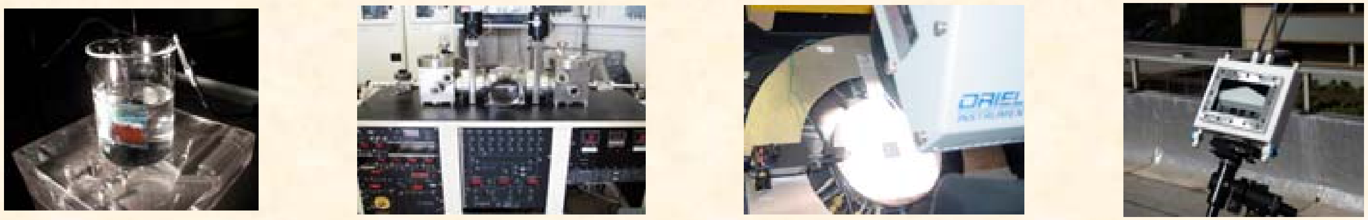


Photoelectrochemical Hydrogen Production Program

Eric L. Miller

Bjorn Marsen, Daniela Paluselli

University of Hawaii

25 May 2004

Objective

To assist DOE in the development of technology to produce hydrogen using solar energy to photoelectrochemically split water

- **Develop cost-effective materials-systems for efficient photoelectrochemical (PEC) hydrogen production**
- **Demonstrate viability of such a PEC system**
- **Initiate plans for future development to commercialization**

Budget

	DOE	UH	Total
Phase I- FY '01	$249,527	$82,573	$332,100
Phase II- FY '02	$241,176	$60,294	$301,470
Phase III- FY '03	$237,108	$60,056	$297,164

- **No current FY '04 funding**
- **No-cost extension using '03 funds through June '04**
- **Currently seeking additional funds for further development**

Technical Barriers and Targets

- Durable materials with the appropriate characteristics for photoelectrochemical hydrogen production that meet the program goals have not been identified…

- Materials with smaller bandgaps more efficiently utilize the solar spectrum, but are often less energetically favorable for hydrogen production because of the bandedge mismatch with respect to either hydrogen or oxygen redox potentials…

- Hybrid designs combining multi-layers of materials could address issues of durability and efficiency.

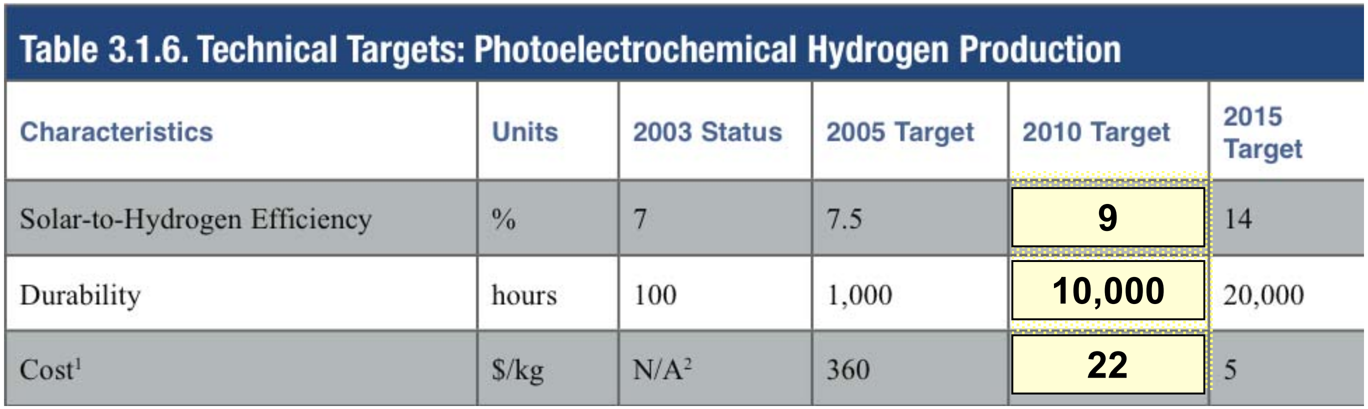
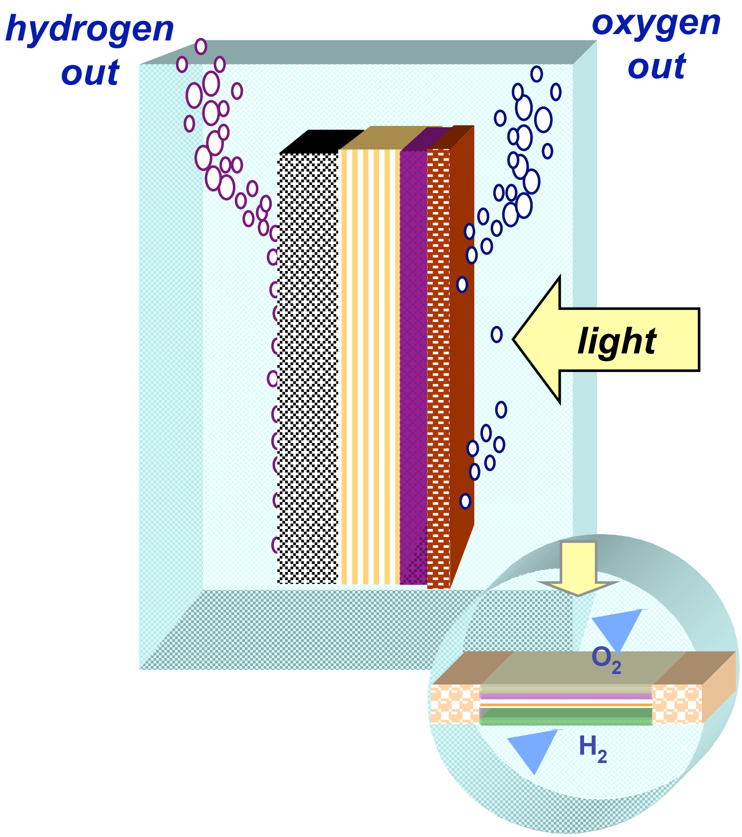


Table 3.1.6. Technical Targets: Photoelectrochemical Hydrogen Production

Characteristics	Units	2003 Status	2005 Target	2010 Target	2015 Target
Solar-to-Hydrogen Efficiency	%	7	7.5	9	14
Durability	hours	100	1,000	10,000	20,000
Cost[1]	\$/kg	N/A[2]	360	22	5

U.S. DOE Multi-Year Research-, Development-, and Demonstration Plan, June 2003 Draft

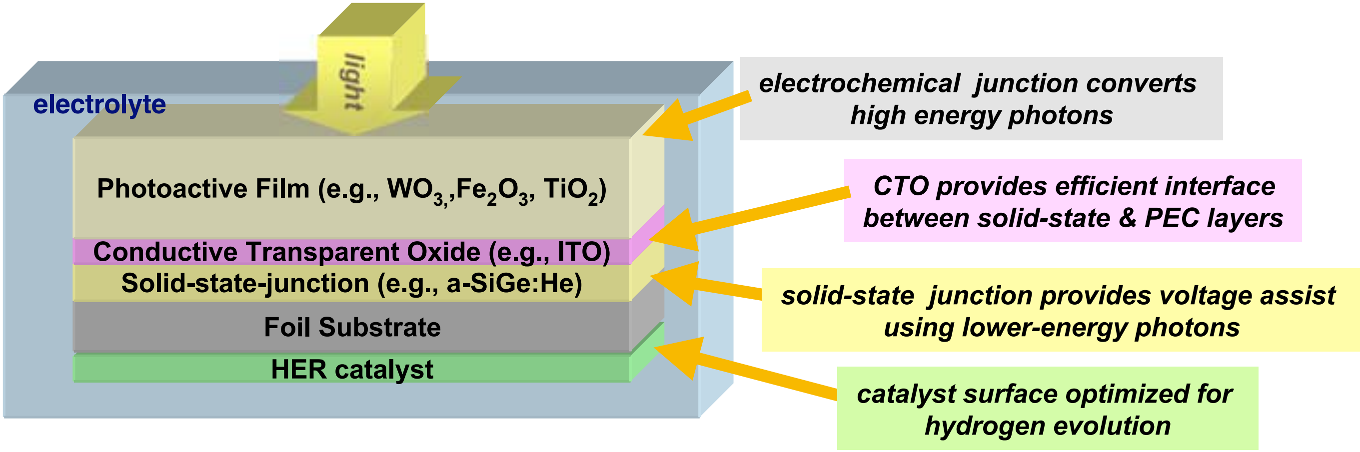
UH Approach to PEC



- **Multi-Junction planar photoelectrodes for direct water splitting**
- **Focus on low-cost materials**
  - –Stainless steel foil substrates
  - –Amorphous silicon thin films & devices
  - –Metal oxide thin films & devices
  - –CIGS thin films & devices
- **Utilize scalable fabrication processes for commercial manufacture**

The Hybrid Photoelectrode

- *a Key Enabling Technology Developed at UH (patent in progress)*



electrochemical junction converts high energy photons

CTO provides efficient interface between solid-state & PEC layers

solid-state junction provides voltage assist using lower-energy photons

catalyst surface optimized for hydrogen evolution

- **Integrates low-cost photovoltaic (PV) and photoactive oxide materials to provide voltage needed for direct water splitting**
- **Simple planar structure allows easy fabrication and scalable manufacture**
- **No need for complex and corrosion-prone electrical interconnects**
- **Leverages DOE investments in other programs (such as PV)**

Project Safety

- **For the “Hawaii Fuel Cell Test Facility”, UH has developed extensive hydrogen safety plans. Elements include:**
  - **Complete database of relevant codes and standards**
  - **Failure modes and effects analysis (FMEA)**
  - **Review by industrial partner of FMEA and safety compliance**
  - **Generation of in-house safety manuals**

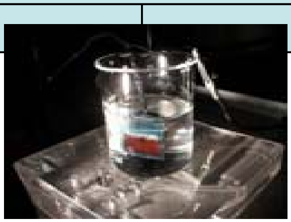
- **For this project, UH has implemented the appropriate safety plans to accommodate the small quantities of hydrogen produced in the lab-scale PEC experiments*, including:**
  - **Specification of adequate ventilation of the laboratory space**
  - **Training of personnel in H_2 handling procedures & emergency protocols**

at 9% STH efficiency under 1-sun, a 3 cm^2 lab-scale device produces less than 1 milligram of H_2 per hour.

Project Timeline

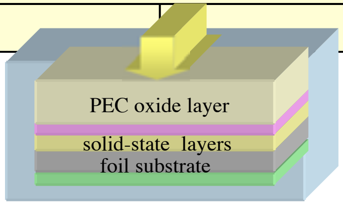
MILESTONES HAVE BEEN CONSISTENTLY MET…

Phase I – FY '01



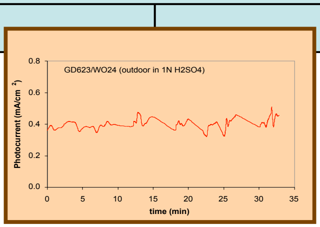
- Evaluation of competing photoelectrode configurations

Phase II – FY '02



- Development of the Hybrid Photoelectrode design

Phase III – FY '03



- Hybrid Photoelectrode proof of concept
- Key focus areas identified
- Partnerships established for future development

Progress Summary

- The “Hybrid Photoelectrode” developed cost-effective materials-systems for efficient (PEC) hydrogen production
  - Pathways to success identified and pursued
  - Critical research issues in materials R&D, and in photoelectrode design, fabrication & testing identified and attacked
- Viability of a “Hybrid Photoelectrode” system demonstrated
  - Proof of concept demonstrated based on WO_3 and amorphous silicon prototype in acid electrolyte
  - Efficiency enhancements in progress
- Plans initiated for further development to commercialization
  - Industry, academic and government lab partnerships established
  - Proposals submitted for extended funding

Identification of Promising Pathways

tungsten trioxide has good photoactivity, but the high bandgap limits photocurrent

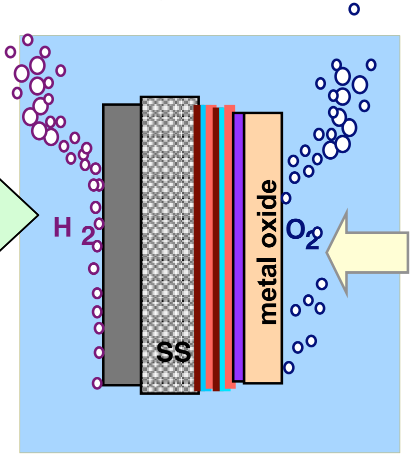
WO_3 with reduced bandgap
(doping, surface mod, etc)

iron oxide has near-optimal bandgap, but recombination losses limit photocurrents

Fe_2O_3 with improved electronic properties
(doping, surface mod, etc)

Integration with optimized solid state materials/devices

Viable PEC System



others may arise through combinatorial discovery, etc…..

Critical Research Focus Areas

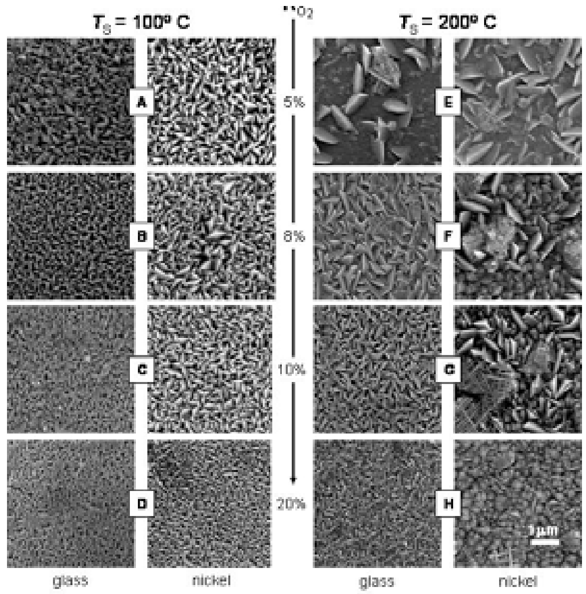
- **Development of ‘low-temperature’ (<300°C) metal oxide films compatible with Hybrid Photoelectrode fabrication & operation**
  - **Film engineering using reactive sputtering**
  - **Comparative film characterizations**
  - **Combinatorial Discovery / First Principle Calculations *(new)***
  - **Post deposition film modification *(new)***

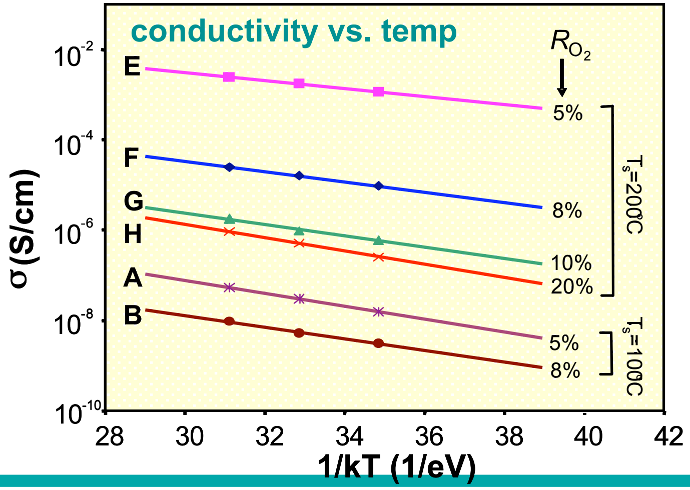
- **Continued development of optimized solid-state materials**
  - **Amorphous silicon device optimization**
  - **CIGS -based device configurations**
  - **Microcrystalline materials**

- **Integrated device optimization using best-available materials**
  - **Voltage tailoring, and current and spectral matching**
  - **Compatible processes for planar film fabrication**
  - **Scaled-up fabrication for commercial manufacture**

Low-Temperature Fe_2O_3 Progress

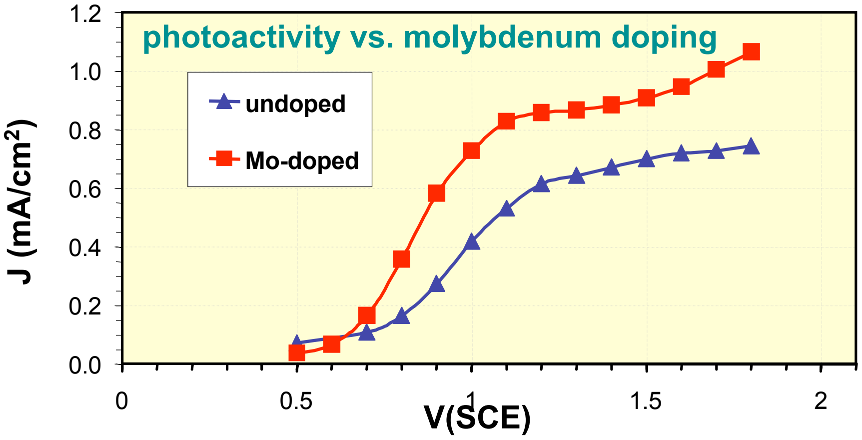
process-dependent grain structure

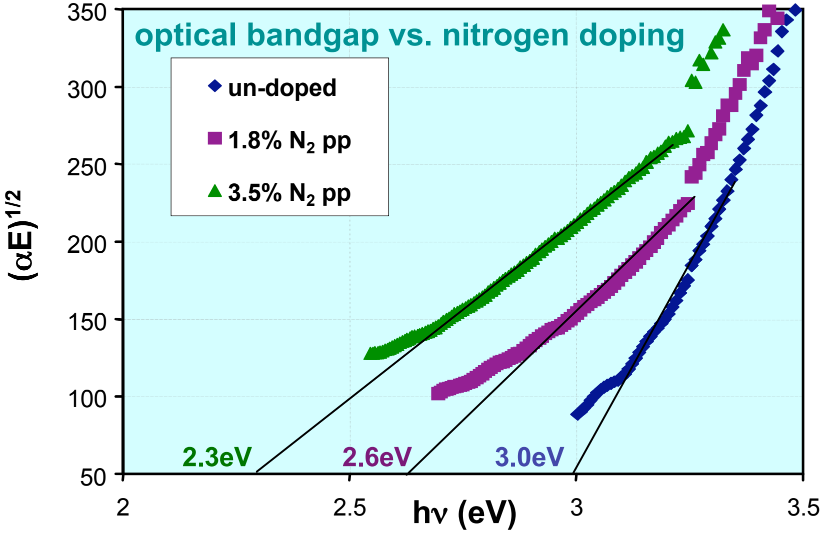




- **Grain structure modified by process parameters**
  - substrate temperature
  - gas composition & pressure
- **Conductivity improved in large-grained films**
  - range from 10^{-10} - 10^{-3} S/cm
- **Photocurrents remain low**
  - in the sub 0.1 mA/cm^2 range
- **Possible enhancement of photocurrent with film doping**

Low-Temperature WO_3 Progress

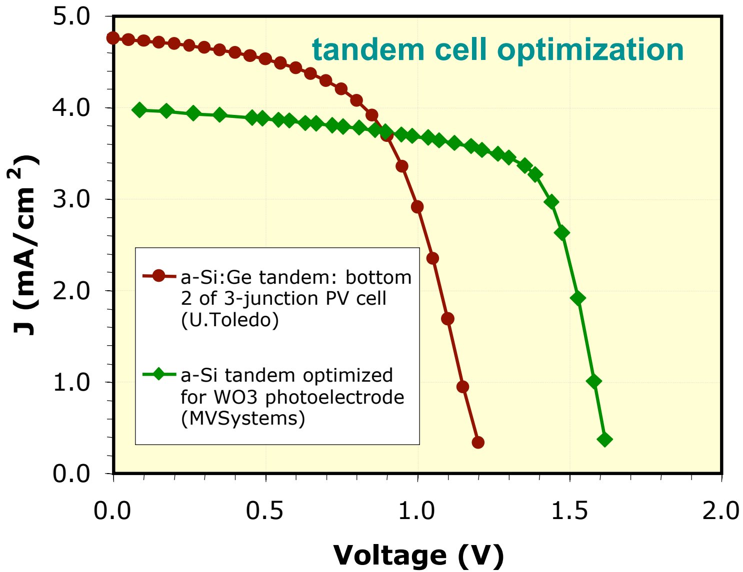




- **Good electronic properties**
  - conductivities up to 10^{-1} S/cm
- **Photocurrents readily achieved in 'pure' WO_3 sputtered films**
  - consistently in mA/cm^2 range
  - theoretically limited to ~$4mA/cm^2$ (achieved in hi-temp films)
- **Molybdenum doping improves photoactivity in sputtered films**
  - enhanced voltage and current characteristics
- **Nitrogen doping decreases bandgap in sputtered films**
  - reductions from 3.0 to 2.3 achieved

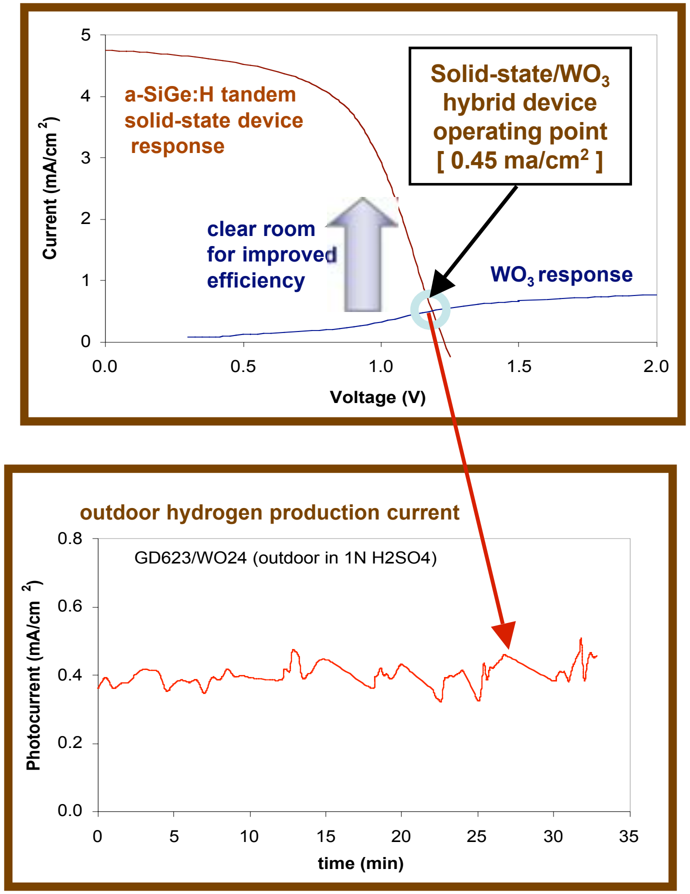
Solid-State Device Progress

Amorphous silicon deposition system



- **Amorphous silicon/germanium tandem devices demonstrated on foil substrates**
  - tuned to photons not used at PEC junction
- **Tandem device optimized for WO_3 photoelectrodes demonstrated using no germanium**
  - enhanced voltage
  - current levels adequate for matching to PEC junction
- **Microcrystalline silicon and CIGS based systems considered for future high-efficiency devices**

Photoelectrode Demonstration



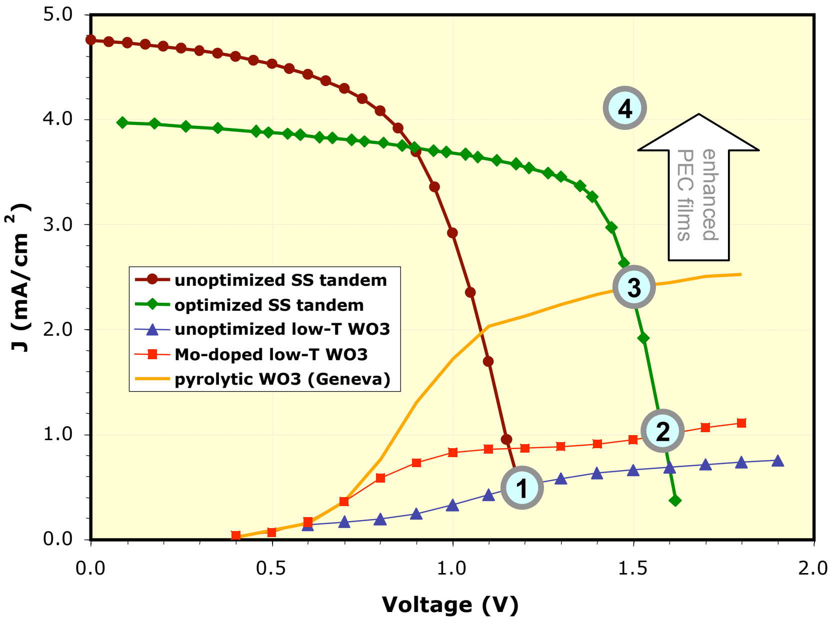
DEVICE STRUCTURE:

- Un-optimized silicon-alloy tandem
- Unoptimized low-T sputtered WO$_3$
- 2.85 cm^2 area

PERFORMANCE:

- Currents up to 0.5mA/cm^2 (0.7%STH)
- Stable operation in acid over 8 hours
- Photocurrents consistent with measured properties of the WO$_3$ material and the tandem silicon cell
- Significant efficiency enhancement expected with improved metal-oxide properties and optimized tandem

Pushing the Efficiency



① 0.7% STH demonstrated with un-optimized low-temp sputtered WO_3 and a-S:Ge tandem

② 1.3% STH expected using Mo-doped sputtered WO_3 with optimized a-Si tandem

③ >3.0% STH expected from a pure WO_3 system based on performance of pyrolytic materials

④ >5.0% STH requires enhanced PEC oxides (e.g. reduced-bandgap WO_3 or enhanced Fe_2O_3) and further optimization of the solid-state layers

Goals will be met by continued development and optimization of:

- The PEC junction material (e.g., WO_3, Fe_2O_3)
- The solid-state junction layer (e.g., a-Si tandem)
- The integrated device (lab and manufacture scale)

Recent Collaborations

THE UNIVERSITY OF TOLEDO

- Amorphous silicon/germanium solar cell design & fabrication

MVSystems

- Amorphous silicon solar cells
- Fabrication process scale-Up

NREL

- Materials R&D guidance

DUQUESNE UNIVERSITY

- Pyrolitic oxide research

Others over the past three years include:

IEC Delaware, UNAM Mexico, IEA annex 14 (University of Geneva, etc.)

Future Work: the PEC "Dream Team"

- **Plans initiated for development toward commercialization**
  - –Industry, academic and government lab partnerships established
  - –Critical development issues identified & pathways to success established
  - –Proposals submitted for extended funding

HNEI

- Technical Management
- PEC Device Integration
- Materials Research Coordination

MVSystems

- Amorphous Silicon Solar Cells
- Fabrication Process Scale-Up

Intematix

UCSB
- Rapid PEC Screening Methods
UCSB

- Combinatorial Materials Discovery

NREL

- *Materials Research*
- *Device Certification*

Southwest Research Institute

- *Film Modification*
- *Roll Processes*

DUQUESNE UNIVERSITY

- *Pyrolytic Materials*

Response to Reviewer Comments

"This project would benefit from better coordination or task sharing with other material research and maybe combinatorial discovery."

> ***Expanded collaboration is critical… Since last review, we have invested significant effort to establish our "PEC Dream Team" for further development, including combinatorial discovery as a major emphasis.***

"More emphasis is needed on scaling-up to a complete PEC system as well as finding better materials."

> ***Emphases on process-scale-up and on development of better materials have been boosted by introduction of key industry/government partners into the "team", such as MVSystems (fabrication specialists), Intematix (combinatorial discovery), NREL (materials characterizations), and others.***

"I see continued improvements in this area being made but I do not see the type of improvements needed to meet 2010 goals and beyond."

> ***Again, the expanded collaborative effort is the key to effect the improvements in PEC materials, solid-state junctions, integrated device fabrication and scale-up needed to meet the long-term goals.***

Publications

- E. Miller, D. Paluselli, B. Marsen, R. Rocheleau, “Low Temperature Reactively-Sputtered Iron Oxide for Thin Films Devices”, Thin Solid Films, in press (2004).
- E. Miller, D. Paluselli, B. Marsen, R. Rocheleau, “Development of Reactively Sputtered Metal Oxide Films for Hydrogen-Producing Hybrid Multijunction Photoelectrodes”, International Journal of Hydrogen Energy, in press (2004).
- E. Miller, R. Rocheleau, S. Khan, “A Hybrid Multijunction Photoelectrode for Hydrogen Production Fabricated with Amorphous Silicon /Germanium and Iron Oxide Thin Films”, International Journal of Hydrogen Energy, in press (2004).
- E. Miller, R. Rocheleau, and X. Deng, “Design Considerations for a Hybrid Amorphous Silicon/Photoelectrochemical Multijunction Cell for Hydrogen Production”, International Journal of Hydrogen Energy, 28(6), 615-623 (2003).
- R. Rocheleau, E. Miller, and A. Misra. “High-efficiency Photoelectrochemical Hydrogen Production using Multijunction Amorphous Silicon Photoelectrodes”, Energy and Fuels, 12, 3-10 (1998).
- R. Rocheleau, E. Miller, “Photoelectrochemical Production of Hydrogen: Engineering Loss Analysis”, *International Journal of Hydrogen Energy* 22, 771-782 (1997).

Acknowledgements

U.S. Department of Energy

- **University of Hawaii**
  - Dr. Richard Rocheleau
  - Fred Matsunaga
  - Dr. Sylvain Marsillac
  - Susanne Dorn
  - Kent Ross
  - Tina Weatherby

- **MVSystems, Inc.**
  - Dr. Arun Madan

- **University of Toledo**
  - Dr. Xunming Deng

- **Intematix Corporation**
  - Dr. Young Yoo

- **National Renewable Energy Lab**
  - Dr. Mowafak Al-Jassim
  - Dr. John Turner
  - Dr. Yanfa Yan

- **Duquesne University**
  - Dr. Shahed Khan

- **CNR Bologna (Italy)**
  - Dr. Clara Santato

- **Southwest Research Institute**
  - Dr. James Arps
  - Dr. Bruce Lanning

MAHALO NUI LOA