bSi Photocathodes

4.4.1 SEM of Ag/MaCE substrate bSi-12

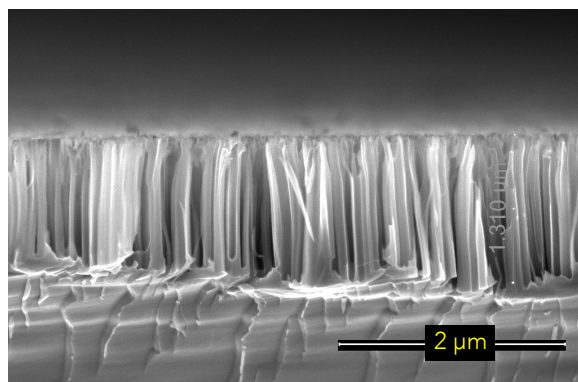


Figure 37 SEM micrograph for Ag/MaCE fabricated photocathode bSi-12 captured at 50000x magnification showing a nanostructural length as estimated by SEM measurement tool to be 1.3 μm .

Continuing from Figure 31 the SEM image for bSi-12 is displayed in Figure 37. This sample was etched for 40 mins in one-step Ag/MaCE etching, which has resulted in a different morphology. Specifically, a dense array with a nanostructural length of 1.3 μm was produced. Hence it can be concluded that for Ag/MaCE, the initial 30 minutes resulted in irregular nanostructures, which is attributed to the low activity of the Ag metal particles, has also been observed in other reports.^[190] Figure 40 displays the nanostructural lengths obtained for many of the samples investigated in this chapter. Sample bSi-13 which was etched for a duration of 60 min, was not analysed by SEM.

4.4.2 PEC performance for Au, Ag/MaCE and nanostructure lengths

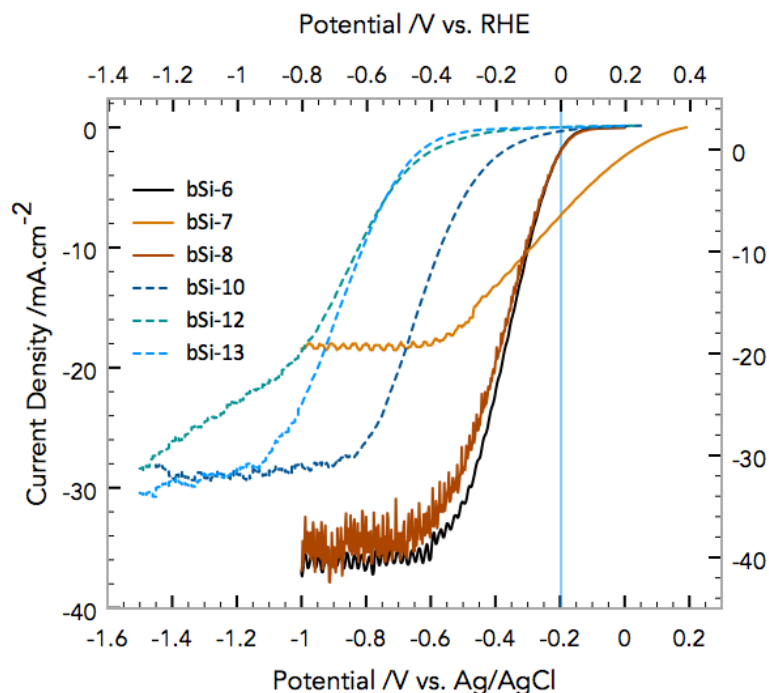


Figure 38 Comparison of linear sweeps of photocathodes bSi-(6-8,10,12,13). All J - V data were measured at the start of the lifetime of the photocathode. 1 M H_2SO_4 , Scan rate 50 mV.s^{-1} , (100 mW.cm^{-2}).

To compare the initial performance of all photocathodes under illumination, the cathodic LSV for the forward cycles measured for each of bSi-(1-13) are displayed in Figure 38. Direct correlation between nanostructure morphology and the PEC properties (V_{OS} , J at $E(H^+/H_2)$, J_{LIM} and V_{LIM}) can be drawn. The sample that shows highest photocurrent density at 0 V *vs.* RHE is bSi-7. This electrode interface features low-density nanowires $\sim 30 \mu\text{m}$ in length which are clearly seen to exhibit significant side-etching of the nanostructures, as depicted in Figure 29(k). In contrast, sample bSi-6 shows the highest J_{LIM} . This electrode features nanowires with a similar density interface with nanostructure height of $\sim 18 \mu\text{m}$ as shown in Figure 29(j). Sample bSi-8 shows a similar profile to bSi-6, with slightly lower J_{LIM} . The morphology of the nanowires in bSi-8 exhibits lengthier wires up to $\sim 45 \mu\text{m}$ in length as shown in Figure 29(l).

The variation in performance is believed to be attributable to the interface morphology. The effect of Si interface modification has been shown to give rise to light-scattering features, as discussed preciously in section 3.7. The J - V profiles in Figure 38 show enhanced performance for lesser density nanostructures in samples bSi-(6-8). Light scattering depends largely on factors such as nanowire width, length and interspacing.^[55,56,243] Because the etching profile is dependent on the etchant metal composition, the variation in the performance also depends on the type of metal used. It has been established in Chapter 3 and section 0 that rapid etching is achieved when Au-MaCE method was used. However, the nanostructural density does not solely play a significant role in determining the performance of the bSi photocathode, but also their lengths.

Sim *et al.*^[190] showed that the cathodic photocurrent performance of SiNW in HER conversion increases as the surface becomes more nanostructured due to increased effect of photoabsorption due to scattering. This increase plateaued at a maximum nanostructure height, beyond which the performance decreased. They have attributed this photocurrent threshold to the possibility of Si surface traps/defect sites, but did not show this experimentally. Foley *et al.*^[243] simulated the operation of thin SiNW photoelectrodes for solar energy conversion. They reported high charge recombination for longer nanowires due to the enlarged depletion region.

It is evident from CL analysis in section 3.7.2, that the nanostructures exhibit a variety of defect sites at the interface of the nanowires and also their bulk. Together with the increased recombination in a lengthier nanostructure profile, this explains the lower photocurrent yield from the lengthier nanowires in sample bSi-8 than for bSi-6. Despite, this variation is low for these two electrodes and maybe related to the density of the nanostructures. The density of the nanostructures plays a significant role in the photoelectrode performance as realised in bSi-(10,12,13). The correlation between the nanostructural length and density cannot be established in this study due to the lack of sufficient range of nanostructural profiles. These properties were visited elsewhere in the literature,^[87,190,243] and could be further investigated in future studies.

4.4.3 Effective surface area versus projected area for data analysis of black Si photocathodes

PEC studies, including the present thesis, conventionally report the photocurrent density in units of mA per projected surface area of the 2D interface (A_{2D}). However, the significantly increased geometrical surface areas (GSA) of bSi means that the effective area (A_{eff}), is much larger than A_{2D} . Several techniques exist for experimentally determining the surface area,^[244] including BET gas (nitrogen) adsorption method which measures physical absorption,^[245,246] or the double-layer capacitance method for estimating the electrochemically active surface area (ECAS).^[247] The first method requires invasive abrasion, and is therefore not suitable to examine brittle Si interfaces, while the second method only provides a rough estimate with very low accuracy due to limitations.^[244] For this reason, and to explain the photocurrent yield for bSi, an estimate of an area enlargement factor is considered.

To estimate GSA of the nanowires, on an arbitrary substrate, such as bSi-2 (*cf.* Figure 2(a) p.83 for SEM image). The largest average radius of nanowires, estimated by length measurement tool on ImageJ software, was $r \cong 70$ nm, and the nanowire length, $h \cong 3.57$ μ m. Accordingly, GSA of a hypothetical bSi, was calculated considering the base area to be adjacent to the nanostructure, GSA follows $A_{eff} = 2\pi rh + 2\pi r^2$. This leads to a scaling factor of at least $A_{eff}/A_{2D} > 50$ times for a 1 cm² 2D surface.

The J - V profiles of p -Si and bSi-2 photocathodes are plotted in Figure 39 for their respective A_{2D} and A_{eff} . It can be seen from the curves, that using the A_{2D} -calculated photocurrent density for the bSi photocurrent yield allows for directly comparing features with that of the planar photocathode. For bSi-2, there is a noticeable decrease in overpotential for the HER reaction, as well as an increase in the J_{LIM} (*cf.* Table 1 in the published article, p.86, for the V_{OS} and J_{LIM} values). As established in section 0, the decrease in overpotential is attributed to the increase in A_{eff} , while the increase in J_{LIM} is attributed to the increase in photoabsorption due to the light-scattering effects

as a result of the nanostructural area, under constant illumination power density. Therefore, one can deduce that J_{LIM} gives a measure of the extent of photogenerated charges at the interface, and the photocurrent density at any given potential is a measure of the contribution of these photoactive sites in HER conversion (rate of HER conversion). For the same bSi substrate and incident illumination, an increase in J_{LIM} either implies an increase in photogenerated charges, or an increase in the total number of photoactive sites. These two factors contribute to the significantly increased bSi photocurrent density (J_{eff}) shown by the black curve as compared with that for the planar Si (grey) in Figure 39.

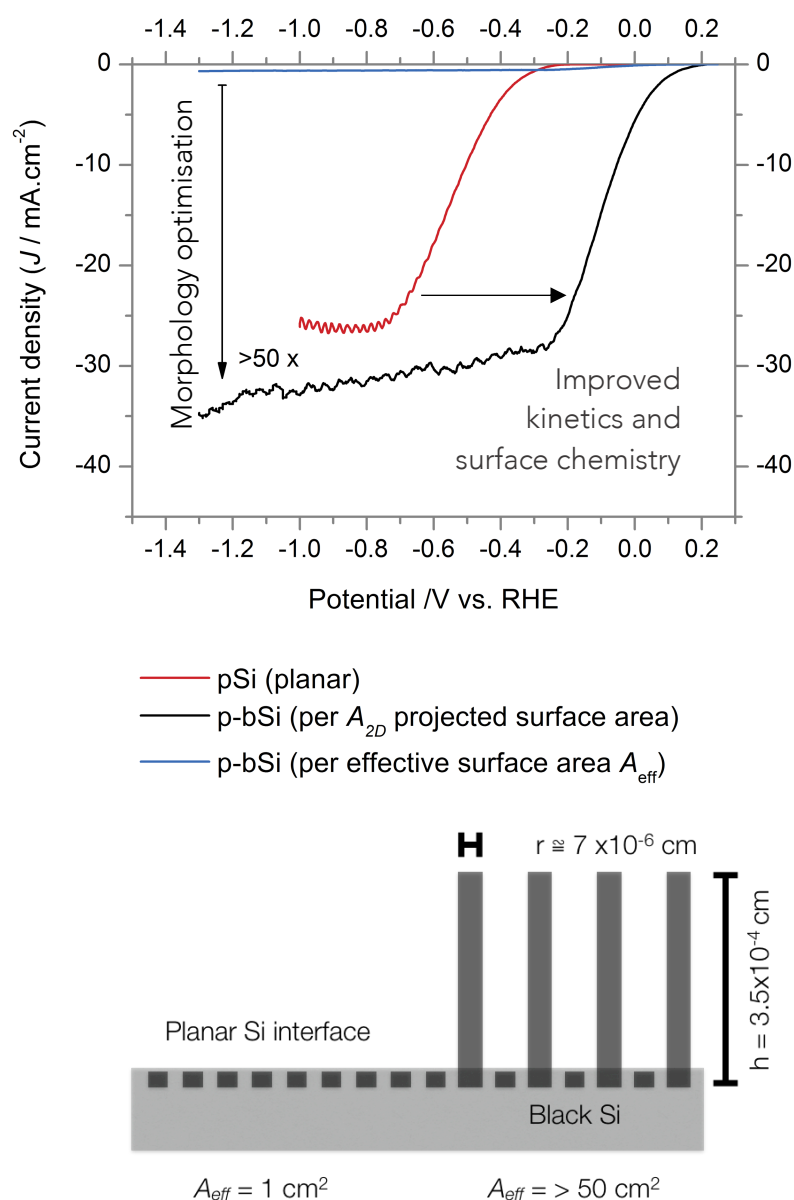


Figure 39

The effect of interface optimisation on the photocurrent yield for bSi compared to planar p-Si photocathodes. The J - V data is adapted from published results in Figure 5(a) of bSi-2 on p.85. The blue curve denotes the photocurrent per A_{eff} as estimated in the right-hand figure. The nanostructuring process not only leads to increased light absorption, but also an enlarged electrochemical interface for the same projected surface (2D) area of the material.

On the other hand, the effective photocurrent density on bSi (blue curve) is significantly lower than that for planar Si due to a lower yield per unit area on the bSi, and hence the small contributions from all the active sites amount to a large photocurrent yield for the 2D surface area of bSi photocathode. This is despite the fact that the absorption to majority of incident light on the bSi (*cf.* Figure 21 for UV-Vis reflectance profiles), therefore implies that not all active sites on the bSi take part in catalysing HER reactions. In contrast, planar Si only offers a flat interface for both light absorption and HER catalysis, and a much higher reflectance to the incident light. Therefore, due to the relatively limited number of catalytic sites, and photoactive interface on planar Si, the contribution of the active sites to the photocurrent yield is higher than that for the bSi. This analysis indicates that bSi offers significantly larger active sites for STH conversion, but not all contribute to produce a photocurrent.

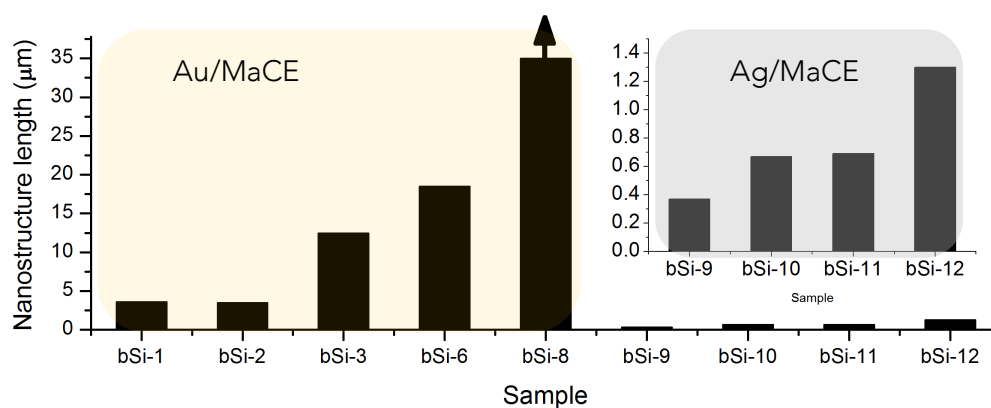


Figure 40 Summary of nanostructural heights obtained on bSi-(1-3,6,8,9-12). The inset shows the heights for the sub-micron nanowires.

Thus the enhancement in bSi can be attributed to the vast number of sites available for redox catalysis, even though not all A_{eff} contributes to the same extent. Since the photocurrent yield is rather limited by the incident illumination and maximum theoretical photocurrent density achievable on Si. This allows the potential to develop better absorption from solar concentrators or catalysts, and hence a lower overpotential for the same photocurrent yield can be achieved. The effective limit for the photocurrent density on bSi would therefore depend on light scattering attributes, to a large extent, before a material-imposed limit is in effect. Similarly, for the planar counterparts, there is a significant limitation in the photocatalytic active sites.

4.4.4 Long term performance of bSi photocathodes

In total, six bSi samples were tested for their STH conversion in long term experiments. Some data were presented for substrates bSi-(3,6) in sections 0 and 4.3, and the remaining results are presented here. The photocathodes are subjected to several CV and CA tests, and were exposed to aqueous acidic electrolyte (1 M H_2SO_4) for a various durations (*cf.* Table 6 for summary of experimental parameters for each photocathode). The exposure time reported for each sample was

inclusive of operation time and idle electrolyte exposure. The stability results are categorised based on their assisting metal used in fabrication (Au, Ag/MaCE). This is due to the significant effect of metal choice on the morphological attributes of the produced nanostructures, and hence on their performance.

4.4.4.1 Stability of Au/MaCE fabricated bSi-(1-8) photocathodes

The long-term performance of Au/MaCE etched photocathodes was performed on bSi-(3,6,8). The difference between these substrates in terms of their morphological traits (*cf.* Figure 29(f,j,l) for respective SEM images) arises from the fabrication conditions outlined in Table 4. The PEC results for these photocathodes were shown in Figure 7 on p.87, Figure 35, Figure 36, Figure 41 and Figure 42. Briefly, and as summarised in Table 6, sample bSi-3 was tested for the longest duration, 115 days of chemical exposure, including potentiostatic CA for 460 h in the same electrolyte at -0.2 V *vs.* RHE. Samples, bSi-(6,8) were tested for a shorter period of time, 120 and 48 hours respectively, both subjected to -0.5 V *vs.* RHE throughout this duration. For all samples, a CV was recorded for freshly fabricated photocathodes, during, and after long-term exposure.

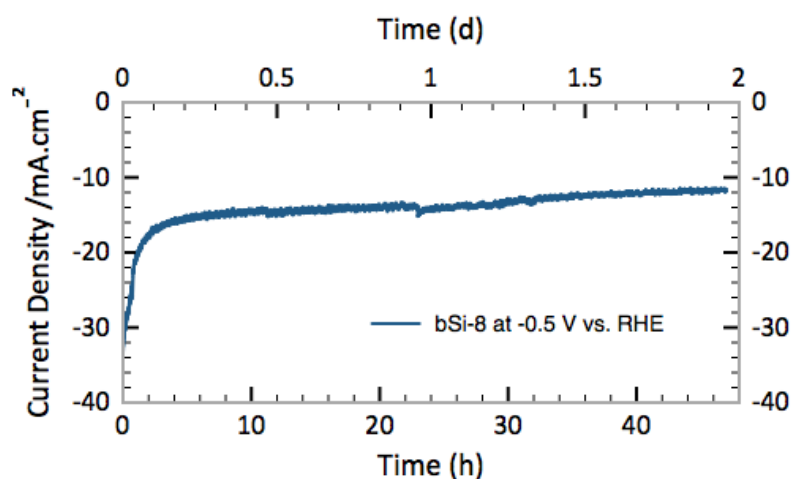


Figure 41 CA on bSi-8 at -0.5 V *vs.* RHE in 1 M H_2SO_4 , 100 mW.cm^{-2}

The electrolyte was replaced frequently when possible, throughout the duration of the experiments to ensure that the decay in photocurrent is not related to changes in the electrolyte, such as the increase in pH. Any prominent photocurrent spikes in the data occurred when the experiment was paused and the cell disassembled to ensure no leakage or breakage had affected the photocathode.

Long-term exposure was shown to degrade the interface of pristine Si dramatically. On the other hand, the stability of bSi-3 over a prolonged 460 h of potentiostatic operation in Figure 35 shows that the photocathode undergoes an increase in photocurrent density over the initial 20 h, from -6 mA.cm^{-2} to -17 mA.cm^{-2} . The photocathode then operates for a further 280 h showing an overall photocurrent density which fluctuates between -15 mA.cm^{-2} and -12 mA.cm^{-2} . After 300 hours, a gradual decrease in the performance was noticed for the following 160 h until

it reached -2 mA.cm^{-2} . In this process, a total charge transfer of $-1.61 \times 10^4 \text{ C.cm}^{-2}$ has taken place across the bSi-3 interface. In contrast, samples bSi-(6,8) showed a higher initial photocurrent density at the start of the test, which then decayed by around half over the first few hours (2 h for bSi-6 and 10 h for bSi-8), and remained stable for the remaining time of the experiment. Sample bSi-6 showed the same spikes as above, due to frequent exchange of the electrolyte, while bSi-8 was tested in a large-volume cell and therefore did not require electrolyte replacement.

Table 6 List of chemical exposure durations for all substrates tested for their durability in 1 M H_2SO_4 without bias, as well as for biased chronoamperometric tests conducted under different potentials.

Method	Sample name	Exposure duration, unbiased (days)	CA test duration (hours), CA potential (V <i>vs.</i> RHE)
Au/MaCE	bSi-3	115	460, -0.2
	bSi-6	6	120, -0.5
	bSi-8	4	48, -0.5
Ag/MaCE	bSi-10	5	60, -1.3
	bSi-12	5	60, -1.3
	bSi-13	7	60, -1.3

The CV analysis for bSi-3 was discussed in the published article. While that for bSi-(6,8), are shown in Figure 42. In brief, the J - V profile of bSi-3 undergoes a positive shift without any effect on J_{Lim} . In contrast, the J - V profile for bSi-6 shows a positive V_{Os} and a crossover can be noticed, which follows a decrease in J_{Lim} . The performance for bSi-8 after long-term testing shows an increase in the overpotential and a decrease in J_{Lim} , as compared with that before the CA tests. The morphology of the interfacial layer of bSi photocathodes evidently affects the stability results, which plays a major role because of the areal density of the nanostructures. Photocathode bSi-3 exhibited a densely-packed topology owing to using relatively lower fluoride concentration. Similarly, the increased fluoride etching concentration during the fabrication of bSi-(6,8) allowed for a faster etching mechanism that lead to a less dense morphology, and hence larger spacing between the nanostructures.

Comparing the performances for bSi-6 and bSi-8 supports this argument further, as the less dense morphology nanowires in bSi-8 deteriorated faster than bSi-6. This morphology variation has therefore shown to affect in turn the strength, light scattering and catalytic activity, and thus their overall photocathode performance. Importantly, bSi-3 was prepared with a quick oxide layer etch for several seconds prior to experiments, bSi-(6,8) were used as stored, with a native

oxide layer on the surface. As discussed before, the effect of the oxide layer on bSi substrates is the reverse of that on the planar Si, due to the enhancement from geometrical orientation of the nanostructures and the vast electrochemical interface, that even with oxide formation, the weak contributions from catalytic sites on bSi amount to the overall photocurrent.

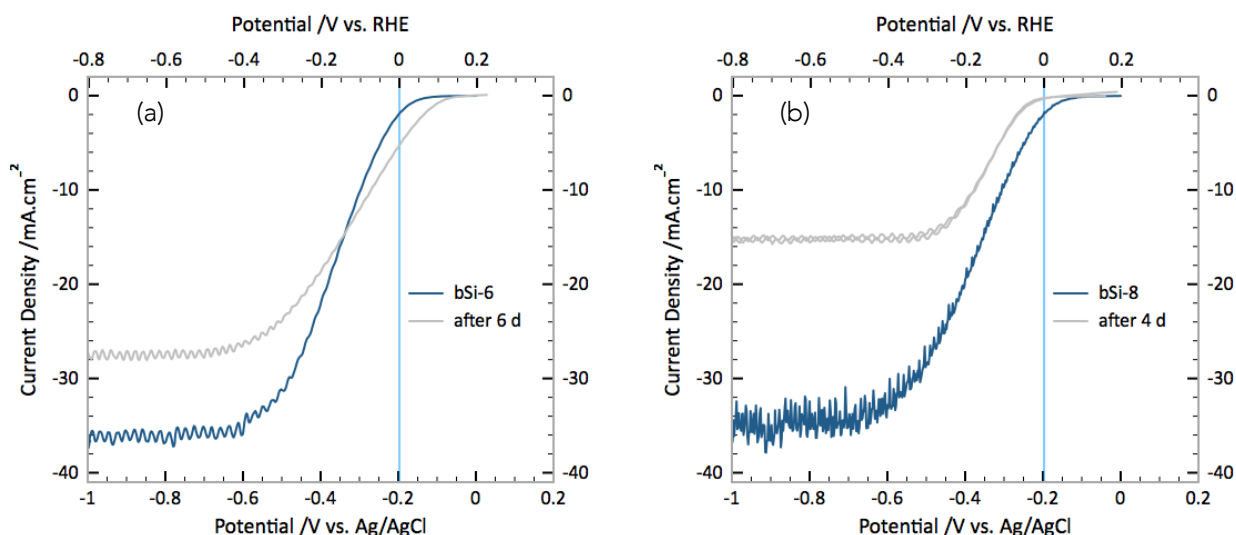


Figure 42 J - V dependence of Au/MaCE fabricated photocathodes bSi-(6,8) before (blue) and after (grey) long-term stability tests in 1 M H_2SO_4 , 50 mV.s^{-1} , 100 mW.cm^{-2} .

The performance after the durability tests can then be revived by removal of the oxide layer (using MaCE-1 for < 1 min) and re-activation, as discussed earlier for the original photocathode. This may be effective in resetting the interface, however, continuous etching has a negative effect in that it will continue to remove Si layers from the nanostructures, leading to their thinning until they no longer have a dense morphology, hence lowering their performance. This is evident from the lower PEC yield discussed below for bSi-(10-13) photocathodes (*cf.* Figure 43), which exhibited less dense nanostructural morphologies. It is therefore a compromise, although perhaps the repeated process of obtaining a new nanostructured layer out of the Si bulk could make this photocathode “re-usable”.

The stability test for bSi-3 is the longest comprehensive experiment conducted under such conditions, which is significantly longer than the stability tests which range from several cycles to one or two days at best, that are reported in the literature.^[28] According to these durability tests, the performance of bSi is considered significantly better than that for planar Si. This performance is despite the use of an acidic electrolyte which is normally corrosive to planar Si, and is known to drive the oxidation of Si according to the Pourbaix diagram,^[79,80] as discussed before in Chapter 2. Therefore, bSi is a promising relatively stable structure for solar water splitting, specifically attractive for use as a platform material.

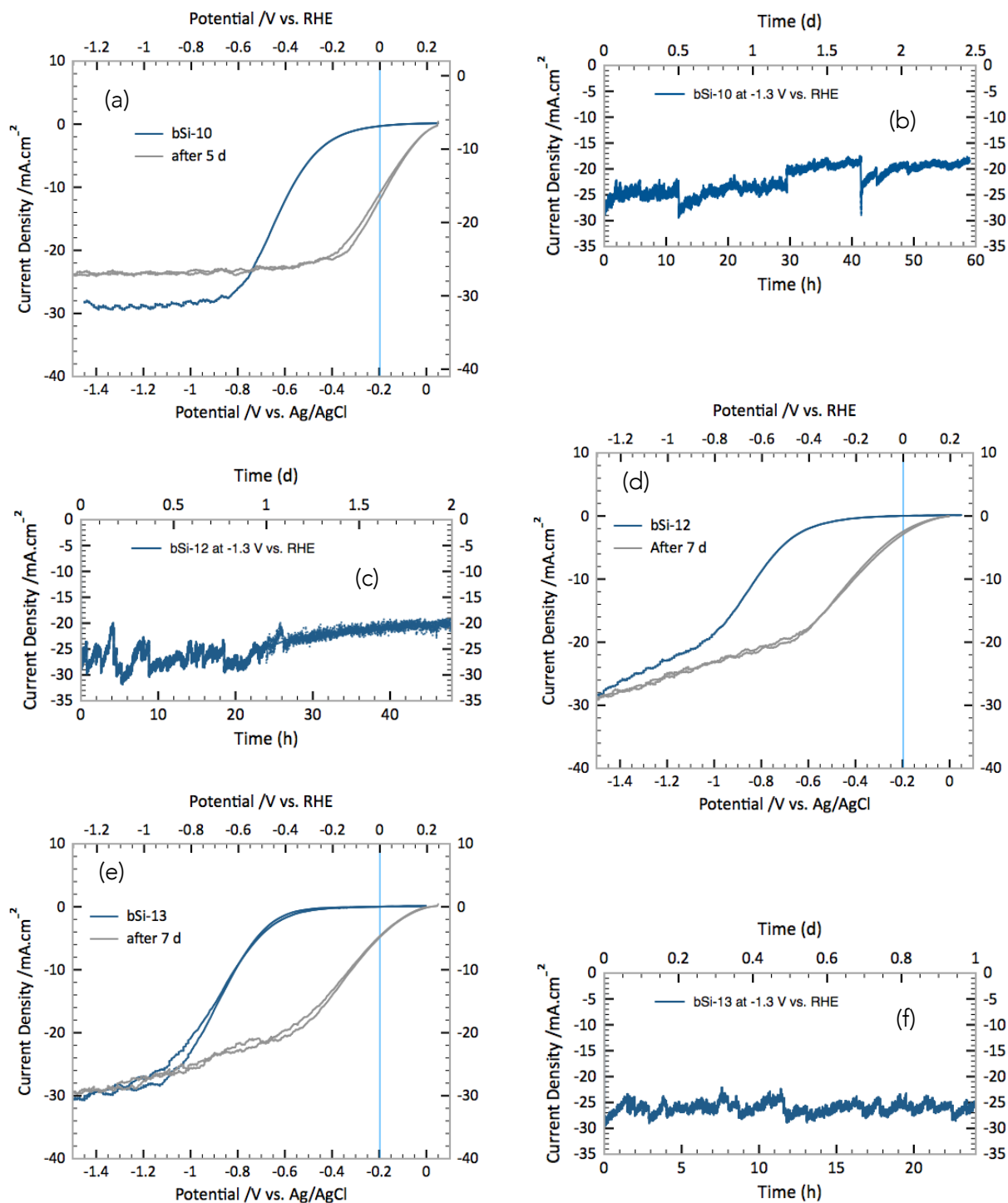


Figure 43 PEC characterisation of Ag/MaCE photocathodes bSi-(10,12,13) compared for their durability and performance in 1 M H₂SO₄. Subfigures (a,d,e) all represent CV measurements (50 mV.s⁻¹, 100 mW.cm⁻²) before (blue) and after (grey) a series of long-term tests involving measurements at -1.3 V *vs.* as shown in subfigures (b,c,e) and exposure in same electrolyte, under no external bias.

4.4.4.2 Stability and performance of Ag/MaCE fabricated photocathodes

The experimental results for Ag/MaCE fabricated samples are considered. The J - V dependence of bSi-(9-13) photocathodes were subjected to the same tests as presented for Au/MaCE. The effect of silver etchant on the resultant nanostructures is evident in Figure 31 and Figure 37. The main difference that prevails is the length of the nanostructures, where Ag/MaCE produced non-defined and relatively shorter nanostructures as compared with Au/MaCE for the same etching durations. The CV results for PEC and stability tests are shown in Figure 43 and the highlights listed in Table 7.

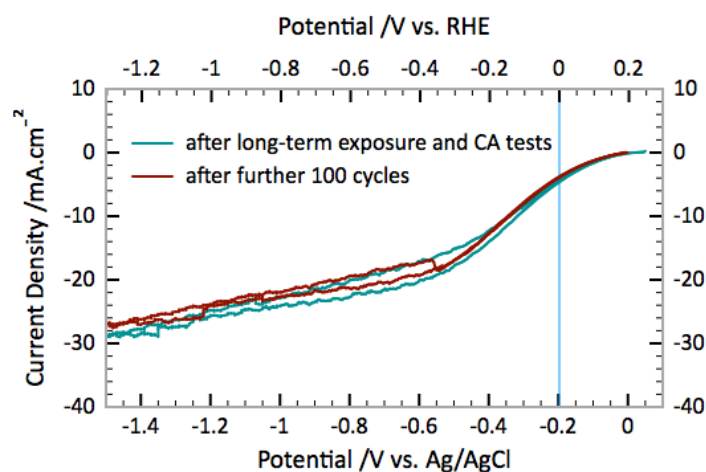


Figure 44 J - V dependence on bSi-13 after long term experiments (red) lasting 24 h of constant potentiostatic STH conversion (Figure 43(f)) and 7-day exposure to aqueous acidic media. The same photocathode was also tested under continuous cycling for 100 cycles without observable deterioration in the performance of the photocathode; measured in 1 M H_2SO_4 , 50 mV.s^{-1} , 100 mW.cm^{-2} .

Light-driven STH conversion was carried out constantly for bSi-(10,12,13) at -1.3 V vs. RHE (*cf.* Table 6). The chronoamperograms (CA) are displayed in Figure 43. The results are consistent with the conclusions drawn above for Au/MaCE, especially with respect to the decrease in overpotential achieved after the long-term potentiostatic experiments. For both bSi-(10,12) the initial cathodic photocurrent was observed to be $\sim 28 \text{ mA.cm}^{-2}$ and deteriorated to $\sim 18 - 20 \text{ mA.cm}^{-2}$ after 60 h of operation. In regards to bSi-13, the CA showed a constant current over the first 25 h of the experiment (data for bSi-12 showed the initial 50 h and for bSi-13 for the initial 25 h, while remaining data could not be retrieved).

An anodic shift in V_{Os} was seen for the Ag/MaCE photocathodes, this shift was directly proportional to the etching time of the photocathode. In addition, another similar trend was obtained for the current measured at 0 V vs. RHE , on the CV profiles recorded after long term performance (*cf.* grey curves in Figure 43). These values were -12 , -2.5 and -4.9 mA.cm^{-2} for bSi-(10,12,13) respectively. The potential difference where these photocurrents were measured for the initial photocathode, were of 0.4 V , 0.43 V , and 0.52 V more positive after the long-term tests

were concluded. This trend is also evidently related to the nanostructural lengths of the bSi layer at the interface. The significant reduction in the overpotential is associated with the increased catalytic activity for STH conversion, as seen from the CV features highlights collated in Table 7. Therefore as concluded from these results, by increasing the nanostructural lengths, within the range studied here, the overpotential is decreased, which conforms with the Au/MaCE results.

Table 7 Highlights from CV results of photocathodes bSi-(10,12,13) before and after the long-term chronoamperometry measurements that were conducted at -1.3 V *vs.* RHE.

Sample	Onset potential (V_{OS}), V <i>vs.</i> RHE ^a	ΔV_{OS}	Overpotential shift (V) at the photocurrent density ($\text{mA}\cdot\text{cm}^{-2}$) ^b	Limiting Photocurrent (J_{LM}) ^c
bSi-10	0.10	0.15	0.4 V, $-12 \text{ mA}\cdot\text{cm}^{-2}$	-29
	0.25			-24
bSi-12	-0.02	0.22	0.43 V at $-2.5 \text{ mA}\cdot\text{cm}^{-2}$	-29
	0.2			-29
bSi-13	-0.05	0.25	0.52 V at $-4.9 \text{ mA}\cdot\text{cm}^{-2}$	-31
	0.2			-31

^a V_{OS} is obtained from the potential value at $-0.001 \text{ mA}\cdot\text{cm}^{-2}$

^b The potential difference at the photocurrent observed for 0 V *vs.* RHE

^c J_{LM} is obtained by determining the maximal cathodic photocurrent value

Substrate bSi-13 was cycled for an additional 100 CV cycles after the 7-day exposure and 60 h CA test. The J - V dependence before and after the 100 cycles is displayed in Figure 44. Its CV profile does not undergo significant change from this test, indicating the stability of the photocathode across dynamic/static potential tests. These results demonstrate a significant link between the nanostructural morphology and the performance of the photocathode, considering the areal density in this case is highly ordered in the case of bSi-12 as compared to bSi-10.

Further to this, the improved photocatalytic activity brought about from continuous catalysis for long durations, also confirms a positive effect of nanostructuring for these photocathodes. Future studies on detailed electrochemical processes are required (perhaps even *in situ*) before a full understanding of the interfacial kinetics on these photocathodes is achieved. However, based on the above discussion, the published article as well as simulated results earlier for the geometrical morphology of the nanostructures, the increase in the activity at the interface is related to the electrochemical surface area for enhancing both, the photocurrent conversion, and the overpotential. Given that the extent of the STH conversion at this interface would be significantly lower than the maximum catalytic capacity of the photocathode, because of the vast effective area, it appears that they are limited by the photoabsorption capacity of the semiconductor, and are also dependent on the effect of nanostructures on the PEC performance.

4.4.5 Solar-to-Hydrogen (STH) Efficiency

For water splitting photocathodes which require an external bias in three-electrode conventional PEC cells, as used here, the efficiency can be calculated separately for the HER compartment. Being able to quantify a solar energy to hydrogen gas (STH) conversion efficiency allows for individual optimization of materials in multi-electrode systems, such as the case for a PEC cell containing a bSi photocathode.

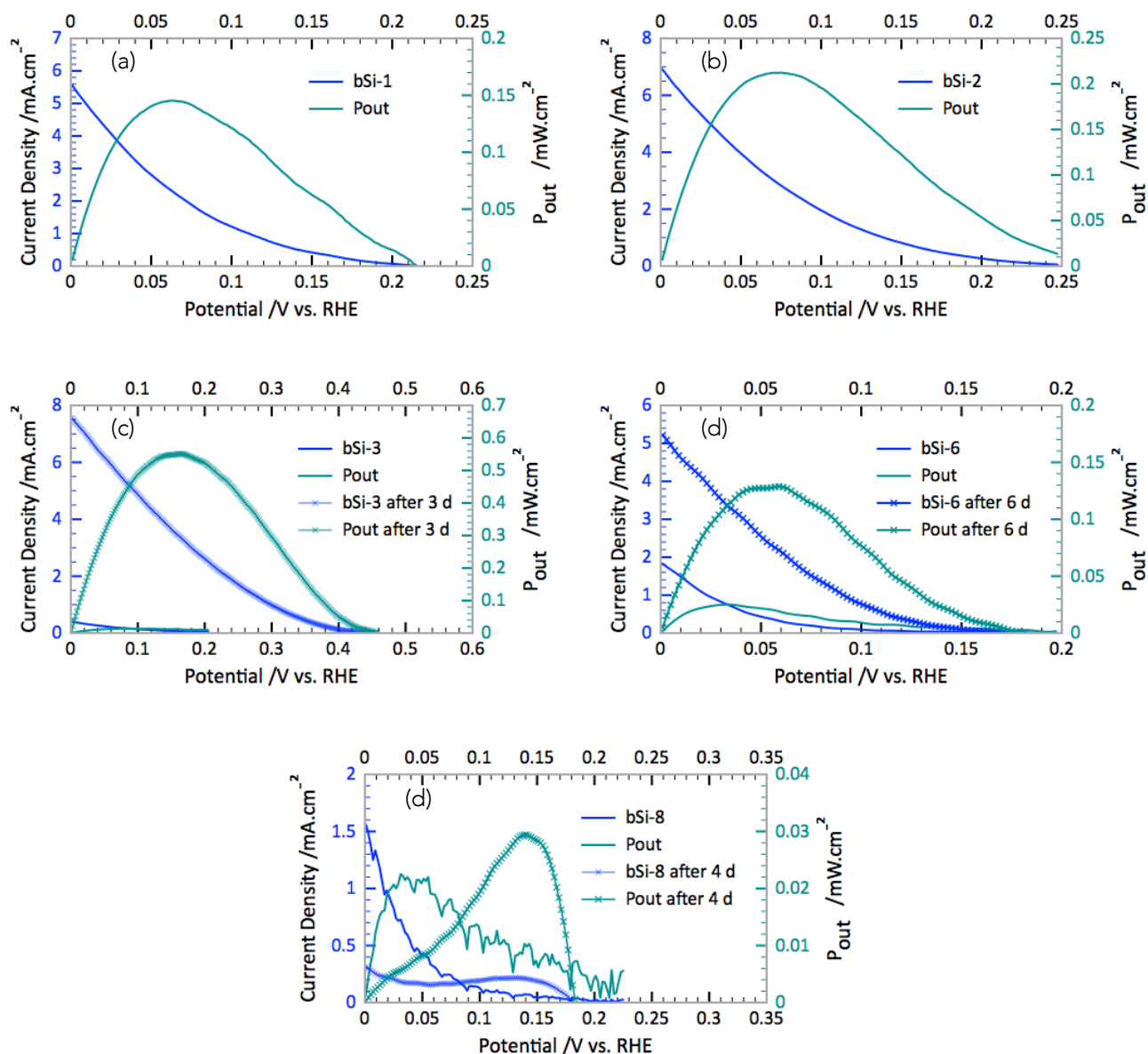


Figure 45

Current density *vs.* overpotential (primary axes) and power output (secondary axes) data for bSi-(1,2,3,6,8) fabricated via Au/MaCE method. The photocathodes were tested before (solid line) and after (dotted lines). The peak for P_{out} corresponds to the respective STH efficiency ($P_{in} = 100 \text{ mW.cm}^{-2}$).

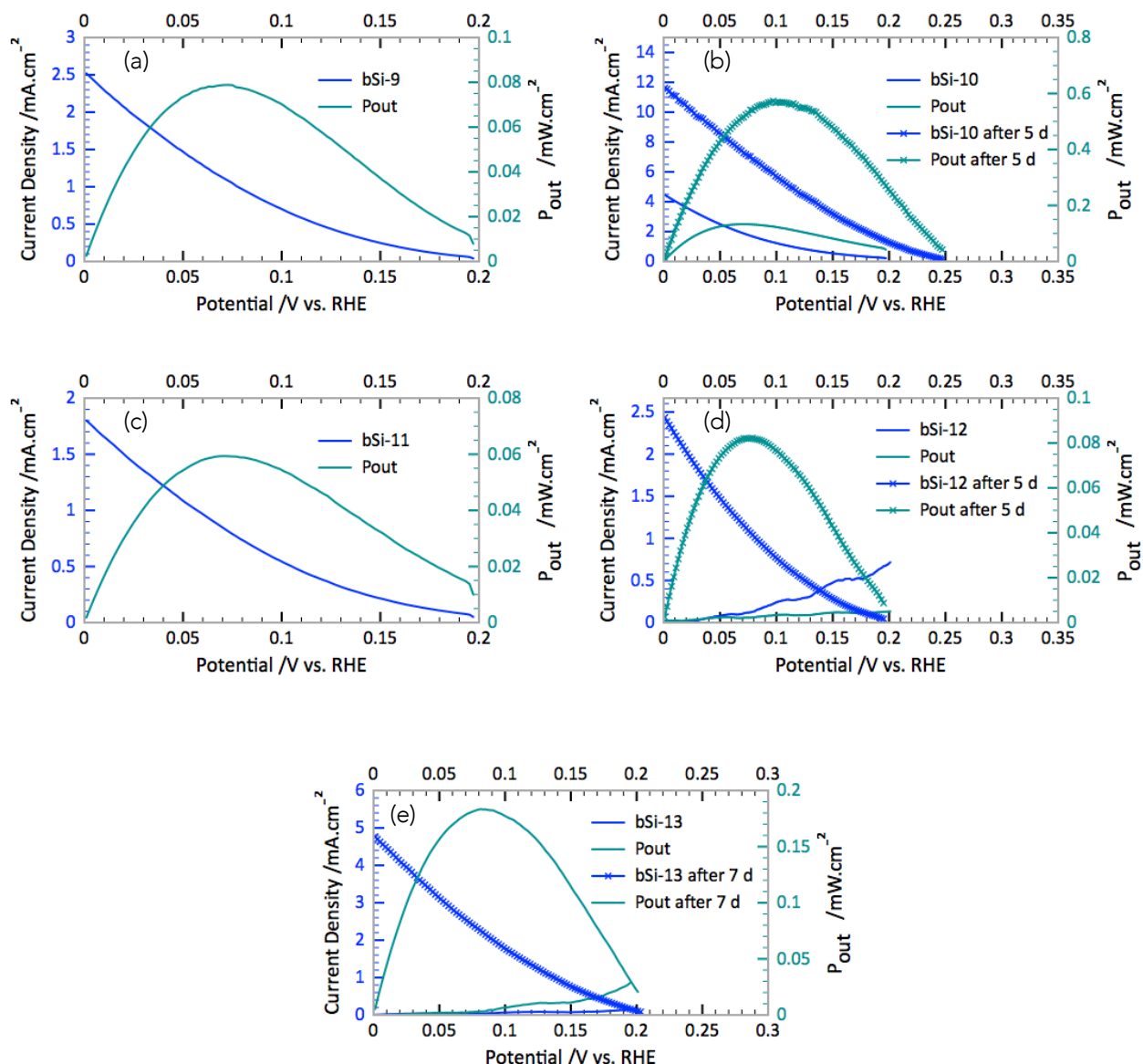


Figure 46 Current density *vs.* overpotential (primary axes) and power output (secondary axes) data for bSi- (9-13) fabricated via Ag/MaCE method. The photocathodes were tested before (solid line) and after (dotted lines). The peak for P_{out} corresponds to the respective STH efficiency ($\text{P}_{\text{in}} = 100 \text{ mW.cm}^{-2}$). Data extracted from CV/LSV measurements displayed in Figure 43.

The efficiency of the HER photocathode can be calculated from respective J - V data. It is important to note that these efficiencies cannot be taken as true faradaic efficiencies because no products were analysed for the STH calculation, therefore it only represents a portion of the total Gibbs free energy involved in the overall water splitting reaction. The STH conversion efficiency for a hydrogen half-cell driven by solar illumination, can be commonly implemented as a measure of cathode performance, and can be calculated according to Equation 13.^[6,190,248]

In regards to the values for STH efficiencies, a general trend is observed for the results before any long-term testing, which is that the STH efficiency is inversely proportional to the nanostructural lengths and therefore to the etch time. For instance, comparing the efficiency for

bSi-(10-13) decreases from 0.13% to 0.02%, as the nanostructural length ranges from 674 nm to more than 1300 nm, the length of bSi-13 nanowires were not measured, but is likely to be greater than that for bSi-12, implying from the trend observed in their etching times. A similar trend is observed regarding the density of the nanostructures; lower STH efficiencies were calculated for more dense nanostructures at the start of the test. For example, bSi-3 was shown to be most dense morphology, and yields the lowest initial STH efficiency.

Equation 13: The solar-to-hydrogen conversion efficiency for a hydrogen half-cell driven by solar illumination, commonly implemented as a measure of cathode performance.^[6,190,248]

$$STH\%(\eta) = \frac{V_{max} \times J_{max}}{P_{max}}$$

Table 8 List of STH conversion efficiencies for bSi-(9-13) fabricated by Ag/MaCE, and their respective plots, before and after long term tests where applicable.

Sample name	Figure	STH efficiency	
		Before long-term tests	After (duration in days)
bSi-1	Figure 45(a)	0.15%	N/A
bSi-2	(b)	0.21%	N/A
bSi-3	(c)	0.01%	0.50% (3 d)
bSi-6	(d)	0.03%	0.13% (6 d)
bSi-8	(e)	0.02%	0.21% (4 d)
bSi-9	Figure 46(a)	0.08%	N/A
bSi-10	(b)	0.13%	0.6% (5 d)
bSi-11	(c)	0.06%	N/A
bSi-12	(d)	0.03%	0.08% (5 d)
bSi-13	(e)	0.02%	0.18% (7 d)

Figure 45 and Figure 46 displays the data used to calculate the maximum power outputs for each of the photocathodes bSi-(1-11), the photocurrent densities are plotted *vs.* the overpotential values for HER, and the product of both corresponding values ($P_{out} = J \times V$) on the secondary y-axis. A List of these photocathodes, together with their STH and corresponding graphs is in Table 8. The results are categorised based on the fabrication method; Au/MaCE fabricated

photocathodes bSi-(1-3,6,8) and Ag/MaCE fabricated photocathodes bSi-(9-13) with results displayed in Figure 45 and Figure 46, respectively. As outlined in the previous section on the long-term stability of both types of photocathodes, only bSi-(3,6,8) and bSi-(10,12,13) were used to calculate the STH efficiencies.

In contrast, after long-term testing the STH efficiency for bSi-3 significantly increases to 0.5%, due to enhanced photocatalytic activity at the interface as a result of its continuous use. This performance is comparable with that previously reported for bSi nanowires, where the STH efficiency of Ag/MaCE was measured to be 0.48% by Sim *et al.*^[190] for bSi photocathodes with 29.3 μm lengths, produced by 300 min etching. However, the performance on metal-free bSi photocathodes developed herein are attributed solely to the performance of pristine bSi, considering that other groups reported possible contribution from remaining metal catalysts at the interface after etching.

4.4.6 Tafel analysis

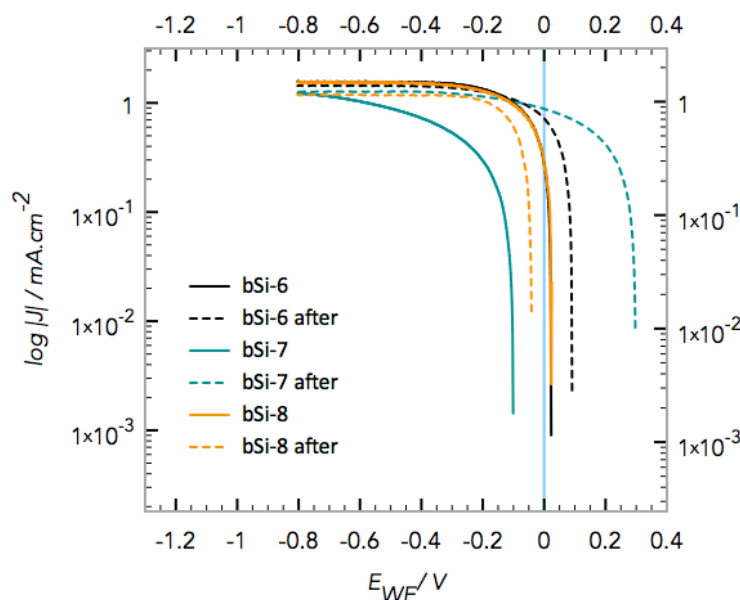


Figure 47 Semilog Tafel plots for Au/MaCE prepared samples; bSi-(6-8) photocathodes, before (solid lines), and after durability tests (dashed lines). Scan rate 50 mV.s^{-1} in 1 M H_2SO_4 .

Tafel-like plots of the logarithm of photocurrent density versus RHE potential are displayed in Figure 47 and Figure 48 for Au, Ag/MaCE fabricated photocathodes bSi-(6-8,10,12,13) that were investigated for durability. The effects of long-term catalysis on their catalytic activity is considered. Several conclusions can be drawn from this analysis regarding the contribution of the nanostructures, the effective area of the electrochemical interface as well as the activation process of the photocathodes. All curves showed a trend of positive potential shift for the same photocurrents, except for bSi-8, which shows some decrease in its catalytic activity after long term tests. We attribute this positive shift for every photocathode to the enhanced catalytic

conversion for HER, for the same morphological interface. This promotes the catalytic activity of the same interface for the adsorption of redox species onto the interface under the same testing conditions. The Tafel curves show that the photocathodes exhibit a flat plateau, indicating the limitation of these photocathodes primarily due to the sluggish kinetics of redox conversion at the interface of pristine interfaces at higher overpotentials, as described previously in Chapter 2. This is observed for all photocathodes except for bSi-7, which demonstrates relatively sluggish activity at low potentials as indicated by the lower slope region before a diffusion limited $\log|j|$ - V stretch is reached. The absence of a linear Tafel region suggests the absence of activation-controlled redox conversion of the photocathodes, except for bSi-7, which demonstrates a low-sloped semi-linear region, again due to the sluggish contribution from local active sites.

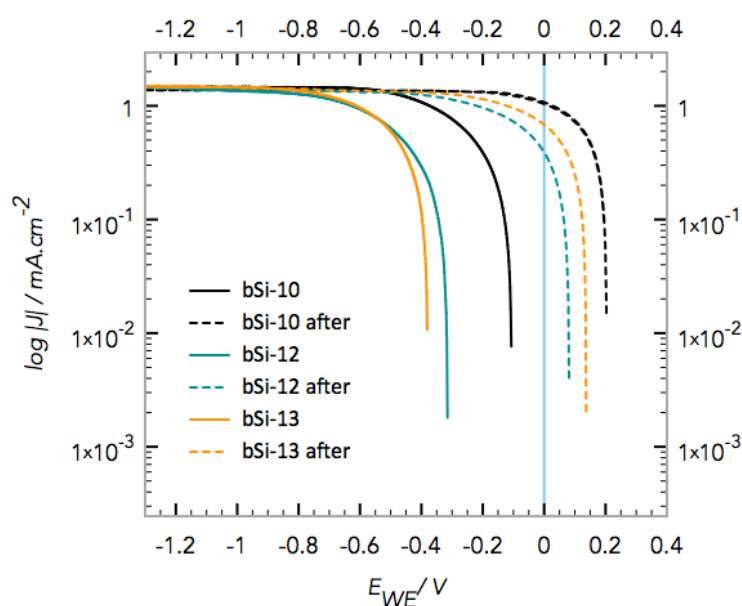


Figure 48 Semilog Tafel plots for Ag/MaCE prepared samples; bSi-(10,12,13) photocathodes, before (solid lines), and after durability tests (dashed lines). Scan rate 50 mV.s⁻¹ in 1M H₂SO₄.

Those photocathodes that demonstrate their catalytic activity positive to 0 V *vs.* RHE, demonstrate HER feasibly for a photocathode system relying on solar-assisted PEC cells. In this case, the maximal catalytic activity is achieved solely by light stimulation of the interface, by generating a photovoltage at the interface. All Ag/MaCE fabricated photocathodes undergo an anodic shift in V_{OS} to become positive of 0 V *vs.* RHE after their long-term use. While for Au/MaCE fabricated photocathodes, bSi-(6,8) initially, and bSi-(6,7) after the long-term tests, demonstrate V_{OS} and reach of maximal activity at potentials above 0 V *vs.* RHE.

4.5 Conclusions and Results Summary

In this chapter, the photocathode characterisation of metal-free bSi photocathodes were investigated for solar-to-hydrogen conversion, considering contributions from the nanostructural

geometries, the STH efficiencies, long-term stability and catalytic activities of bSi materials fabricated by using Ag or Au/MaCE. The J - V responses for each photocathode was measured before, during and after extensive long-term stability tests. The photocathodes demonstrated high photocurrent densities at 0 V *vs.* RHE. Furthermore, the bSi photocathode stability was demonstrated during at least 250 hours in a prototype hydrogen cell. The long-term performance for up to 115 days of continuous exposure to harsh acidic media, was shown on these materials, before the performance diminished.

In addition, STH efficiencies were calculated for the metal-free bSi photocathodes under 1 sun illumination to compare the performance, considering the effects of long-term operation on PEC efficiency. The measured STH efficiency for majority of the photocathodes was lower before the long term experiments, ranging between 0.02 – 0.13% for bSi fabricated by Ag/MaCE, and 0.02 – 0.21% for bSi fabricated by Au/MACE. These values showed overall increase after long-term tests, and the highest STH value was 0.5% after 3 d of continuous HER conversion at – 0.2 V *vs.* RHE (in the case of bSi-3 fabricated by 20 min etching in Au/MaCE, and the metal was completely recycled). This performance is competitive with that previously reported for bSi nanowires which reported STH efficiency of 0.48% by Sim *et al.*^[190] for bSi photocathodes despite contribution from remaining metal catalysts at the interface after etching.

In summary, the PEC analysis explains the enhanced photocatalytic activity as a result of contribution from the nanostructured interface, rather than improvement from the Si itself. The surface modification of Si offers benefits in two ways, a morphological control over the interface leads to enhanced light scattering attributes, and a significant increase of the effective electrochemical interface surface area, which exposes a vast catalytic surface for the electrochemical conversion to take place. The optimum results were demonstrated by moderately-packed and medium-length nanowires, which can be optimised by controlling the fabrication parameters during etching.

CHAPTER 5 METAL NANOCATALYSTS FOR bSi PHOTOCATHODES

5.1 Chapter Overview

This chapter presents PEC characterisation of electrocatalyst-supported bSi nanostructures. There are two parts to this chapter: Section 5.3 investigates the interface of bSi as a nanocatalyst-support photocathode platform, together with an inversion layer, based on Pt and Pd functionalised catalysts. Section 5.4 discusses the fabrication techniques of Cu catalysts in particular on bSi interfaces, and investigates the variety of bSi|Cu nanostructures that arise, their morphological and PEC characterisations for HER in acidic and neutral aqueous electrolytes.

5.2 Role of Co-catalyst Materials in Solar Energy Conversion

To achieve efficient conversion of solar energy to chemical fuel, such as hydrogen, the photocathode must exhibit excellent photovoltaic properties and catalytic efficiency. Previously in Chapter 3 and Chapter 4, nanostructured Si photocathodes were fabricated and characterised in order to develop bSi interfaces that perform enhanced STH conversion. These nanostructures have shown high efficiency due to the vast PEC interface, enhanced light-scattering effects, and long-term stability, as compared to planar photocathodes. These results were achieved on metal-free interfaces. There is yet room for improvement of the overall photocathode efficiency, because pristine Si interfaces were shown to exhibit sluggish kinetics due to poor adsorption of solvated species and poor activation of intermediates.

Therefore, assemblies which incorporate highly efficient co-catalysts are necessary in order to take advantage of the large surface area of bSi and its improved stability. This chapter presents extensive studies on noble metal catalysts on bSi photocathodes for their functionality in the HER catalysis. Several nanocatalyst fabrication techniques can be implemented to achieve catalyst-supported photocathode assemblies.

5.2.1 Efficient HER catalysts

Noble metals have formed the backbone of electrocatalysis for a variety of redox reactions. A range of computational studies have been successful in identifying desirable metal catalysts, based on their interfacial properties and the amount of energy required to facilitate the HER.^[249–251] These models also further validated experimental studies under varying conditions to devise reliable water splitting systems.^[6]

Identifying catalysts with moderate binding strength to absorb solvated species is therefore crucial. This balance is required such that the binding energy for redox intermediates is not too

weak for surface activation, nor so strong as to lead to active site saturation and thus leading to catalyst poisoning. The binding strengths of intermediates on material surfaces can be measured; however for metal-hydrogen in particular, analysis of the Gibbs free energy of hydrogen adsorption (ΔG_H) is sufficient for understanding these principles.

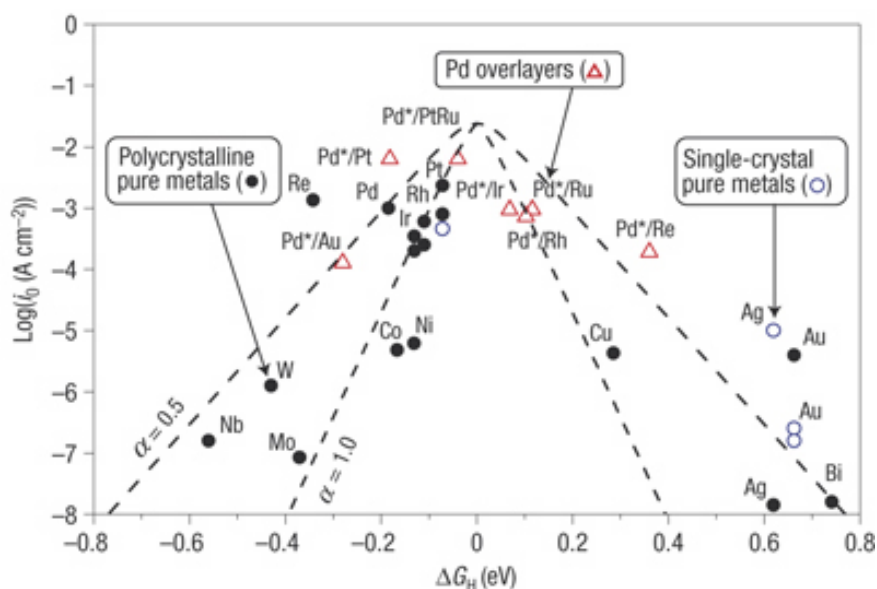


Figure 49 Volcano plot for a range of metal catalysts displays their activity for the HER in terms of the binding energy to hydrogen (ΔG_H), plotted against electrolysis current density for hydrogen evolution, at standard conditions. Image adapted with permission from Greeley et al.,^[249] ©2006, Nature Publishing Group.

When the catalytic activity of a metal is graphed as a function of ΔG_H , a relationship is found in form of a “volcano plot”, as demonstrated in Figure 49. The reason for this typical shape, is that the metals with intermediate binding strength perform the most efficient redox conversion of solvated protons into hydrogen gas, via the HER. Clearly, the most efficient materials are platinum (Pt) group metals. Pt is most commonly used due to being the most efficient and durable catalyst in electrolyser devices. This group of noble metals are regarded as some of the most scarce in the earth’s crust (*cf.* Figure 5 for a graphical representation of the abundance of earth elements).^[252]

The use of platinum in water splitting is advantageous, because it offers unmatched performance especially for low-temperature electrocatalysis.^[6,42] Pt is an expensive noble metal given that its scarce, yet it is being commonly used in its bulk form. For instance, it has been simulated that if all available platinum is collected for manufacturing fuel cells, it would only sustain a hydrogen economy of 500 million fuel cell vehicles for just 15 years, considering the parameters of a study conducted by Gordon *et al.*^[253] This analysis does not take into consideration the demands for platinum for industrial catalysts and catalytic converters, which will draw competition; eventually, platinum will not be an affordable material to rely on for making the hydrogen needed to sustain a reliable economy, or part thereof.

For this purpose, research efforts are focused on the use of such scarce materials in low quantities via nanocatalyst structures that provide the same performance and efficiency as do the catalysts in their bulk form. This has been demonstrated earlier in the published article in Chapter 2, as well as in a plethora of published literature studies.^[28] The advantages of using nanocatalysts include cutting down fabrication and materials costs, combining highly efficient catalysts with effective photovoltaic semiconductors, flexibility with surface modification to achieve nanostructures to enhance material performance and efficiency, and lastly the ability to screen different morphologies of catalysts and semiconductor assemblies to find optimum PEC photocathodes for use in solar water splitting, or other fuel production devices.

5.2.2 Metal Functionalisation on Si Interfaces

A wide-range of techniques can be implemented to obtain metallic and non-metallic dispersions. The physico-chemical properties of the supporting platform and its morphology are quite significant in determining the deposition parameters required. There are many theoretical and experimental studies reported regarding the processes involved in metal decoration of planar Si surfaces.^[28,35,40,114,254–261] The interface morphology, its interaction with chemicals and illumination, are amongst some of the factors that influence such processes. The common deposition methods include, but are not limited to, electroless, electrochemical, or photoelectrochemical (ED, ECD, or PED, respectively), or through physical coating methods such as magnetron sputtering.

The ECD method is the basic method for electroplating metal particles from solution and can be performed by applying an external bias to the working electrode of an electrochemical cell, while connected to a potentiostat. The metal deposition can be driven either potentiostatically, in the case of ECD, or galvanostatically, in the case of ED. The deposition technique and type of metal used affect the final coating quality.

ECD can be achieved via a potential-controlled (potentiostatic or chronoamperometry) method, which provides enhanced control over the kinetics of the system, the solvated redox species and the redox reactions at the interface. This method provides high quality and purity of deposition and additional control over nucleation kinetics, which are important for the fabrication of nanocatalysts. The deposition conditions, such as chemical concentration and illumination intensity, as well as substrate type, also affect the metal-nucleation kinetics due to the interaction of metal redox species with the energetics of the underlying electrode interface.

In contrast, galvanic deposition is performed by applying a specific current, therefore allows for the control over the rate of electrochemical reactions proceeding at the interface. The amount of metal can be calculated according to Faraday's law. The morphology arising from this method can be different to others used for metal deposition. There is however, a downside to this method, that the deposited species may involve impurities from the electrolyte, given that any solvated species can undergo the reduction.

ECD also includes spontaneous electroless reduction of metals via ED. This is because local microscopic "electrochemical cells" are established at the interface allowing metal reduction. The metal work function and band positions of the Si play a significant role. In order for ED to proceed, the metal is required to exhibit adequate oxidising strength to initiate the displacement

of a Si atom at the interface. This is dependent on the work function and electrochemical potential of the metal, in order to inject holes into the valence band of Si, or scavenge electrons to reduce itself at the interface, such as the case in deposition under illumination.

The different conditions associated with deposition on Si, are discussed in detail. Especially for metals whose redox potentials do not allow their spontaneous deposition, such as the case with Cu, deposition can still be performed by using adequate agents that can initiate the chemical displacement of interfacial atoms, in a similar manner to that previously employed for the fabrication of bSi using MaCE (*cf.* Chapter 3).

In regards to PED, illumination is beneficial in providing a photovoltage, which arises due to photogenerated charge carriers. These are necessary for driving the redox reactions associated with metal-deposition at the interface. In this process, the overpotential needed to drive the deposition process can be minimised. The photovoltage is dependent on the energetics of Si, and the relative potential of the metal redox couple compared to that for the Si and the HER/OER. The conditions associated with PED techniques are investigated in detail for Pt, Pd and Cu metal deposition.

5.3 Fabrication and Characterization of Pt- and Pd- Coated bSi with Inversion Layers for Hydrogen Photogeneration in Aqueous Electrolytes

Both Pd and Pt are expected to enhance the performance of the underlying bSi photocathode for proton reduction, according to published literature.^[28,51,52,54] This section of the thesis investigates how Pd and Pt deposition affects the performance of *p*-type bSi nanostructures that have been coated with an *n*⁺-emitter inversion layer, to achieve a core-shell p-n junction. With a *p*-type core, or entirely doped, these nanowires can be prepared by diffusion of a Phosphorous (P) dopant from a solid source in a furnace, under inert atmosphere to avoid Si oxide formation. Through this process, diffusion can be controlled by tuning parameters such as exposure time and dopant type and concentration. Surface inversion provides a way to “unpin” the Si surface energetics and gain control of the Si band edge position, as well as the energy barrier height leading to an enhanced photovoltage.^[262] Furthermore, this method improves the charge mobility at the interface,^[263] as well as enhances the scattering effects due to the absorption coefficients associated with the *p-n*⁺ interface, which gives rise to a range of light-trapping capabilities.^[56,264]

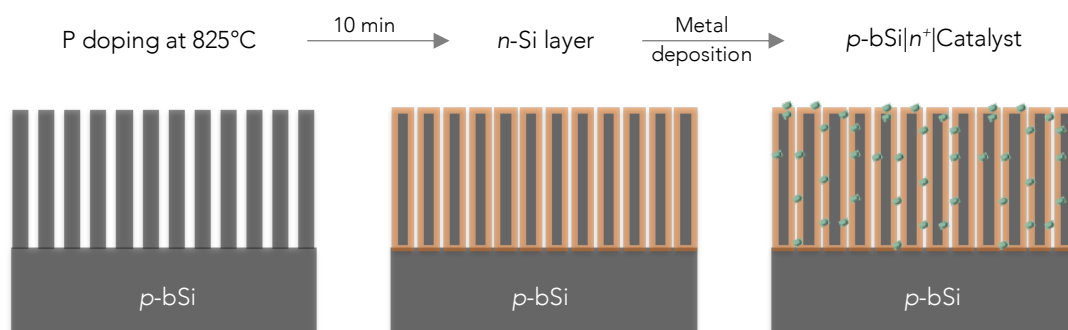


Figure 50 Schematic illustration showing the process involved in preparing catalyst coated core-shell nanostructured bSi, with inverted *n*⁺-emitter layer. Surface inversion can be achieved on bSi by exposing the wafer to a furnace equipped with solid target for P-doping under 825°C for 10 mins in an inert atmosphere. The resulting photocathode assembly can be patterned with metals nanocatalyst, such as by Pt and Pd in this work.

5.3.1.1 Experimental methods

A “dummy” Planar Si wafer (*p*-type, class C) was initially cleaned with piranha solution (*cf.* Table 2 for composition) followed by Marangoni isopropyl alcohol (IPA) drying.^[265] The wafer was cleaned with an HF oxide removal prior to doping, this wafer was used as a reference. The nanostructured bSi wafer (bSi-15, *p*-type, class C) was used for establishing *p*-bSi|*n*⁺ cathodes (*cf.* Table 14 for bSi-15 fabrication parameters). The inversion layer doping was performed¹ by P-diffusion, using solid target (Saint-Gobain, PH-900, active component; Cerium Pentaphosphate (CeP₅O₁₄)), and heated at 825°C for 10 mins under an N₂ atmosphere. This process was performed on two wafers at a time, due to the furnace capacity, and also included the reference wafer. The

¹ Phosphorus doping and conductivity measurements were conducted by staff at the Melbourne Centre for Nanofabrication (MCN). Experiments were performed according to requested parameters.

reference wafer conductivity was tested using four-point probe. Conductivity measurements on the p -bSi/ n^+ interface were not feasible given the 3-dimensional geometry of the surface, and lack of non-invasive measurement technique. The wafers were then cleaved into smaller pieces ready for PEC cell testing.

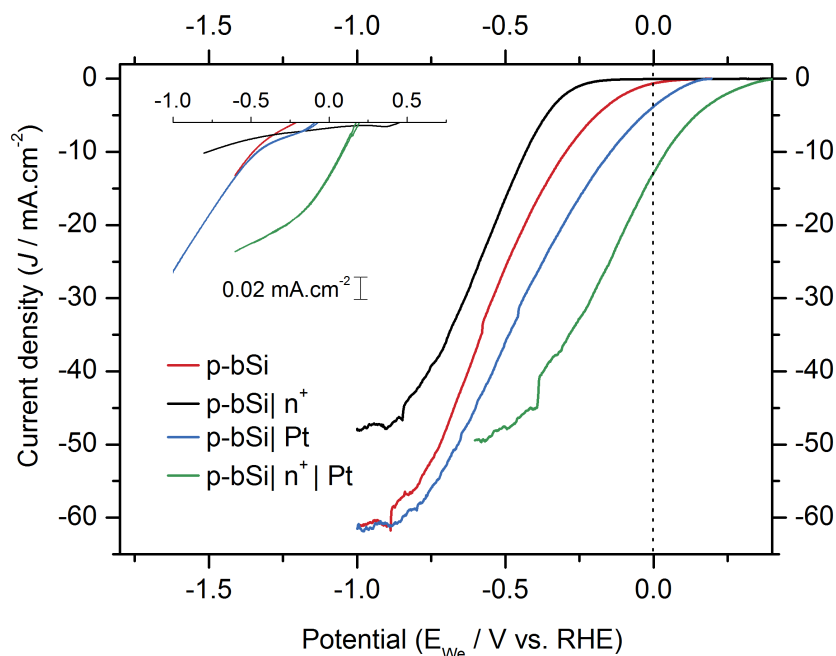


Figure 51 J - V data showing the PEC performance of Pt and n^+ -incorporated on p -bSi (bSi-15, red), p -bSi/ n^+ (black), p -bSi|Pt (blue) and p -bSi/ n^+ |Pt (green) for STH conversion from 1 M H_2SO_4 tested in dark (inset) and under illumination. Scan rate 50 mV.s^{-1} , 100 mW.cm^{-2} .

Pt was deposited from a solution containing 2 mM H_2PtCl_6 in 1 M HCl, and Pd from 0.1 wt% $PdCl_2$ in 1% HCl on bSi-15. For both metals, a standard configuration PEC cell was used to secure the p -bSi WE and expose a surface area of 0.785 cm^2 for orthogonal 1 sun illumination (100 mW.cm^{-2}). In both cases, the first stage of deposition involved scanning the electrode potential from 0.3 V to $-0.1 \text{ V vs. Ag/AgCl}$ ($0.5 \text{ V to } 0.1 \text{ V vs. RHE}$) at a scan rate of 50 mV.s^{-1} for a duration of 8 s. The subsequent deposition at $-0.1 \text{ V vs. Ag/AgCl}$ (0.1 V vs. RHE) for an additional of 60 s. The photocurrent was monitored during the deposition.

5.3.1.2 Results and discussion

Conductivity testing of the reference wafer (p -Si/ n^+) confirmed the P doping via a reduced sheet resistance of the wafer surface from $60 \text{ k}\Omega.\text{cm}^{-2}$ down to $4 \text{ k}\Omega.\text{cm}^{-2}$. To study the PEC response for the HER, the p -bSi, p -bSi/ n^+ , p -bSi|Pt, p -bSi|Pd, p -bSi/ n^+ |Pt and p -bSi/ n^+ |Pd photocathodes were subjected to cycling under both dark and illumination conditions in 1 M H_2SO_4 . Figure 51 and Figure 53 both display the results for the forward scans of the CVs obtained for the photocathodes in order to compare the effects of surface inversion and metal type on their

HER performance. The J - V features, including the onset potentials (V_{OS}) and values of photocurrent density (J) at the theoretical standard potential for the HER ($E^\circ = 0$ V *vs.* RHE), were extrapolated from the forward sweeps and are presented in Figure 52 for Pt- and Figure 53 for Pd-deposited photocathodes.

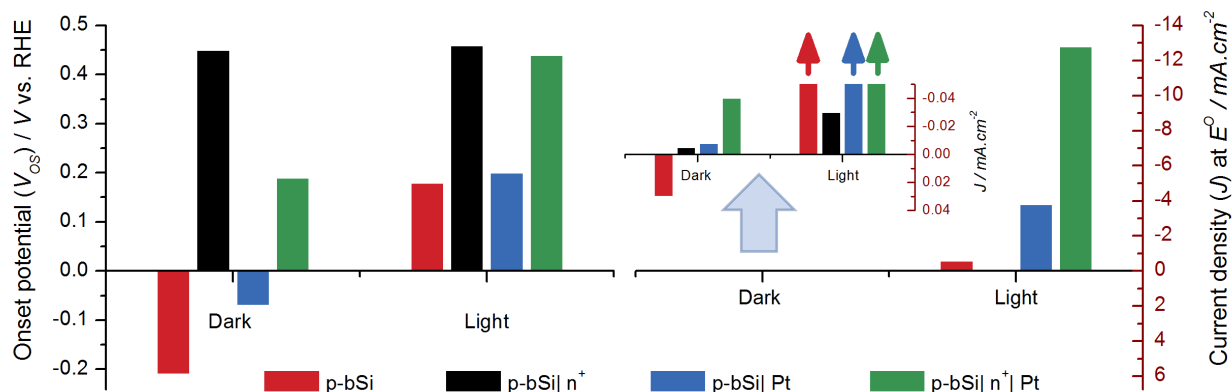


Figure 52 A comparison of the onset potentials (V_{OS}) (left) and the output dark current and photocurrent densities at $E^\circ = 0$ V *vs.* RHE (right), extrapolated from J - V data in Figure 51, for pristine p -bSi (red), p -bSi| n^+ (black) p -bSi|Pt (blue) p -bSi| n^+ |Pt (green), in dark and illumination conditions. The current densities in dark for all samples, light for p -bSi| n^+ (black) and p -bSi|Pt (blue) are displayed in the inset. Data values are in Table 12.

For p -bSi, the photovoltage produced from illumination is almost 0.4 V, which shifts V_{OS} anodically by that magnitude. In contrast, the V_{OS} for p -bSi| n^+ does not show this photovoltage effect, because of the unpinning of the band edge energies at the interface, which meant that the optimum onset potential of the surface was achieved regardless of illumination. Normally for Si, the magnitude of currents at potentials negative to the onset are significantly higher under illumination than in dark conditions due to the provision of photogenerated charges which partake in the reduction process. Furthermore, the V_{OS} on p -bSi| n^+ was anodically shifted by 0.28 V for illumination conditions, from that on p -bSi as a result of equipping the interface with the inversion layer. This value is a considerable enhancement of the performance, which means better charge-transfer kinetics towards proton reduction.

On the other hand, the forward scan in the cathodic direction for p -bSi was found to exhibit higher photocurrent for the HER compared to p -bSi| n^+ photocathodes under illumination for all potentials scanned in the range. This indicates that the p -bSi photocathode exhibits a higher catalytic activity towards the HER, before factorising the influence of the noble metals in catalysing this reaction. In addition, the currents produced by p -bSi| n^+ under illumination are lower at 0 V *vs.* RHE than that produced from p -bSi. This shows that the interface of p -type Si is more catalytically active towards HER than n -type, which is expected given p -Si has been the preferred type of semiconductor for cathodic PEC schemes. According to the review by Sun *et al.*,^[28] using an inversion layer substantially enhances the photovoltage. Hence, the contrasting observation here for p -bSi| n^+ and its decreased catalytic performance can be attributed to not optimizing for maximal

photocurrent by tuning the diffusion parameters in the processing to yield a thinner layer, which can comprise future studies. Nevertheless, the performance of Pt and Pd catalysts functionalised on p -bSi/ n^+ is of particular interest in this study.

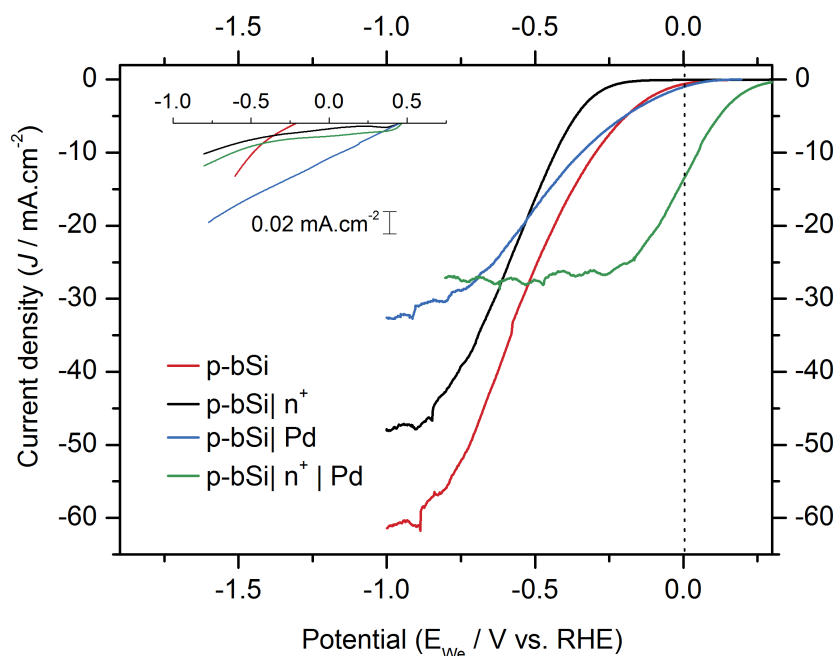


Figure 53 J - V data showing the PEC performance of Pd and n^+ -incorporated on p -bSi (bSi-15, red), p -bSi/ n^+ (black), p -bSi/ n^+ /Pd (green) for STH conversion from 1 M H_2SO_4 tested in dark (inset) and under illumination. Scan rate $50 \text{ mV}\cdot\text{s}^{-1}$, $100 \text{ mW}\cdot\text{cm}^{-2}$.

The linear sweeps for p -bSi/Pt in Figure 51 show that the Pt nanoparticles lead to an enhancement in the HER catalysis, as inferred by an overall reduction in the overpotential required to produce photocurrents for a range of applied bias values, a positive onset shift, and an increase of the magnitude of the current density at the onset potential in the dark and under illumination. This enhancement was also observed for p -bSi/Pd photocathodes (*cf.* Figure 53), where the overall J - V profile for the Pd-coated sample shifted anodically, as compared to p -bSi. However, the maximum cathodic photocurrent density is limited at approx. $30 \text{ mA}\cdot\text{cm}^{-2}$, half that produced by p -bSi ($J > 60 \text{ mA}\cdot\text{cm}^{-2}$), despite showing a similar V_{Lim} . This difference can be attributed to the coverage of Pd, which seems to hinder the light absorption of the underlying photocathode.

For both p -bSi/ n^+ /Pt and p -bSi/ n^+ /Pd photocathodes, the combination of metal nanoparticles and surface inversion led to an overall enhancement in the HER catalysis, and both metals demonstrate relatively similar onset potentials under illumination. Despite this minor enhancement of onset potentials, a significant increase in the photocurrent density at $E^\circ = 0 \text{ V vs. RHE}$, was noted for both catalysts ($-12.8 \text{ mA}\cdot\text{cm}^{-2}$ for p -bSi/ n^+ /Pt and $-13.8 \text{ mA}\cdot\text{cm}^{-2}$ for p -bSi/ n^+ /Pd). The enhanced performance of these photocathode assemblies is attributed to the improved charge-transfer kinetics caused by reducing the energy barrier at the Si/liquid interface

and an enhanced charge separation and therefore suppressing charge recombination.^[266] These effects led to an improved photocurrent and photovoltage. The charge-transfer kinetics allow for better delivery of charges to the metal catalysts, and thus better catalytic activity, particularly for p -bSi| n^+ |Pd compared to p -bSi|Pd.

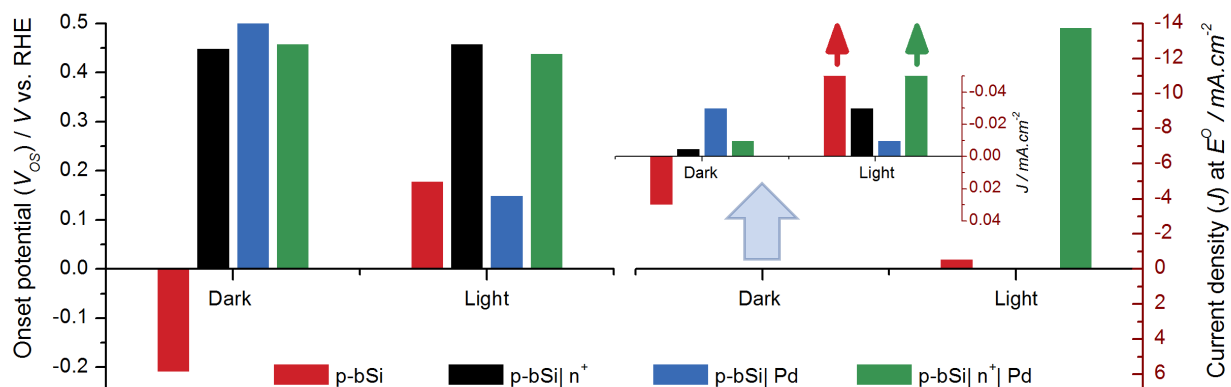


Figure 54

The onset potentials (V_{os}) (left) and the output dark current and photocurrent densities at $E^\circ = 0$ V vs. RHE (right), extrapolated from the J - V data presented in Figure 53 for Pd-coated bSi photocathodes. The bars represent p -bSi (red), p -bSi| n^+ (black) p -bSi|Pd (blue) p -bSi| n^+ |Pd (green), in dark and illumination conditions. The current densities in dark for all samples, light for p -bSi| n^+ (black) and p -bSi|Pd (blue) are displayed in the inset. Data values are shown in Table 12.

5.4 Fabrication and Characterization of Cu-coated bSi for H₂ Photoreduction in Acidic and Neutral Electrolytes

5.4.1 Literature review on Cu nanocatalysts fabrication methods and applications

Many studies investigated aspects of deposition of different metals on Si.^[35,40,203,260,261,267–270] For ED methods, the commonly addressed metals include Au and Ag because the energy band positions of Si allow for their spontaneous deposition.^[31] In contrast, there are few studies on different techniques for deposition of copper (Cu), although Cu plays an important role in the electronics industry and in modern technologies, such as solar to fuel conversion,^[6,154,271–273] or in conjunction with Si for application in Li-ion batteries.^[274–276] Cu has been especially attractive in the field of biomaterials due to the excellent bactericidal properties of both, Si and Cu.^[153,277,278]

A number of methods have been exploited for incorporating Cu on Si/bSi, including, but not limited to: electroless,^[260,279–281] electrochemical,^[114,202,205] and sputtering^[274,276,282] techniques. However, little attention has been given to the mechanism of copper deposition on bSi under illumination by PED techniques. In this section, the controlled deposition of Cu nanocatalysts is investigated, especially the different deposition techniques and growth mechanism which arise from different substrate morphologies in both *p*- and *n*-type Si.

5.4.2 Factors affecting Cu metal deposition on bSi platforms

The kinetics of metal deposition on semiconductor interfaces are influenced by a number of factors that dictate the type and characteristics of the deposited interfaces. The energetics involved in the interaction between metal ions and Si are relatively weak in nature, and hence deposition proceeds by the formation of dispersed 3D growth following the Volmer-Weber mechanism, which describes early stage metal nucleation mechanisms on semiconductors.^[204,257,261,283] There are three pathways in which metal reduction may occur at the interface of the semiconductor: via excited states in the conduction band, ground states in the valence band, or via any surface states induced by the process of doping or surface modification.^[261] This means that the deposition can proceed under adequate conditions electrolessly at open-circuit potential, under an applied bias and/or stimulated by a photovoltage with illumination.

The surface of Si does not facilitate the progress of electrochemical reactions due to the sluggish kinetics for charge transfer across the interface. However, once a driving force allows the surface to receive a metal ion, and a metal nucleus forms, this nucleus acts as a “hotspot” for electrochemical reactions to channel charges to the bulk through the deposited surface, due to the better charge-transfer kinetics involved with the deposited metal. Therefore the challenge posed Cu deposition is from the seeding of Cu particles onto Si via heterogeneous nucleation. Once seeding is successful, the reaction rate for homogenous depositions of Cu ions on Cu nanoparticles is much faster and hence favours the growth of existing nuclei, than nucleation at new sites on the pristine Si surface.

Furthermore, the redox potential for Cu is 0.34 V *vs.* RHE, which is located just above the valence band of Si (*cf.* Figure 3 for the energy band positions of Si). This means that for the ED of Cu particles on Si, the band positions do not align well for establishing an electrochemical charge transfer in order to nucleate Cu particles on the Si interface. This is contrary to what has been previously shown for Au and Ag metal ions, which are suitable for ED because their deposition proceeds via valence band hole-injection, as previously discussed in Chapter 3 and

Chapter 4. Therefore, a driving force is required: either through illumination during electrodeposition or through chemical patterning via electroless deposition or chemical displacement. Chemla *et al.*^[268] have studied the first stages of trace Cu metal deposition in detail in fluoride-containing electrolyte under electroless conditions, while Yae *et al.*^[260] conducted their study for deposition from higher Cu concentrations. Magagnin *et al.*^[114] have reported on uniform Cu layers of submicron depths from deposition times of up to 2 hours. Ogata *et al.*^[35] reviewed the mechanism involved in the electrochemical deposition of Cu structures. While some of these studies resulted in formation of porous metal due to the presence of fluoride they were all focused on planar Si materials.

The formation of Cu deposits from the combination of nucleation types can be explained by the fact that Cu nucleation onto *p*-Si proceeds via hole-injection in the valence band as well as charge transfer via the conduction band.^[35,204,261] The favoured pathway depends on the alignment of the redox level with the energy bands under the applied potential and illumination. It has been reported that less-noble metals, such as Ni, undergo deposition only by charge transfer via the conduction band, and hence heterogeneous growth predominates and even without surface activation of the underlying Si.^[35,261] Therefore it is essential in this case to illuminate the surface to achieve deposition via photoexcited electrons in the E_{CB} .

Table 9: Types of Cu deposition techniques that were used for coating bSi photocathodes with nanoparticles and dispersed coatings and the composition of the electrolytes used.

Type of technique	Deposition method	Source
(Photoelectrodeposition) - PED	LSV scan from 0 V to -0.8 V <i>vs.</i> Ag/AgCl (0.46 V to -0.33 V <i>vs.</i> RHE)	0.2 M CuSO ₄ , 0.1 M H ₃ BO ₃ , 0.1 M H ₂ SO ₄ (pH = 4.5)
	CA at -0.8 V <i>vs.</i> Ag/AgCl (-0.33 V <i>vs.</i> RHE)	
	CA at -0.8 mA.cm ⁻²	
Electroless deposition - ED	Immersion in chemical bath containing copper and Si etchant	Cu/MaCE 1 M NH ₃ , 1 M (NH ₄)HF ₂ , 1.89 M HNO ₃ , 0.01 M CuSO ₄
Sputtering	Coating of Cu particles physically from Cu target, 40 mA, 60 s in Q-150T (S), Quorum Technologies	Cu metal disc target

LSV = Linear sweep voltammetry, CA = Chronoamperometry

However, the deposition of metal particles on *n-type* Si are much more feasible without the assistance of illumination, hence more studies have investigated the morphology of metal deposition onto *n*-Si than *p*-Si wafers.^[35,261] The present study investigates light-driven

electrochemical processes on *p*-type wafers. The following case study investigates the mechanism of Cu nanoparticles deposition and coating on bSi. The resulting modified interfaces have been characterised and tested as photocathodes in PEC electrocatalysis of the HER in a variety of aqueous electrolytes. Furthermore, the nucleation, growth mechanism and catalyst morphology were investigated using SEM.

5.4.3 Experimental methods

Copper was coated onto bSi by of the following techniques: ED, and PED involving a standard configuration PEC cell described before, or physical coating using a sputtering machine (*cf.* Table 9 for further details). The fabrication parameters and bSi characterisation was previously discussed in Chapter 3.

5.4.3.1 Cu deposition

PED was carried out under applied potential in buffered electrolytes containing Cu^{2+} ions (*cf.* Table 9 for electrolyte composition). For comparison, Cu was initially deposited on planar *p*-Si (class C) and the deposit compared with that formed on bSi-15. The WE ($\text{SA} = 0.785 \text{ cm}^2$) was exposed to 30 mL electrolyte, and a coiled Pt wire CE, and a Ag/AgCl were used, along with orthogonal illumination by 1 sun (equivalent to 100 mW.cm^{-2}).

For the planar sample, a constant potential was applied at $-0.8 \text{ V vs. Ag/AgCl}$ (-0.33 V vs. RHE) for a total duration of 600s. For bSi, two techniques were compared: a variable voltage step or galvanostatic conditions. The former method involved an initial potential ramp from 0 V to $-0.8 \text{ V vs. Ag/AgCl}$ (0.46 V to -0.33 V vs. RHE) at a scan rate of 50 mV.s^{-1} followed by a potentiostatic deposition, at $-0.8 \text{ V vs. Ag/AgCl}$ (-0.33 V vs. RHE) for a range times of 0s, 10s, 20s, 50 s, 100 s, 200 s, and 600 s, resulting in catalyst coated *p*-bSi|Cu-(0s, 10s, 20s, 50s, 100s, 200s and 600s) substrates, respectively. Alternatively, galvanostatic deposition of copper obtained *p*-bSi|Cu-PED by applying a cathodic current of -0.8 mA.cm^{-2} for a duration of 30 s.

In the case of ED, Cu/MaCE was carried out by immersing substrates in Cu-containing etchant (refer to Table 9 for the composition) for 30 - 40 s. This was carried out for three samples, bSi-16, bSi-17, and bSi-18, as shown below in

Table 10: Sample names and Si wafer specifications used in ED deposition with Cu/MaCE.

Sample name after ED	Specifications	Class
<i>p</i> -bSi-16 Cu-ED	<i>p</i> -type Si, 200 μm , 0-100 ohm.cm, (100)	D
<i>n</i> -bSi-17 Cu-ED	<i>n</i> -type Si, 500 μm , 1-10 ohm.cm, (100)	E
<i>p</i> -bSi-18 Cu-ED	<i>p</i> -type Si, 500 μm , 1-10 ohm.cm, (100)	C

For the physical metal-coating process, sputtering was used for incorporating Cu particles on *p*-bSi|Cu-Sputt using a Q-150T (S) sputtering instrument from Quorum Technologies. The sputtering was conducted from a Cu disc target at a current of 40 mA and a sputter time of 60 s.

5.4.3.2 SEM/EDX microscopy

All deposited metal morphologies have been inspected using a range of electron microscopy instruments using an FEI Nova NanoSEM 450 FEGSEM instrument.

5.4.3.3 PEC testing

The PED prepared photocathodes were tested for their PEC performance driven by GAMRY interface 1000 potentiostat and using a NEWPORT ORIEL solar simulator equipped with Xenon lamp tuned to 1 sun intensity using a calibrated solar cell.

5.4.4 Results and discussion

5.4.4.1 Morphology of PED deposited Cu particles

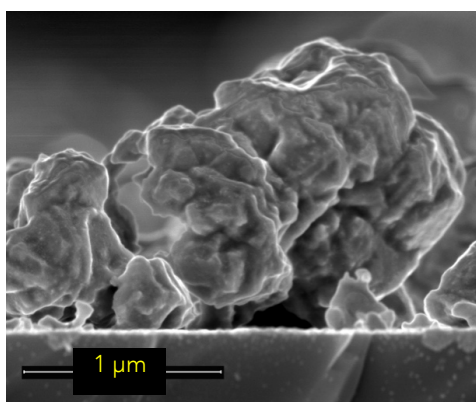


Figure 55 Cross-sectional SEM micrograph of a planar Si photocathode coated with a copper deposit that was achieved by variable potential photoelectrodeposition for 600 s.

Figure 55 shows a cross-sectional micrograph of Cu processed by PED through a constant potential on a planar *p*-Si photocathode. The growth of large micrometre-sized Cu clusters on Si is initiated by heterogeneous nucleation via reduction of Cu metal ions onto Si, and progresses by homogenous nucleation of Cu to develop the large metal clusters. Because of the limited planar interface and the kinetics involved for Cu deposition, a varying voltage method would also yield similar results due to the mechanism under illumination conditions also being dominated by homogenous deposition of the Cu metal. The observed large cluster deposition suggests that the photocurrent channelled from the Cu surface is much higher than that from the Si interface. Figure 61 shows cross-sectional micrographs of Cu deposited via PED. The initial variable-potential step results in the growth of nanoparticle sized Cu (< 150 nm in diameter) initiated by heterogeneous nucleation from the reduction of Cu metal ions mostly at the tips of the nanostructures.

Further metal deposition was achieved by holding the photocathode under potentiostatic conditions for an additional duration (10 s - 600 s). The shorter deposition durations resulted in the nanoparticle size increase up to micron sized clusters (*cf.* Figure 57 for samples *p*-bSi|Cu-(50s, 100s, 600s)). The nanoparticle coverage spans the top-half region of the nanostructures while the larger clusters grow at the pore bottom during a 50 s deposition. Longer durations (>200 s) resulted

in the formation of a copper film as a result of homogenous growth on the clusters until they formed the thick layer at the base of the nanostructures.

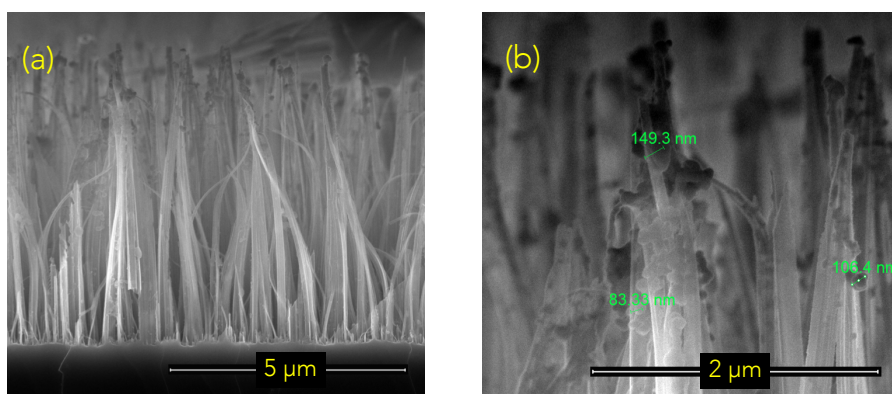


Figure 56 SEM images of cross sections of *p*-bSi|Cu-0s showing the effect of the initial step of varying potential PED in an electrolyte containing 0.2 M CuSO₄, 0.1 M H₃BO₃, 0.1 M H₂SO₄ (pH = 4.5), results in a Cu deposition of scattered amorphous shaped nanoparticles with sizes < 150 nm in diameter.

For comparison with the variable potential technique, a galvanostatic technique involving passing a photocurrent of $-0.8 \text{ mA}\cdot\text{cm}^{-2}$ for a duration of 30 s was used to prepare *p*-bSi|Cu-PED. Results in Figure 62 suggest that mostly homogenous nucleation took place during this process, because the nanostructures are decorated with scattered nanoparticles. The density and size of particles on the surface was governed by the nucleation, which was proportional to deposition time and magnitude of photocurrent applied. Passing a small constant current density allows control of the rate of the deposition.

It can be deduced from galvanostatic conditions that nanoparticles are seeded at low potentials (within 200 - 300 mV). Scanning towards cathodic potentials truncates the growth of the nucleation of nanoparticles at new sites, and hence leads to formation of relatively large clusters via homogenous nucleation. Literature reports suggest that this occurs regardless of illumination conditions.^[35,261] Energetically, the applied potential results in the downward band-bending effect near the surface of Si. The occupancy of the surface states by electrons is dependent on the position of the Fermi level, whose position is not changed by illumination. The surface states can be populated from CB de-excitations, and hence the electrons can participate in the deposition process via these surface states. Consequently, it is adequate to achieve charge transfer at low potentials via the surface states of Si to catalyse the reduction of Cu.

When a moderate cathodic potential is applied, the metal redox potential remains within the band gap, while for higher cathodic potentials, this level exhibits better overlap with the valence band. Therefore, in the latter case, one can achieve deposition via hole injection into the valence band, even in dark, regardless of the doping type of Si, and the Cu nucleation proceeds via ($\text{Cu}^{2+} \rightarrow \text{Cu}_{(s)} + 2\text{h}^+$) if the energy bands appropriately align. At this stage, nucleation follows a progressive homogenous metal deposition onto pre-existing Cu particles which grow larger in size with the

increase in deposition time. While these clusters develop in an amorphous geometrical shape, they seem to augment evenly in all directions. This indicates that the surface of the metal particles facilitates the reduction of solvated ions in these conditions. Furthermore, extended deposition times resulted in the growth of a thicker layer ($< 3 \mu\text{m}$ thickness) at the base of the nanostructures, due to the metal clusters merging to form this layer.

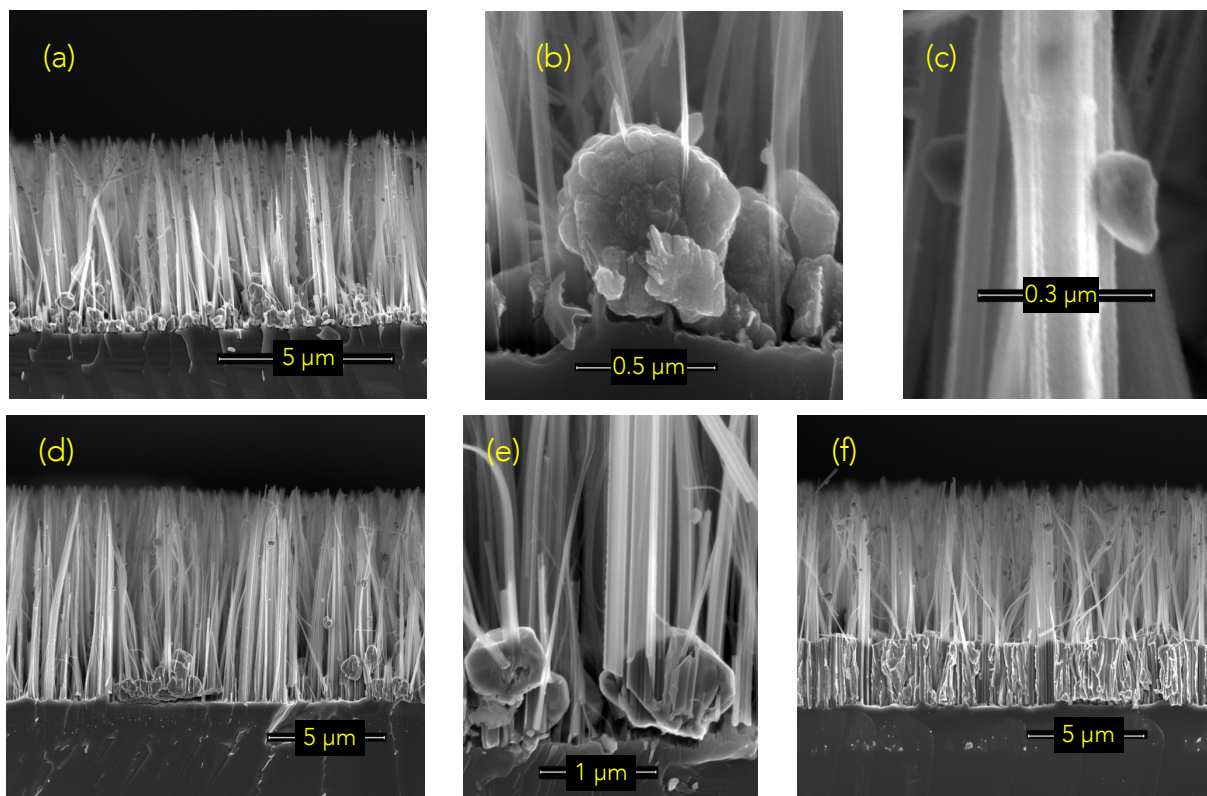


Figure 57 SEM images of cross sections of: (a-c) $p\text{-bSi/Cu-50s}$, (d,e) $p\text{-bSi/Cu-100s}$, and (f) $p\text{-bSi/Cu-600s}$ coated with copper catalysts using photoelectrodeposition in 0.2 M CuSO_4 , $0.1 \text{ M H}_3\text{BO}_3$, $0.1 \text{ M H}_2\text{SO}_4$ ($\text{pH} = 4.5$) under the illumination of 1 sun light (100 mW.cm^{-2}). For each deposition, the potential was ramped from 0 V to $-0.8 \text{ V vs. Ag/AgCl}$ (0.46 V to -0.33 V vs. RHE) at a scan rate of 50 mV.s^{-1} before a potentiostatic deposition was carried out at $-0.8 \text{ V vs. Ag/AgCl}$ (-0.33 V vs. RHE) for (a-c) 50 s , (d,e) 100 s and (f) 600 s .

The fact that the Cu layer develops around the base of nanostructures and is defined by a flat surface, which suggests that only homogenous growth takes place at higher cathodic potentials. This phenomenon confirms that the current density at this potential is higher on the surface of Cu than that on the Si surface. This can be confirmed in $J\text{-}V$ analysis of PEC performance later in this section (*cf.* Figure 64). If it were otherwise, a non-uniform Cu layer would be produced, which is not the case for substrates prepared with longer depositions $p\text{-bSi/Cu-}(50\text{s} - 600\text{s})$. Hence this supports that homogenous growth dominates at more cathodic potentials. These results conform with metal particle growth models previously reported,^[261] where initial seeding of the metals by heterogeneous nucleation is followed by diffusion-limited particle growth to form the observed 3D clusters.

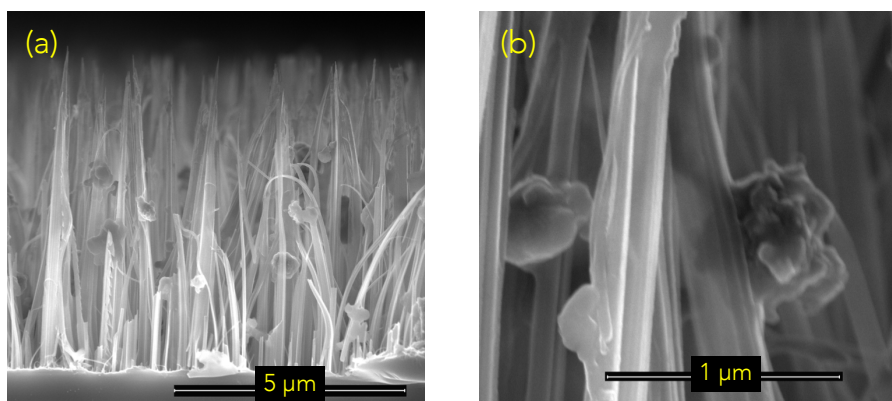


Figure 58 SEM images of cross sections of p -bSi|Cu-PED substrates with Cu particles deposited by PED method in an electrolyte containing 0.2 M CuSO_4 , 0.1 M H_3BO_3 , 0.1 M H_2SO_4 (pH = 4.5) with a galvanostatic step of $-0.8 \text{ mA}\cdot\text{cm}^{-2}$ *vs.* Ag/AgCl (-0.33 V *vs.* RHE) for a duration of 30 s, in illumination of 1 sun light ($100 \text{ mW}\cdot\text{cm}^{-2}$).

5.4.4.2 Morphology of ED of Cu on bSi

Cu deposition via electroless methods is also investigated on bSi nanostructures by immersion in Cu/MaCE (*cf.* Table 2 for chemical composition). The purpose of this is to achieve chemical displacement of surface Si atoms or to establish miniature local galvanic cells, which promote charge transfer to drive the metal reduction process.^[261] The possible mechanisms for this zero-current mechanism are illustrated in Figure 60 for the different energetic pathways. These pathways involve hole-driven chemical displacement of Si atoms, or driving a redox process at the interface involving the metal particle reduction. Figure 59 shows the SEM cross-sections for the cylindrical p -bSi-16|Cu-ED nanostructures before and after the Cu deposition process.

Several observations can be noted: the Cu deposits formed a variety of morphologies including crystalline particles in the form of cubic-shaped clusters as well as scattered amorphous growth. The deposits were observed to mainly grow at the tip of the nanostructures. A large quantity of the crystalline cubic nanostructures range between 60 - 70 nm in width, are scattered around different sites of bSi nanowires. This suggests that both homogenous and heterogeneous depositions take place spontaneously on the nanostructures.

Although no significant growth proceeds at the pore bottom, in contrast to the deposition morphology previously observed when using the PED method. This variation arises from local electrochemical cells present at the nanoscopic scale, as a result of the interaction of Si with the electrolyte. A concentrated difluoride etchant generates a potential at V_{OCP} to hold the cell at highly cathodic potential, which largely depends on the composition and concentration of the etchant.^[29,35,261]

These conditions may not be achieved during the low cathodic potentials that were initially applied in the PED method, where seeding was observed for a short duration, followed by a potential-controlled deposition. In the current experiment, the sufficiently negative potential (in excess of -0.5 V *vs.* RHE under conditions similar to that used here)^[29] facilitates diffusion-controlled deposition of the ions. Furthermore, the nucleation of new metal particles can proceed

throughout the deposition process. The deposited particles can also create pits in the nanostructures, hence stimulate the formation of defect sites in the substrate, where further Cu growth can take place, besides other defect sites created as a result of the Si etching process.

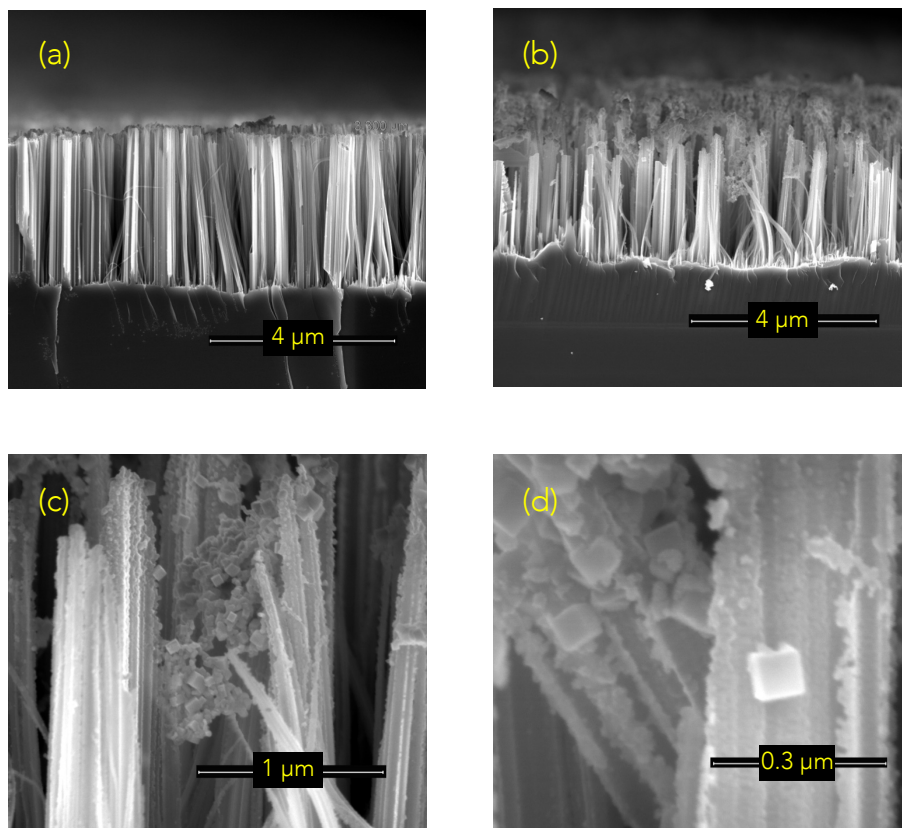


Figure 59 SEM micrographs of (a) uncoated bSi-16 and (b-d) p -bSi-16|Cu-ED after electroless deposition in Cu/MaCE for a duration of 30 s on bSi cylindrical nanostructures modified on p -type Si, class D.

Electroless Cu deposition on lower-resistivity Si with needle-like morphology produces larger clusters of Cu aggregates. Such deposits were likely facilitated by the larger spaces between the nanostructures, which can be observed in the SEM images taken for p -bSi-18|Cu-ED (*cf.* Figure 61) before and after the electroless deposition. Cu aggregates arose from nucleation sites at defect sites closer to the apex, while no significant clusters were deposited below that region.

The same ED technique was tested on n -type bSi etched under similar conditions to p -bSi, where it resulted in very different metal coverage (*cf.* Figure 62). In this case, the deposited Cu showed uniformly defined nanoparticle morphology, with larger particles growing at the tip of the wires and smaller nanoparticles towards the base of the structures. It is inherently easier to deposit noble metals, and even non-noble metals, on n -type Si, without assistance from illumination. This is because Cu deposition can proceed by hole injection via the valence band as well as charge transfer via the conduction band. It is believed that the resulting morphology is stabilised in the presence of fluoride- and oxidant-containing media.

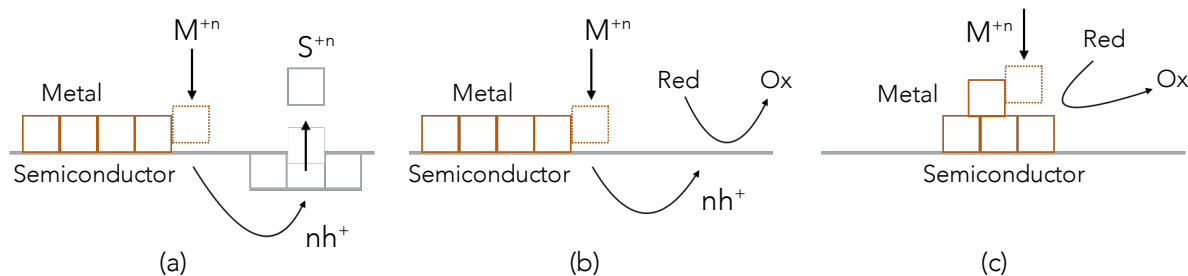


Figure 60 Schematic diagram showing the different mechanisms involved in metal deposition via electroless pathways from a M^{+n} -containing electrolyte (in this case Cu^{2+}). Holes are injected from the metal into the valence band of Si via $(M^{+n} \rightarrow M_{(s)} + nh^+)$ either: (a) oxidise the surface atoms (S) in the vicinity, and if the products are soluble, such as in the fluoride-containing electrolyte, and lead to their dissolution (cf. Equation 7 and Equation 8 for SiO_2 dissolution to fluorosilicates in different pH conditions). (b) injected holes drive an oxidation reaction of a reductant at the interface, if available, or (c) homogenous nucleation driven by electrons which are donated by an oxidation reaction at the interface of the metal, in favor of the enhanced charge-transfer kinetics on the metal surface as compared to that on the Si surface. The concepts and mechanisms illustrated were developed by Oskam et al.^[261]

In regards to the etching effect on nanostructured Si wires in both Si wafer types, the substrate undergoes further etching either by Si oxidation or hole-injection from the neighbouring Cu deposition (cf. Figure 60 for the different mechanisms involved in ED of a metal), and in turn dissolution takes place to produce fluorosilicates. The rate of etching of Si in the fluoride solution is relatively slow, however it is significantly increased under the influence of metal deposition, as outlined before for MaCE mechanisms in Chapter 3. The nanostructures undergo thinning or shortening in this process; however substrate immersion for a duration of 30 s - 40 s, is sufficient to obtain a significant catalyst coverage while preserving a high degree of the nanostructures, as shown in all cases of electroless depositions.

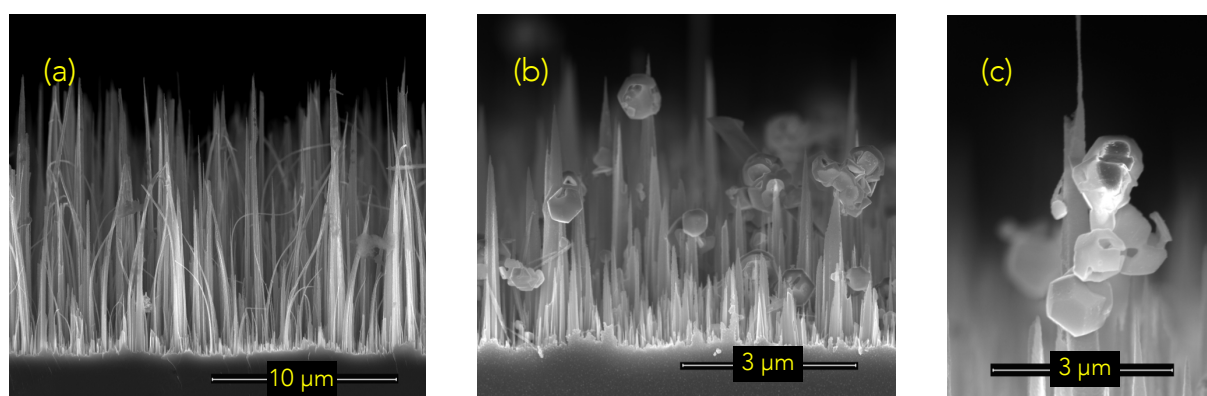


Figure 61 SEM micrographs of p -bSi-18|Cu-ED before and after electroless deposition in Cu/MaCE solution for a total duration of 40 s on needle-like textured bSi modified on p -type Si wafers (class C).

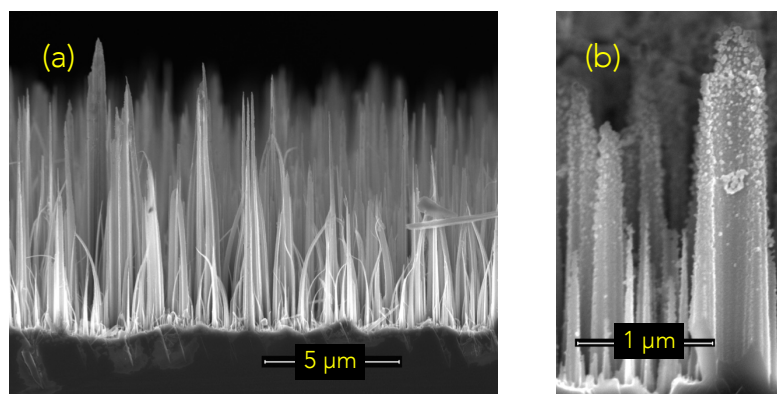


Figure 62 SEM micrographs of (a) uncoated bSi-17 nanostructured surface and (b) n -bSi-17|Cu-ED after electroless deposition in Cu/MaCE solution for a total duration of 40 s on n -type bSi (class E).

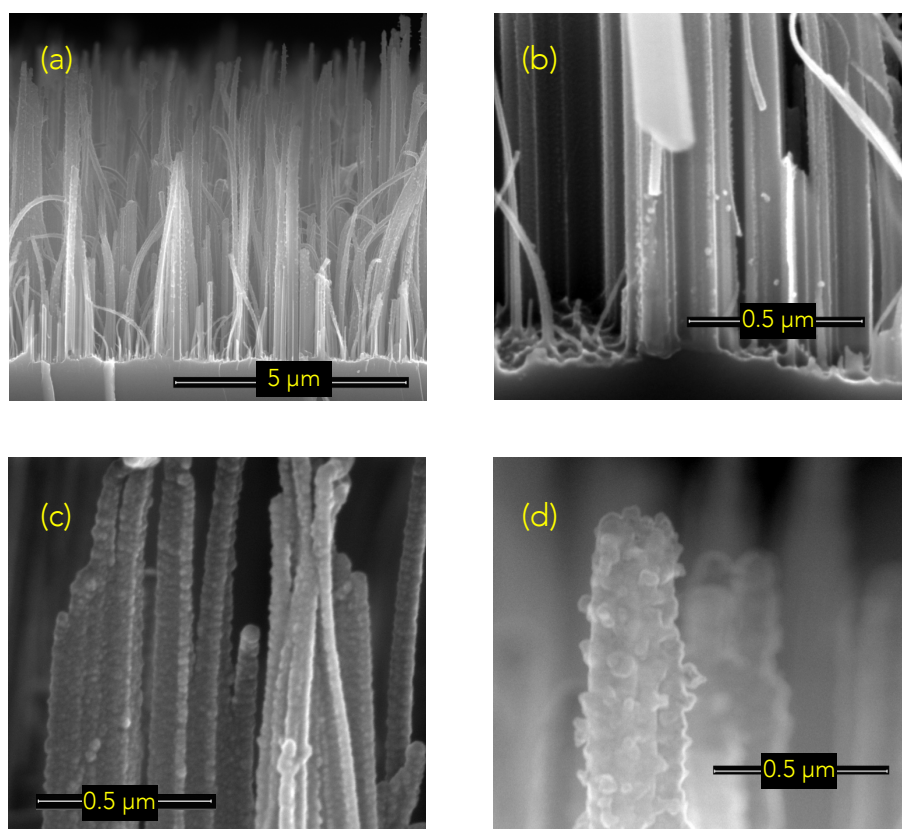


Figure 63 SEM images of cross sections of p -bSi|Cu-Sputt showing the type of Cu coating that arises from physical coating of Cu particles by means of sputtering technique.

The scattered nanoparticle deposits observed in the studied electrochemical methods can be explained by the nature of metal-ion interaction with semiconductor interfaces. A general rule, nanoparticle nucleation from solution onto foreign surfaces is favoured on active sites such as surface defects, where the substrate is a semiconductor, and the deposition didn't take place via either of the energy bands.^[261] Following nucleation, deposition proceeds by diffusion-limited

three-dimensional growth, obeying the Volmer-Weber mechanism,^[204,257,261,283] and therefore giving rise to the scattered islands observed in the Cu deposits.

5.4.4.3 Physical metal deposition by sputtering

In an alternative approach to electrochemical deposition, sputtering can produce more uniform Cu coatings on bSi. Figure 63 shows a sputtered Cu layer, sample *p*-bSi|Cu-Sputt, with uniform coverage except for at the bases of the nanostructures. This implies that physical deposition means are key for uniform coating of bSi nanostructures with Cu metal. In contrast, the electrochemical and chemical methods studied here resulted in dispersed metal clusters or thick homogenous coatings at the base of these nanostructures.

5.4.4.4 EDX composition analysis

All substrates were inspected for their elemental composition using EDX spectroscopy: the results are collated in (*cf.* Figure 66). Cross-sectional regions from the interface were scanned under high (10 - 20 keV) accelerating voltage, which is higher than that used to collect the SEM micrographs. For some samples, such as, *p*-bSi-16|Cu-ED, EDX analysis was possible from accelerating potentials as low as 5 keV. The nanoparticles observed from the deposition are all indeed copper, attached to different regions of the nanowires. The spatial resolution for EDX does not permit high-resolution imaging for small nanoparticles, it is clear that the deposition does take place, giving rise to a range of metal particle sizes.

5.4.5 Photoelectrochemical cell characterization of Cu-coated bSi

The performance of bSi|Cu photocathodes is investigated for the HER in 1 M Na₂SO₄ (pH = 6) or 1 M H₂SO₄ (pH = 0) electrolytes. Experiments were carried out in a typical three-electrode PEC cell configuration. A series of CV scans were performed on the WE against an Ag/AgCl RE, and a coiled Pt wire CE. The photocathode was orthogonally illuminated with the Xenon lamp of a Newport solar simulator, tuned for one sun-equivalent power density (100 mW.cm⁻²) using a solar cell. The potential scale was converted to reflect the measured potentials to the RHE scale, according to $E_{RHE} = E_{Ag/AgCl} + 0.197 + (0.059 \times \text{pH})$.

Figure 64 compares *J-V* characteristics of samples *p*-bSi|Cu-(0s - 20s) prepared by variable PED method, with those of uncoated *p*-bSi, for their dark and illuminated performance in both electrolytes. The HER onset potentials (*V*_{OS}), are shown for all photocathodes in Figure 65. Several observations can be made about the effects of Cu nanoparticles. The onset potential for metal-free nanostructured bSi in acidic and dark conditions is close to the standard onset potential for HER at = 0 V *vs.* RHE. For all other conditions, as well as for the Cu-functionalised photocathodes, the onset is much more positive than this value, which indicates an enhancement by a lower overpotential required to drive HER.

Introducing a Cu nanoparticle coating generally resulted in an anodic shift in the onset potential. Varying the amount of Cu deposition produced varying results, as will be discussed. Furthermore, the magnitude in anodic onset potentials shift from the control photocathode according to the illumination conditions and electrolyte pH. For acidic conditions, the shifts are much larger in dark, while minor variation can be observed under illumination.

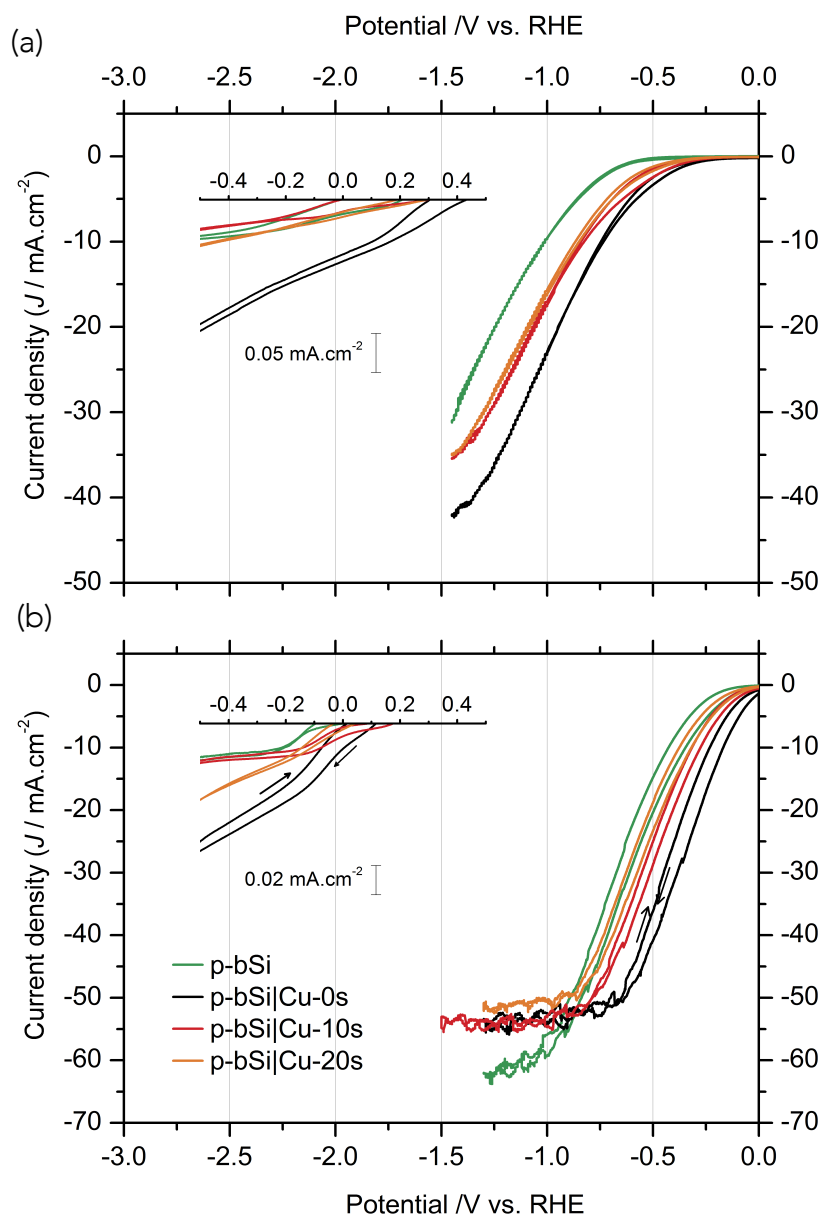


Figure 64 J - V data showing the different PEC performance on p -bSi|Cu-(0s - 20s) in (a) 1 M Na_2SO_4 and (b) 1 M H_2SO_4 illuminated and in dark (inset). In all (b) curves, the forward scan is the one with higher overpotential than the corresponding backward scans, as indicated by the arrows. Scan rate 50 mV.s^{-1} , 100 mW.cm^{-2} .

5.4.5.1 Effect of particle morphology

It seems that the increase of Cu nanoparticle size by extending the deposition time on the constant potential step to 20 s, does not improve performance. For instance, p -bSi|Cu-20s showed the least positive onset potential compared to all Si/Cu interfaces. This result suggests that a nanoparticulate morphology is favoured for the catalytic activity for STH conversion, such as in the case with p -bSi|Cu-0s which was prepared via a variable potential step. This photocathode showed the most anodic onset, hence better catalytic activity for the HER.

5.4.5.2 Effect of electrolyte pH

The onset values in Figure 65 do not show a specific trend within each set of experimental conditions, however for acidic media are lower than those for the corresponding photocathode in neutral conditions. This shows that the catalysis for the HER in the neutral electrolyte is better than that in acidic media for the Cu-functionalised photocathodes. This can be observed regardless of the deposition thickness of copper particles, and is also the case for the pristine Si nanostructures. This could be attributed to the high binding energy for protons on Cu, meaning that, with the abundance of protons in acidic media, and low electrolysis current, the HER is limited by the availability of the active sites on the catalyst interface (*cf.* Figure 49 for the proton binding energy and electrolysis current for a variety of noble-metal catalysts). In neutral electrolytes, with a far lower concentration of protons, Cu-functionalised photocatalysts perform better.

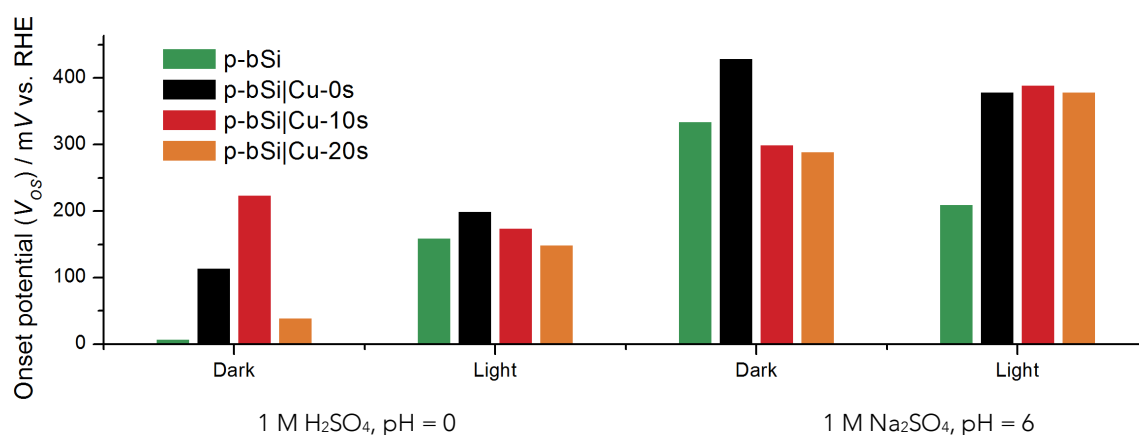


Figure 65 The onset potentials (V_{os}) in mV extrapolated from J - V data in Figure 64, for pristine p -bSi (green), Cu-coated p -bSi|Cu-0s (black), p -bSi|Cu-10s (red) and p -bSi|Cu-20s (orange), in dark and illumination conditions in both electrolytes. The onsets are all positive to the standard HER potential (0 V *vs.* RHE). There is no specific trend observed within each set of conditions, however V_{os} values are seen to increase in neutral conditions.

In terms of driving the HER, the photocurrent yield on p -bSi|Cu-0s is also optimal compared with those seen on the metal-free photocathode or other Cu-coated substrates, in both acidic and neutral media. The photocurrents are higher for the same overpotential in the case of acidic electrolyte, given that the potential across the interface is at the same value *vs.* RHE. This is due to the abundance of protons in the solution. In other words, when the adsorbed protons are reduced to gaseous hydrogen driven by the applied overpotential, the rate at which this process occurs is much higher in a highly concentrated (acidic) medium. Furthermore, a limiting photocurrent $J_{lim} > -60 \text{ mA.cm}^{-2}$ was achieved on the uncoated p -bSi photocathode, which is onset at a higher overpotential than that for p -bSi|Cu-0s, which measures $\sim -55 \text{ mA.cm}^{-2}$ of photocurrent density. The CV curves for all photocathodes show that the back scan occurs at a lower over-potential from the forward scan. The forward and backward scans are indicated with arrows in Figure 64(b). The difference in the overpotentials indicate that the catalysis is enhanced in the backward scan for each of the photocathodes.

5.5 Conclusions and Results Summary

This study chapter has presented a preliminary investigation of bSi interface optimisation by a P-doped inversion layer, and the performance for the HER using Pt and Pd co-catalysts, has been studied. Results demonstrated that an anodic shift in the onset potentials shifts: 0.24 V and 0.29 V and an increase in photocurrent value by 9 mA.cm⁻² and 13.8 mA.cm⁻², respectively at 0 V *vs.* RHE, as a result of introducing the emitter layer.

Furthermore, this chapter investigated the deposition of a range of copper nanostructures and coatings optimised using various electrochemical techniques namely; photoelectrochemical (PED) and electroless (ED), as well as physically via sputtering. The deposition parameters were optimised for shape- and rate-controlled Cu deposition. The resulting *p*-bSi|Cu nanostructures were used as photocathodes for HER catalysis in neutral and acidic electrolytes. Results have shown that PED deposition showed desirable PEC performance, where nanocatalysts ranging below 150 nm in size. Results show that the onset potentials are anodic in both neutral (up to 0.38 V *vs.* RHE) and acidic (up to 0.2 V *vs.* RHE) under 1 sun illumination. On the other hand, the yield at -0.5 V *vs.* RHE was -3.4 mA.cm⁻² at neutral conditions, -36.2 mA.cm⁻² in the case of the acidic electrolyte, due to the abundance of protons in the latter electrolyte.

5.6 Supplementary Information

5.6.1 Pt- and Pd-coated bSi

Table 11: List of all data points for the onset potentials (V_{OS}) and current densities at the theoretical $E^\circ = 0$ V *vs.* RHE, collected from *J-V* curves displayed in: Figure 51 for Pt nanocatalysts, and Figure 53 for Pd nanocatalysts, deposited on inversion layer (n^+) coated and non-coated bSi nanostructures. These data points were compared in bar-plot format in Figure 52 and Figure 54 for Pt and Pd respectively.

Sample	Onset potentials (V_{OS}) V <i>vs.</i> RHE		Current density at $E^\circ = 0$ V <i>vs.</i> RHE	
	Dark	Light	Dark	Light
<i>p</i> -bSi	-0.21	+0.18	+0.03 mA.cm ⁻²	-0.6 mA.cm ⁻²
<i>p</i> -bSi n^+	+0.45	+0.46	-0.005 mA.cm ⁻²	-0.03 mA.cm ⁻²
<i>p</i> -bSi Pt	-0.07	+0.20	-0.008 mA.cm ⁻²	-3.8 mA.cm ⁻²
<i>p</i> -bSi n^+ Pt	+0.19	+0.44	-0.04 mA.cm ⁻²	-12.8 mA.cm ⁻²
<i>p</i> -bSi Pd	+0.5	+0.15	-0.03 mA.cm ⁻²	-0.01 mA.cm ⁻²
<i>p</i> -bSi n^+ Pd	+0.46	+0.44	-0.01 mA.cm ⁻²	-13.8 mA.cm ⁻²

5.6.2 Cu-coated bSi

Table 12: List of onset potentials (V_{OS}) extrapolated from J - V curves displayed in Figure 64 for Cu nanocatalysts on bSi nanostructures. The PEC features were displayed in bar-plot format in Figure 65.

Sample name	Onset potentials (V_{OS}) V <i>vs.</i> RHE			
	1 M H ₂ SO ₄ , pH = 0		1 M Na ₂ SO ₄ , pH = 6	
	Dark	Light	Dark	Light
<i>p</i> -bSi	0	0.16	0.34	0.21
<i>p</i> -bSi Cu-0s	0.12	0.20	0.43	0.38
<i>p</i> -bSi Cu-10s	0.23	0.18	0.30	0.39
<i>p</i> -bSi Cu-20s	0.04	0.15	0.29	0.38

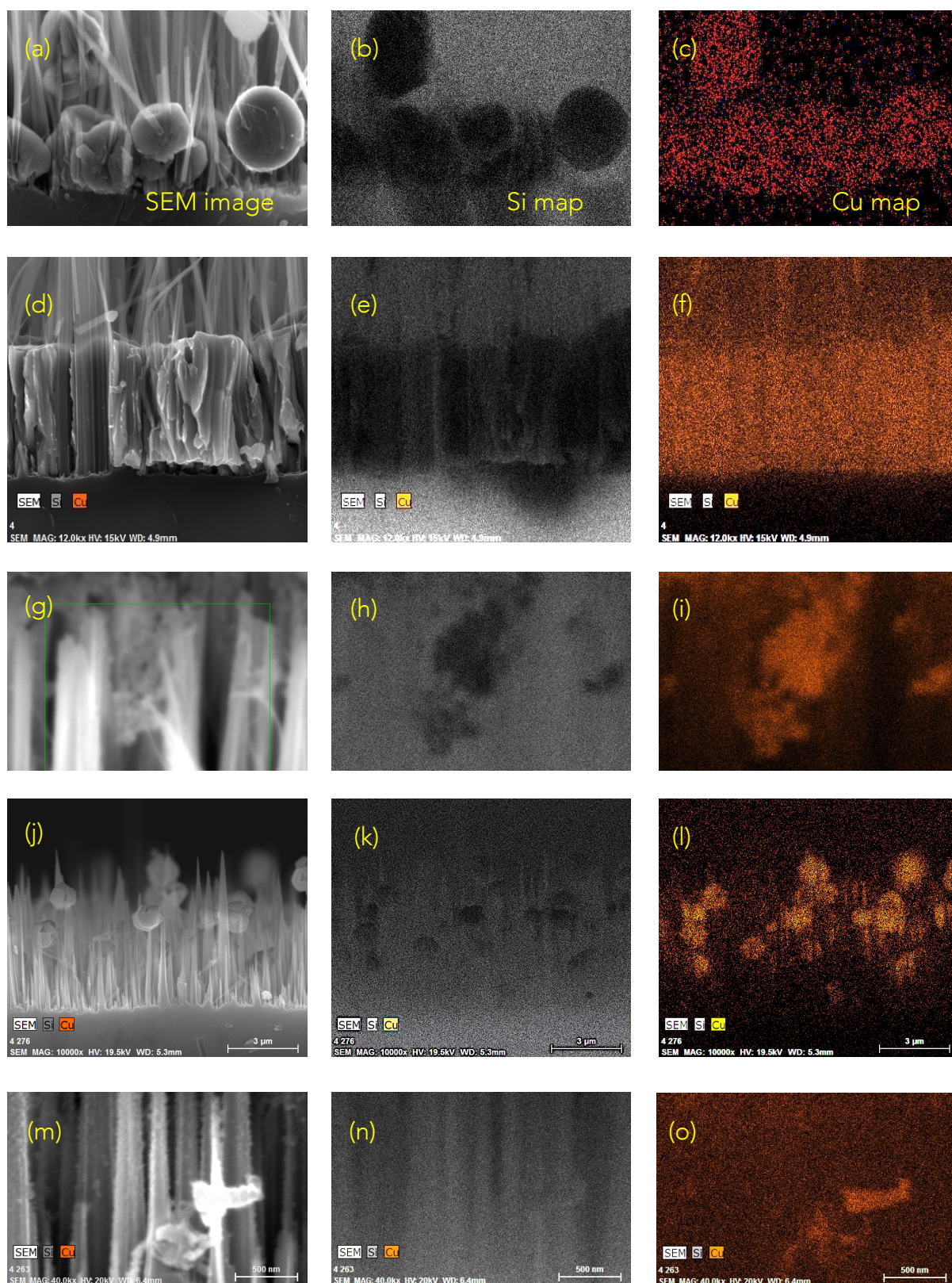


Figure 66

EDX analysis on cross sections of (a-c) p -bSi|Cu-100s, (d-f) p -bSi|Cu-600s, (g-i) p -bSi-16|Cu-ED, (j-l) p -bSi-18|Cu-ED and (m-o) n -bSi-17|Cu-ED, showing the varying morphology of Cu coatings prepared by ED/PED techniques.

6.1 Overview

Throughout the course of this thesis, a range of mechanistic studies were presented to establish theoretical and experimental background concerning the development of Si-based photocathode materials for PEC devices, particularly for the HER reaction in solar water splitting. This work benchmarks Si as a multidisciplinary platform that can also be implemented in other energy storage pathways, such as CO₂ or N₂ reduction reactions, and in conjunction with other important catalysts.

The reason for Si being a promising candidate electrode material for PEC applications is owing to the sustainability requirements. Si, being the second most abundant element, can be easily procured off-the-shelf in a variety of specifications and morphologies. Consequently, the physico-chemical properties of Si materials have been investigated in great depth, making it the most studied semiconductor material, and its use in a wide-range of applications is prominent in the electronics industry, and recently, the solar fuel-cell industry. However, in its application in solar-energy conversion to chemical fuels, the Si interface poses major challenges for supporting adequate kinetics; the interface is rendered sluggish towards redox photo- and electro-catalysis mainly because of poor interaction with redox species as well as extreme susceptibility to corrosion.

6.2 Enhancing the long-term performance of Si using diamond protective coatings

The first objective in this thesis entailed a preliminary investigation of the corrosion problem on Si interfaces and the influence of the spontaneously formed oxide on the PEC performance of a photocathode assembly. Experiments in Chapter 2 showed that corrosion entirely diminishes the performance within hours. To address this, a single encapsulating and protective interface is proposed in this work; built from boron-doped diamond (BDD), and synthesized to cater for desirable chemical inertness, pin-free morphology, ultra-high conductivity, UV-absorbing semiconducting attributes, more than 70% transparent to the solar spectrum ($E < 5.5 \text{ eV}$), and most importantly, a robust 2 μm thin layer, was developed on *p*-Si wafers to yield a cathode ensemble. From a diamond materials fabrication perspective, Si already is the material of choice for the diamond growth due to matching crystallographic and physical attributes. The fabrication of diamond coatings was carried out by FRAUNHOFER USA, according to the parameters and Si specifications provided to them, which were selected based on literature reports on the resultant BDD characterisation and physicochemical studies.^[284]

The functionality of the obtained electrodes was experimentally tested under stringent electrochemical conditions, which are known to be highly-corrosive to pristine Si. These were

successfully shown to have little or no-effect on the *p*-Si|BDD electrode. Exhaustive tests performed over the course of 280 h of continuous exposure did not yield any resistance change across the Si/diamond interface. In fact, the BDD interface has demonstrated better electrocatalytic activity after this duration and after continuous cycling, as compared with its performance at the start of the experimental tests, or even that of pristine *p*-Si. The *p*-Si|BDD electrode showed an onset for HER at -0.5 V vs. SCE (-0.26 V vs. RHE) as compared to -0.85 V vs. SCE (-0.61 V vs. RHE) for the pristine *p*-Si cathodes. This excellent performance was attributed to the nature of the grain-boundaries in BDD, in that it contains catalytic sp^2 -hybridised structures which are electrochemically significant. Therefore, the BDD coatings have demonstrated success in simultaneously protecting the underlying Si photocathode, as well as further electrochemical functionality, as compared with other protective coating materials in the literature.

However, in order to drive HER reactions in an efficient manner, these kinetics still proceeded at a significant overpotential, which indicates that external energy is required to facilitate HER at the BDD interface. Nano-sized Pt particles were electrochemically deposited in low quantities from salt solution using applied potential. The developed electrode ensemble demonstrated that BDD coatings served as an excellent corrosion-free substrate material, while the Pt particles exhibited electrochemical proton reduction kinetics almost as facile as a reference bulk Pt wire. At such low quantities, the performance of nanoscopic amounts of Pt can compete with that for a significantly larger electrode geometry. This work was published in a peer-reviewed publication.

6.3 Materials fabrication and characterisation of Si-based nanostructured interfaces

It is evident that the design of electrodes in the nanodomain is a promising approach to developing Si-based photocathodes for efficient PEC devices. To study this, chemical fabrication of Si nanostructures (bSi) was achieved by chemically etching wafers to develop a range of nanosized features. Metal-assisted chemical etching (MaCE) using Au, Ag, or Pd, was implemented as simplest generic method which allowed control of the interface morphology by tuning the etchants' compositions, as discussed in Chapter 3. Typically, the fabrication of black Si involved the use of hazardous hydrofluoric acid, or costly dry reactive ion etching techniques. Herein, etching was improved using a fast and cost-effective method that avoided HF. A range of bSi wafers of different types (*p*- and *n*-type) were fabricated by etching for 10, 20, 30, 40, or 60 minutes in ammonium difluoride (NH_4HF_2)-based etchants, containing oxidants (H_2O_2 or HNO_3) of varying concentrations. In this manner, Si nanostructures were produced with varying areal densities, shapes and dimensions. The resultant nanostructures ranged in their topology, due to variation of the chemical composition of the etchants, and the duration of etching times. The nanostructures exhibited different shapes, such as nanowires, needle-like and cone-like structures. The heights ranged from $\sim 0.3\text{ }\mu\text{m}$ to more than $35\text{ }\mu\text{m}$. Ag/MaCE has resulted in the shorter range, Au/MaCE resulted in the intermediate lengths, while Pd/MaCE resulted in lengthier nanostructures, due to a high catalytic activity of Pd. Increasing concentrations of the difluoride and oxidant both resulted in lengthier nanostructures.

Some of the physical properties investigated in this work included characterisation of: the nanostructures by electron microscopy, the interface morphology and compositions, using spectroscopic techniques to examine and quantify the surface reflectance and luminescence by

photostimulation. The reflectance was significantly decreased in the case of bSi as compared with planar Si, resulting in reflectance just above 10% of the incident light, as measured by diffuse reflectance UV-Vis spectroscopy. The absorbed portion was shown to induce excitons in the different nanostructures of the material, hence evidence of surface and bulk defects. The luminescence patterns from nanoscopic SiO_x structures show characteristic emissions in the visible and IR wavelength range, based on SEM microscopy and cathodoluminescence spectroscopy technique. This indicated that the absorbed photons generated transitions in a variety of nanostructures which possessed individual band gaps due to their nanoscale dimensions. Hence, this achieves a better understanding of the etching mechanism on Si interfaces, the morphology of the bSi nanostructures and their optical properties.

6.4 Si-based nanostructures as photoelectrodes for solar to hydrogen generation

The photocathode characterisation of metal-free bSi photocathodes were investigated thoroughly for PEC solar-to-hydrogen conversion. Accordingly, a metal recycling method was implemented to achieve dendrite free photocathodes after Au/MaCE was performed. Chemical treatments were studied for the metal-removal, and further spectroscopic tests showed evidence, for the first time in the literature, to show that metal-free bSi photocathodes were successfully obtained. The PEC performance for a range of bSi substrates was tested using voltammetry methods, and the results were reported in an article publication which was presented in Chapter 4. The *J-V* responses for each photocathode was measured before, during and after extensive long-term stability tests. The photocathodes demonstrated high photocurrent densities at 0 V *vs.* RHE, which marks the standard onset potential for the HER, while that for planar Si photocathodes showed insignificant STH conversion (-0.01 mA.cm^{-2}). The highest photocurrent recorded for the bSi photocathodes at 0 V *vs.* RHE was -12 mA.cm^{-2} for bSi-10 (Ag/MaCE), with a limiting photocurrent of -29 mA.cm^{-2} achieved at -0.64 V vs. RHE . On the other hand, the highest limiting photocurrent measured was -36 mA.cm^{-2} for bSi-(2 and 6) (Au/MaCE) at a saturation potential of -0.25 V vs. RHE , with a lower photocurrent at 0 V *vs.* RHE measured at -7.1 mA.cm^{-2} and -0.19 mA.cm^{-2} , respectively. In regards to the potentials at which HER was onset, V_{Os} was shown at 0.1 V *vs.* RHE for bSi-10, 0.25 V *vs.* RHE for bSi-2 and 0.19 V *vs.* RHE for bSi-6. The photocathodes exhibited varying nanostructural lengths; $0.67 \mu\text{m}$ for bSi-10, $3.5 \mu\text{m}$ for bSi 2 and $18.5 \mu\text{m}$ for bSi-6.

The results indicate that both the nanostructural lengths and the areal density of the modified layer influence the STH performance, such that a trend is observed for the photocathodes. Accordingly, shorter nanostructures with thicker wire diameter showed high photocurrent density yield at 0 V *vs.* RHE, with intermediate onset potential and a lower limiting current, indicating reflection of some proportion of the incident light, as is the case with bSi-10. In contrast, intermediate nanowire lengths of highly ordered nanostructures (in bSi-2) resulted in more positive onset potentials and high limiting photocurrent, achieved without significant overpotential for the maximal STH conversion rate. This was also achieved for largely disordered areal density of nanostructures in the case of thin, needle-like and height-variable wires (bSi-16), indicating that the morphology of the two photocathodes contributed to the STH performance by enhanced light-scattering effects. Considering the 1 sun illumination, these results are close to the maximum theoretical value reported for the same Si specifications, at -43 mA.cm^{-2} , assuming all

absorbed photons are converted into electron-hole charge carriers.^[285] The difference in the acquired limits is likely attributed to light reflection, or minor efficiency losses due to some charge recombination, and leaves room for future development of these photocathodes. Furthermore, future studies can be dedicated to reducing the potential for maximal performance of the photocathodes, ideally to an anodic value for the use of bSi as a standalone photocathode in an HER cell.

The bSi photocathode stability was demonstrated during at least 250 hours in a prototype hydrogen cell. Furthermore, the long-term performance for up to 115 days of continuous exposure to harsh acidic media, was shown on these materials, before degradation of the performance, but not the morphology. Furthermore, the HER onset potentials undergo anodic shifts for all the photocathodes; bSi-10 for example experienced an onset potential shift of + 0.15 V after continuous HER for 60 h at -1.3 V *vs.* RHE. Such results are quite promising for bSi in a functional PEC device.

In addition, STH efficiencies were calculated for the metal-free bSi photocathodes under 1 sun illumination to compare the performance, considering the effects of long-term operation on PEC efficiency. The measured STH efficiency for majority of the photocathodes was lower before the long term experiments, ranging between 0.02 – 0.13% for bSi fabricated by Ag/MaCE, and 0.02 – 0.21% for bSi fabricated by Au/MACE. These values showed overall increase after long-term tests, and the highest STH value was 0.5% after 3 d of continuous HER conversion at – 0.2 V *vs.* RHE (in the case of bSi-3 prepared by 20 min etching). This performance is competitive with that previously reported for bSi nanowires which reported STH efficiency of 0.48% by Sim *et al.*^[190] for bSi photocathodes with 29.3 μm lengths, produced by 300 min etching. However, the performance on metal-free bSi photocathodes developed herein are attributed solely to the performance of pristine bSi, considering that other groups reported possible contribution from remaining metal catalysts at the interface after etching.

6.5 Nanomaterial electrocatalysts supported by bSi photoelectrodes

In Chapter 5, the use of surface-functionalised HER nanocatalysts and development of the bSi interface is investigated for better photocathode performance. Accordingly, this study encompassed two objectives; firstly, to develop the interface for enhanced charge transfer and energetics, via surface inversion, and studying its PEC performance with known excellent HER catalysts, secondly, to study the capability of bSi as an electrocatalyst support photocathode for copper, whose redox electrochemistry does not allow spontaneous deposition on Si.

Regarding the first part of this study, the *p*-type interface was developed via surface inversion using P-doping to yield an n^+ -emitter layer. This was implemented due to its known enhancement in terms of increasing the photovoltage, charge mobility, control over the energy band edges of the semiconductor, as well as optical scattering attributes demonstrated by the *p-n* junctions. For this purpose, the PEC performance of these interfaces was investigated together with common HER nanocatalysts in acidic electrolytes. Pt and Pd nanocatalysts were functionalised on the surface of *p*-bSi and *p*-bSi/ n^+ . The PEC tests on *p*-bSi/ n^+ photocathodes showed that for both metal nanoparticles (Pt and Pd), the catalytic activity for proton conversion is increased, as evident by an anodic shift in the onset potentials shifts: 0.24 V and 0.29 V and an increase in photocurrent

value by 9 mA.cm^{-2} and 13.8 mA.cm^{-2} , respectively at 0 V vs. RHE , as a result of introducing the emitter layer.

Functionalising bSi with Pt and Pd nanocatalysts using common PED methods was straight-forward, as a result of the alignment of the Si energy bands with the redox potentials for both metals. Several other metals are beneficial, such as Cu which is attractive for biomedical applications or has shown high efficiency in CO_2 conversion. However, functionalising Cu on the interface of bSi is a challenging process considering the redox potential does not align well for simple deposition. For this purpose, the deposition of a range of copper nanostructures and coatings optimised using various electrochemical techniques namely; photoelectrochemical (PED) and electroless (ED), as well as physically via sputtering. The deposition parameters were optimised for shape- and rate-controlled Cu deposition. The resulting *p*-bSi|Cu nanostructures were used as photocathodes for HER catalysis in neutral and acidic electrolytes.

Detailed morphological and PEC characterisation of the photocathodes concluded that the PED deposition via variable potential ramp, from 0.46 V to -0.33 V vs. RHE at a scan rate of 50 mV.s^{-1} , showed desirable PEC performance among the tested PED photocathodes (which included photocathodes prepared with up to 20 s additional PED deposition at -0.33 V vs. RHE after the variable potential ramp step). The *J-V* measurements showed that the HER onset potentials were positive in the case of neutral electrolytes (up to 0.38 V vs. RHE) in contrast to that obtained in acidic ones (up to 0.2 V vs. RHE) under 1 sun illumination. The limited concentration of protons in the neutral solution resulted in lower photocurrents than the yield in the acidic medium, at the same cathodic potentials. For instance, the yield at -0.5 V vs. RHE was -3.4 mA.cm^{-2} in neutral conditions and -36.2 mA.cm^{-2} in the case of acidic electrolyte. These results have identified that the smaller nanosized catalysts performed better for STH conversion, where the best performance has been demonstrated by Cu deposits that ranged below 150 nm in size.

6.6 Future work

Nanostructured black silicon-based photocathodes and nanocatalysts were developed in this research for the hydrogen evolution reaction from solar water splitting, which in the future, could be implemented in solar-to-fuel conversion technologies. There are several ways in which this work could be progressed:

6.6.1 Optimising BDD coatings for solar water splitting

Chapter 2 has covered the use of inert, highly conductive diamond coatings for stabilising the HER reaction on quasimetallic Si electrodes, intended to test the stability in dark conditions. Further research in this topic can include testing these photocathode ensembles for solar water splitting. In fact, significant research can be generated in developing the BDD coatings on nanostructured bSi, which has been shown to exhibit significant enhancement in performance, as compared with planar Si. These materials could potentially be used as the functional electrodes in many solar-to-fuel conversion applications.

6.6.2 Black Si cathodes and anodes

The advanced fabrication and characterisation techniques described for the development of p -bSi in Chapter 3 can be further extended to n -bSi such that anodes are fabricated in conjunction with stabilising coatings, as described above, and can be studied for photoelectrochemical oxidation reactions, such as the oxygen evolution reaction. This way, tandem cells can also be designed in future work, and make use of the performance of these materials and their stability. Furthermore, the results from luminescence studies, show a significant amount of surface and bulk defects were developed in the nanostructures, and therefore a systematic study could be adapted in the future such that the influence of various etchants, metal precursors, and oxidants, is studied considering their effects on the defects and the overall PEC performance. Further physicochemical characterisation is needed to fully understand the energetics and contributions from these defects to the final performance and stability of the photocathode.

6.6.3 Testing a range of co-catalysts

In this work, the performance of nanocatalysts fabricated from Pt, Pd, or Cu, have been studied mainly for the solar-to-hydrogen conversion on p -bSi|catalyst ensembles. This work can be extended to a range of catalysts such as Ru, Au, Ag, *etc.*, which may also be beneficial for other fuel reduction schemes.

6.6.4 Optimisation of p - n junction-based bSi

Chapter 5 presented preliminary results for using inversion layers as emitters in core-shell nanostructured p -bSi| n^+ photocathodes. The experiment requires significant optimisation for fully understanding the effect of the doping thickness and nanostructural morphology on the final performance of the photocathode as well as using different catalysts that are specific to other reduction reactions. In this manner, future electrode interface optimisation is key for progressing solar-to-fuel conversion towards implementation in technologies.

REFERENCE INDEXES

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Table 13 Silicon wafer specifications as obtained from supplier (University Wafer Inc.)

Class	Specifications (type, wafer thickness, resistivity, crystallographic orientation)
A	<i>p</i> -type Si, 1000 μm , <0.002 ohm.cm, (111)
B	<i>p</i> -type Si, 500 μm , 0.003-0.007 ohm.cm, (111)
C	<i>p</i> -type Si, 500 μm , 1-10 ohm.cm, (100)
D	<i>p</i> -type Si, 200 μm , 0-100 ohm.cm, (100)
E	<i>n</i> -type Si, 500 μm , 1-10 ohm.cm, (100)

Table 14 List of bSi substrates studied in Chapter 3 - Chapter 5. Samples were initially degreased using de-ionised (DI) water, acetone, ethanol and isopropanol prior to etching. Furthermore, a standard Piranha clean was performed for surface preparation.

Sample name	Si wafer class	Fabrication steps
<i>p</i> -Si Au	Class C	1 min coat in Au/MaCE-2
bSi-1	Class C	1 min coat in Au/MaCE-2 20 min etch in MaCE-1 (aged) 1 d immersion in Au-wash

bSi-2	Class C	3 min coat in Au/MaCE-2 20 min etch in MaCE-1 (aged) 1 d immersion in Au-wash
bSi-3	Class C	3 min coat in Au/MaCE-1 20 min etch in MaCE-1 (fresh) 1 d immersion in Au-wash
bSi-4	Class C	3 min coat in Au/MaCE-2 20 min etch in MaCE-1 (fresh) 1 d immersion in Au-wash
bSi-5	Class C	1 min coat in Au/MaCE-1 10 min etch in MaCE-2 1 d immersion in Au-wash
bSi-6	Class C	1 min coat in Au/MaCE-2 20 min etch in MaCE-2 1 d immersion in Au-wash
bSi-7	Class C	1 min coat in Au/MaCE-2 30 min etch in MaCE-2 1 d immersion time in Au-wash
bSi-8	Class C	1 min coat in Au/MaCE-2 40 min etch in MaCE-2 1 d immersion in Au-wash
bSi-9	Class C	10 min etch in Ag/MaCE 1 d immersion in Ag-wash
bSi-10	Class C	20 min etch in Ag/MaCE 1 d immersion in Ag-wash
bSi-11	Class C	30 min etch in Ag/MaCE 1 d immersion in Ag-wash
bSi-12	Class C	40 min etch in Ag/MaCE 1 d immersion in Ag-wash
bSi-13	Class C	60 min etch in Ag/MaCE 1 d immersion in Ag-wash
bSi-14	Class C	3 min coat in Au/MaCE-2 20 min etch in MaCE-1 1 d immersion in Au-wash

bSi-15	Class C	3 min coat in Au/MaCE-2 20 min etch in MaCE-1 1 d immersion in Au-wash
bSi-16	Class D	3 min coat in Au/MaCE-2 20 min etch in MaCE-1 1 d immersion in Au-wash
bSi-17	Class E	3 min coat in Au/MaCE-2 20 min etch in MaCE-1 1 d immersion in Au-wash
bSi-18	Class C	3 min coat in Au/MaCE-2 20 min etch in MaCE-1 1 d immersion time in Au-wash
<i>n</i>-bSi Pd	Class E	3 min coat in Pd/MaCE 20 min etch in MaCE-1
<i>p</i>-bSi <i>n</i>*		P-doping 10 mins at 825 °C (PH-900)
<i>p</i>-bSi Pt	Class C	3 min coat in Au/MaCE-2 20 min etch in MaCE-1 1 d immersion time in Au-wash
<i>p</i>-bSi Pd		Pt deposition by: LSV from 0.5 V to 0.1 V <i>vs.</i> RHE, + 60 s CA at 0.1 V <i>vs.</i> RHE Pd deposition by: LSV from 0.5 V to 0.1 V <i>vs.</i> RHE, + 60 s CA at 0.1 V <i>vs.</i> RHE
<i>p</i>-bSi <i>n</i>* Pt		Same as <i>p</i> -bSi Pt with P-doping layer
<i>p</i>-bSi <i>n</i>* Pd		Same as <i>p</i> -bSi Pd with P-doping layer
<i>p</i>-Si Cu	Class C	—
<i>p</i>-bSi Cu-0s	Class C	—
<i>p</i>-bSi Cu-10s		CA at – 0.33 V <i>vs.</i> RHE for 10s

<i>p</i> -bSi Cu-20s		20 min etch in MaCE-1	CA at – 0.33 V <i>vs.</i> RHE for 20s
<i>p</i> -bSi Cu-50s		1 d immersion time in Au-wash	CA at – 0.33 V <i>vs.</i> RHE for 50s
<i>p</i> -bSi Cu-100s		Cu deposition by LSV 0.46 V to – 0.33 V <i>vs.</i> RHE	CA at – 0.33 V <i>vs.</i> RHE for 100s
<i>p</i> -bSi Cu-200s			CA at – 0.33 V <i>vs.</i> RHE for 200s
<i>p</i> -bSi Cu-600s			CA at – 0.33 V <i>vs.</i> RHE for 600s
<i>p</i> -bSi Cu-PED	Class C	3 min coat in Au/MaCE-2 20 min etch in MaCE-1 1 d immersion time in Au-wash – 0.8 mA.cm ^{–2} for 30 s in 0.2 M CuSO ₄ , 0.1 M H ₃ BO ₃ , 0.1 M H ₂ SO ₄ (pH = 4.5)	
<i>p</i> -bSi Cu-Sputt	Class C	3 min coat in Au/MaCE-2 20 min etch in MaCE-1 1 d immersion time in Au-wash Cu target, 40 mA, 60 s in Q-150T (S), Quorum Technologies	
<i>p</i> -bSi-16 Cu-ED	Class D	Same as bSi-16 Immersed in Cu/MaCE 30 - 40 s	
<i>n</i> -bSi-17 Cu-ED	Class E	Same as bSi-17 Immersed in Cu/MaCE 30 - 40 s	
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