Photoelectrochemical Hydrogen Production: UNLV-SHGR Program Subtask

Eric L. Miller
University of Hawaii

Robert Perret
UNLVRF

16 May 2006

#PD6

This presentation does not contain any proprietary or confidential information

Overview:
Photoelectrochemical (PEC) H_2 Production

Timeline

- **Project start date:** 1 Oct. 2004
- **Project end date:** 31 Dec. 2005
- **Percent complete:** 100% (Phase I)

Barriers

- **Barriers addressed: PEC H_2 production**
  - *AP: Materials Efficiency*
  - *AQ: Materials Durability*
  - *AR: Bulk Materials Synthesis*
  - *AS: Device Configuration Designs*

Budget

- **Total project funding:** $508.6k
  - *DOE share: $400k*
  - *Contractor share: $108.6k*
- **FY04 Funding :** $ 508.6k
- **Funding for FY05:** $ 684k

Partners

- **UH Collaborators:**

  MVSystems Inc., Intematix Corp., NREL, UNLV

- **SHGR team partners:**

  CU-Boulder, SNL, GA, GE, APS

Objectives: PEC Research

The primary objective is to assist DOE in the development of technology to produce hydrogen using solar energy to photoelectrochemically split water- *specifically focusing on multijunction thin film devices using metal oxides and other low-cost materials.*

DOE "Multi-Year Program Plan" Target Table

Table 3.1.11. Technical Targets: Photoelectrochemical Hydrogen Production[a]

Characteristics	Units	2003 Status	2010 Target	2015 Target[b]
Usable semiconductor bandgap[c]	eV	2.8	2.3	2.0
Chemical conversion process efficiency (EC)[d]	%	4	10	12
Plant solar-to-hydrogen efficiency (STH)[e]	%	not available	8	10
Plant durability[f]	hr	not available	1000	5000

***solar-to-hydrogen conversion efficiency (STH)**

$$= \frac{\text{chemical energy in hydrogen produced (lower heating value)}}{\text{energy in the sunlight over the collection area}} \approx \underbrace{1.23 \times J_{ph}}\ \%\text{for AM 1.5 solar irradiation}$$

J_{ph} is photocurrent in mA/cm^2

Objectives:
Phase I Goals and Targets

- Develop low temperature tungsten trioxide (WO_3) thin film material which forms a photoactive PEC interface in electrolyte
  Target: 1.6 mA/cm^2 minimum photocurrent under AM 1.5 light

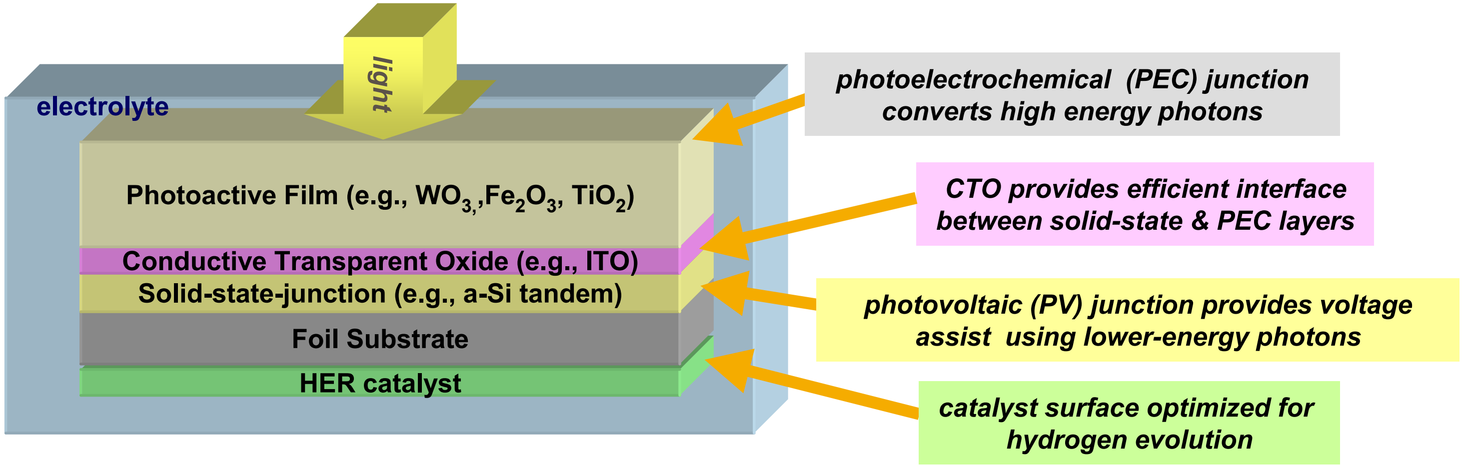
- Demonstrate functional "Hybrid Photoelectrode" device incorporating WO_3 and amorphous silicon active films
  Target: 2 - 4 % STH efficiency under AM 1.5 illumination

- Explore avenues, utilizing combinatorial discovery with bulk film research techniques, toward reduced band-gap material (e.g., modified WO_3) for higher photocurrents and enhanced STH efficiency in future devices

- Explore avenues toward manufacture scaled devices utilizing reel-to-reel vacuum deposition and other fabrication techniques

Approach:
The Hybrid Photoelectrode

➢ *a Key Enabling Technology: UH-patented structure (patent # 6887728)*



- Multijunction device integrating low-cost PEC and PV materials 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 research programs (such as PV)
- Development of appropriate process-compatible PEC & PV materials is critical to success

Approach:
Specific PEC Tasks- Phase I

Level 1: Advanced Materials Research & Development

i. Development of low-temperature sputtered WO_3 photoactive films
ii. Combinatorial discovery of photoactive WO_3 compounds *(Intematix)*
iii. Comparative evaluation of available pyrolytic photoactive oxides
iv. Theoretical studies of oxide materials for bandgap engineering

Level 2: Data Acquisition and Analysis

i. Integrated hybrid photoelectrode design, fabrication and testing
ii. Hybrid photoelectrode performance certification *(NREL)*
iii. Production of customized photovoltaic devices for HPE *(MVSystems)*

Level 3: Concept Design and Analysis

i. Process scale-up studies *(MVSystems)*
ii. Cost and profitability estimates

HNEI MVSystems Intematix NREL

Progress: Phase I Summary

- **Low temperature reactively-sputtered WO_3 films developed**
  3.2 mA/cm^2 photocurrents achieved *(meeting Task 1.1 targets)*
  – Optimization of reactive-sputter process parameters
  – Comprehensive materials characterization to enhance understanding
  – Initial work on bandgap reduction through nitrogen- and sulfur- doping

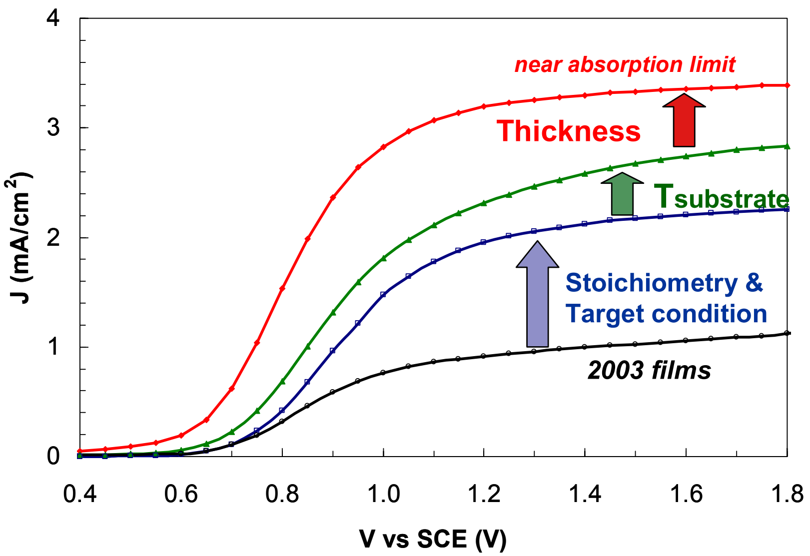
- **"Hybrid Photoelectrode" device based on sputtered WO_3 demonstrated**
  3.1% STH efficiency achieved *(meeting Tasks 2.1, 2.3 targets)*
  – Mechanically-stacked device using custom designed a-Si tandem PV cell
  – Fabrication technique for fully-integrated device in development

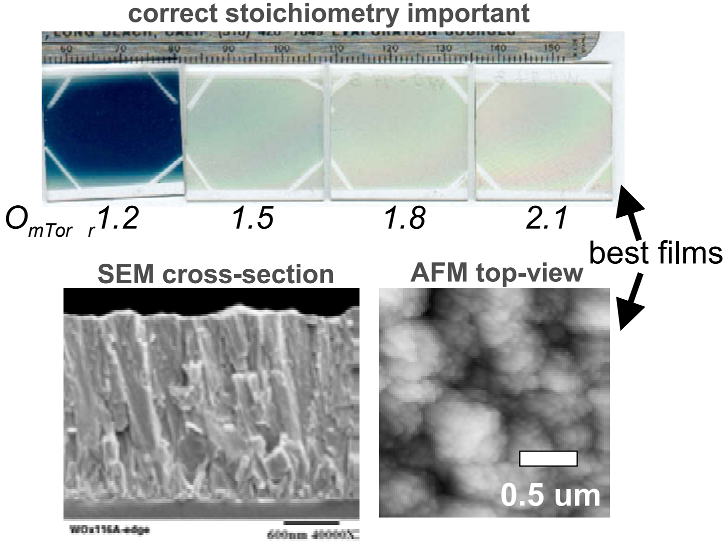
- **Rapid throughput bandgap screening technique demonstrated to facilitate discovery of new lower-bandgap PEC materials** *(meeting Task 1.2 targets)*
  – "Laser Modulated Differential Spectroscopy" technique developed at Intematix
  – LMDS successfully demonstrated on WO_3 films (undoped & sulfur-doped)

- **Scaled-up fabrication technology demonstrated** *(meeting Task 3.1 targets)*
  – Patented process using reel-to-reel cassettes in a vacuum cluster tool installed at MVSystems Inc.

Progress: WO_3 Film Optimization

Critical achievement: photocurrents optimized in low-temperature sputtered WO_3





- **Films optimized by adjustments to reactive-sputter process parameters using feedback from comprehensive film characterizations**
  - –Including substrate T (<300°C), oxygen partial pressure, deposition rate, etc.

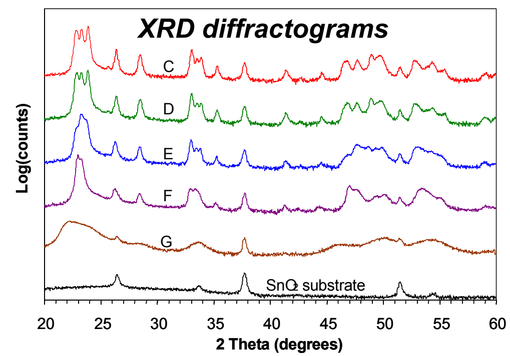
- **Photocurrents in acid under AM1.5 illumination enhanced 320%**
  - –Levels improved from ~1 mA/cm^2 to over 3.2 mA/cm^2 (near theoretical max for WO_3)
  - –Levels in our optimized samples EXCEED project target of 1.6 mA/cm^2
  - –These levels exceed reported levels in films synthesized at higher-temperature

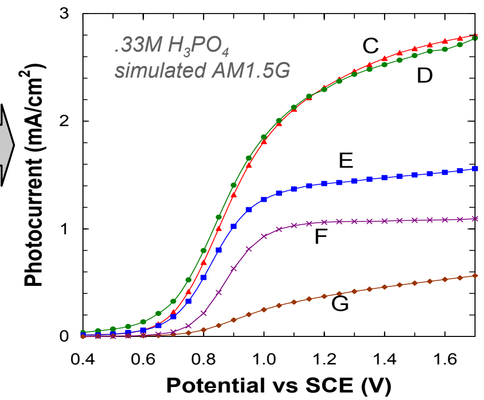
    {2.4 mA/cm^2, Santato, Augustynski et al. JPCB 105, 936 (2001)}

Progress: Key Correlations in WO_3 Films

CRYSTALLITE STRUCTURE:

– Films with larger crystallites show higher photocurrent performance





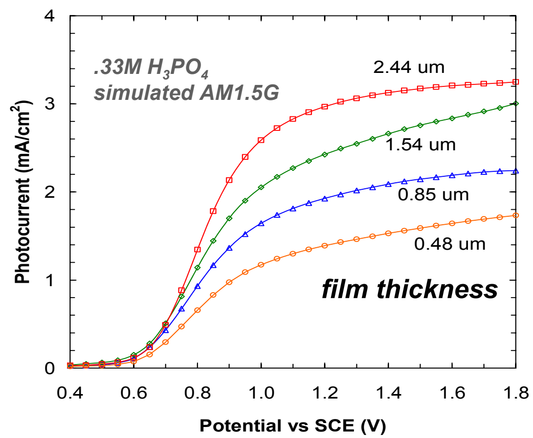
FILM THICKNESS:

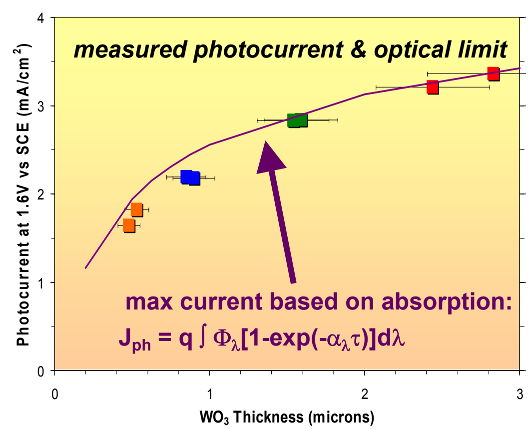
– Observed performance close to bandgap-dependent absorption limit *(quantum efficiencies close to 100%)*

– Thicker films approach the 'total absorption' limit for WO_3

– Validates the ***BULK ELECTRODE*** model of the PEC junction *(J_{ph} not limited to 'surface' effects)*

– 'Tailoring' bulk properties is possible *(bandgap grading, etc.)*





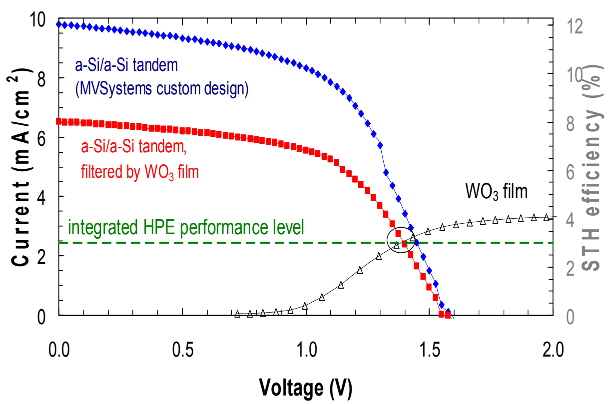
Progress: HPE Device Demonstration

2003 prototype performance: **0.7% STH efficiency (un-optimized WO_3/a-SiGe/a-SiGe: materials)**

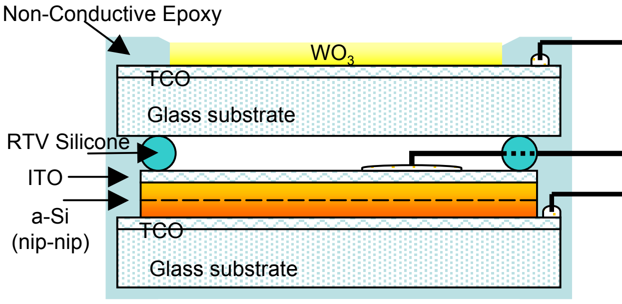
2005 prototype performance: **3.1% STH in mechanically-stacked device with optimized materials**

- **CONFIGURATION:**
  - PV and PEC layers fabricated separately, then mechanically interconnected and sandwiched together
- **RESULTS:**
  - STH conversion 3.1% consistent with predictive models, and meeting 2-4% target
- **INTEGRATED DEVICE:**
  - Monolithically integrated HPE devices still suffer from fabrication damage, but progress is being made
  - Fewer losses (higher STH) expected in successfully integrated device

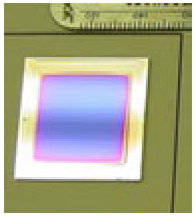
device modeling



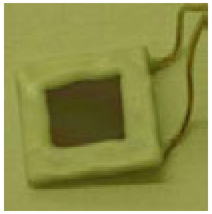
stacked HPE configuration



device fabrication

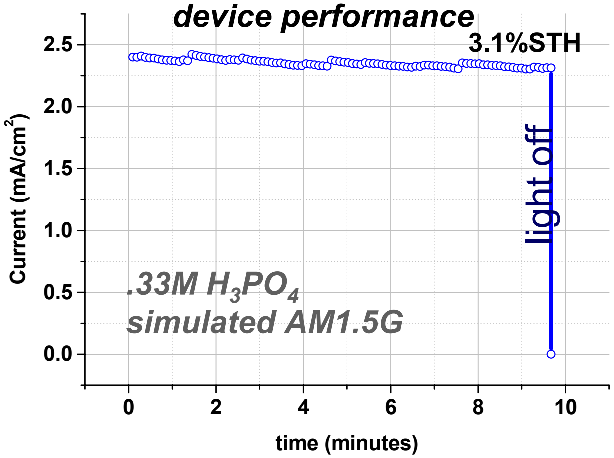


custom a-Si/a-Si tandem solar cell



fabricated photoelectrode

device performance

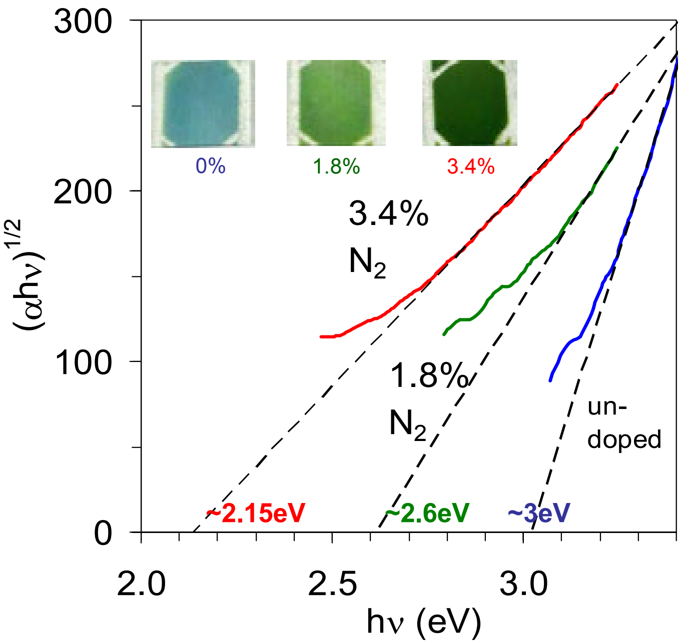


Progress: Bandgap Reduction Work at UH

Reactive Sputtering of Nitrogen-Doped WO_3 Films

Asahi et al., (on N-doped TiO_2): "Substitutional doping of N was the most effective because its p states contribute to the bandgap narrowing by mixing with the O 2p states" (Science 293, p. 269, 2001)

- **Initial Experiments: observed bandgap shift in WO_3:N on glass**
  - Paluselli et. al., Electrochem. Solid State Lett. 2005
- **Initial work on glass substrates produced highly amorphous WO_3 films, which are not PEC quality**
- **New doping experiments are needed using substrates (such as the SnO coated glass) which 'seed' more crystalline PEC-active films**
- **Broader set of material fabrications and characterizations needed**

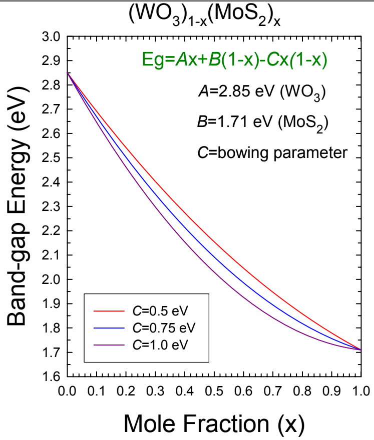


Progress: Bandgap Reduction Work at Intematix

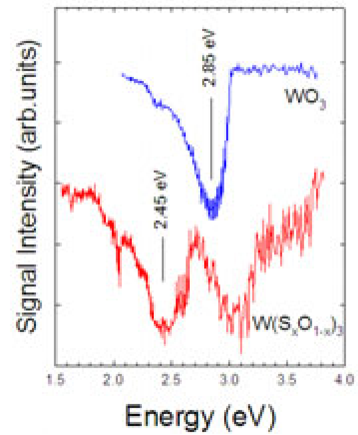
Intematix

- **EXPERIMENTAL BASIS:**
  - Alloying W with Mo, or O with S in WO_3 should result in a reduction of the compound material band-gap.
- **APPROACH:**
  - Combinatorial library fabricated using ion-beam sputtering
  - Rapid band-gap screening using Laser Modulated Differential Spectroscopy (LMDS)
- **RESULTS:**
  - LMDS validated on WO_3-based films
  - Initial W/Mo/O/S combinatorial samples synthesized and tested
  - Sulfur doping of WO_3-based films appears to reduce optical band-gap

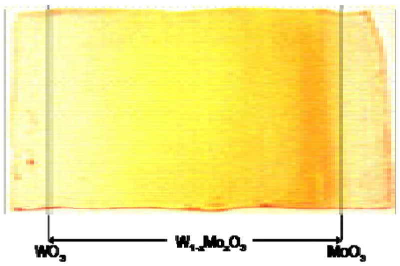
Variation of band-gap energy is calculated based on virtual crystal approximation



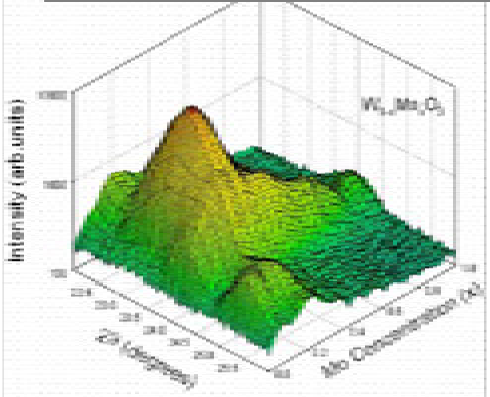
LMDS band-gap screening applied to WO_3 and S-doped WO_3



$W_{1-x}Mo_xO_3$ synthesized using combinatorial ion beam sputtering



Crystallographic analysis for $W_{1-x}Mo_xO_3$ Library

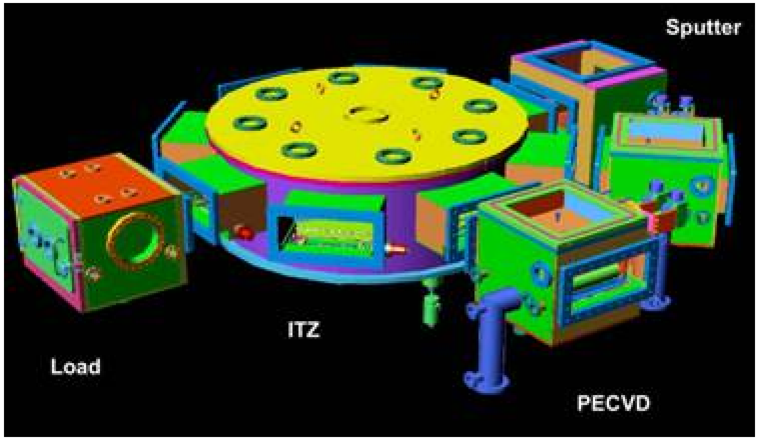


Progress: Process Scale-up Technology

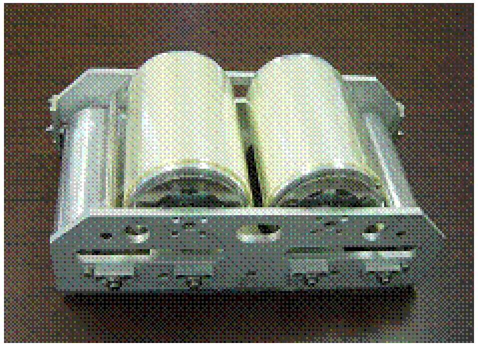
MVSystems

- **CLUSTER TOOL APPROACH:**
  - Multi-chamber thin-film deposition system designed, installed, and validated by MVSystems
  - Fully compatible with all HPE materials and device fabrication steps
  - Fabrication of 30 cm x 40 cm films and devices demonstrated at MVSystems
  - Fabrication of 30 cm x 13 meters possible using patented reel-to-reel cassette technology
  - Basis for initial cost estimates

model of a basic cluster tool system



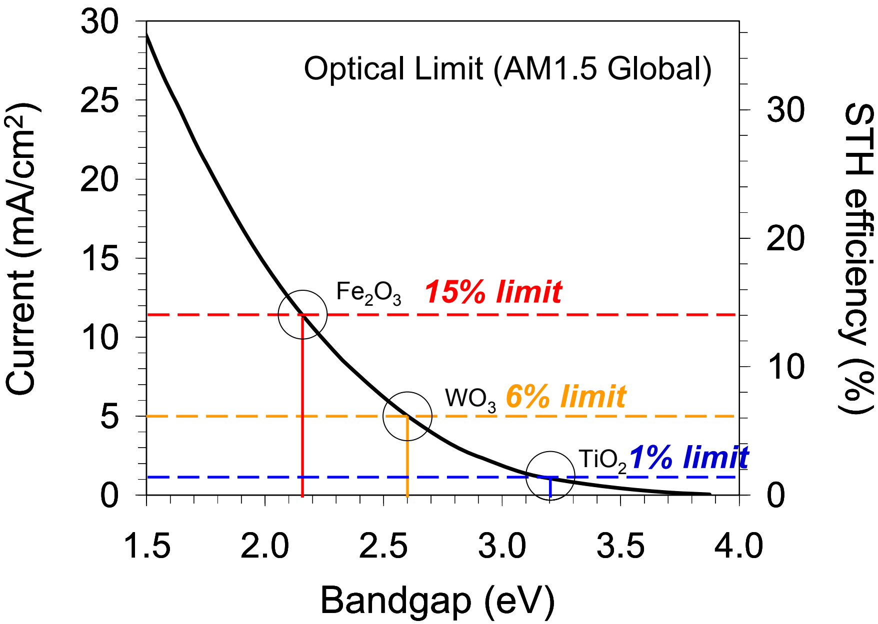
cluster tool installation



reel-to-reel cassette*

* US patent #6,258,408B1: **MVSystems**

Future Work: Need for New PEC Materials



To meet long-term DOE goals of 10-20% STH efficiency in a PEC H_2 production system, cost-effective semiconductor materials with band-gaps less than 2.4eV need to be discovered and developed.

In addition to the band-gap criteria: optical absorption, band-edge alignment, surface catalytic activity, electronic transport, and photoelectrochemical stability all need to be optimized in the new materials.

The primary goal is the efficient and reliable production of hydrogen using devices incorporating the new PEC materials .

- **PHASE I Efforts:** **Developed critical infrastructure and protocols for evaluating the electronic and photoelectrochemical characteristics of PEC semiconductor films, and for incorporating of these films into functional H_2 producing devices.**

- **Phase II Efforts:** **Current & Future work will focus extensively on the discovery and development of new PEC semiconductor materials for high-efficiency devices, drawing on infrastructure and experience from Phase I work, and using an expanded collaborative effort.**

Future Work: Expanded Collaborations

HNEI

UNLV UNIVERSITY OF NEVADA LAS VEGAS

NREL

UCSB

Intematix

MVSystems

- An expanded collaborative network of world-leaders in materials research has been assembled to expedite discovery and development of new PEC cost-effective semiconductor materials for use in high-efficiency hydrogen production devices, with particular focus in areas of:

- **Advanced Materials & Interface Characterization Techniques:**
  - –Micro-structural and Nano-scale Properties (XRD, SEM, AFM ,SKPM…)
  - –Solid-State Electronic/Optoelectronic Properties (PES/ IPES…)
  - –Solid-Solid & Solid-Liquid Interface Characteristics (XES, EXAFS…)
  - –Photoelectrochemical Behavior Analysis (i-V, IPCE, EIS…)
- **Advanced Materials Discovery & Synthesis Techniques:**
  - –Theoretical Calculations of Compound Semiconductor Band Structures
  - –Rapid-Throughput Combinatorial Synthesis and Screening
  - –Physical and Chemical Vapor Deposition of Novel Compounds
- **Hydrogen Production Device Development & Certification:**
  - –Design, Fabrication & Testing of Photoelectrodes Incorporating New Materials
  - –Standardized Device Certification Procedures

Future Work: Expanded Materials Classes

HNEI

UNLV UNIVERSITY OF NEVADA LAS VEGAS

NREL

UCSB

Intematix

MVSystems

➢ The Research Team will utilize its collective expertise and infrastructure in materials synthesis, screening and characterization to explore an expansive set of promising PEC materials classes, including:

- **Metal and Mixed-Metal Compounds**
  - Modified Tungsten Oxide Compounds
  - Modified Zinc Oxide Compounds
  - Combinatorial Synthesis & Screening of Iron-Based Compounds
  - Combinatorial Synthesis & Screening of Ternary Metal Oxide/Sulfide Films
- **Silicon Compound Based Films**
  - Silicon Carbide Alloy Films with p- and n- type Doping
  - Silicon Nitride Compound Films
- **Carbon Compounds Based Films**
  - Diamond Like Carbon Films
- **Chalcopyrite Alloy Films**
  - Copper-Indium-Gallium-Selenium-Sulfur Alloys

SUMMARY

- **All Major Technical Targets Met in Phase I Materials & Device Tasks:**
  - Photocurrent target (>1.6mA/cm^2) met in metal-oxide films:
    World-record levels of 3.2 mA/cm^2 demonstrated in WO_3 films fabricated using low-temperature device-compatible sputtering process
  - Conversion efficiency target (2-4% STH) met in "Hybrid Photoelectrode" devices:
    STH efficiency of 3.1% demonstrated in a-Si/a-Si/WO_3 based structure

- **Critical Experience and Infrastructure Developed in Phase I Work:**
  - Versatile synthesis tools established for fabricating PEC materials & devices
  - Comprehensive characterization protocols established for PEC materials & devices
  - Rapid-throughput synthesis & screening techniques developed to facilitate materials discovery
  - Manufacture scale process demonstrated for HPE device fabrication

- **New PEC Materials Needed for Higher Efficiency H_2 Production Devices:**
  - Engineering of semiconductor compounds with band-gaps below 2.4 eV is needed
    (such as modified WO_3, different mixed-metal oxides or sulfides, and others)

- **Expanded Research Collaboration has been Established to Expedite the Materials Discovery and Development Process in Future Work:**
  - UH, UNLV, NREL, UCSB, Intematix & MVSystems to form core PEC research team
  - Increased emphasis on materials/interface theory, characterization and discovery
  - Expanded range of promising PEC materials classes to be investigated

Acknowledgements

✷ U.S. Department of Energy / UNLVRF

- **University of Hawaii**
  - Dr. Richard Rocheleau
  - Dr. Bjorn Marsen
  - Dr. Brian Cole
  - Dr. Daniela Paluselli
  - Misti Lum
  - Fred Matsunaga
  - Susanne Dorn
  - Zey Tong
- **UNLV / UNLVRF**
  - Dr. Clemens Heske
  - Dr. Bob Perret
  - Dr. Lothar Weinhardt
  - Monika Blum
  - Linda Smith
  - Pam Levins
- **US DOE**
  - Roxanne Garland
  - Mark Paster
- **MVSystems, Inc.**
  - Dr. Arun Madan
  - Dr. Jian Hu
  - Dr. Alex Stavrides
  - Dr. Augusto Kunrath
  - Richard Treglio
- **Intematix Corporation**
  - Dr. Xiaodong Xiang
  - Dr. Qizhen Xue
  - Dr. Wei Shan
- **NREL**
  - Dr. Mowafak Al-Jassim
  - Dr. John Turner
  - Dr. Yanfa Yan
  - Dr. Chunsheng Jiang
  - Dr. Helio Moutinho
  - Bobby To
  - Maggie Mann
- **UCSB**
  - Dr. Eric McFarland
  - Dr. Thomas Jaramillo

MAHALO NUI LOA

Publications and Presentations

Journal Publications & Patents

- E. Miller, B. Marsen, B. Cole , M. Lum, "Low-Temperature Reactively-Sputtered Tungsten Oxide Films for Solar-Powered Water Splitting Applications", *Electrochemical and Solid-State Letters* 2006, 9, in press
- B. Marsen, E. Miller, D. Paluselli, R. Rocheleau, "Progress in Sputtered Tungsten Trioxide for Photoelectrode Applications", *International Journal of Hydrogen Energy,* 2006 in press.
- E. Miller, B. Marsen, D. Paluselli, R. Rocheleau, "Optimization of Hybrid Photoelectrodes for Solar Water Splitting", *Electrochemical and Solid-State Letters,* 2005, 8, A247-249.
- E. Miller, D. Paluselli, B. Marsen, R. Rocheleau, "Development of Reactively Sputtered Metal Oxide Films for Hydrogen-Producing Hybrid Multijunction Photoelectrodes", *Solar Energy Materials and Solar Cells,* 2005, 88, 131-144.
- ***PATENT:*** E. Miller, R. Rocheleau, "Hybrid Solid State/Electrochemical Photoelectrode for Hydrogen Production", Patent number: 6887728 issued 05/03/05

Conference Participation

2005 IPHE Renewable Hydrogen Workshop, Seville Spain

- E. Miller: "Photoelectrochemical Hydrogen Production" Symposium Co-chair

2005 XIV-IMRC Materials Conference, Cancun Mexico

- B. Marsen: Oral Presentation- "Progress in Sputtered Tungsten Trioxide for Photoelectrode Applications"

Response to Reviewer Comments

Reviewer Comments from May 2005 (covering five months of Phase I work)

Strengths
- Ability to assemble a photocatalyst assembly and effort to extend the photo response into the visible via bandgap engineering.
- A good collaborative research partnership.
- Methodical work with a systematic approach to development of the WO3 large-scale films.
- Good combination of skill sets in thin film fabrication, evaluation of devices as photocells and photoelectrodes, and characterization.

Weaknesses
- A better understanding of the energetic considerations for hydrogen and oxygen production (band energies and water redox potentials) is needed while exploring new catalytic systems.
- The value of solar-to-hydrogen efficiency is based on current measurements. Actual hydrogen evolution data is necessary to justify the claims. (Define acronyms next time -- the term STH is not well defined in the presentation).
- Progress to date is not particularly remarkable. More discussion of this status would be interesting.

Specific recommendations and additions or deletions to the work scope
- A colloidal approach of synthesizing WO3 particles and deposition as thin films can provide a low temperature film casting method. Similar method has been employed in casting TiO2 films for solar cell applications.
- Spectroscopic investigation to identify charge recombination/separation process at different stages of modification can provide insight into the loss of photogenerated charge carriers.
- None suitable at this point in the project.

Response to Reviewer Comments

Comments on the whole were reasonable, technically-sound and greatly helpful. In the past, the state of the art in PEC hydrogen production has been overstated; Phase I of this effort has taken a step back to build the infrastructure and expertise needed for a more legitimate R&D effort incorporating better characterization and certification standards. As a result of this initial leg-work, continued phases embracing a larger collaborative effort are expected to result in a more comprehensive understanding of fundamental underlying principles, and more productive pathways toward discovery and development of new catalytic materials and systems needed for viable PEC hydrogen production.

Critical Assumptions and Issues

- **Critical Issue 1**: Discovery & Development of New PEC Materials:

  A collaborative team of world leaders in materials modeling, synthesis, characterization, an discovery has been assembled by this program to address this paramount issue

- **Critical Issue 2**: Integration of New PEC Materials in Efficient H_2O Splitting Devices:

  Experts in device design, fabrication, testing and certification have been included in the team

- **Critical Issue 3**: Incorporation of Devices into H_2 Production Plants

  Experts in systems design and integration will be brought into the team as needed