

PHOTOELECTROCHEMICAL SYSTEMS FOR HYDROGEN PRODUCTION

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Abstract

Two important research areas that are part of NREL's effort towards a photoelectrochemical-based (PEC) direct water splitting system include surface modification to improve system energetics and triple junction amorphous silicon structures (α -Si) as a low-cost thin-film water spitting system. In the area of surface modification, p-GaInP₂ surfaces were tailored by adsorption of metallated porphyrins and transition metals with the aim of moving band edge energies as well as catalyzing interfacial charge transfer for photoelectrochemical hydrogen generation. Mott-Schottky analyses in pH 4 buffer showed that adsorption of RuOEP CO with either RuCl₃ or platinum sol shifted band edges in a positive direction by 0.48 V which is sufficient to allow the overlap of the bandedges with the water redox potentials in the dark. Charge transfer analysis showed that adsorption of RuOEP CO with RuCl₃, catalyzes charge transfer for the p-GaInP₂ surface up to a photocurrent of 1 mA/cm². However, despite these surface modifications, two-electrode I-V curves show no improvement over unmodified systems. In the area of an α -Si-based system the work involved the characterization of various α -Si triple junction structures, and a study on the ability of α -SiC to protect the surface from corrosion. Samples underwent current-voltage tests, corrosion measurements, and metal-ion catalyst treatments. The α -SiC samples were tested for their characteristics relating to their effect on the overall efficiency of water splitting, and the ability of α -SiC for protecting the underlying semiconducting material.

Introduction

A photoelectrochemical (PEC) system combines the harvesting of solar energy with the electrolysis of water. When a semiconductor of the proper characteristics is immersed in an aqueous electrolyte and irradiated with sunlight, the energy can be sufficient to split water into hydrogen and oxygen. Depending on the type of semiconductor material and the solar intensity, this current density is 10-30 mA/cm². At these current densities, the voltage required for electrolysis is much lower, and therefore, the corresponding electrolysis efficiency is much higher. At a current density similar to short-circuit photocurrent from an ideal PEC water splitting system, hydrogen and oxygen generation is achieved at an effective applied voltage of approximately 1.35 V, giving rise to an electrolysis efficiency of 91% [LHV]. One of the major advantages then of a direct conversion photoelectrochemical system is that it not only eliminates most of the costs of the electrolyzer, but it also has the possibility of increasing the overall efficiency of the process leading to a further decrease in costs.

For direct photoelectrochemical decomposition of water to occur, several key criteria of the semiconductor must be met: the semiconductor system must generate sufficient voltage to split water, the energetic of the semiconductor must overlap that of the hydrogen and oxygen redox reactions, the semiconductor system must be stable in aqueous electrolytes, and finally the charge transfer from the surface of the semiconductor must be fast enough not only to prevent corrosion but also reduce energy losses due to overvoltage. Our approach has been to look for new semiconductor materials with bandgaps in the ideal range and then attempt to catalyze their surface and engineer their bandedges if necessary. We are also reviewing PV device structures to determine if any could be easily modified to effect the direct splitting of water.

Gallium indium phosphide, with a band gap of 1.8-1.9 eV, meets the band gap energy criteria, its band edges are, however, 0.2-0.4 V too negative to achieve the band edge overlap criteria and they are pH sensitive. The electrode also accumulates photogenerated charges at its surface, thus contributing to surface corrosion and band edge migration away from the desired electrode energetics. Chemical modifications of the semiconductor electrode surface can help the system ameliorate both these problems. By performing different chemical treatments at the semiconductor surface, the band edges can be shifted to appropriate energetic positions and the interfacial charge-transfer can be catalyzed. Previous reports have shown that adsorption of organic and inorganic molecules at p-type GaInP₂ can shift the band edges of the semiconductor positive or negative.

Solid state multijunction devices can deliver the energy required for hydrogen production from water while accessing a large fraction of the solar spectrum, providing high efficiency. The lowest cost multijunction system is one based on amorphous silicon (a-Si). Triple junction a-Si devices have voltages greater than 1.8 volts, sufficient for water splitting, and the cells can be tailored to produce voltages matched to the energetic requirements of the water splitting reaction, maximizing the overall efficiency. Because of the instability of α -Si in an aqueous environment, we have proposed a surface coating of amorphous silicon carbide (α -SiC) to stabilize and protect the system. While other protective coating are being considered, the advantage of a-SiC is that it can be deposited under the same conditions and in the same chamber as the a-Si triple junction solar cells.

Results

In this section we combine two surface modification approaches mentioned above by investigating the effects of adsorption of organometallic compounds to simultaneously affect band edge shift as well as act as an electrocatalyst for the p-GaInP₂/water interface. The porphyrins were deposited onto a new p-GaInP₂ electrode after initial characterization and etching with concentrated sulfuric acid. The testing was done in pH 4 buffer. Repeated Mott-Schottky scans were performed in the cathodic and anodic directions to determine the stability of the surface treatment. The results in Table 1 are the average of all of the scans in both cathodic and anodic directions.

Table 1. Flat band potentials for drop-evaporated porphyrin treatments in pH 4 buffer. OEP = Octaethyl porphyrin, TPP = Tetraphenyl porphyrin.

Treatment	Shift in V_{FB} (V)	Standard Deviation (V)
CoOEP	0.117	0.017
CoTPP	0.121	0.053
FeOEP Cl	0.102	0.058
FeTPP Cl	0.100	0.043
RhOEP Cl	0.138	0.082
RuOEP CO	0.266	0.182
RuTPP CO	0.161	0.091

All of the porphyrins show a statistically significant shift in flat band potentials, with the ruthenated porphyrins showing the greatest shift. The band edges shifted into overlap conditions about 20% of the time with the RuOEP CO treatment (OEP = octaethyl porphyrin; CO = carbonyl). Two factors cause the large standard deviation in the flat band potential (see Table 1), neither of which is a lack of precision in measurements. The first is the varying application thickness. As we increase the porphyrin application thickness on the p-GaInP₂ surface, the shift in flat band potential increases (see Figure 1).

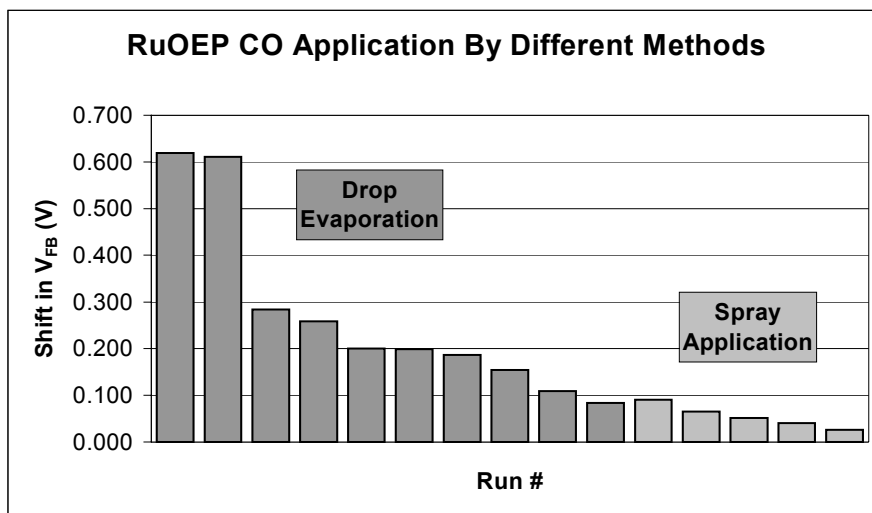


Figure 1. Comparison of drop evaporation and spray application of RuOEP CO. The magnitude of the shift in band edge position correlates well with the thickness of the RuOEP CO application. Shift in V_{FB} is the change in the Fermi level position between a treated and untreated electrode. The results are sorted by the extent of shift in the flat band potential.

The drop-evaporation method is capable of depositing greater amounts of porphyrins on the p-GaInP₂ surface than the spray application method. This apparently leads to a greater shift in the measured band-edge position with the drop-evaporation method. With the RuOEP CO drop-evaporation treatment, the flat band potential shifted as much as 600 mV when a large amount of porphyrin was applied to an electrode with a small surface area. Conversely, the flat band potential shifted as little as 100 mV when a small amount of porphyrin was drop-evaporated onto a larger surface area. The RuOEP CO spray application applied only minute amounts of the porphyrin to the electrode surface, causing only slight shifts in flat band potentials. The flat band potential shifted as little as 26 mV when the electrode is sprayed for 5 seconds, and as much as 90 mV when sprayed for 80 seconds. An outcome of this observation is that RuOEP CO may not be the best band edge-shifting agent of all the porphyrins that we studied. Because the porphyrin thickness may have varied between runs, we may have inadvertently applied more RuOEP CO than other porphyrins to the p-GaInP₂ surface during initial testing. This would make the grounds for comparison between different porphyrins unequal. Further testing is needed to normalize the differences between application techniques.

The second factor causing a large standard deviation in the flat band potential is the electrode age. After several etchings in concentrated sulfuric acid, the response to porphyrin treatments decays. We hypothesize that the decrease in response is due to the decrease in surface defects (and an increase in the surface smoothness) of the p-GaInP₂ as the electrode is etched more. Previous work in our laboratory showed that the photoluminescence of p-GaInP₂ increases as the etch time increases. In fact, the photoluminescence increases the fastest when etched in concentrated sulfuric acid, as compared with the other etchants studied. The increase in photoluminescence is indicative of fewer surface states, suggesting that the p-GaInP₂ has a cleaner surface with fewer defects. As the number of surface states and defects decrease, there is less opportunity for the porphyrin to attach to the surface. Thus, with less porphyrin attached to the surface, the band edge shift substantially decreases.

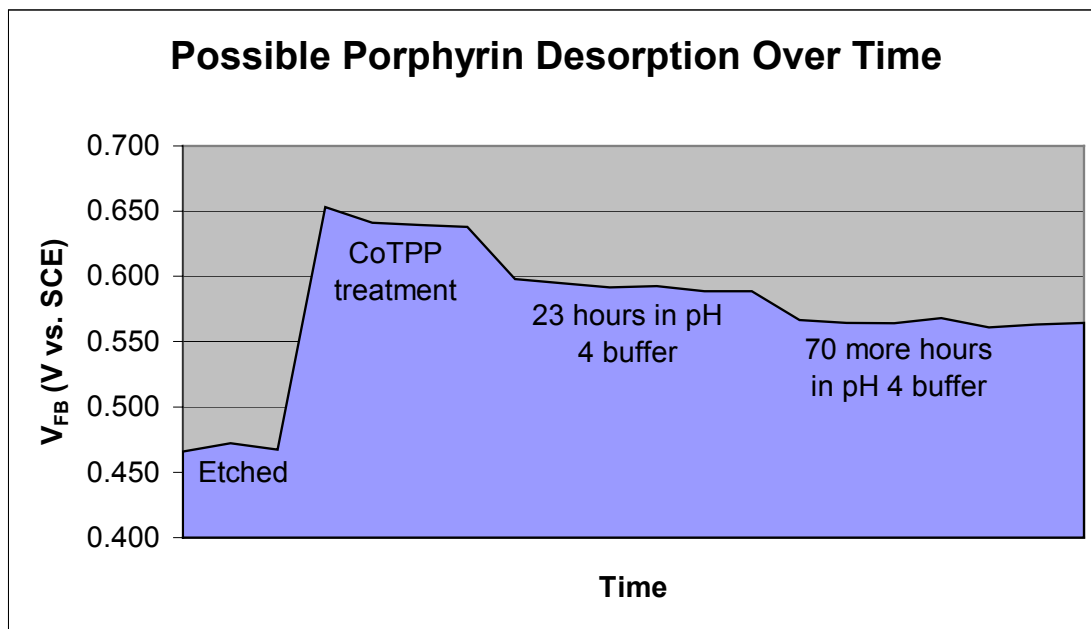


Figure 2. Flat band potential of an electrode during extended immersion in pH 4 buffer.

Another area for further work is on the stability of the porphyrin on the p-GaInP₂ surface. Figure 2 shows the possible desorption of CoTPP in pH 4 buffer over a period of days. As shown, the shift in band edge position decreases after immersing a treated electrode for extended periods in pH 4 buffer, suggesting that the CoTPP is desorbing. The flat band potential decreases by 50 mV after 23 hours and by another 25 mV after an additional 70 hours. Fortunately, light irradiation does not contribute to the decrease in band edge position during extended immersion. Further work will focus on improving the porphyrin stability on the surface. Increasing the surface roughness and covalently attaching the porphyrins to the p-GaInP₂ surface are options worth exploring.

The results for RuOEP CO in combination with transition metals is shown in Table 2.

Table 2. Flat band potential of combination treatments in pH 4 buffer.

Treatment	Shift in V_{FB} (V)	Standard Deviation (V)
Pt sol + RuOEP CO	0.481	0.012
RuCl ₃ + RuOEP CO	0.488	0.207

Both treatments of RuOEP CO with either Pt sol or RuCl₃ showed substantial shifts in band edge position. In order for the cell to split water without any external voltage assistance, the measured flatband potential for a p-type semiconductor must be below (more positive of) the H₂O/O₂ redox potential. These combination treatments allowed overlap of the water redox potentials to occur in the dark.

Figure 3 displays the effects of testing in a range of pHs on a treated and untreated electrode.

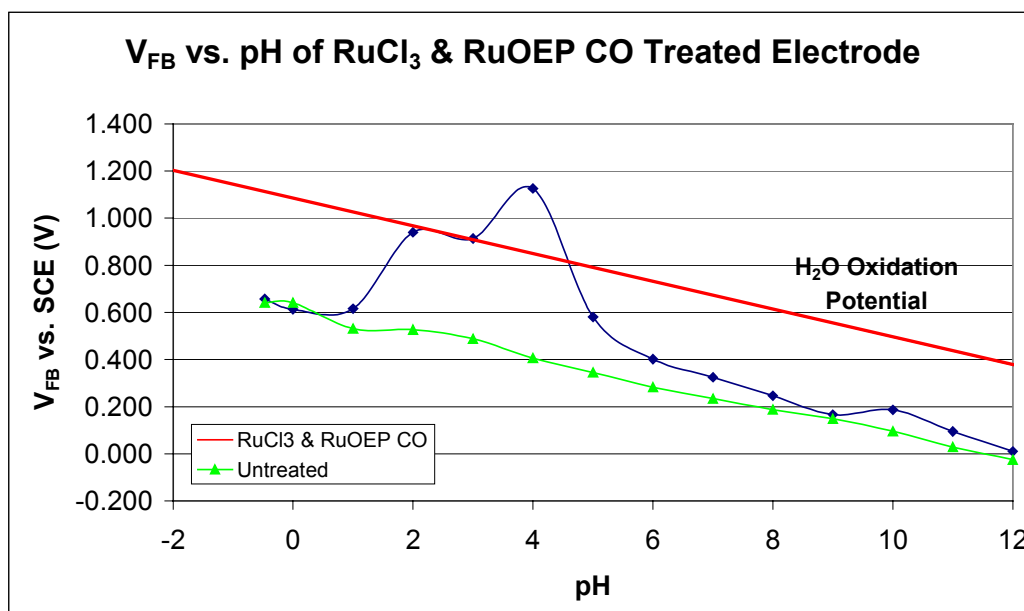


Figure 3. The effect of pH on the flat band potential of an untreated electrode and an electrode treated with both RuCl₃ and RuOEP CO. Dip-coating an untreated electrode with RuCl₃ and then drop-evaporating RuOEP CO vastly improves charge catalysis properties up to a photocurrent of 1 mA/cm². Testing is in pH 4 buffer. The most substantial shift in flat band potential occurs at pH 4, hence the testing at that pH.

We performed testing almost entirely in pH 4 buffer since the largest shifts in flat band potential occurred at that pH. However, the short circuit current (SSC) is substantially improves at a lower pH. Further testing will focus on improving porphyrin response at lower pHs so as to improve the photocurrent and water-splitting efficiency. Figure 4 demonstrates the effect of a combined porphyrin-metal ion treatment under illumination. Dip-coating an untreated electrode with RuCl_3 and then drop-evaporating RuOEP CO vastly improves charge catalysis properties up to a photocurrent of 1 mA/cm^2 .

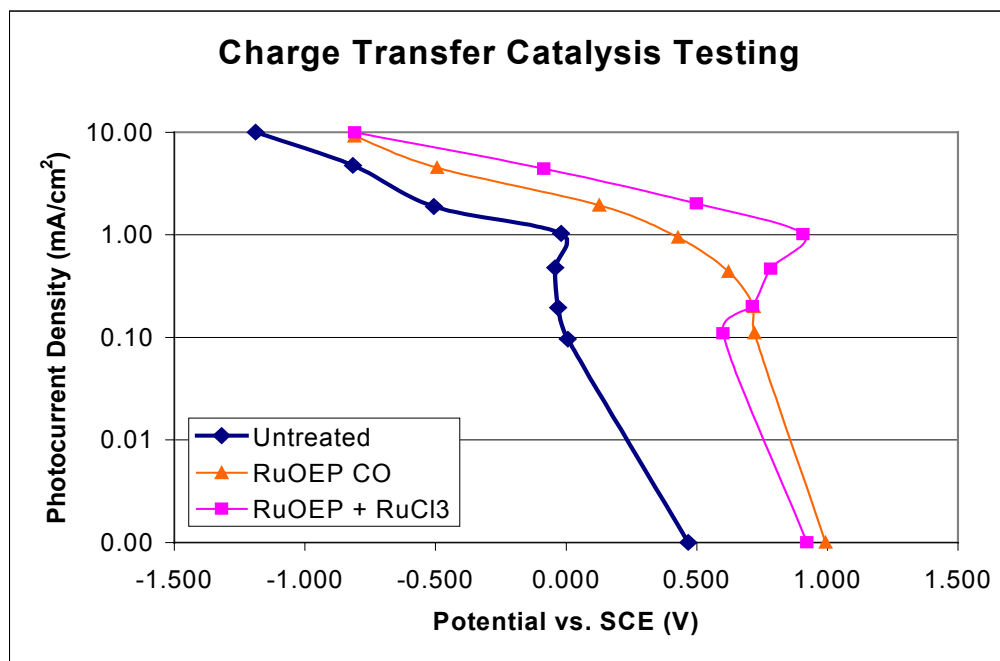


Figure 4. Charge transfer catalysis of various treatments. Testing performed in pH 4 buffer.

Testing of charge transfer catalysis at the p-GaInP_2 surface showed that the RuOEP CO and the RhOEP Cl catalyze charge transfer up to a photocurrent of 0.2 mA/cm^2 . By adding platinum or ruthenium in addition to the porphyrin, the flat band potential and charge catalysis improved markedly. Despite the improved placement of band edges, no significant change in the two-electrode I-V curve was perceptible. Differences in the open cell potential (OCP) between modified and unmodified systems were not statistically significant; at a photocurrent of 1 mA/cm^2 the unmodified electrodes' OCP was $-0.368 \pm 0.048 \text{ V}$ and the modified electrodes' OCP was $-0.399 \pm 0.041 \text{ V}$ (both vs. SCE). Further research must be done to determine why the OCP does not shift positive, despite the improvements in surface energetics as measured by Mott-Schottky analysis and the improved catalysis.

Band Edge Engineering Summary

The surface of p-GaInP_2 can be modified by adsorption of metallated porphyrins and transition metals, resulting in improved energetics and catalysis for photoelectrochemical water splitting. Our survey of porphyrins as band edge-shifting agents showed that RuOEP CO shifts band edges a substantial amount in the correct direction. When combining the RuOEP CO with a transition metal, such as ruthenium or platinum, the band edge shift increases up to 0.48 eV in the positive direction. In addition, the band edges and Fermi level overlap the water redox potentials under light irradiation at a photocurrent of 1 mA/cm^2 , which is the photocurrent

generated by approximately one-tenth of one sun. However, the improvement in band edge position did not improve the open-circuit cell potential and the two electrode I-V characteristics of the system. Further work will focus on understanding and enhancing the band edge and catalysis properties of the porphyrins and transition metals to improve the potential of this water splitting system.

Characterization of triple junction amorphous silicon systems.

This section will review our results from work to characterize various a-Si triple junction samples, and the ability of a-SiC to protect the surface from corrosion. The various samples underwent current-voltage tests, corrosion measurements, and metal-ion catalyst treatments. The a-SiC samples were tested for their characteristics relating to their effect on the overall efficiency of water splitting, and the ability of a-SiC for protecting the underlying semiconducting material.

Semiconductor Electrodes

The a-Si triple junctions along with the a-SiC samples were obtained via a subcontract with Energy Conversion Devices. The a-Si films (p-i-n/p-i-n/p-i-n solar cells) were deposited on 2" by 2" stainless steel substrates via plasma-enhanced chemical vapor deposition (PECVD). Some triple-junction samples were topped with heavily doped a-SiC p-layers of varying characteristics. Individual a-SiC samples were also obtained to study their properties independent of the solar cells. These were deposited under the same conditions as the a-Si films. Each sample then cut into small pieces ($0.02 \text{ cm}^2 - 2.2 \text{ cm}^2$), and attached to a copper wire with electrically conductive silver epoxy and placed in an oven for over an hour at 80°C . After curing the Ag epoxy, the side and the back of the electrode was covered with a non-conductive epoxy so that only the sample's surface ($0.05\text{-}0.21 \text{ cm}^2$) was exposed to the solution.

Electrochemical Measurements

Capacitance-voltage (C-V) and Current-voltage (I-V) tests were performed in a conventional three-electrode apparatus with a platinum counter electrode, a saturated calomel electrode (SCE) as the reference, and the a-Si sample as the working electrode. The C-V tests were conducted on a Solartron 1287 Electrochemical Interface and a Solartron 1260 Impedance/Gain-Phase Analyzer in 1 M KOH and 1 M H_2SO_4 solution with a scan range of -1.0 V to $+0.7 \text{ V}$. The I-V measurements were conducted on a Voltalab PGZ 301 potentiostat in 1 M KOH, pH 7 buffer, and 1 M H_2SO_4 . Corrosion tests were done under illumination at a constant -500 mV bias applied to the samples for a period of 30 min to 60 min. A fiberoptic illuminator with a tungsten bulb was used for these tests.

Results and Discussion

In order to show the effectiveness of a-SiC's when used as a protective layer on a triple-junction a-Si device, a comparison test was done with two triple-junction a-Si devices and two triple-junction a-Si devices with a-SiC deposited on the surface. Figure 5 shows the results these samples under $.481 \text{ W/cm}^2$ illumination with RuCl_3 in 1 M KOH for an hour. Figure 6 shows the samples under the same illumination and metal-ion treatment in a solution of 1 M H_2SO_4 . The two samples without the a-SiC protection were chosen based on their relatively high current output and high stability in solution. It is clear that while a-SiC offers some protection, especially in chemically "aggressive" solutions such as 1 M KOH, when compared in acid (figure 6) no

noticeable difference occurred between the protected samples vs. the non-protected samples. Some samples appear to be stable in acid without the protective coat. The only difference in the samples that displayed little corrosion is the production parameters. This suggests that a-SiC may not be necessary to protect the device, especially when the electrolyte solution is acidic. Furthermore, figure 7 shows that in some cases, the a-SiC actually decreases the current density as compared to an unprotected sample. To determine the cause for the current decrease, additional experiments were performed.

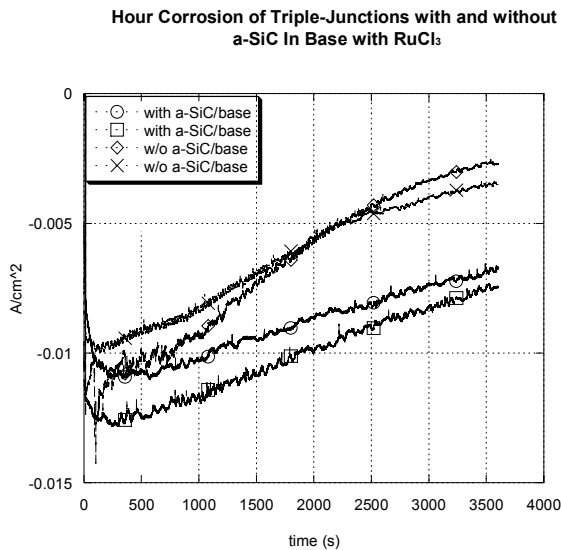


Figure 5. Photocurrent stability under .481 W/cm^2 illumination with $RuCl_3$ in 1 M KOH.

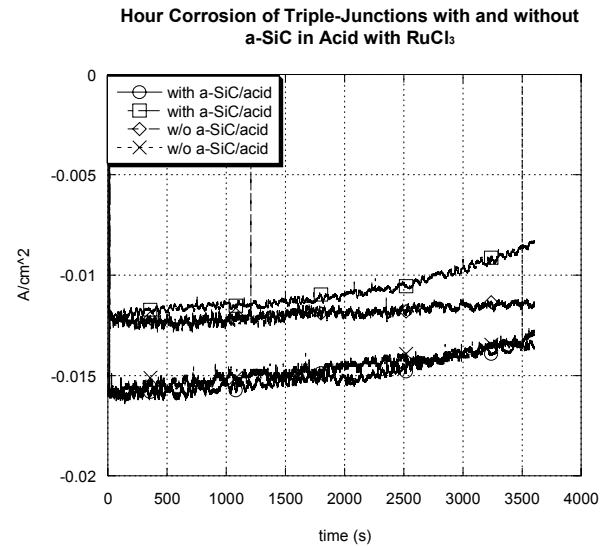


Figure 6. Photocurrent stability in a solution of 1 M H_2SO_4

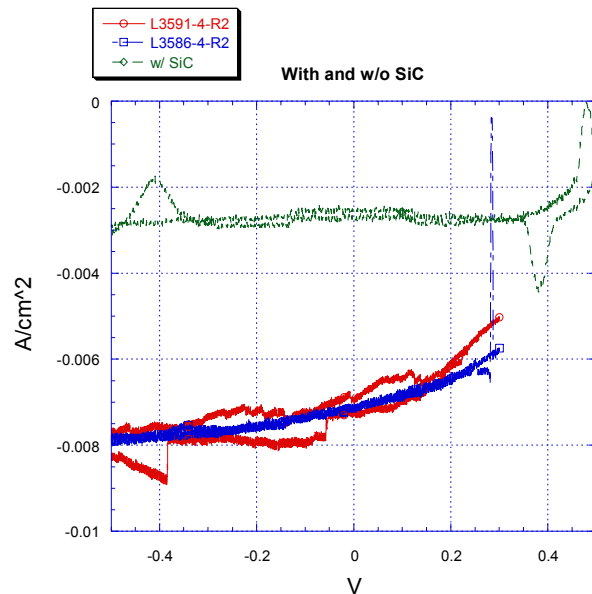


Figure 7. Comparison of the photocurrent for coated and uncoated samples in acid

Since the a-SiC film is deposited on the surface of the semiconductor, its physical and optical properties must be optimized to work with the a-Si triple-junction that it is designed to protect. The triple junction a-Si solar cell is composed of three a-Si cells stacked on top of each other, with decreasing bandgap energy as you move to the back of the device. Cell 1 absorbs photons with energies from 1.9 eV and above, Cell 2 to absorb energies within the range of 1.6 eV to 1.9 eV, Cell 3 absorbs energies between 1.4 eV to 1.6 eV. The entire visible spectrum is not absorbed in one junction. It is apparent that an ideal protective coating for a PEC device will be transparent and highly conducting. For a-SiC to be effective in this device without hindering the photocurrent, band gaps in the 2.5 eV range and higher would be ideal.

Table 3 shows the band gap values for the various a-SiC samples after plotting (photocurrent / photon flux)^(1/2) vs. photon energy (eV).

Table 3

Sample Number	Band Gap (eV)
<u>GD498-4</u>	1.95
<u>GD499-4</u>	1.93
<u>SiC113</u>	1.67
<u>SiC114</u>	1.62

Note that two of the a-SiC samples have band gap values of 1.67 eV and 1.62 eV. This suggests that these films would hinder the photovoltaic process by absorbing the photons that Cell 1 normally absorbs; therefore, causing the device to not function until Cell 2. This would drastically reduce the photocurrent in the system. The films with values of 1.95 eV and 1.93 eV would be better candidates because more light would be allowed to pass through the protective film into the a-Si triple-junction. The sample growth parameters that produced the higher bandgap material will be what we focus on for further work.

Since the a-SiC is deposited on the surface of the electrode, the electrons have to move through the a-SiC to effect water splitting. As it has a finite thickness, there will be some resistance associated with it. Impedance analysis was used to determine the resistance of the a-SiC films. Samples GD498-4 and GD499-4 were tested under .481 W/cm² illumination in 1 M H₂SO₄ solution with Triton X added so that the hydrogen bubbles would not block the surface. The results show that GD498-4 has a resistance of about 0.8 Ω and GD499-4 a resistance of about 1. Ω. At 15 mA/cm² (typical photocurrent values), a 1 Ω resistance causes a 15 mV decrease in voltage. For a typical reversible electrochemical reaction, a 60 mV decrease in voltage causes a decade decrease in current density. That means that a 15 mV loss drops the current and the corresponding hydrogen production by a factor of 2.5. Clearly additional work needs to be done to optimize this material before it can be used as a protective coating, this includes increasing the a-SiC's band gap and decreasing the resistance, or possibly integrating the top cell in the device with a-Si and a-SiC.

Testing metal-ion treatment effects included a look at I-V curves as well as corrosion measurements. Some of the metal-ion catalyst solutions did have a positive effect on the

electrodes by increasing current density, but none of the solutions affected electrode corrosion. The iridium solution catalyzed charge the most on sample L3591-4 and platinum catalyzed the most on L3586-4. Further testing should be done to see which metal-ion solutions catalyze charge transfer the most for an extended period of time.

Conclusions

While semiconductors in direct contact with the electrolyte solutions offer the simplest and lowest cost approach for a direct water splitting system, there has been considerable debate as to the viability of this approach. The criticism has been that applying pinhole free transparent protective coatings is difficult at best. However, this work clearly shows that it is feasible to utilize amorphous silicon devices in direct contact with aqueous electrolytes without an additional protective coating. The samples show stability without the added a-SiC coating. While the exact composition of the surface is still unknown, this is an important discovery in that the combination of an optimized protective coating and an inherent underlying stability in the semiconductor material itself can lead to an extended lifetime in operation. A breach in the protective layer would not be fatal to the device. Continued work with ECD to optimize the triple junction for increased efficiency, and tune the top layer for optimum stability is clearly indicated.

Acknowledgement

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