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PHOTOELECTROCHEMICAL HYDROGEN PRODUCTION

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Abstract

At the University of Hawaii (UH), the approach to developing high-efficiency, low-cost photoelectrochemical (PEC) processes for the direct production of hydrogen has included the use of integrated electrochemical/optical models to design photoelectrodes based on multijunction thin-film technology; materials research to identify critical issues on photoelectrode efficiency and stability; and the fabrication and testing of photoelectrodes for optimization and life-testing. In recent years, we designed photoelectrodes using monolithically stacked triple-junctions of amorphous silicon (a-Si) and mechanically interconnected side-by-side copper-indium-gallium-diselenide (CIGS). This year, significant progress was made in optimizing constituent films for these photoelectrode designs. Photoelectrodes using both a-Si and CIGS were fabricated and tested. Both types of photoelectrodes were fabricated using optimized NiMo, Fe:NiOx, ITO (indium-tin-oxide), and polymer-encapsulation films deposited at the University of Hawaii. The a-Si solar cells used in these studies were deposited by the University of Toledo using a process that yielded electrical efficiencies as high as 12.7%. The 13% efficient CIGS cells were provided under subcontract by the University of Delaware. Based on the electrical efficiency of the cells and prior experiments using these catalytic coatings, solar-to-hydrogen efficiencies of 6% to 8% were expected for the a-Si based photoelectrodes. However, peak efficiencies of only 2.5% were measured in outdoor tests. The discrepancy has been attributed to handling-induced degradation in the a-Si triple-junction performance. Severe degradation also occurred in CIGS diodes when cut for photoelectrode fabrication. Open-circuit voltage in the CIGS triple-stacks was reduced from 1.8 V to below 1 V, making water-splitting impossible, despite predicted solar-to-hydrogen efficiencies in excess of 10%. Planned future work includes development of improved handling techniques to demonstrate the true hydrogen production potential in the photoelectrodes, with greater emphasis on the higher-efficiency CIGS devices. Plans also include continued development of the hybrid solid-state/PEC photoelectrode described at the FY 2001 Annual Review Meeting. This design combines a double-junction amorphous silicon cell with a dye-sensitized TiO_2 or WO_3 photoelectrochemical junction.

Introduction

Under the sponsorship of the U.S. Department of Energy, research at the Hawaii Natural Energy Institute of the University of Hawaii has aimed at developing high-efficiency, potentially low-cost, photoelectrochemical (PEC) systems to produce hydrogen directly from water using sunlight as the energy source. The main thrust of the work has been the development of integrated multijunction photoelectrodes, comprising semiconductor, catalytic, and protective thin-films deposited on low-cost substrates (such as stainless steel), for solar hydrogen production (Rocheleau et al. 1998). In the illustration of a generic hydrogen photoelectrode shown in Figure 1, sunlight shining on photoactive regions of the electrode produces electric current to drive the hydrogen and oxygen evolution reactions (HER, OER) at opposite surfaces. Hydrogen photoelectrode operation represents a complex interaction of photovoltaic, optical, and electrochemical effects, and an important part of the UH research has been the development of integrated models combining these effects (Rocheleau and Vierthaler 1994). Figure 2 shows a schematic of the model used in the analysis of a triple-junction photoelectrode.

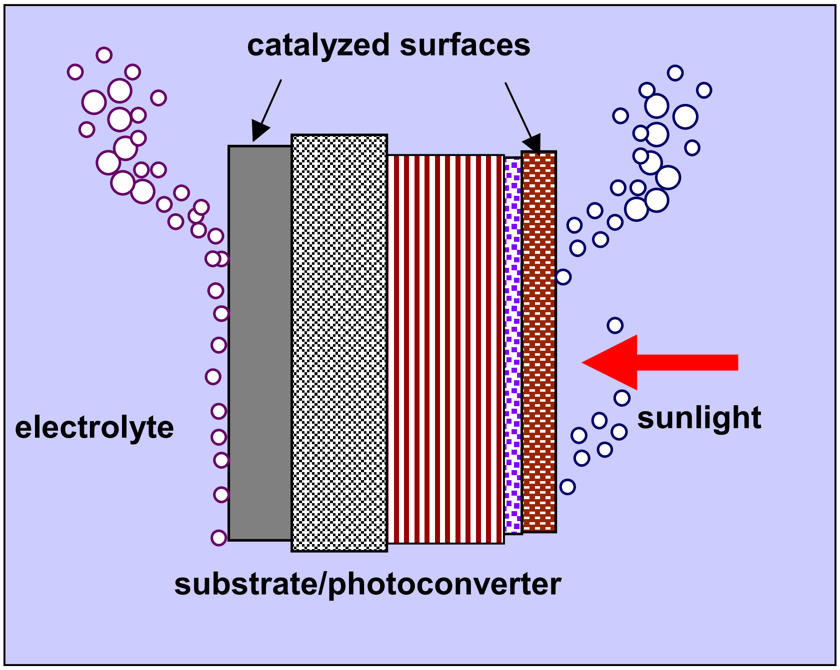


Figure 1. Photoelectrochemical hydrogen production

In order to meet DOE goals, a PEC system must be low-cost, operate at solar-to-chemical conversion efficiencies greater than 10%, and have long operating lifetimes. Numerous approaches involving a variety of semiconductors have been explored since the early 1980s, but none have successfully satisfied both the efficiency and stability criteria. The high voltage required to dissociate water and the corrosiveness of the aqueous electrolytes have been major hurdles. Based on results from numerous modeling and proof-of-concept experiments conducted at UH over the course of the PEC research, our approach has been to develop photoelectrodes incorporating multijunction thin-film photoconvertors (for high voltage) and thin-film catalyst and protective layers (for stability).

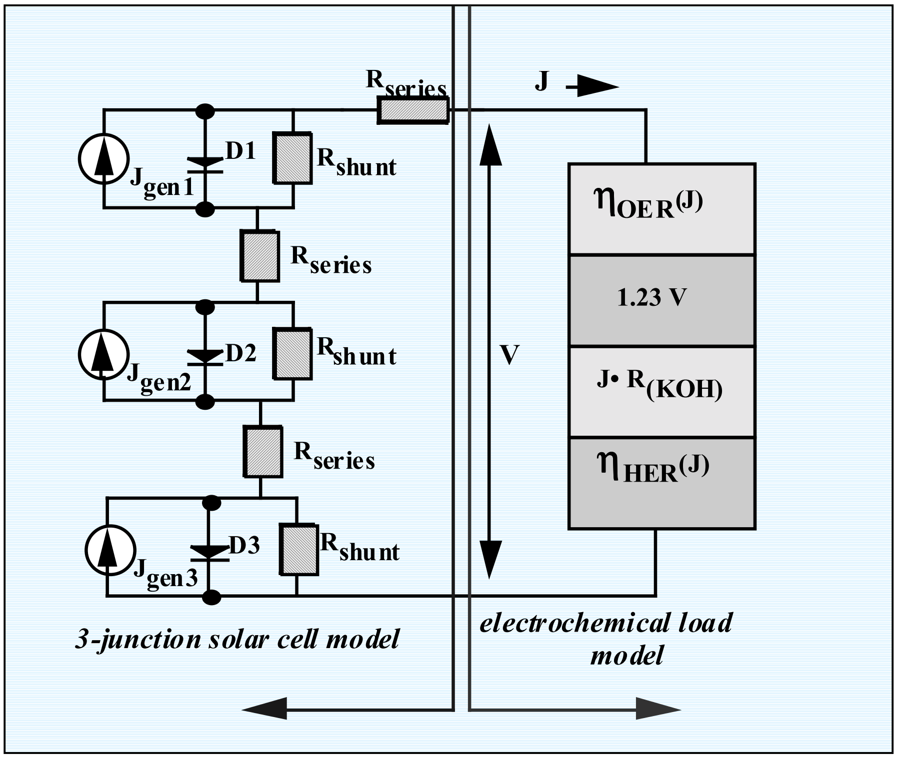


Figure 2. Model of triple-junction photoelectrode

Specifically, our work has provided strong evidence that direct solar-to-hydrogen conversion efficiency of up to 10% can be expected using photoelectrodes fabricated from low-cost, multijunction amorphous silicon (a-Si) (Rocheleau and Miller 1997), while conversion efficiencies approaching 15% are possible using advanced photoelectrode designs based on multijunction copper-indium-gallium-diselenide (CIGS) cells stacked in a side-by-side configuration (Miller and Rocheleau 2000). Both the a-Si and CIGS photoelectrode systems have the potential for low cost based on the very thin semiconductor layers involved and on compatibility with high-throughput manufacturing processes.

Over this past year, we have modified the basic integrated photoelectrode to allow both a-Si and CIGS structures to be used. Schematics of the most recent designs are shown in Figures 3a and 3b for a-Si and CIGS devices, respectively. Using high-efficiency a-Si triple-junction solar cells deposited by the University of Toledo, and high-efficiency CIGS/CdS cells deposited by the Institute for Energy Conversion (IEC) at the University of Delaware, we fabricated simple proof-of-concept test structures for both these photoelectrode designs. Fabrication of the test structures, as described in detail in following sections, was completed at UH using the thin-film catalyst and protective layers developed through our PEC research (Miller and Rocheleau 1999; Miller and Rocheleau 2000).

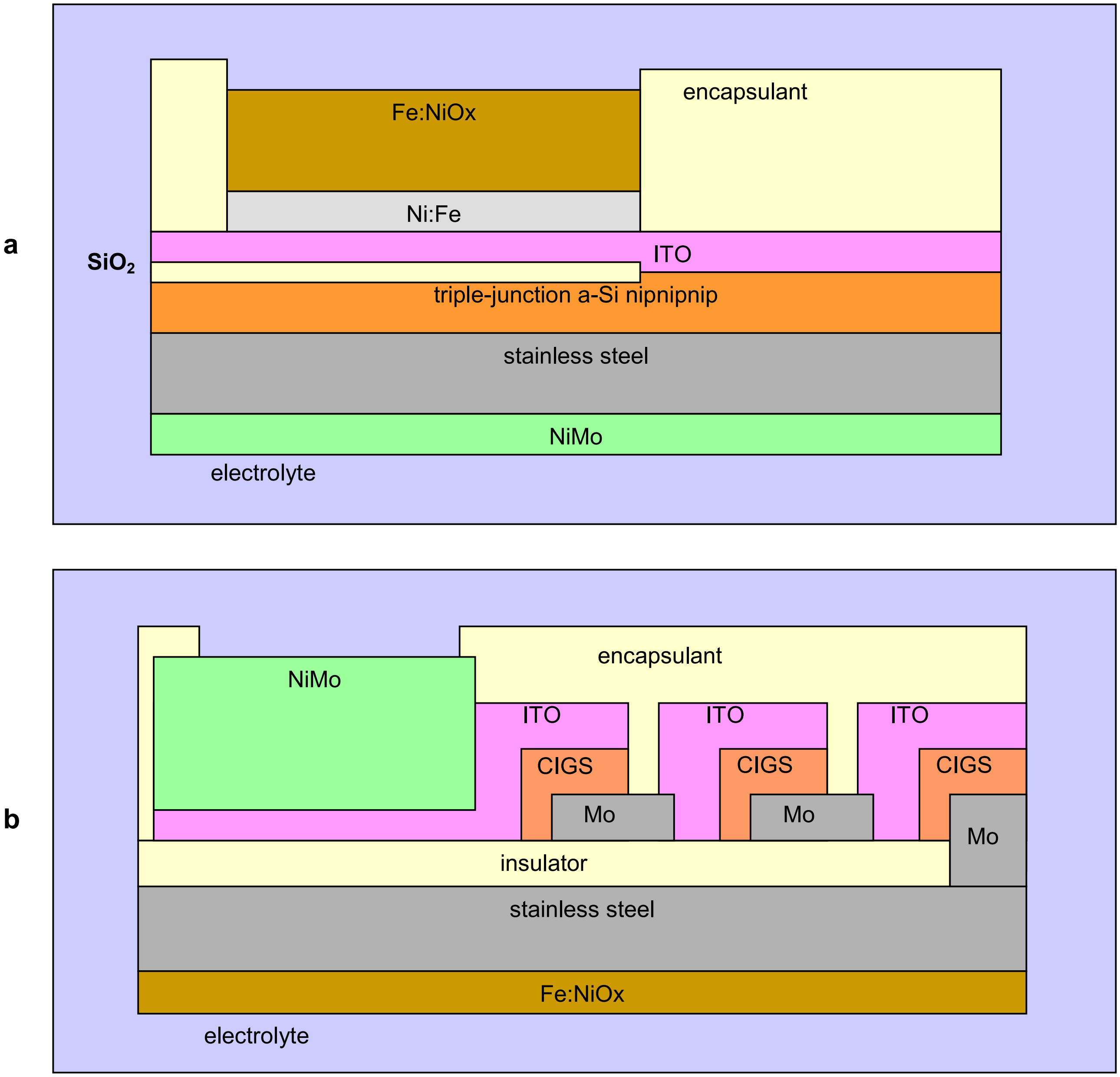


Figure 3. Structure of photoelectrode test devices

Under current funding, in addition to the proof-of-concept photoelectrode fabrications, we developed the conceptual design for a "hybrid" multijunction photoelectrode, incorporating current-matched solid-state and electrochemical photojunctions. This structure, as illustrated in Figure 4, is most easily implemented using a double-junction a-Si device deposited on stainless steel foil. In the configuration shown, the back surface of the foil substrate is treated with a thin-film HER catalyst, and the front surface of the solid-state solar cell component is coated with a thick photoactive material, such as dye-sensitized TiO_2 or WO_3, which replaces the top junction in the original triple-junction a-Si design.

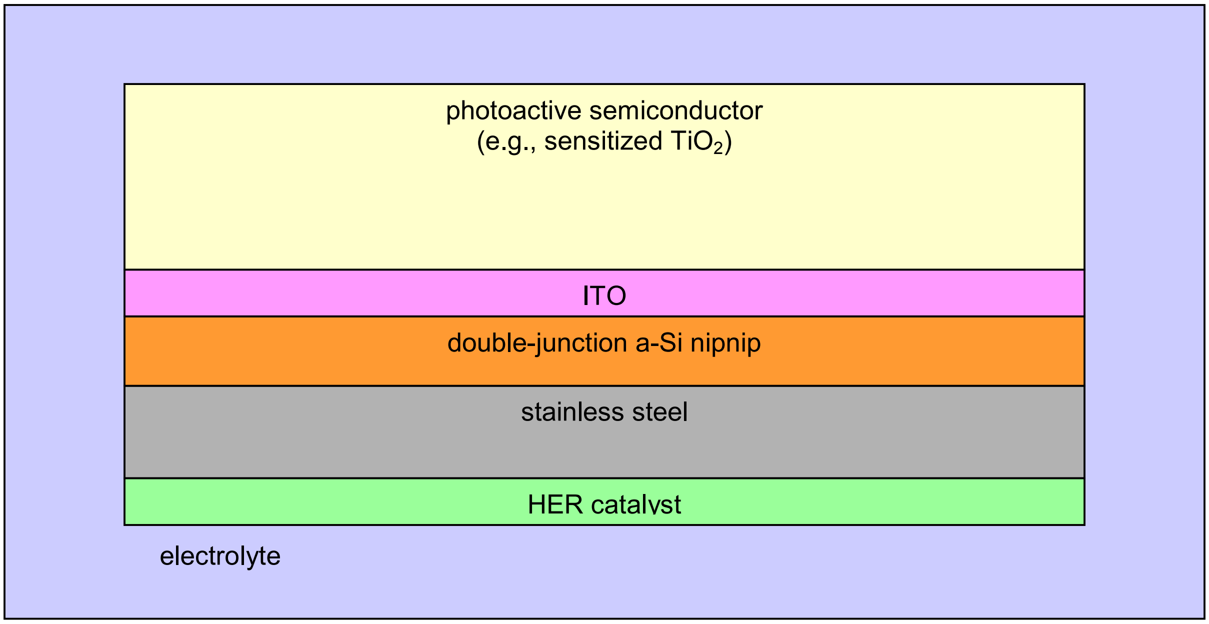


Figure 4. Basic structure of the hybrid photoelectrode

Potential advantages of the hybrid design include simplified fabrication, greater stability, and lower cost. In addition, elimination of lateral current collection loss and reduction of front-surface OER overpotential loss could lead to improved photoelectrode performance. A more detailed description of this new design and its features is presented in later sections.

Goals and Objectives

The ultimate goal of this research has been the development of a high-efficiency, low-cost photoelectrochemical process for the direct production of hydrogen. Over the course of our PEC development work, we have developed integrated electrochemical/optical models to identify materials and multijunction electrode designs with potential for high efficiency, and have fabricated and tested photoelectrodes engineered to maximize efficiency and stability for given material properties.

The primary goals for this past year have included:

- The development and evaluation of multijunction a-Si based photoelectrodes based on the design illustrated in Figure 3a, optimized for operation in KOH.
- The development and evaluation of mechanically interconnected, high-efficiency, CIGS-based photoelectrodes, based on the design depicted in Figure 3b.
- The design of advanced photoelectrode designs using new materials or configurations (such as the hybrid photoelectrode shown in Figure 4) to obtain enhanced stability and efficiency, and to minimize cost.

Progress in achieving these goals is described in the Progress Status section below.

Progress Status

Under previous contracts at UH, the efforts focused on demonstrating the feasibility of the photoelectrochemical approach using thin-film solar cell materials. Optimizing the optoelectronic performance and chemical stability of each of the thin-film components of the photoelectrode, including semiconductor layers, the hydrogen and oxygen catalysts, and transparent contact and protective films, was a significant part of the effort. After the successful demonstration of the proof-of-concept using separated anode/cathode configurations (Rocheleau et al. 1998), the primary goal became the development of photoelectrodes configurations based on planar fabrication of thin-films onto inexpensive substrates without external interconnects. In this report, photoelectrodes without anode/cathode interconnects are referred to as "integrated photoelectrodes."

Activities during Phase I of this contract have focused on fabricating and testing proof-of-concept photoelectrodes using both a-Si and CIGS thin-film solar cells, and the development of the conceptual design for a new hybrid configuration in which the outermost junction is a true electrochemical junction. Specific tasks have included:

1) Model Development: Continued upgrade of the integrated electrical/optical model for PEC analysis.

2) Materials Research: Continued optimization of the catalyst and protective coatings for use in the a-Si and CIGS integrated photoelectrodes.

3) Amorphous Silicon Photoelectrodes: Fabrication and outdoor testing of triple-junction a-Si photoelectrode structures based on the design shown in Figure 3a.

4) CIS/CIGS Photoelectrodes: Construction of a mechanically interconnected CIGS photoelectrode device approximating the more complex structure of Figure 3b.

5) Advanced Photoelectrodes: Formulation of the new hybrid design, as shown in Figure 4, with a specific implementation incorporating a-Si solid-state junctions and an outer layer of a material such as dye-sensitized TiO_2 or WO_3 to form the PEC junction.

The progress status of tasks 1 through 5 is discussed below.

Integrated Model Development

For several years, we have been developing electrical and optical models for design and optimization of hydrogen photoelectrodes. The electrical model, based on an equivalent circuit model, was developed at UH to simulate solid-state junction performance in conjunction with electrochemical loads (Rocheleau and Miller 1997). The optical model, based on the commercially available analysis package, *Essential Macleod*, is used to derive the absorption profiles in the multijunction structures of interest. To date, the electrical and optical components are independently operational, but not fully integrated into a single user-friendly package. Integrating the models, as well as upgrading them to analyze the advanced hybrid photoelectrode design, are efforts that are currently underway.

Materials Research

This year, we continued research to optimize component films necessary to the integrated photoelectrode structures under investigation. Significant progress was made in developing improved catalyst films, in the deposition of high-efficiency a-Si and CIGS cells onto metallic substrates (IEC at the University of Delaware and University of Toledo, respectively), in the optimization of indium-tin oxide (ITO) films for transparent contact layers, and in the use of a highly transparent and stable polymer adhesive as a photoelectrode encapsulant.

In recent years, we have relied on cobalt-molybdenum (CoMo) thin-films sputter-deposited from an alloy target as the HER catalyst in our photoelectrode structures. These films have demonstrated good HER activity and excellent long-term stability over a three-year continuous operation test (Rocheleau et al. 1998). One major drawback has been the difficulty obtaining hot-pressed CoMo alloy targets from the vendors. This year, we spent considerable effort investigating alternative mixed-metal films as the HER catalyst, including nickel-molybdenum (NiMo), nickel-iron (NiFe), and cobalt-nickel (CoNi). Each of these materials was sputter-deposited from alloy targets. Target compositions of 50:50 for the NiMo and CoNi, and 81:19 for the NiFe permalloy were evaluated.

Figure 5 shows voltammetry scans of the three new catalyst materials, with traces for Ni and CoMo included for reference. It is clear that all the alloy films exhibit lower hydrogen overpotentials compared to the plain nickel substrate. Of the materials tested, the NiMo films exhibited the lowest hydrogen overpotentials, slightly outperforming CoMo. Figure 6 shows SEM scans of as-deposited CoMo, NiMo, CoNi, and NiFe films taken at a magnification of 80,000x. Clear differences in the surface morphologies of the four films are evident. In comparison to the CoNi and NiFe films, CoMo and NiMo exhibit a finer grain structure, which is possibly a factor in the lower overpotentials in these materials. Based on results from these experiments, the NiMo alloy films were selected as a lower-cost replacement for CoMo in our photoelectrode designs. Long-term stability tests are in progress to further assess the applicability of these films.

In addition to the HER catalyst development, we also made further improvements to the reactively sputtered Fe:NiOx films developed at UH as an OER catalyst (Miller and Rocheleau 1997). Specifically, the effects of oxygen partial pressure in the reactive sputter gas on OER activity were explored. Figure 7 shows current-overpotential curves for three films sputtered from the same NiFe permalloy target, but with slightly different oxygen partial pressures in the argon-oxygen sputtering ambient. Film 2 (with 14% oxygen content) exhibits a clear improvement in OER activity compared to Film 1 (previous standard conditions, with 21% oxygen) and Film 3 (17.5% oxygen), indicating the existence of a local maxima for catalytic activity as a function of oxygen partial pressure in the processing environment. Further investigation of this observed effect is in progress.

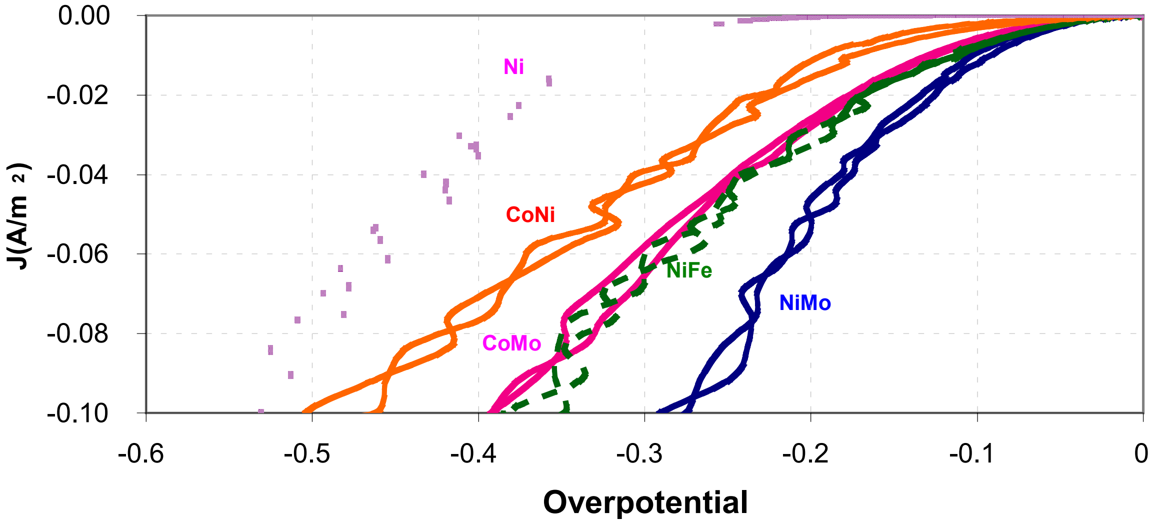


Figure 5. Comparison of HER catalyst film activities

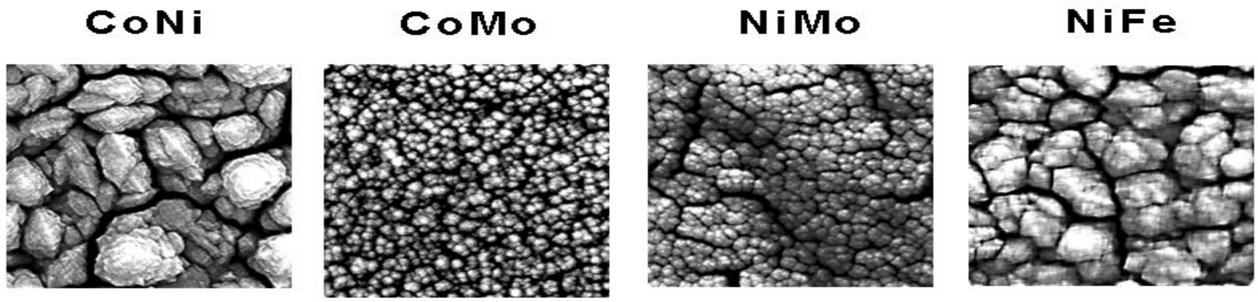


Figure 6. Surface morphology of HER catalyst films

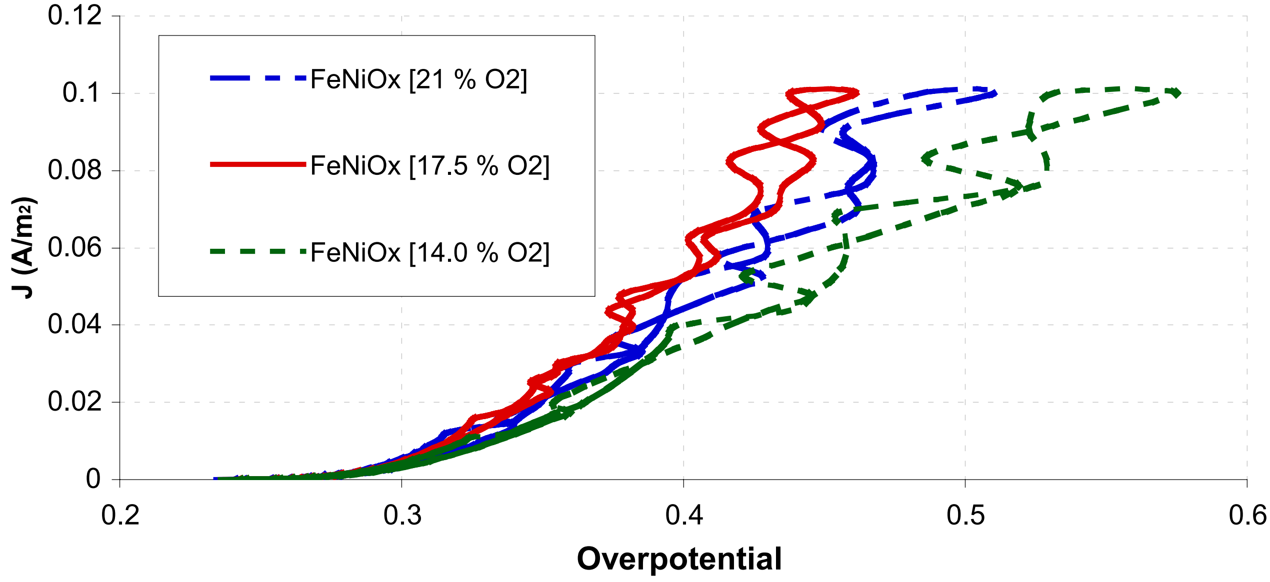


Figure 7. Comparison of Fe:NiOx catalyst film activities

Last year, we reported efforts to fabricate integrated photoelectrodes using triple-junction amorphous silicon cells. These structures used sputter-deposited ITO (top contact layer), CoMo (HER catalyst), Fe:NiOx (OER catalyst), and TiO_2 (encapsulant). Apparent shorting at device edges and at TiO_2 surfaces was observed in these devices. This year, we modified the a-Si photoelectrode design to eliminate this problem. The TiO_2 was replaced with a highly stable transparent polymer as the encapsulant. Other changes included improved a-Si cells, use of CoMo in place of NiMO, and improved chemical resistance of the ITO.

The high-efficiency, triple-junction, amorphous silicon solar cells used in this work have been provided by Xunming Deng of the University of Toledo. This year, Toledo researchers successfully demonstrated photovoltaic efficiencies up to 12.7% in their triple-junction cells deposited onto stainless steel (SS) foil. This is the highest efficiency to date for their laboratory (Wang et al. 2001). The quantum efficiency characterization for one of these devices is shown in Figure 8.

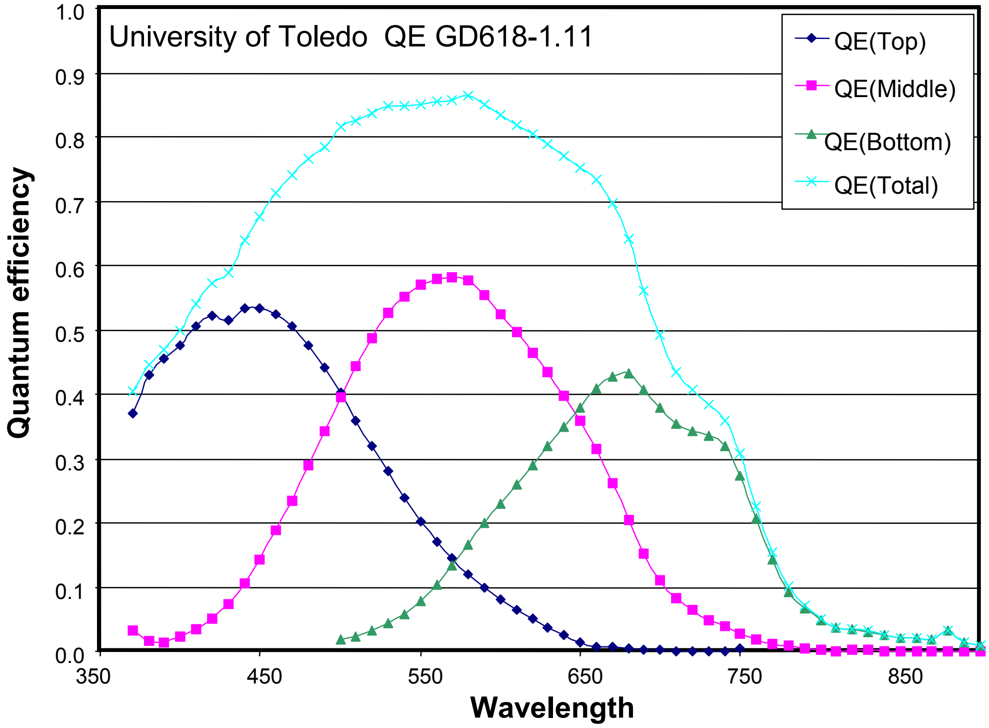


Figure 8. Quantum efficiency of high-performance a-Si triple-junction

For photoelectrode applications, the University of Toledo researchers deposited their new high-efficiency cells onto stainless steel foil pre-coated on the reverse side with NiMo HER catalyst. We subsequently completed the devices with ITO, Fe:NiOx OER catalyst, and encapsulant.

Corrosion-resistant ITO films deposited under process conditions that also yielded high conductivity and transparency were reported last year (Chin 2000). These ITO films were specifically developed for photoelectrode applications. Figure 9 shows the measured percentage weight loss of ITO films deposited under various conditions (on stainless steel 302) as a function of time immersed in 1N KOH. A substantial fraction of the film mass was removed in the samples deposited at 100°C, while little to no change was observed in the films deposited at 200°C. This past year, we completed an analytical correlation between film structure and the observed ITO film properties. Figure 10 summarizes the measured the X-ray diffraction (XRD) parameters, normalized counts per second, and grain size at primary crystal orientations, for the different deposition conditions. Of these samples, film sample 2 (deposited at 200°C and with 0.125% oxygen in the sputtering ambient) was the most resistant to corrosion, but also exhibited the best transparency and conductivity. The optimization of these three properties is well-correlated with enhanced film grain-size and preferred <222> orientation.

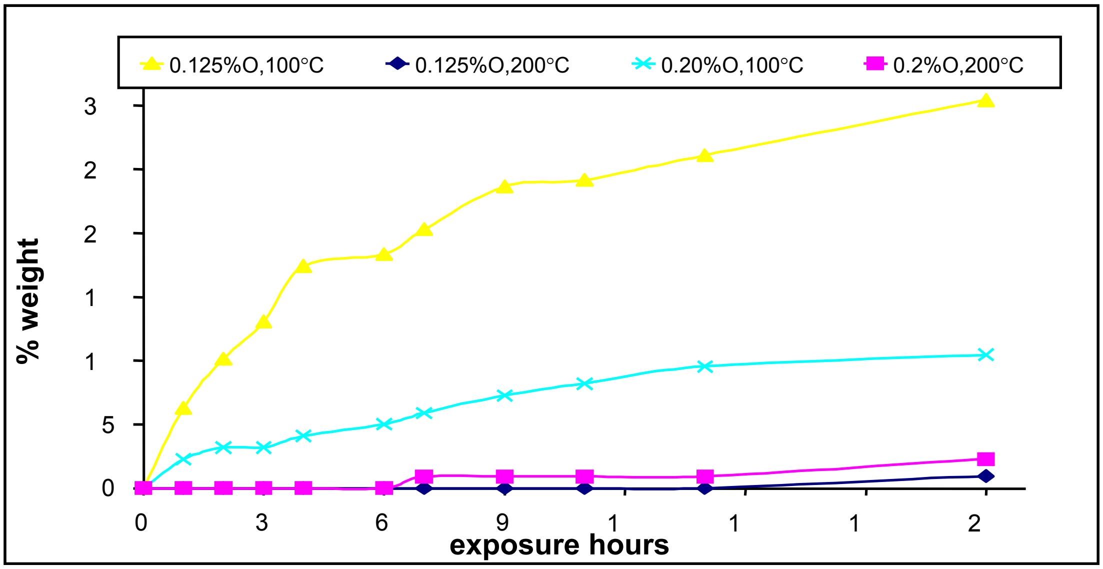


Figure 9. Comparison of ITO film stability in 1N KOH

Results of initial efforts to develop a chemically stable integrated photoelectrode were reported at the FY 2000 Program Review Meeting (Miller and Rocheleau 2000). These devices were fabricated using sputter-deposited TiO_2 as the transparent encapsulant, selected based on its reported compatibility in KOH and results from initial stability experiments. During testing, however, it was evident the TiO_2 surfaces were being driven to potential levels sufficient to drive oxygen evolution and other active corrosion reactions. This year, we conducted a thorough search to find a replacement for TiO_2 as the protective window layer. Of several materials tested, the best results were obtained using the Mater Bond polymer system EP39-2, a transparent epoxy polymer, designed specifically for potting optoelectronic devices. This material was found to have excellent optical properties, as shown in the transmission and reflectance plots in Figure 11, and good stability in KOH. In addition, the material was compatible with traditional screen-printing techniques, which could be readily applied to the planar photoelectrode structure.

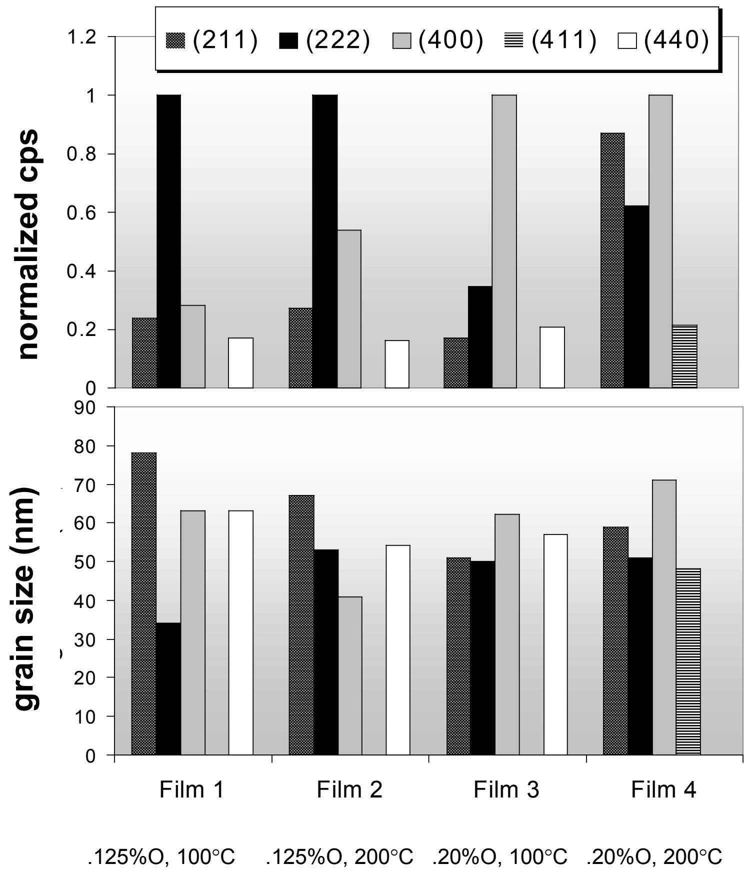


Figure 10. Crystallography of ITO films

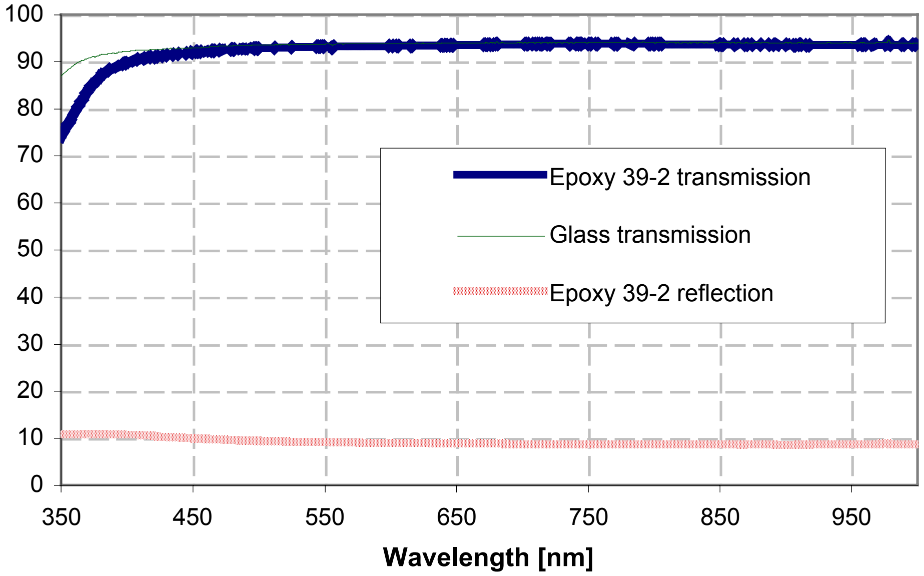


Figure 11. Optical properties of polymer encapsulation film

Amorphous Silicon Photoelectrode Development

A key milestone for this past year was the fabrication and testing of integrated amorphous silicon photoelectrodes. The a-Si photoelectrode structure was modified from last year's design to incorporate the University of Toledo's high-efficiency cells, NiMo (instead of CoMo) catalyst, and EP39-2 polymer (instead of TiO_2) encapsulant. The processing sequence for fabricating these devices, the status of a prototype reactor for photoelectrode testing, and results from preliminary testing of the fabricated photoelectrode structures are discussed below.

Photoelectrode Fabrication

The triple-junction amorphous silicon photoelectrode structure shown schematically in Figure 3a was fabricated onto 1" x 1" stainless steel squares using the following procedure:

1) Sputter-deposit a NiMo film (about 1µm thick) on back of cleaned stainless steel (SS) substrate.

2) Deposit triple-junction a-Si nipnipnip (by PECVD at University of Toledo) on front SS surface.

3) Sputter-deposit a thin SiO_2 insulation layer (about 500Å thick) through mask over approximately half the Si area.

4) Sputter-deposit the ITO top contact film (about 1200Å thick) through a shadow mask over entire active area.

5) Sputter-deposit a NiFe/Fe:NiOx film (about 1µm thick) through mask on front in-line with the SiO_2 insulator.

6) Screen-print polymer encapsulant (about 3µm thick) over uncatalyzed portion of the active Si.

The devices were cleaned using methanol and DI (deionized) water between processing steps. In total, 36 photoelectrodes were fabricated using a-Si cells from four separate PECVD runs (nine substrates per run). Completed devices are shown in Figure 12.

Small-Scale Reactor

At the FY 2000 Program Review, we reported the design of a small-scale hydrogen photoreactor with gas collection and solar-tracking features intended for photoelectrode testing. This year, we completed the construction of the reactor, shown in Figure 13. The calibrated burettes mounted at the top of the reactor are connected to gas collection ports for hydrogen and oxygen collection. The gases are generated at opposite sides of the photoelectrodes. The reactor body is mounted onto the tripod using an equatorial-mount to facilitate solar tracking during outdoor tests.

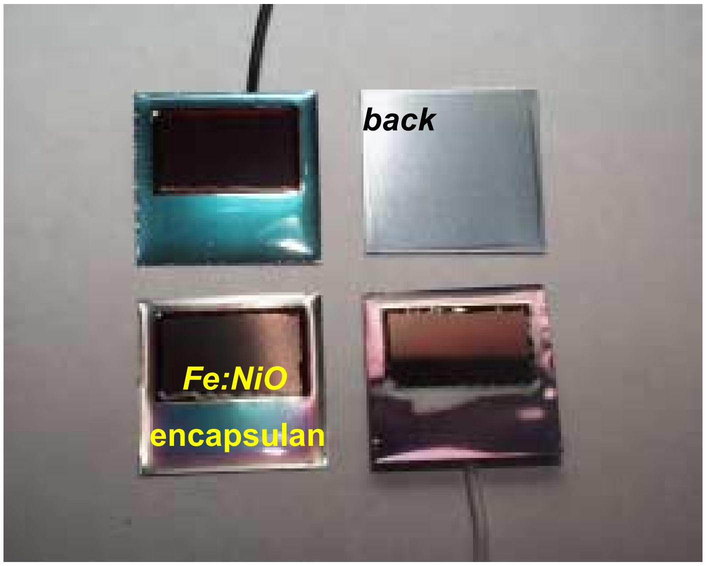


Figure 12. Completed a-Si test photoelectrode

Figure 13. Hydrogen photoreactor for photoelectrode tests

Initial testing was performed using the small-scale reactor; however, characterization of the solar-to-hydrogen efficiency using gas evolution measurements was limited by incomplete gas collection. At the relatively low rates achieved in these tests, bubbles became trapped in the narrow pathway leading to the burettes. Hydrogen efficiencies were obtained by modifying some of the fabricated photoelectrodes, as described below, to allow direct measurement of the current passing between the anode and cathode. Plans have been developed to modify the reactor to allow more efficient gas collection.

Photoelectrode Testing

The a-Si photoelectrodes were modified, as shown in Figure 14, by attaching electrical leads between the anode and cathode sides of the electrode. The electrical leads were attached at the back HER surface, which was then potted over with an insulating polymer layer to prevent any hydrogen evolution from the surface. This lead was then connected through an ammeter to a secondary HER electrode placed behind the photoelectrode. This allowed measurement of hydrogen photocurrent for calculation of hydrogen efficiency.

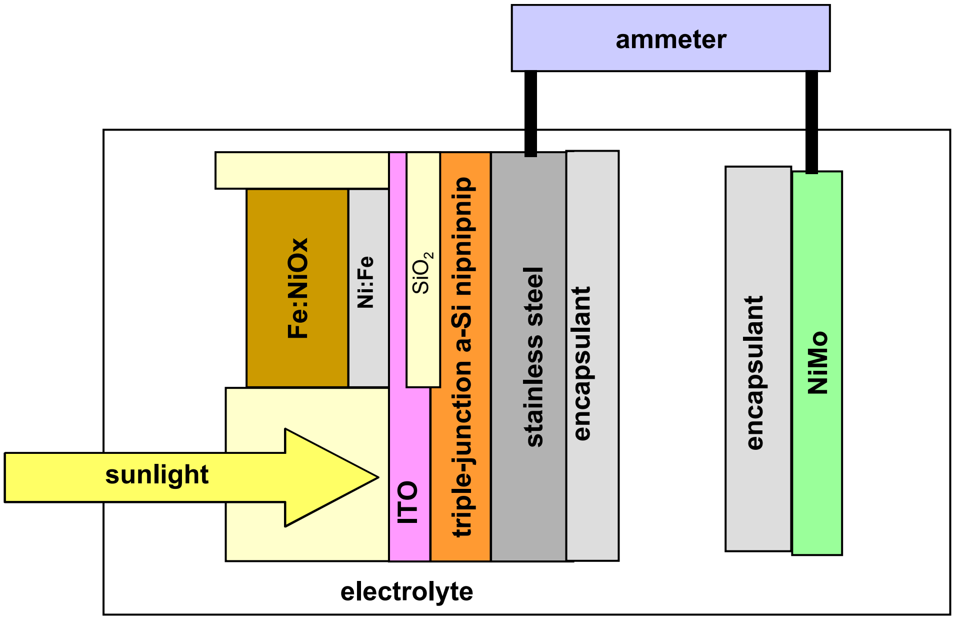


Figure 14. Photoelectrode structure modified for efficiency measurements

Of the 36 photoelectrodes that were fabricated, 12 were modified per Figure 14 for efficiency measurements. These 12 were tested in 1N KOH under simulated solar illumination (ELH lamps) and outdoors under sunlight. In all 12 devices, gas bubbles were observed evolving from the catalyst surfaces. Figure 15 is a photograph of one of the photoelectrodes under test. Unfortunately, significant shortcomings in both efficiency and stability were observed over the course of these tests.

The triple-junction a-Si cells fabricated at the University of Toledo exhibited as-deposited photovoltaic efficiencies up to 12.7% and open-circuit voltages up to 2.3 V. Based on these parameters, our models indicated solar-to-hydrogen efficiencies ranging from 6% to 8% were expected. The loss from the electrical efficiency and range is based on lost area and estimated ranges for optical, electrical, and electrochemical losses. However, only 3 of the 12 devices tested under outdoor conditions demonstrated hydrogen efficiencies exceeding 1%, and the highest observed efficiency was 2.5%. This disappointing result was later traced to degradation in the solar cell performance as a result of the processing steps used in photoelectrode fabrication.

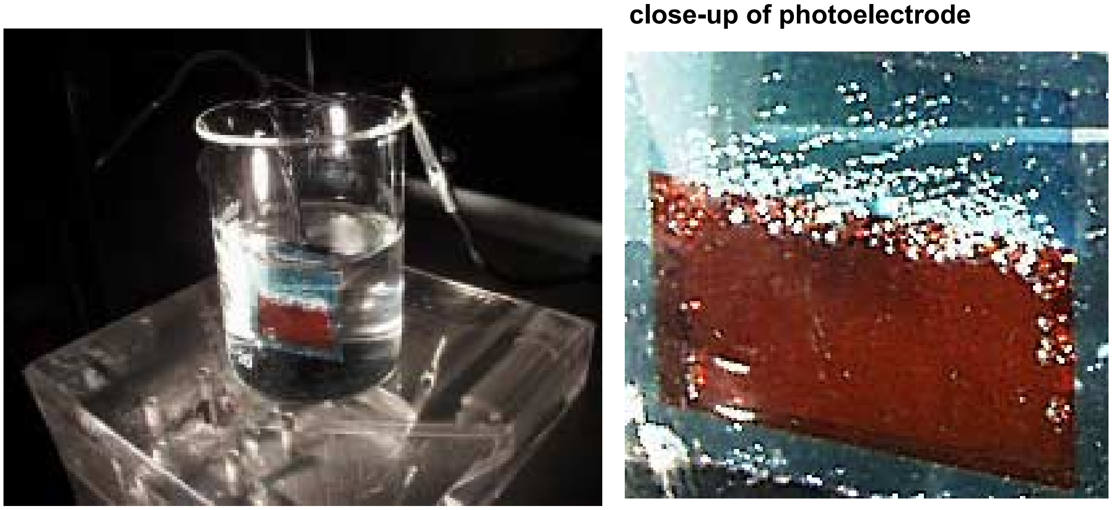

close-up of photoelectrode

Figure 15. Gas evolution at a-Si photoelectrode surface

When the photoelectrodes were tested as solar cells in air, the open-circuit voltage in all devices was found to have degraded to less than 1.5 V (from initial values around 2.2 V to 2.3 V). In a few cases, voltages as low as 0.3 V were measured. This level of degradation in the photovoltaic performance provided sufficient explanation for the low solar-to-hydrogen efficiencies. After in-depth discussions with the University of Toledo, we concluded that the triple-junction cells were being damaged over the course of fabricating them into photoelectrodes, despite the fact that standard planar fabrication techniques were being employed. Our experiments in previous years to modify solar cells into photoelectrodes did not result in such severe solar cell degradation. There is evidence that the processing procedures used to produce the high-efficiency 12.7% solar cells also result in devices that were more susceptible to handling damage. The tradeoff between efficiency and yield is not uncommon in solid-state device research. It was agreed that near-term follow-up work to fabricate hydrogen photoelectrodes from a-Si cells should utilize more established triple-junction recipes giving slightly lower PV efficiencies (10-11%) but higher yield.

In addition to the lower than expected efficiencies, an unanticipated mode of instability was observed in some of the photoelectrodes during testing. In half of the modified photoelectrodes tested in KOH under outdoor conditions, the OER catalyst layer on the front surface separated from the underlying layers after approximately 30 minutes of operation. Although the catalyst films did not appear to have dissolved or be completely removed, the appearance of “wrinkles” in the OER catalyst film surfaces and a corresponding drop in performance made it clear that they were no longer effectively connected with the rest of the device. This effect did not appear in the remaining 6 test devices, even after 4 hours of testing.

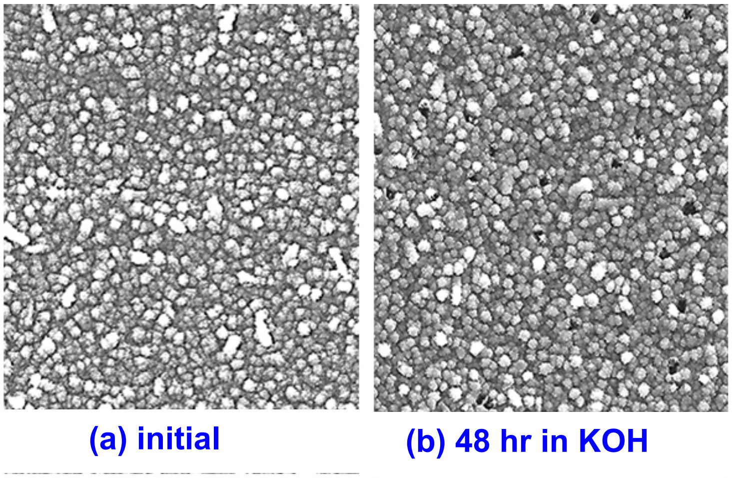
Film separation in planar devices is often an indication of adherence problems due to inadequate surface preparation prior to deposition. The separation effect was not observed in the long-term stability tests in KOH of the Fe:NiOx catalyst material deposited on nickel foil (Rocheleau et al. 1998). The nickel foil substrates, however, were thoroughly cleaned and etched in HCl before deposition of the oxide film, whereas only methanol/DI water rinses were used between layering steps in the photoelectrodes. The acid etch was not included to avoid damaging underlying photoelectrode component layers. Clearly, an improved method of surface preparation for the Fe:NiOx sputtering step needs to be devised to eliminate the film adhesion problem. One effective approach that has been employed with success in other labs (Inal 1997), but would require some hardware modifications to our sputtering system at UH, involves sputter-etching the surface in a low-vacuum argon ambient immediately prior to film deposition.

CIS/CIGS Photoelectrode Development

Another key milestone for this year was completion of our preliminary investigation of CIGS photoelectrodes, including corrosion testing of CIS/CIGS materials, and fabrication of a mechanically interconnected test structure simulating the side-by-side series connected configuration. Results in these areas are discussed below.

Corrosion Tests

The basic structure of a CIS or CIGS photoelectrode in the side-by-side series connected configuration was shown in Figure 3b. Although the CIS or CIGS material in this arrangement is completely encapsulated and has no direct contact with the electrolyte, long life in a commercial unit is expected to be enhanced by corrosion resistance in all constituent films. Preliminary testing of CIS films deposited on molybdenum foil indicated reasonably good corrosion resistance in KOH electrolyte. Figure 16 shows SEM images of the CIS surface taken before and after 48 hours of immersion in 1N KOH. Although sparsely scattered vacancies appear in the film grain structure after KOH exposure, the basic surface morphology remains unchanged.


(a) initial

(b) 48 hr in KOH

Figure 16. SEM images of CIS films before and after 48-hour KOH exposure

Completed CIGS diodes deposited on molybdenum-coated glass substrates were fabricated by the Institute for Energy Conversion (IEC) at the University of Delaware for evaluation in our photoelectrode development program. Attempts to evaluate the stability of these devices in

KOH were hampered by tendencies of the films to separate from the substrates, an effect similar to that seen in the OER catalyst films in the a-Si photoelectrodes. The CIGS diodes tended to peel away from the substrates after several minutes immersed in 1N KOH, but did not appear to be dissolved. The substrate adhesion problem needs to be addressed before the corrosion resistance of the diodes can be properly evaluated.

Photoelectrode Fabrication

The integrated multijunction CIGS photoelectrode in the side-by-side configuration of Figure 3b is clearly more complex than the corresponding monolithic structure in Figure 3a for the a-Si devices. Despite the complexity, industrial processes have been developed for production of similar structures for PV modules (Gay 1998). A commercially available PV module produced by Siemans Solar Industries that is so configured is shown in Figure 17.

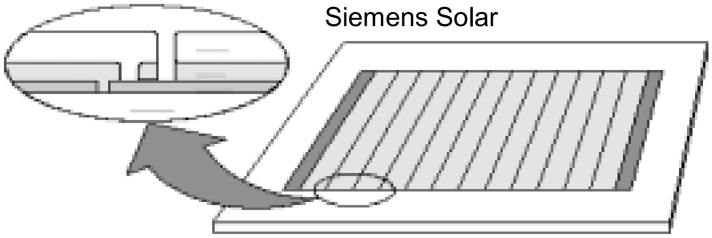


Figure 17. PV module with side-by-side CIS cells

Since the techniques for side-by-side cell fabrication are currently beyond the scope of our laboratory capabilities at UH, our initial attempts to explore the CIGS photoelectrode used mechanically interconnected CIGS devices as shown in Figure 18.

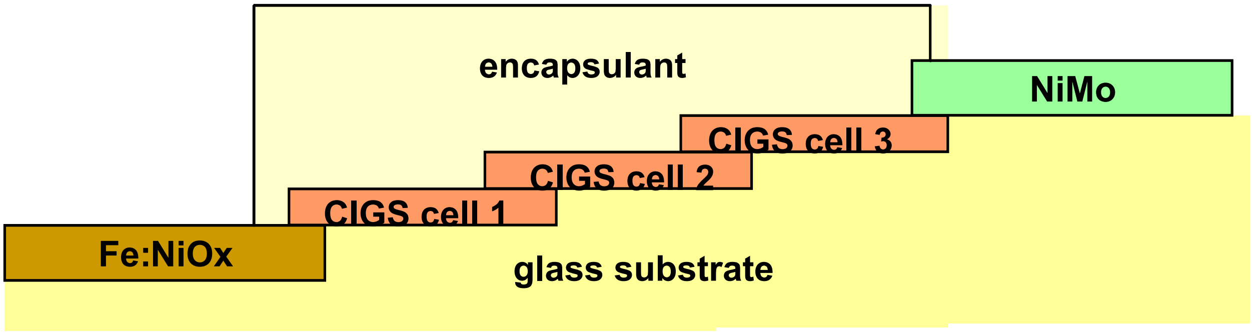


Figure 18. Mechanically stacked configuration for CIGS test photoelectrode

CIGS diodes with as-deposited PV efficiencies of 13% and open-circuit voltages of 0.6 V were deposited onto 1” square molybdenum foil substrates by the IEC in Delaware. These samples were cut and stacked along with NiMo and Fe:NiOx coated nickel foil pieces in the configuration shown in Figure 18. Conductive epoxy was used to interconnect front-to-back of successive layers, and the EP39-2 polymer was used as the transparent encapsulant over the photoactive region. The resulting test device is pictured in Figure 19.

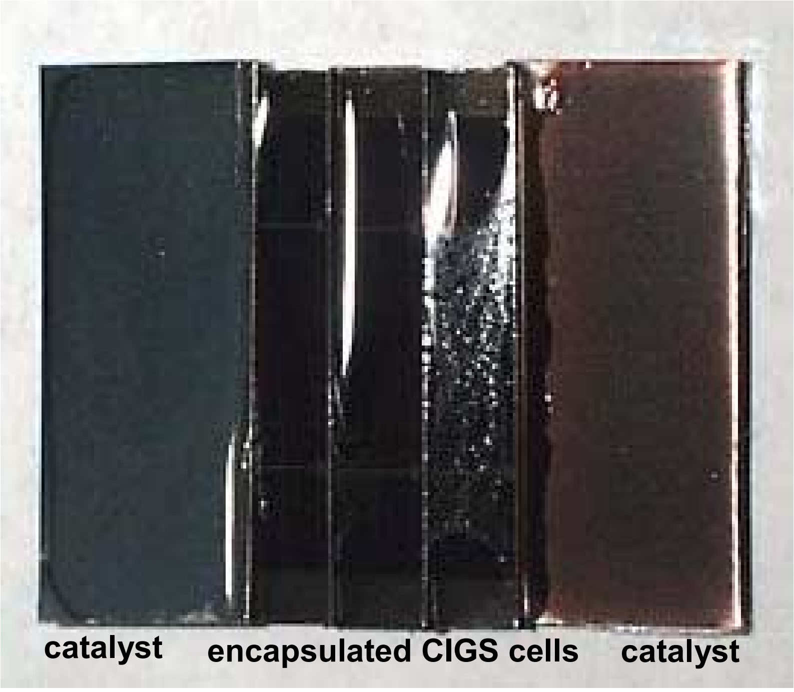


Figure 19. Mechanically stacked CIGS test device

Prior to testing in KOH, the assembled CIGS device was tested for PV properties under sunlight. It was found that the expected open-circuit voltage of 1.8 V for the triple-junction had been reduced to below 0.9 V after photoelectrode assembly. Further investigation revealed that the process of mechanically cutting the devices degraded the open-circuit voltages by about a factor of 2, consistent with the observed result in the triple-junction. Since the voltage had dropped below the levels necessary for water-splitting, the device was not tested as a photoelectrode. Alternate methods of fabricating CIGS photoelectrode test devices that do not compromise the CIGS diodes are being explored.

Advanced Photoelectrode Designs

A third key milestone this year was the conceptual design development for the hybrid solid-state/PEC photoelectrode shown in Figure 4. This design was motivated both by recent advances in semiconductor materials (such as dye-sensitized TiO_2 and WO_3) for photoelectrochemical applications (Graetzel 2000; Swiss Federal Institute of Technology 1996), and by our models. In the high-efficiency, triple-junction, amorphous silicon solar cells deposited by the University of Toledo for our photoelectrode research this year, the top “nip” junction was designed to absorb most strongly in the 350-500 nm range, as was shown in the quantum efficiency curves in Figure 8. In principle, this top cell could be replaced by a PEC junction with strong absorption in a similar range to form a water-splitting photoelectrode for hydrogen production. As was shown in Figure 4, this hybrid photoelectrode could be fabricated on SS with the back surface catalyzed for the hydrogen evolution reaction (HER), and the front surface deposited with a double-junction “nipnip” topped with an ITO/photoactive-semiconductor layer. The semiconductor top layer forms a PEC junction in electrolyte, and must have appropriate conduction band alignment for the oxygen evolution reaction (OER). In addition, the PEC junction must be strongly absorbing in the 350-500 nm region for current matching to the underlying solid-state junctions. Research advances in dye-sensitized TiO_2 and tungsten trioxide (WO_3) indicate that these may be suitable candidate materials for the hybrid photoelectrode. For example, Figure 20 shows the quantum efficiencies of TiO_2 PEC junctions as a function of sensitizing dye (Swiss Federal Institute of Technology 1996). The junction sensitized with the RuL_3 dye exhibits peak absorption near 500 nm, consistent with the requirements for the hybrid photoelectrode.

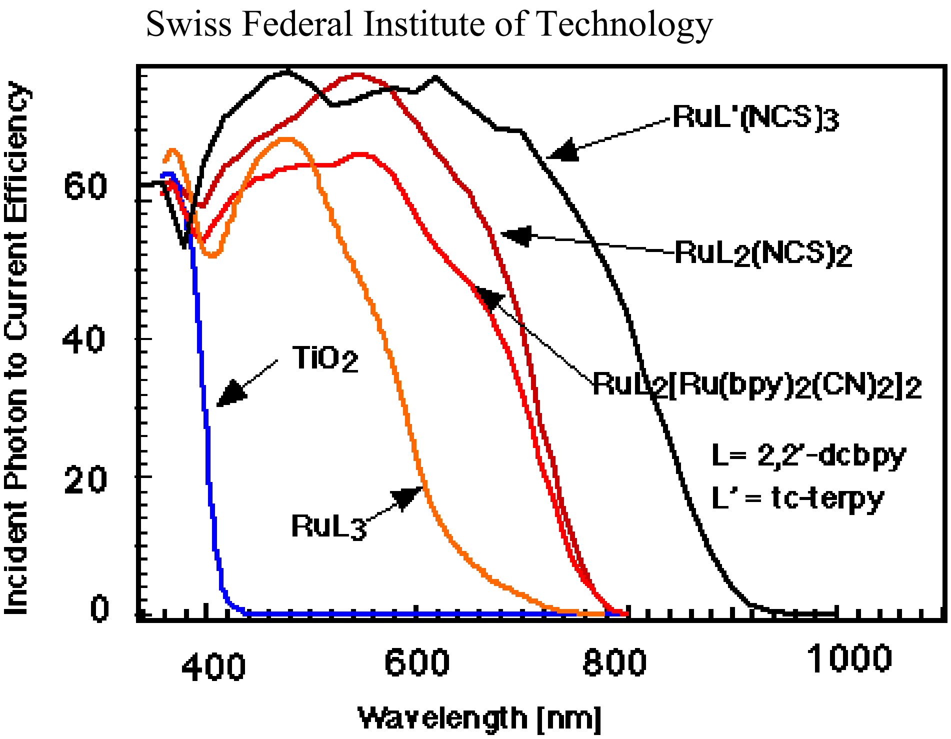


Figure 20. Quantum efficiencies of dye-sensitized TiO_2 PEC junctions

Important issues in development of the hybrid photoelectrode design include the voltage and current-matching requirements in the solid-state and electrochemical junctions. Once updated with material properties of the TiO_2/WO_3, our integrated models incorporating electrical, electrochemical, and optical analyses will be a powerful tool in this development effort. Material optimization and electrolyte selection for stable and efficient PEC interfaces are also critical to the hybrid photoelectrode design.

Summary

This year, we made significant progress in three areas of research: 1) the optimization of constituent films for integrated multijunction photoelectrodes based on amorphous silicon and CIGS semiconductors; 2) the fabrication of test devices for the a-Si and CIGS integrated photoelectrode configurations; and 3) the design of a hybrid solid-state/PEC photoelectrode design.

Progress in materials optimization was made on several fronts. High-efficiency a-Si triple-junction devices (12.7%) were successfully deposited by the University of Toledo on stainless steel foil precoated with HER catalysts. CIGS devices with efficiencies exceeding 13% were deposited by the IEC, University of Delaware, on molybdenum foil, also compatible with photoelectrode designs. At UH, high-activity NiMo and Fe:NiOx film catalysts were developed to maximize solar-to-hydrogen efficiencies in the photoelectrode configurations. Indium-tin-oxide (ITO) used as transparent contact films in all designs was further optimized for corrosion resistance. Several candidate materials for photoelectrode encapsulation were evaluated for transparency, adhesion, and chemical stability, with the EP39-2 polymer adhesive demonstrating the best overall performance.

Using results from the material optimization effort, proof-of-concept test devices were fabricated for both a-Si and CIGS integrated multijunction photoelectrodes. Test devices for the amorphous silicon, monolithically stacked, integrated photoelectrode incorporated the high-efficiency a-Si material from Toledo, and test devices for the CIGS side-by-side integrated photoelectrode used the high-efficiency CIGS material from Delaware.

Unfortunately, there was limited success in test results using the integrated photoelectrodes. Although 6% to 8% solar-to-hydrogen efficiencies were expected for the a-Si photoelectrodes, the peak efficiency measured in outdoor tests was only 2.5%. We attribute the difference to severe degradation in the triple-junction a-Si PV cells as a result of handling and further processing steps for photoelectrode fabrication. Fe:NiOx film separation from the underlying layers was also observed in about half the a-Si photoelectrodes tested. We attribute this problem to inadequate cleaning between processing steps. As with the a-Si test devices, manual cutting of the CIGS diodes deposited on molybdenum foil also resulted in severe degradation in PV performance. In the CIGS photoelectrodes, the open-circuit diode voltages were reduced below the point where water-splitting is possible. Alternative methods for forming the side-by-side junctions for successful demonstration of the CIGS photoelectrode concept are being investigated.

Based on reported advances in photoactive semiconductor materials, we applied our integrated electronic/optical/electrochemical models in developing the conceptual design for a hybrid solid-state/PEC photoelectrode. The initial design incorporates a double-junction a-Si solid-state device coated with a thick protective transparent material such as dye-sensitized TiO_2 or WO_3, which also forms a third junction, an electrochemical junction with the electrolyte. With proper design of voltage and current characteristics, the hybrid triple-junction is expected to split water with good efficiency and improved stability.

Conclusions and Plans

As a result of this year's work, we have arrived at some fundamental conclusions regarding the relative advantages and disadvantages of the various integrated photoelectrode configurations under consideration. Based on these conclusions, we have reprioritized our efforts and formulated specific plans for future work, emphasizing the CIGS side-by-side configuration and the hybrid configuration.

The integrated solid-state, triple-junction photoelectrode designs, either with amorphous silicon or CIGS, offer promising efficiency and stability, but there are also inherent disadvantages. First, electronic losses due to the lateral collection of current through the front-surface ITO are inevitable. Second, the lateral design with separated photoactive and catalyzed areas on the front surface complicates commercial-scale manufacture and increases the potential for long-term degradation along material seams exposed to electrolyte. In the a-Si version, an additional loss term is the high effective OER overpotential due to the limited Fe:NiOx area on the front surface. The integrated triple-junction a-Si photoelectrode, using state-of-the-art a-Si processing to obtain PV efficiencies around 13%, is expected to split water with solar-to-hydrogen efficiencies between 6% and 8%, based on integrated models including all losses.

On the other hand, CIGS diodes using state-of-the-art processing can have PV efficiencies exceeding 18% (Tuttle et al. 1995). In addition, the catalyst at the front surface is the HER catalyst, which, although still limited by area, has inherently lower overpotential. Solar-to-hydrogen efficiencies exceeding 10% are readily achievable using the CIGS devices. There are added complexities in the fabrication of the side-by-side CIGS photoelectrodes, which require further development. However, large-scale manufacturing processes for such a configuration are already in place in the PV industry (Gay 1998). The disadvantages in complexity are outweighed by the potential for higher efficiency in the integrated CIGS photoelectrodes. We have therefore decided to emphasize development of these devices over the triple-junction a-Si counterparts.

The advanced hybrid photoelectrode offers advantages over both the a-Si and CIGS solid-state designs. The lateral current collection loss is eliminated, the front surface overpotential loss is reduced, and the geometry is greatly simplified, easing fabrication. In addition, greater long-term stability is expected, a result of the thick uniform outer layer of TiO_2 or WO_3. The simplified fabrication and inherently low cost of the oxide junction could significantly lower system cost. We have therefore concluded that the primary emphasis needs to be placed on developing the hybrid photoelectrode design to take advantage of the inherent benefits.

Based on our conclusions, we propose the following plan for future work in photoelectrode development:

1) Triple-junction amorphous silicon integrated photoelectrodes:
    - Complete testing of photoelectrodes in process for publication.
2) Triple-junction CIGS integrated photoelectrodes:
    - Continue development and optimization of the side-by-side design.
    - Identify potential partners to produce side-by-side CIGS test structures.
    - Fabricate and test photoelectrodes based on industry partner’s structures.

3) Hybrid solid-state/PEC photoelectrodes:

- Establish partnerships with research organizations developing dye-sensitized TiO_2 and WO_3 for photoelectrochemical applications.
- Obtain current optical and electrochemical data for sensitized TiO_2 and WO_3.
- Adapt integrated model to design hybrid systems with optimized efficiencies.
- Fabricate test devices using a-Si solid-state double-junction and a dye-sensitized TiO_2 or WO_3 PEC junction (with ITO interconnect layer).

We plan to continue our cooperative partnerships with the University of Toledo and the IEC of the University of Delaware to obtain high-efficiency a-Si and CIGS devices. Additional partnerships will be sought in both academia and industry for the fabrication of side-by-side CIGS junctions, and for the development of sensitized TiO_2 and WO_3. Through participation this year in the 2000 IEA meeting of Annex 14 on Photoelectrochemical Hydrogen Production, we have already established important contacts with members of the Swiss-Federal Institute of Technology and with the Centro de Investigacion en Energia in Mexico.

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