Chapter 2

HYDROGEN EVOLUTION WITH MINIMAL PARASITIC LIGHT ABSORPTION BY DENSE CO-P CATALYST FILMS ON STRUCTURED P-SI PHOTOCATHODES

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2.1 Introduction

Low filling fractions of catalyst islands on planar photocathodes minimize optical losses but yield increases in overpotential due to the concentration of current density at the catalyst-coated regions of the electrode.³² Moreover, the approach either requires an emitter layer for efficient carrier transport to the catalyst-coated regions, or requires that the islands are separated by less than the minority-carrier collection length and optimally operate in the pinch-off regime to avoid excess majority-carrier recombination.⁵⁶ Microstructured electrode morphologies also have been used, and films of opaque catalyst nanoparticles (NPs) can yield minimal photocurrent losses when deposited strategically on emitter-containing p-Si microwire arrays.⁵⁷⁻⁶⁰ Specifically, high-lifetime n⁺p-Si microwire-array (μ W) cathodes with CoP NPs loaded at the base of the μ Ws yield an ideal regenerative cell efficiency (η_{IRC}) of 1.9% under 1 Sun illumination, but these devices

exhibit low fill factors.⁵⁹ Designs using n⁺p Si μ W-array cathodes with NiMo loaded at the base of the μ Ws, beneath a layer of TiO₂ NPs, or directed to the tips by an insulating, antireflective SiO₂ layer, yielded $\eta_{IRC} = 2.9\%$ and 10.8% respectively.^{58, 60} These systems require a radial emitter to facilitate carrier transport axially from the site of photogeneration to the location of the catalyst. We demonstrate herein that three-dimensionally structured semiconductors allow dense films of Co-P to be integrated with photocathodes in designs that place the opaque catalysts in the path of incident sunlight, but produce minimal parasitic absorption because the catalysts are primarily placed on surfaces that are orthogonal to the incident rays. This strategy is beneficial in the presence or absence of an emitter layer, and thus is a promising design for efficient photoelectrodes for solar fuel production.

2.2 Experimental Methods

Randomly textured micropyramidal, μ P, Si structures were formed via anisotropic etching of an unpatterned P-type Si <100> wafer with resistivity 10-20 Ω -cm that was first cleaned in 3:1 H₂SO₄ to 30% wt H₂O₂ for 10 min. The wafer was then etched for 1 h at 80 °C in an aqueous solution of 2% wt potassium hydroxide/20% v isopropyl alcohol. Silicon microwire arrays 30 µm in height and 3 µm in diameter were formed via deep reactive-ion etching in an SF₆/O₂ plasma, with a photolithographically patterned alumina mask used to define the microwire dimensions. (**A.1**) All Si samples were cleaned in a RCA SC1 bath (5:1:1 H₂O/NH₄OH/H₂O₂, 80 °C for >10 min), buffered oxide etch (at room temperature for 5 min), and a RCA SC2 bath (6:1:1 H₂O/HCl/H₂O₂, 70°C for >10 min) to remove SiO₂, Al₂O₃ and trace metal impurities. An n⁺p junction was formed via diffusion doping with CeP₂O₁₄ doping wafers (**A.1**). Si samples were coated with a Co-P catalyst via lowtemperature, scalable photoelectrochemical deposition.²⁶ The cathodic charge density passed during deposition, normalized to the projected area of the individual electrode, was used to determine the catalyst loading. Immediately after deposition of the catalyst, electrodes were tested for hydrogen evolution in a cell filled with 0.50 M H₂SO₄(aq) (TraceMetals grade, Fisher) that was continuously purged with 1 atm of H₂(g) and illuminated with 100 mW cm⁻² of simulated AM1.5 sunlight. The acidic testing environment leached excess Co from the films, reduced the absolute overpotential for hydrogen evolution until a stable value was reached within 30 min, and left islands of Co-P with an elemental Co/P ratio of ~2:1 on the substrates. The ~2:1 Co/P ratio obtained after the catalyst-activation step is in close agreement with values measured for electrochemically deposited Co-P.^{26, 61}

2.3 Results

Figure 2.1 shows scanning-electron micrographs (SEMs) of each of the p-Si/Co-P cathode structures examined in this work: planar p-Si, as well as p-Si microwires (μ W) or p-Si micropyramids (μ P on a planar, photoactive substrate). After etching, the height of the vertical Si microwires was 30 μ m and the heights of the <111> Si micropyramids were $\leq 3 \mu$ m. Photoelectrodeposition of Co-P resulted in discontinuous islands of Co-P distributed over the planar or microstructured p-Si surface. The vertical sidewalls of the μ Ws comprised the majority of the geometric surface area for the p-Si μ W-on-planar substrate. Electrodeposition directed the opaque catalyst preferentially to the surface of the μ Ws and away from the planar portion of the substrates, which remained mostly bare. Notably, deposition at high, mass-transport limited, current densities directed the catalyst deposits towards the tips of the microwires (**Figure 2.1D**). Electrodeposition of Co-P onto

n⁺-Si μ W substrates in the dark produced a similar distribution of catalyst along the length of the μ W as was observed for p-Si μ W substrates. Top-down comparisons of microwires and planar substrates with equal amounts of charge passed for Co-P electrodeposition showed that a substantially larger portion of the light-absorbing face of the semiconductor remained exposed than for deposition on planar Si electrodes (**Fig 2.1A,C**).



Figure 2.1: Scanning-electron micrographs of photoelectrochemically deposited Co-P particles after 400 mC cm⁻² charge was passed. (**A**) Top-down image of planar p-Si, inset: magnified image of individual particle showing nanoscale roughness; (**B**) Top-down image of p-Si microwire array showing minimal deposition along the base and caps of the wires; (**C**) Image at 30-degrees tilt of p-Si micropyramid array; (**D**) Image at 20-degrees tilt of p-Si microwire array.

Figure 2.2 compares the current density vs potential (*J-E*) behavior for representative planar p-Si, μ P p-Si, and μ W p-Si/Co-P cathodes for a 400 mC cm⁻² loading of electrodeposited and activated Co-P HER catalyst. Planar p-Si loaded with 400 mC cm⁻²

² of Co-P exhibited substantial parasitic absorption as well as low fill factors, and these devices yielded short-circuit (i.e. at 0 V vs RHE) current densities of -13.6 ± 0.6 mA cm⁻² and cathodic current densities > 10 mA cm⁻² at an average potential of 74 ± 10 mV vs RHE. Structured p-Si/Co-P devices exhibited a larger cathodic current density at all potentials relative to planar devices, or equivalently, a more positive potential vs RHE at all operational current densities. For example, μ P p-Si/Co-P and μ W p-Si/Co-P devices exhibited cathodic current densities > 10 mA cm⁻² at potentials of 181 ± 19 mV and 211 ± 11 mV, respectively, vs RHE.

Table 2.1: Average figures of merit for different p-Si structures loaded with Co-P and tested at 100 mW cm⁻² of simulated sunlight in 0.50 M H₂SO₄(aq). The short-circuit current density, J_{sc} is the current density at the equilibrium potential for hydrogen evolution, RHE. The limiting current density, J_{lim} , was recorded at -0.3 V vs RHE and is proportional to the total number of photons collected by the underlying Si. These values are compared to the limiting current density recorded for the bare Si devices. The potential at -10 mA cm⁻² and 0 mA cm⁻², as well as V_{oc} , determined by the difference between the open-circuit potential and RHE, are also reported. Data points were recorded during scans at 50 mV s⁻¹ after the device performance had stabilized.

Cathode structure	J _{max} (mA cm ⁻²)	Co-P loading = 400 mC cm^{-2}			
		$ J_{sc} \text{ (mA cm}^{-2})$	Voc (V vs RHE)	<i>V</i> 10 (V vs	J _{sc} /J _{max}
				RHE)	
p-Si/Co-P planar	27 ± 0.5	13 ± 1	0.265 ± 0.026	0.074 ± 0.010	0.51 ± 0.02
p-Si/Co-P μP	31 ± 2	18 ± 1	0.286 ± 0.011	0.181 ± 0.019	0.58 ± 0.05
p-Si/Co-P μW	28 ± 1	22 ± 2	0.342 ± 0.024	0.211 ± 0.012	0.78 ± 0.05

The difference in V_{oc} between μW and μP p-Si/Co-P compared to planar p-Si/Co-P electrodes cannot be explained solely by the decrease in light-limited photocurrent densities, and hence must be due to some interfacial phenomena, including possibly oxide formation or other interfacial kinetic processes differentially affecting the anodic and cathodic current densities that determine the potential of net zero current for the electrode/electrolyte system of interest. A comparison of these figures-of-merit is provided as **Table 2.1**. Prior to deposition of the catalyst, the photocathode structures exhibited similar limiting current densities while in contact with $0.50 \text{ M H}_2\text{SO}_4(\text{aq})$ and under 100 mW cm⁻² of simulated AM1.5 illumination. The limiting current density was 26.7 ± 0.5 mA cm⁻² for planar p-Si, 31 ± 2 mA cm⁻² for p-Si μ P, and 28 ± 1 mA cm⁻² for bare p-Si μ W devices. These values represent the maximum photocurrent densities, $|J_{max}|$, obtainable for each device type before losses due to parasitic absorption by the catalyst are introduced. The measured $|J_{max}|$ was consistent with the theoretical maximum photocurrent density simulated for a planar Si slab, after correcting for losses due to reflection at the Si/0.50 M $H_2SO_4(aq)$ interface and absorption in the ~1 cm of electrolyte between the cell window and the surface of the sample.⁶²⁻⁶³



Figure 2.2: *J-E* behavior of p-Si photocathodes with 400 mC cm⁻² of Co-P catalyst in 0.50 M $H_2SO_4(aq)$ under simulated 1 Sun illumination. Scans were recorded at 50 mV s⁻¹ at potentials negative of the open-circuit potential, to avoid oxidation of the Si/catalyst interface.

For each structure, $|J_{sc}|$ was lower than $|J_{max}|$ for the respective bare p-Si structured electrode, indicating that in all cases addition of the Co-P catalyst introduced some parasitic optical absorption. However, equivalent catalyst loadings impeded light absorption differently depending on the structure of the Si substrate. The 400 mC cm⁻² loading of Co-P blocked more light for the planar p-Si/Co-P and μ P p-Si/Co-P devices, which yielded J_{sc} / J_{max} values of 0.51 and 0.58, respectively, than for the μ W p-Si/Co-P devices, which yielded J_{sc} / $J_{max} = 0.78$ (**Table 2.1**). Thus, the Si μ W structure reduced parasitic optical absorption due to deposited Co-P deposition by a factor of 2 relative to the planar surface.

Figure 2.3 illustrates the effect of electrode structuring on obscuration by opaque films, by displaying the photocurrent obtained from each of the device structures during photoelectrodeposition of the opaque Co-P catalyst-precursor film, i.e. prior to the activation step that removed excess Co and structured the film as islands, leaving exposed areas on the substrate. The planar and µP p-Si devices both exhibited a rapid rate of decrease in photocurrent as the loading of the opaque film was increased, whereas the p-Si μ W photocathode showed a much lower rate of decrease in photocurrent with increased loading of the opaque film than the other types of Si photocathodes. The decrease in $|J_{sc}|$ after catalyst deposition for planar and µP Si devices was due to masking of the lightabsorbing surfaces by the catalyst film. For Si µW devices, the high-aspect ratio structure of the substrate provided a geometric surface area that was several times larger than the projected surface area, allowing the total mass of catalyst supported on the electrode to be increased without proportionately increasing shadowing of the planar surfaces of the structure. Most of the geometric surface area of the Si µW-on-planar devices is on the sidewalls of the Si µWs and oriented normal to the direction of illumination, so additional catalyst deposition did not substantially increase the parasitic optical absorption, and large catalyst loadings can be used without substantial losses of $|J_{sc}|$.



Figure 2.3: (A) Loss in photocurrent during deposition of Co-P on various p-Si structures, expressed as the light-limited current density vs. passed cathodic charge density. For clarity, the current density was normalized to the initial current density recorded for the bare photocathode in the deposition cell. (B) The measured photocurrent density in the deposition cell was highly correlated with J_{sc} for hydrogen evolution prior to dissolution of excess cobalt during activation. The predicted values of J_{sc} under 100 mW cm⁻² of simulated solar illumination in 0.50 M H₂SO₄(aq) were calculated based on the ratio of the initial photocurrent and final photocurrent during deposition, multiplied by the limiting photocurrent measured for the bare photocathode in 0.50 M H₂SO₄(aq) under nominally identical illumination conditions

Activation of the catalyst-precursor films resulted in a catalyst structured as islands, allowing more light to reach the semiconducting substrate after activation of the catalyst than during electrodeposition. Upon activation, $|J_{lim}|$ remained stable for > 30 h of continuous operation. Higher photocurrents were thus obtained from devices with activated catalyst islands (**Figure 2.2**) than from devices with an equivalent loading of catalyst structured as a continuous film (**Figure 2.3B**). When catalysts with low Tafel

slopes are used, structuring opaque catalyst films as islands has been shown to lead to improved efficiencies in planar devices relative to structuring the catalyst as a continuous film,³² but the catalyst-island strategy for minimizing parasitic absorption is limited for most catalyst-deposition methods other than lithography, because increases to the surface area of the catalyst typically result in lateral growth of the islands and therefore increased shadowing of the semiconductor by the catalyst. The structuring of the Co-P films as islands improved the performance of these devices relative to devices having continuous films, but the strategic placement of the catalyst onto a three-dimensionally structured electrode is the predominant factor responsible for the improvement in performance of the μ W Si devices relative to μ P and planar Si cathodes observed herein. To assess the effect of the increased surface area available for catalyst loading provided by the Si μ W structure, the dark catalytic behavior was compared for electrodeposited Co-P on planar n⁺-Si and μ W n⁺-Si electrodes (Figure 2.4A). The overpotential required to reach -10 mA cm⁻² was reduced to 170 mV from 190 mV for the n⁺-Si µW sample relative to a planar n⁺-Si substrate. Figure 2.4B presents a comparison of the photoelectrochemical behavior of planar p-Si and µW p-Si electrodes at increased loading, 800 mC cm⁻², of Co-P. When the illumination intensity was increased to 125 mW cm⁻² on the planar p-Si sample, J_{lim} increased to a value comparable to that of the μW device, but the increase in J_{sc} did not proportionally reflect this change. Furthermore, the potential at which -10 mA cm⁻² was produced increased slightly, but remained over 100 mV more negative, for the planar p-Si sample relative to that of the μW p-Si electrodes. This behavior demonstrates that the improved light absorption by the μW device is not sufficient to explain the increased photoelectrochemical performance of these devices relative to the planar controls.



Figure 2.4: (A) Dark catalytic behavior of Co-P on planar n⁺-Si and on an n⁺-Si μ W array with 7 μ m pitch and 3 μ m diameter in 0.50 M H₂SO₄(aq). (B) Comparison at increased light intensity of the behavior of a high loading (800 mC cm⁻² of cathodic charge density passed) of Co-P on planar p-Si with the behavior of Co-P loaded p-Si microwires, demonstrating that the observed increases in performance for the p-Si μ W/Co-P array cannot be explained solely by an increase in the collection of photons.

The potential vs RHE required to reach an absolute current density of 10 mA cm⁻², E_{10} , is a figure of merit that relates the performance of a component half-cell measured using a three-electrode experiment, such as the photocathode described herein, to the performance that would be expected for a full cell with an operating current density of 10 mA cm⁻² and containing the component half-cell.⁶⁴⁻⁶⁵ The average E_{10} obtained for a p-Si μ W-array photocathode in this work, +211 mV versus RHE, is a substantial improvement relative to the +134 mV versus RHE reported for photoelectrochemically deposited Co-P on porous 'black' p-Si or +150 mV versus RHE for NiCoSe_x on nanopillar 'black' p-Si.⁵⁰,

⁶⁶ With the inclusion of an emitter layer, the champion E_{10} for μ W n⁺p-Si/Co-P, +310 mV vs RHE (**Figure 2.5**), is slightly less positive than the $E_{10} = +345$ mV versus RHE value observed for crystalline, nanometer-thick films of CoP on planar n⁺p-Si cathode. The latter comparison is noteworthy because the n⁺p-Si μ W-array photocathode exhibited a more rapid onset to -10 mA cm⁻² relative to V_{oc} , indicating that the catalyst film was able to compensate for the decreased photovoltage relative to the planar film in the earlier study. When utilizing earth abundant catalysts with low Tafel slopes, the photovoltage lost from increased junction area can be offset by the lower overpotential that results from the increased area available for catalyst loading. The improved E_{10} for μ W Si relative to planar and μ P counterparts, with and without a buried junction, is a direct demonstration of this design principle.



Figure 2.5: Power-conversion efficiencies for top-performing μ W devices under 1 Sun illumination (100 mW cm⁻²). The efficiency was calculated assuming 100% faradaic efficiency towards hydrogen evolution. n⁺p-Si devices outperformed p-Si devices due to the increased voltage provided by the solid-state junction relative to the p-Si/liquid junction. The maximum efficiency of p-Si μ W devices approached that of a planar n⁺p-Si device, due to the more efficient catalyst utilization on the surface of the microstructured photocathode.

2.4 Discussion

For Si photocathodes decorated with earth-abundant catalysts, the device efficiency can thus be increased substantially by minimizing the geometric footprint of the opaque catalyst over the light-absorbing surfaces of the semiconductor. Structured substrates allow for the catalyst footprint to be minimized without a reduction in the active surface area of the catalyst. The performance of the silicon microwire devices reported herein relied on long carrier-collection lengths in the axial direction. Free-standing microwire

arrays achieve optimal performance when minority carriers are collected radially, which requires that the catalyst loading be distributed along the length of the microwire to match the local carrier generation rate. The more general approach should be also useful for other semiconductor materials that can be structured such that the majority of the electrochemically active surface area is located on surfaces orthogonal to incident illumination,³⁷ provided that optical carrier generation is maximized and is spatially comparable to the photogenerated charge-carrier collection distances and catalyst location.⁶⁷⁻⁶⁸ Structuring Si into an array of microwires improved the peak power conversion efficiency by 250% while shifting the maximum power point positive by 65 mV (Figure 2.5). The photoactive planar substrate supporting the Si μ W-on-planar device described herein is not desirable for a completely membrane-embedded water-splitting device, hence study of catalyst placement onto Si µW arrays that have been removed from the planar Si substrate and embedded in ion-exchange membranes, and testing of the membrane-embedded Si µW arrays under a variety of device conditions, e.g. back-side illumination through the membrane, will be needed to evaluate these approaches in the context of specific device designs.³¹ Such studies may include selective deposition of the catalyst onto selected regions of structured semiconductors, e.g. the tips of the Si µWs, using wavelength-dependent photoelectrochemical deposition to further reduce parasitic absorption by the catalyst.⁶⁸ The bare Si µW-arrays in this study were not optimized to minimize reflection, absorbing < 65% of incident photons. Silicon photocathodes textured to minimize reflection have achieved measured photocurrents near the absorption limit of silicon under AM1.5 illumination^{49-50, 66, 69}. Texturing High-aspect ratio structures with

antireflective surfaces could further improve the utilization of earth-abundant catalysts in photocathodes used for the HER.

2.5 Conclusion

P-type Si photocathodes incorporating high-aspect ratio microwire structures and supporting high mass loadings of an opaque earth-abundant catalyst showed substantially improved values of $|J_{sc}|$ relative to planar p-Si devices or p-Si devices textured with micropyramids. The vertical sidewalls of the microwires provided surfaces that supported high surface areas of the catalyst in an orientation that minimized the area of the semiconductor shadowed by the catalyst, thereby reducing parasitic optical absorption by the catalyst and improving $|J_{sc}|$ relative to the other photocathode structures. The potential required to reach -10 mA cm⁻² of current density for hydrogen production using the microwire-based devices was +210 mV vs RHE for p-Si and +300 mV vs RHE for n⁺p-Si, both of which are among the most positive reported values for Si-based HER photocathodes utilizing earth-abundant materials, without and including a solid-state junction, respectively. Hence, catalyst placement on sidewalls of high-aspect ratio structures is a viable strategy for incorporating large loadings of opaque catalysts directly on the surface of light absorbers.