Photoelectrochemical Hydrogen Production

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1907

ACKNOWLEDGEMENTS

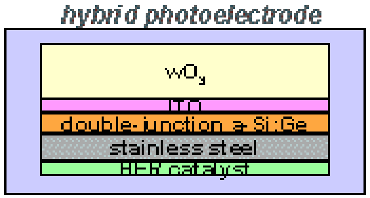
-U.S. Department of Energy for continued support of research

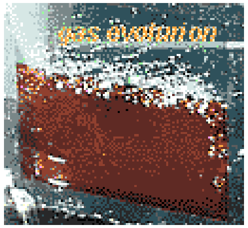
- HNEI Thin Films Lab Staff (D. Paluselli, B. Marsen, et al.) for tireless efforts

- Dr. Shahed Khan of Duquesne University

- Dr. Xunming Deng from the University of Toledo

Poster Outline



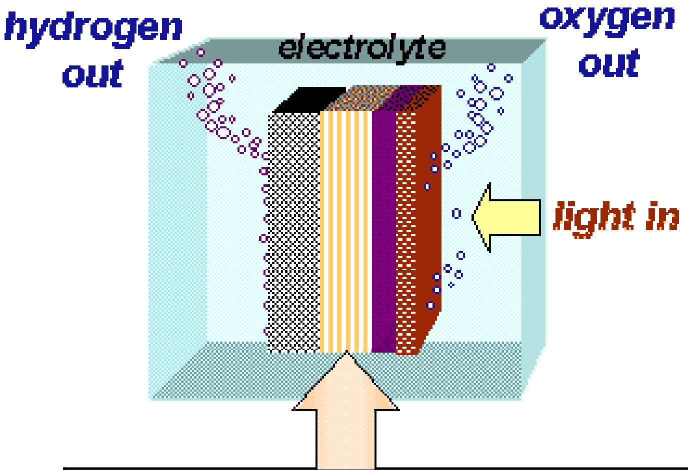


- **Approach and Goals:**
  - *Low-cost' Multijunction planar photoelectrodes for hydrogen production*
- **Hybrid Photoelectrodes**
  - *True photoelectrochemical device based on electrochemical interface at metal oxide films with integrated solid-state voltage assist*
- **Technical Barriers**
  - *General barriers to photoelectrochemical production*
  - *Hybrid photoelectrode development issues*
- **Approach to Technical Barriers**
  - *Materials research and development*
  - *Photoelectrode research and development*
  - *Advanced integrated desings*
- **Progress Status**
  - *Major milestones met*
  - *Materials: Critical metal oxides developed*
  - *Photoelectrodes: Stable hybrid demonstrated*
- **Summary and Future Directions**
- **Important Research Partnerships**

General Approach & Goals

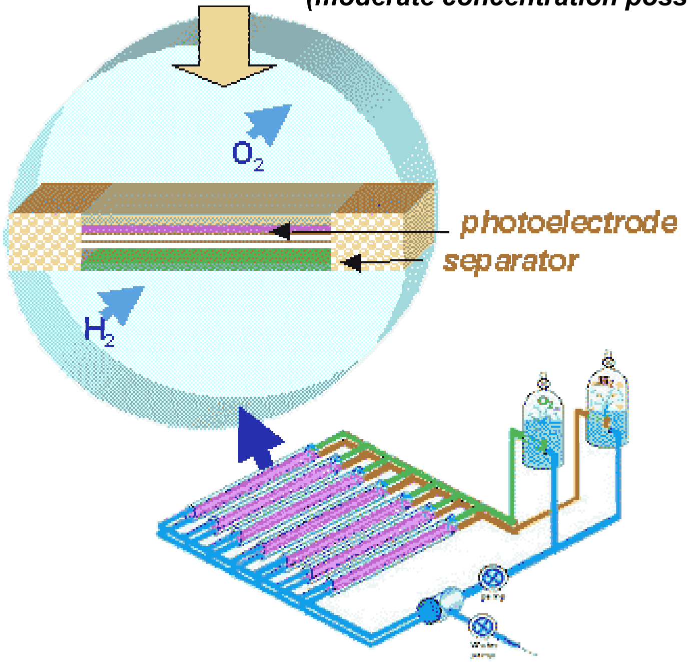
Multi-junction Planar Photoelectrodes using Low-Cost Thin Film Materials

GOALS: 7.5% STH by 2005 @ $360/kg; 9% STH by 2010 $22 /kg



Focus Materials for Planar Photoelectrodes	
low-cost solid state semiconductor films	*amorphous Si/Ge:H*
	μ-crystalline Si
	CIS, CIGS
electrochemical metal oxide semiconductor films	*iron-oxide*
	tungsten trioxide
	titanium dioxide
catalyst films	*mixed metals (Ni, Mo, Co, etc.)*

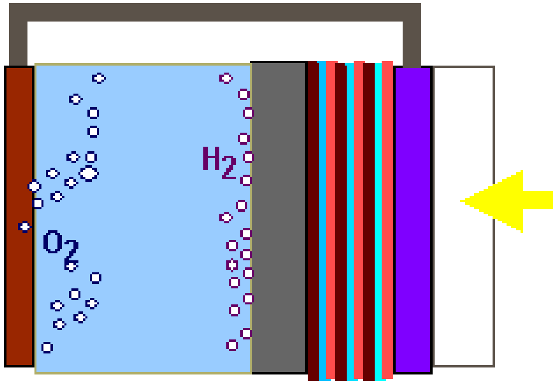
Incident light
(moderate concentration possible)



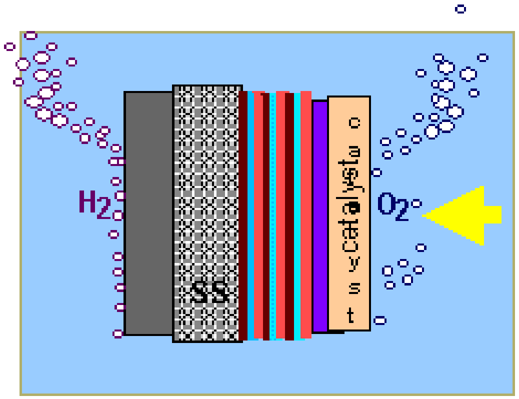
tube array with gas collectors

Multijunction Photoelectrodes

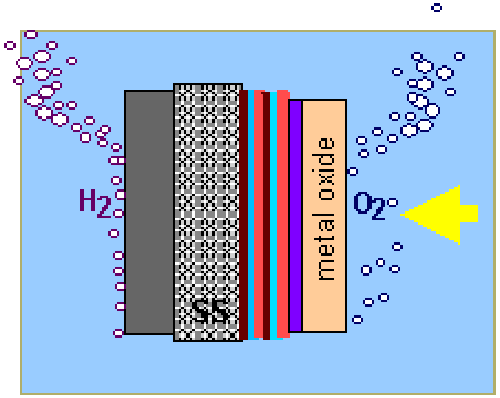
Key Finding from Analytical and Experimental Work:
Efficient utilization of sunlight for water splitting requires multi-junction systems to provide sufficient voltage and current



1997:
Triple junction amorhpous silicon device on glass/ITO superstrate connected to separated OER & HER electrodes demonstrates stable hydrogen production at 7.8% STH.



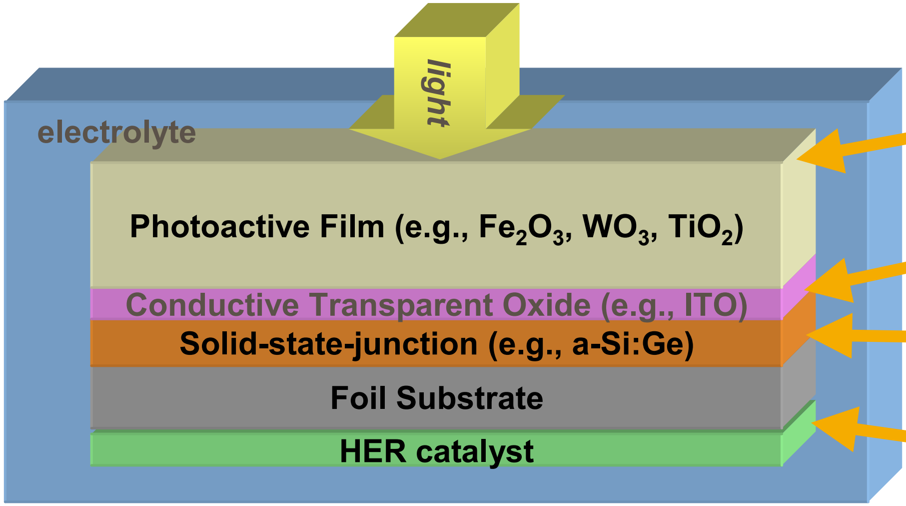
1999:
Triple junction amorhpous silicon device on stainless steel substrate coated with HER catalyst on back & with OER catalyst on front- operated with limited success- OER layer thin enough for transparence offered little corrosion protection



Present:
Multijunction Hybrid Photoelectrode: true electrochemical device where the front catalyst from the 1999 structure Is replaced by a photo-active oxide. The embedded solid-state junction provides a voltage assist to the metal-oxide/electrolyte junction: Hydrogen Is evolved on catalyzed back surface

Hybrid Photoelectrodes

integrated multijunction electrochemical device to provide sufficient photo-generated current & voltage for efficient water splitting *(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

KEY FEATURES:

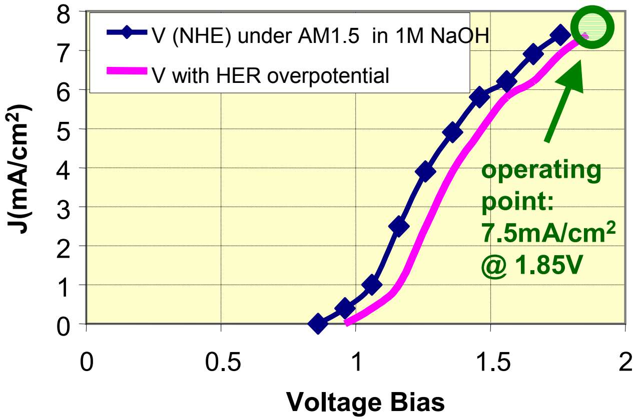
- Oxide interface provides corrosion resistance & long life
- Solid-state junction reduces metal-oxide/electrolyte interface voltage requirements
- Proven metal oxides can be used in hybrid devices for efficient, un-biased water splitting
  - Iron oxide, tungsten trioxide, modified titanium dioxide
- Simple planar structure allows easy fabrication
- Leverages DOE investments in other programs (e.g., Photovoltaics for solid-state materials)

Hybrid Photoelectrode Material Systems

➢**Initial conceptual designs based on spray-pyrolysis nano-structured oxides**

Iron Oxide Films

Duquesne University. Khan & Akikusa



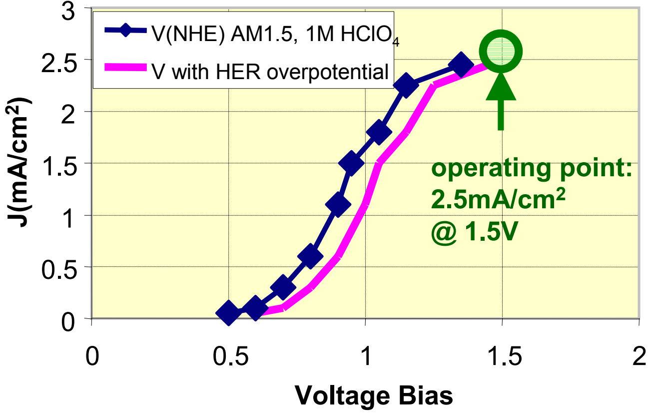
operating point: 7.5mA/cm² @ 1.85V

Incorporation in Hybrid Photoelectrodes

- Photojunction formed in alkaline media
- High photocurrents / low voltage

Tungsten Trioxide Films

University of Geneva ,C. Santato et al.



operating point: 2.5mA/cm² @ 1.5V

Incorporation in Hybrid Photoelectrodes

- Photojunction formed in acid media
- Moderate photocurrents / better voltage

TECHNICAL ISSUES:

- **Pyrolysis deposition temperatures (400-500°C) *Too High* for hybrid structure**
- **High efficiency water splitting requires modification of oxide properties**

Technical Barriers

GENERAL BARRIERS TO PEC HYDROGEN PRODUCTION

from "Multi-Year Plan (draft 3-20): Hydrogen Production"

"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. "

SPECIFIC HYBRID PHOTOELECTRODES ISSUES

- **CRITICAL ISSUE: Development of 'low-temperature' (<300ºC) processes which yield photoactive & stable metal oxide films**
- **ONGOING CONSIDERATIONS: Continued development of optimized materials and device designs are needed to meet program goals. Compatibility of semiconductor and catalytic layers, voltage tailoring, and current matching remain important considerations**

Approach to Technical Barriers

- MATERIALS RESEARCH: Current focus on developing low-temperature reactive sputtering process to produce photoactive & stable metal oxide films
  - Partnership Support (Duquesne University): develop further understanding of structure & composition of photoactive metal oxides for engineering new, process-compatible materials, including Fe_2O_3 , WO_3 & modified TiO_2
- PHOTOELECTRODE RESEARCH: Current focus on incorporating best available materials into hybrid photoelectrode structures to evaluate performance & stability
  - Partnership Support (University of Toledo): design & fabricate multi-junction amorphous-silicon alloy devices with specified voltage and current characteristics
- Continued development of optimized materials and device designs for use in high-performance / low-cost hybrid photoelectrodes

Progress: Timeline and Milestone

All Milestones ON or AHEAD of Schedule
(as of May 2003)

start 1/1/03

from "2003 Spend Plan"

TASK 1: Materials R&D	Comparative evaluation of available a-Si:Ge materials/devices	2nd quarter	*completed*
	Comparative evaluation of available Fe_2O_3 materials	2nd quarter	
	Comparative evaluation of available CIS/CIGS materials	3rd quarter	*in progress*
	Identification of alternative materials for hybrid applications	4th quarter	
TASK 2: photoelectrode R&D	Preliminary designs: a-Si:Ge/Fe_2O_3 photoelectrode test devices	1st quarter	*completed*
	Performance database of fabricated test devices	2nd quarter	
	Optimized design of a-Si:Ge/Fe_2O_3 photoelectrodes	3rd quarter	*in progress*
	Performance database of fabricated optimized devices	4th quarter	
	Design for CIGS-based high-efficiency hybrid photoelectrode	4th quarter	

end 12/31/03

Progress: Materials R&D

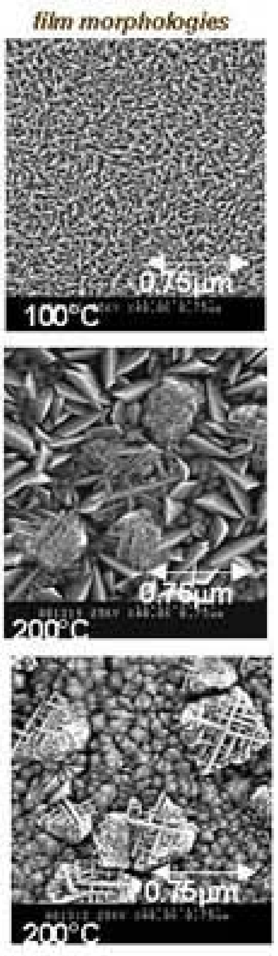
Low-Temperature Photoactive Metal Oxides

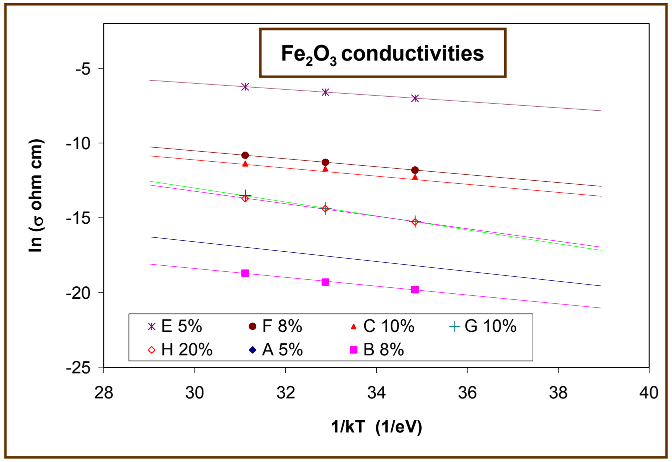
- Fe_2O_3 films successfully deposited using low temperature sputter process
  - Ability to engineer key film properties successfully demonstrated
  - Excellent film adhesion and stability in alkaline media achieved
  - Photocurrents up to 0.1 mA/cm^2 achieved under 1-sun in films deposited to date
- WO_3 films successfully deposited using low temperature sputter process
  - Ability to engineer key film properties successfully demonstrated
  - Excellent film adhesion and stability in acid media achieved
  - Photocurrents up to 0.9 mA/cm^2 achieved under 1 sun in films deposited to date

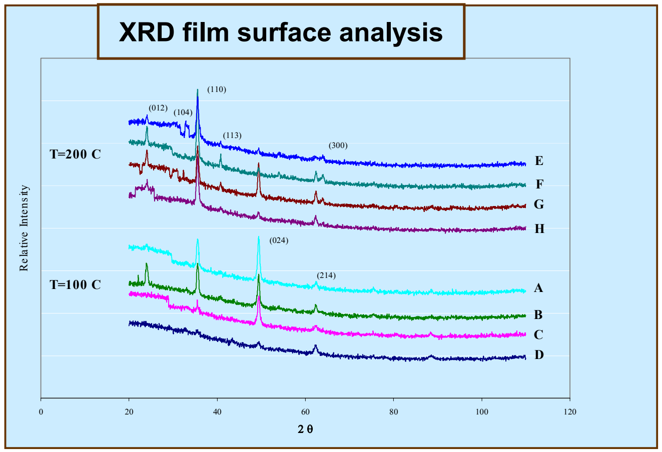
Advanced Solid-State Materials

- Amorphous silicon devices for current photoelectrode tests obtained from partners
- Micro-crystalline silicon films developed in-house (for advanced tandem cells)
- High efficiency copper-indium-gallium-diselenide (CIGS) produced in house
  - 14% efficient 4cm^2 CIGS cell on foil substrate demonstrated

Progress: Fe_2O_3 Film Research

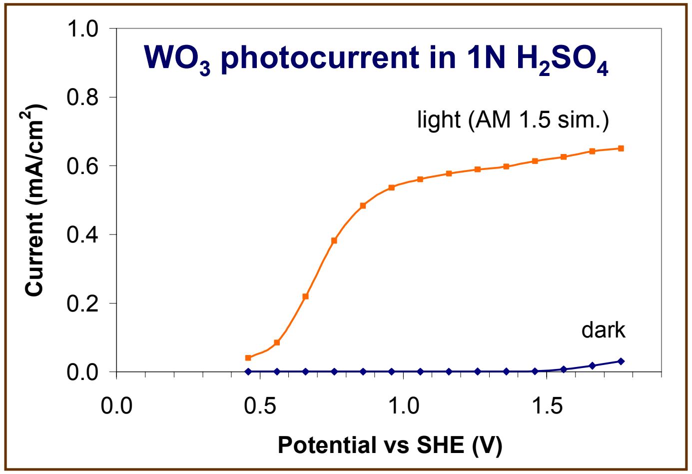

film morphologies

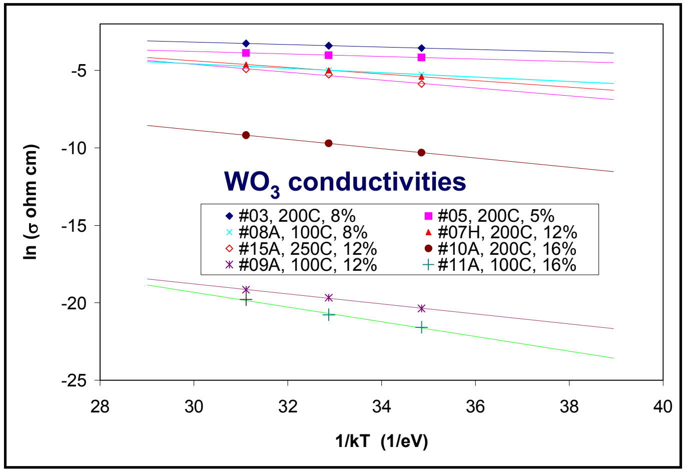

Fe_2O_3 conductivities

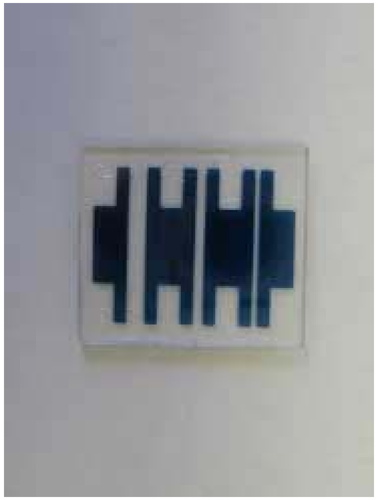

XRD film surface analysis

- Low temperature (<300°C) reactive sputtering from iron target
- Variable substrate temperature and oxygen partial pressure
- Structure/electronic properties vary strongly with deposition parameters
- High-purity Hematite in all films with bandgaps from 1.8 - 2.0 eV
- Film resistivities range from 10^3 - 10^9 ohm cm
- Withstands long-term exposure to 1N KOH (tested for 6 months)
- Films to date: photocurrents up to 0.1 mA/cm^2 under 1 sun in alkaline

Progress: WO_3 Film Research







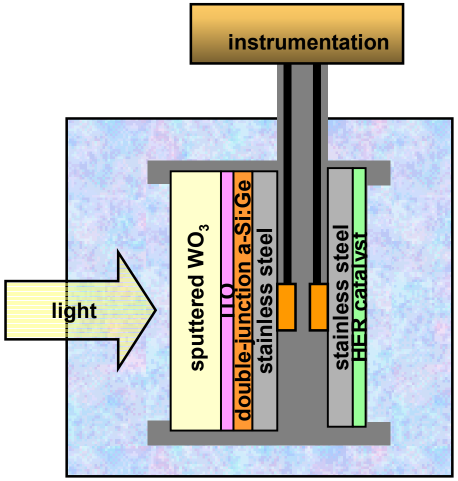
- Investigation initiated February 2003
- Low temperature (<300°C) reactive sputtering from tungsten target
- Variable temperature and oxygen partial pressure
- Measured bandgaps ranging from 3.0-3.2 eV
- Film resistivities range from 10^1 - 10^{10} ohm cm
- Excellent chemical stability in in 1Normal H_2SO_4
- Films deposited to date: photocurrents from 0.2-0.6 mA/cm^2 under 1 sun illumination in sulfuric acid

Progress: Photoelectrode Breakthrough

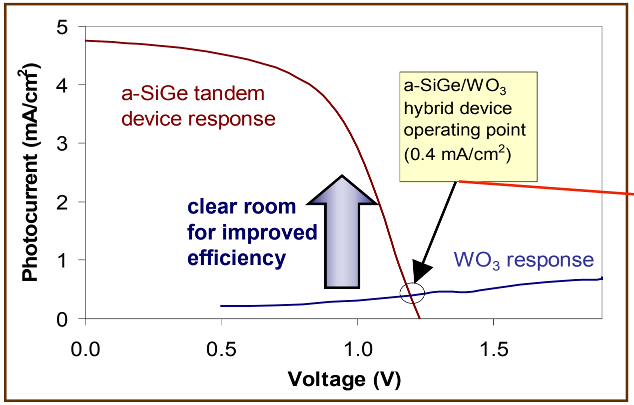
Stable Operation of Hybrid Photoelectrodes Demonstrated!

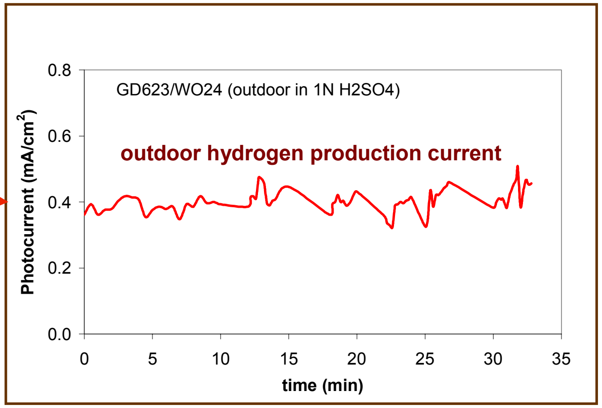
(using best low-temperature materials fabricated to date)

- **DEVICE STRUCTURE:**
  - amorphous silicon-alloy tandem (U. Toledo)
  - Low-temperature sputtered WO_3 (U. Hawaii)
  - 2.5 cm^2 area with separated counter electrode (for photocurrent measurement)



- **DEVICE PERFORMANCE:**
  - Currents up to 0.5mA/cm^2 in 1-sun outdoor tests (.7%STH)
  - Stable operation in 1N H_2SO_4 measured for over 5 hours
  - Photocurrents consistent with measured properties of the WO_3 material and the tandem silicon cell
  - Analysis indicates significant efficiency enhancement with improved metal-oxide properties





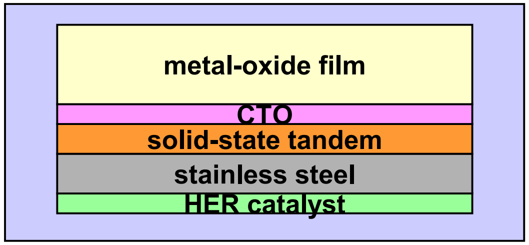
Summary & Future Directions

Status Summary

- **STABLE OPERATION of integrated thin-film Hybrid Photoelectrodes in aqueous electrolyte under 1-sun illumination has been demonstrated for the first time! This is an extremely encouraging indication that we are on a *right track* toward *commercialize-able* photoelectrochemical hydrogen production.**
- **We have identified optical/electronic properties of the present hybrid-compatible metal-oxides as the KEY limiting factor to efficiency… clearly defining the primary focus for continued research efforts.**

Future Directions

We plan to continue development of the Hybrid Photoelectrode, with expanded effort to optimize hybrid-compatible materials for efficiency and long-life. We are confident that by continuing this approach, we will be able to meet the 2005 and 2010 program goals.



Important HNEI Collaborations

CURRENT:

- **Duquesne University:** fabrication of nano-structured Fe_2O_3 films.
- **University of Toledo:** design & fabrication of a-Si:Ge multijunctions.
- **"IEC" University of Delaware:** design & fabrication of high efficiency CIGS.
- **DayStar Technologies:** design & in-house fabrication of CIGS materials.
- **"UNAM" Mexico:** evaluation of alternative materials, μcr-SiC corrosion studies.
- **General Motors:** PEC development lab for device evaluation.
- **IEA Annex 14 connections:** Fe_2O_3, WO_3 and TiO_2 film studies.

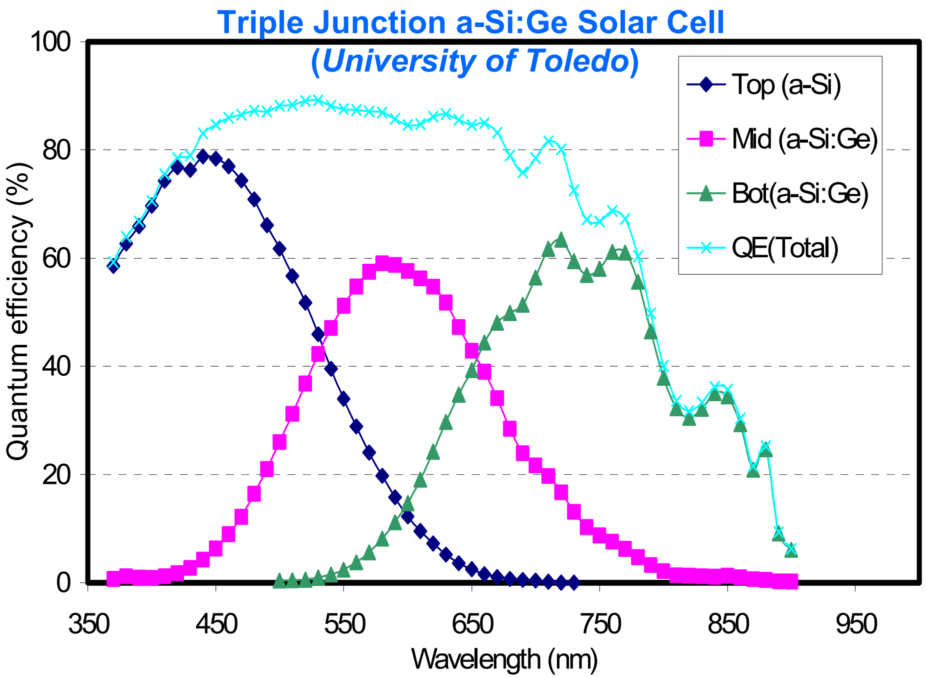
FUTURE:

- **NREL, UCSB & SRI:** Fe_2O_3, WO_3 ,TiO_2 & mixed metal catalyst film screening

Supporting Information Slides…

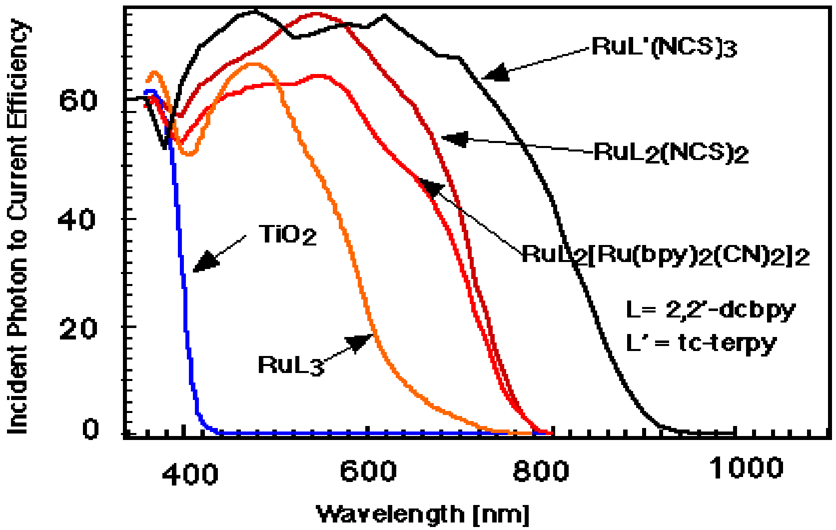
not included in poster

Hybrid Photoelectrode Concept



Triple Junction a-Si:Ge Solar Cell
(University of Toledo)

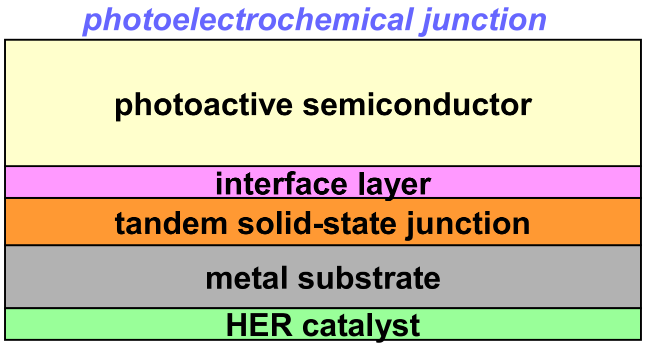
Dye-sensitized TiO_2 PEC Junction
(Swiss Federal Institute)



- Top cell in the solid-state stack can be replaced with an electrochemical junction.
- Each junction must be current matched for high efficiency.
- Series connection of all three junctions needed to generate bias required to split water.
- Top layer must be stable under OER…. (NOT dye-sensitized TiO_2!)

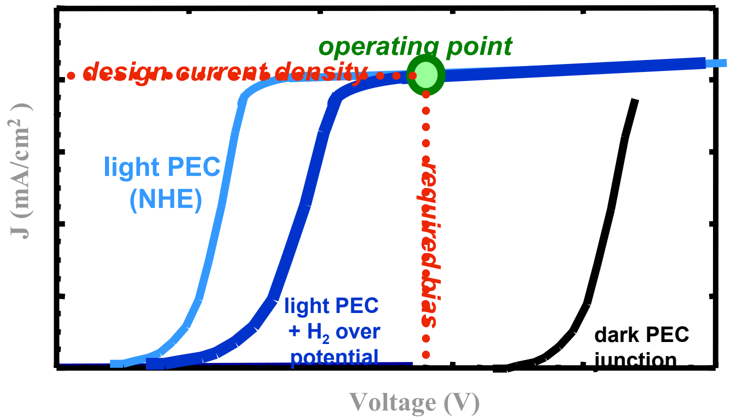
Hybrid Photoelectrode Design

Basic Structure:



- ♦ No lateral current collection loss.
- ♦ Reduction of front surface overpotential loss.
- ♦ Back surface overpotential minimized by catalyst & texturing.
- ♦ Solid-state junctions minimized.
- ♦ Simple planar geometry for fabrication.
- ♦ Uniform stable outer layer for good chemical resistance.
- ♦ Potential for LOW COST MATERIALS

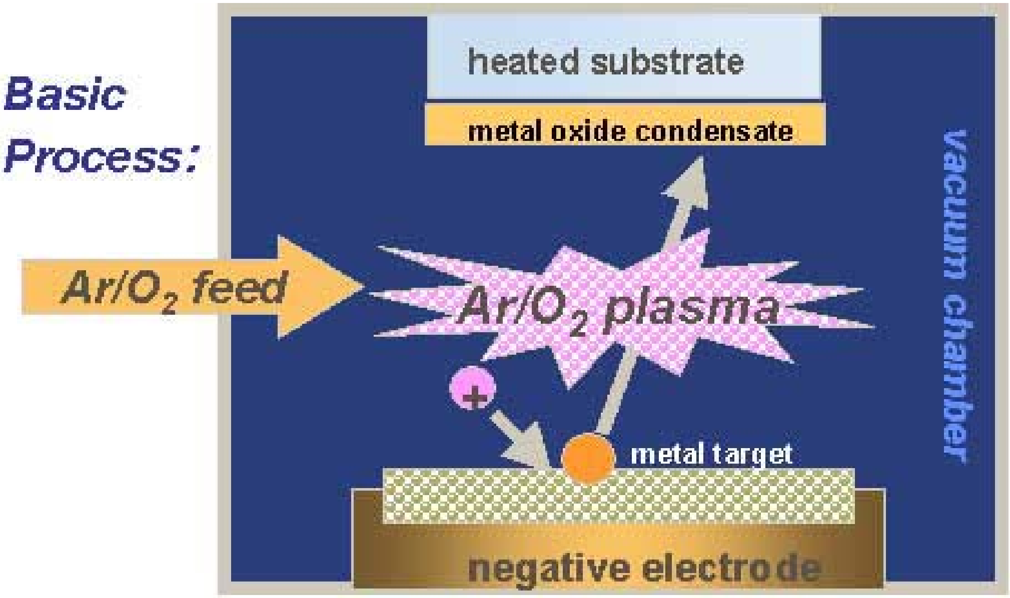
Modeling:



- ♦ Light JV and quantum efficiency for PEC junction needed.
- ♦ JV response of the PEC junction is photoshifted.
- ♦ Correction for the hydrogen overpotential loss is added.
- ♦ Intersection with the design current density establishes the necessary voltage bias.
- ♦ Tandem solid-state cell designed to drive current at the operating point using available photons.
- ♦ CURRENT MATCHING critical: efficiency limited by lowest-current cell in stack.

Reactive Sputtering of Metal Oxides

Basic Process:



- ‘Low-temperature’ reactive r.f. sputter from metallic target
- High-purity films attainable in vacuum deposition process
- Important process parameters influencing film properties:
  - Ambient P, Oxygen PP, Substrate T, r.f. Power, Geometry, Substrate material
- Important film properties for photoelectrochemical applications:
  - Thickness, Uniformity, Composition, Morphology, Optical Bandgap, Conductivity, Chemical Stability, OER Activity, Photoactivity

support

Relevant Reference Material

- **Invited Lectures** (E.L. Miller)
  - International Conference on Advanced Materials (*ICAM 2001*):
  - International Materials Research Congress 2002 (*IMRC XI*)
  - International Conference on Advanced Materials (*ICAM 2003*):
- **Relevant Publications** (E.L. Miller, et al.)
  - "Design Considerations for a Hybrid Amorphous Silicon/Photoelectrochemical Multijunction Cell for Hydrogen Production", *International Journal of Hydrogen Energy*, 28 (2003) 615-623.
  - "A Hybrid Multijunction Photoelectrode for Hydrogen Production Fabricated with Amorphous Silicon/Germanium and Iron Oxide Thin FIlms", *IMRC XI Conference Proceedings.*
  - Manuscripts on sputtered Fe_2O_3 and WO_3 film research under preparation.
- **Patent Disclosure** (E.L. Miller, R. E. Rocheleau)
  - "Hybrid Solid-State/Electrochemical Photoelectrode for Hydrogen Production".

Past-Reviewers Comments

Comments from reviewers of the 2002 Program Review were generally supportive our approach and accomplishments, and indicated encouragement for continued progress.

We appreciate the support, and hope to sustain the forward momentum toward efficient solar-powered hydrogen production.