

# Photoelectrochemical Hydrogen Production: SHGR Program Subtask

*(please attend SHGR presentation #PD28 5/25/05 at 11:05AM )*

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**#PD20**

*This presentation does not contain any proprietary or confidential information*



# Overview

## Timeline

- **Project start date:** 1 Oct. 2004
- **Project end date:** 31 Dec. 2005
- **Percent complete:** 50%

## Budget

- **Total project funding:** \$508.6k
  - *DOE share: \$400k*
  - *Contractor share: \$108.6k*
- **Funding received in FY04:** \$0
- **Funding for FY05:** \$508.6k

## Barriers

- **Barriers addressed: PEC H<sub>2</sub> production**
  - *AP: Materials Efficiency*
  - *AQ: Materials Durability*
  - *AR: Bulk Materials Synthesis*
  - *AS: Device Configuration Designs*

## Partners

- **SHGR team partners:**  
*UNLV, CU-Boulder, SNL, NREL, GA, GE, APS*
- **UH Subcontractors:**  
*MVSystems Inc., Intematix Corp.*



# Objective

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*

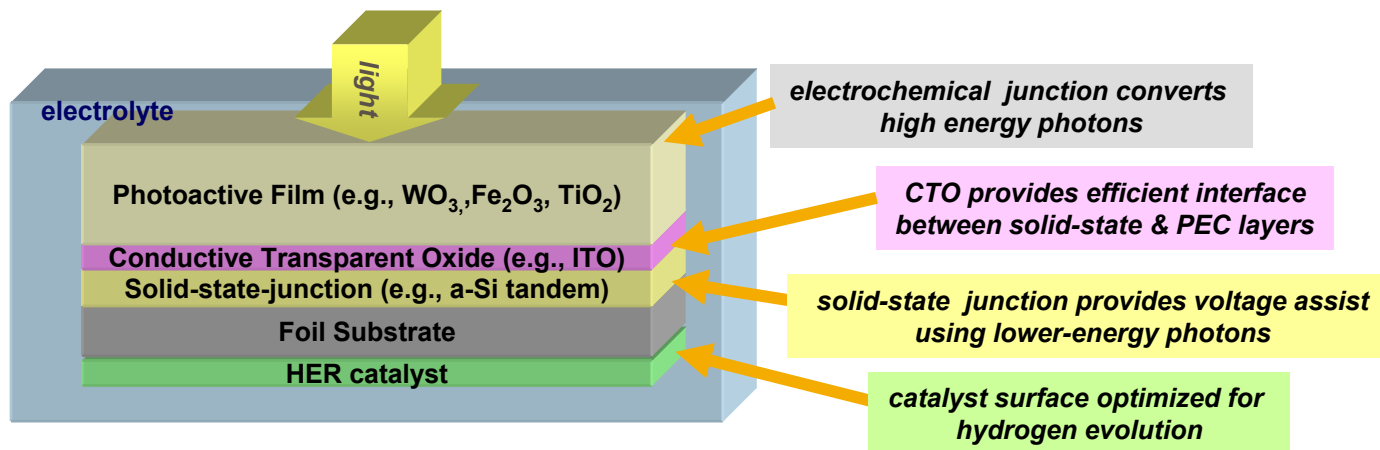
## *specific goals*

- Develop low temperature tungsten trioxide ( $\text{WO}_3$ ) thin film material with photocurrents exceeding  $1.6 \text{ mA/cm}^2$  under AM 1.5 light
- Demonstrate functional “Hybrid Photoelectrode” device based on  $\text{WO}_3$  and amorphous silicon active films with STH efficiency exceeding 2% under AM 1.5 illumination
- Explore avenues toward reduced bandgap  $\text{WO}_3$  for higher photocurrents and enhanced STH conversion potential, utilizing combinatorial discovery with bulk film research techniques
- 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



- 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)
- Initial prototype devices using tungsten trioxide films demonstrated 0.7% STH efficiency
- Development of appropriate process-compatible top layer oxide is critical to enhanced STH
- Development of appropriately matched PV layer is also essential



# Approach: Specific SHGR-PEC Tasks

## Level 1: Advanced Materials Research & Development

- i. Development of low-temperature sputtered  $\text{WO}_3$  photoactive films
- ii. Combinatorial discovery of photoactive  $\text{WO}_3$  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



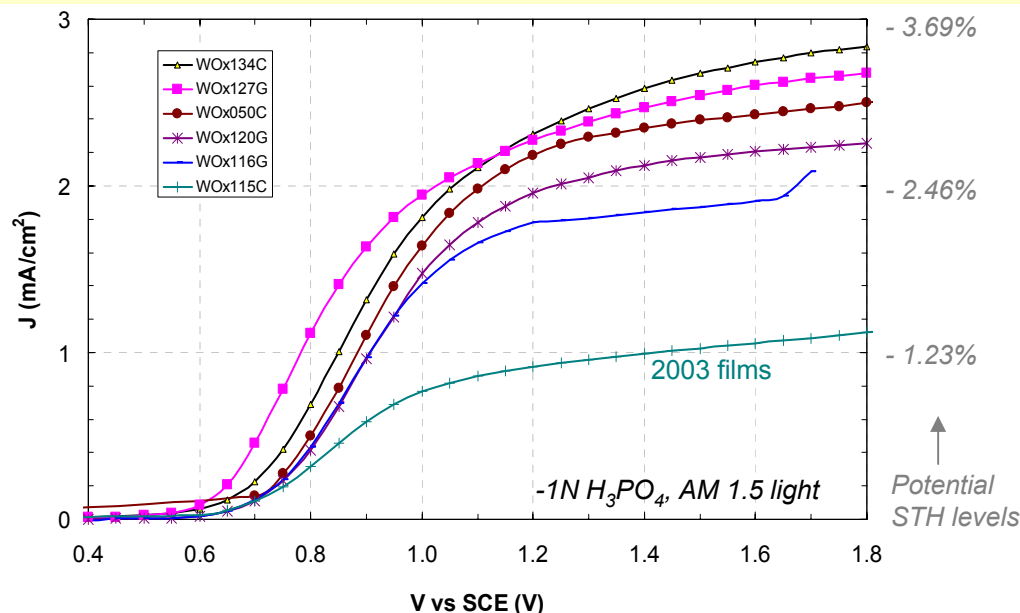
# Progress Summary

- **Low temperature reactively sputtered films with photocurrents exceeding  $2.5\text{mA}/\text{cm}^2$  demonstrated (*Task 1.1*)**
  - Optimization of reactive-sputter process parameters used
  - Process stability for high-performance needs improvement
  - Materials characterization in progress to enhance understanding
  - Initial work performed on bandgap reduction through nitrogen doping
  
- **“Hybrid Photoelectrode” design based on high-performance  $\text{WO}_3$  completed (*Tasks 2.1, 2.3*)**
  - Matched PV layer using a-Si tandem designed, fabricated and tested
  - Plans underway for HPE device fabrication and testing
  - 2.2% STH expected
  
- **Rapid throughput bandgap screening technique developed (*Task 1.2*)**
  - LMDS technique chosen over SEMP technique
  - To be applied to CD of reduced bandgap materials for enhanced STH
  - Research focus on doped oxides (initially, reduced bandgap  $\text{WO}_3$ )
  
- **Fabrication technology selected for initial scaled-up cost analysis (*Task 3.1*)**
  - Reel-to-reel cassette in vacuum cluster tool (MVSsystem patented)



# Progress: WO<sub>3</sub> Film Development

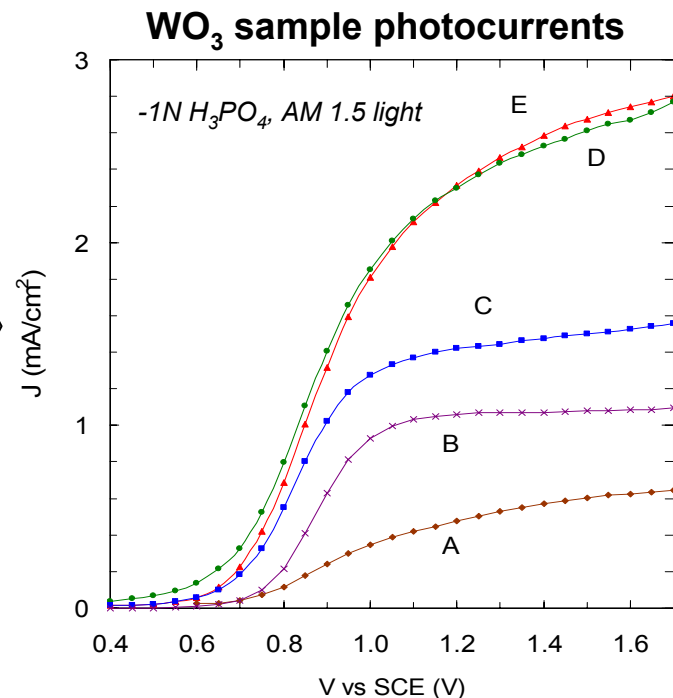
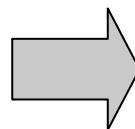
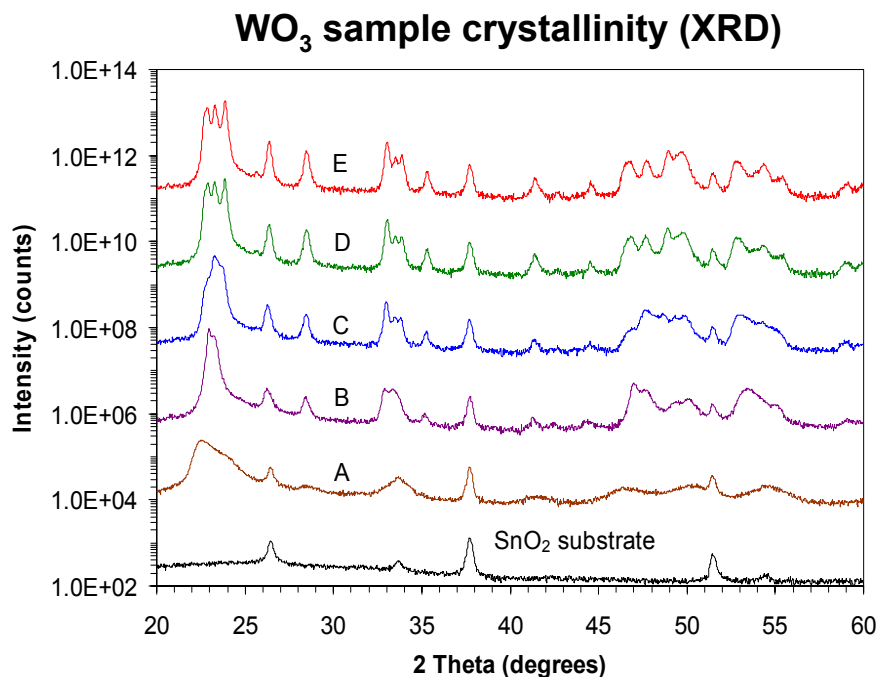
**Critical achievement: photocurrents improved in low-temperature sputtered WO<sub>3</sub>**



- Films optimized by adjustments to reactive-sputter process parameters
  - Including substrate T (<250°C), oxygen partial pressure, deposition rate, etc.
- Photocurrents in acid under AM1.5 illumination enhanced 250%
  - Levels improved from ~1 mA/cm<sup>2</sup> to over 2.5 mA/cm<sup>2</sup> (near theoretical max for WO<sub>3</sub>)
  - Levels in current samples EXCEED project target of 1.6 mA/cm<sup>2</sup>
  - Levels in current samples EXCEED all reported levels in low-temperature films
- Process repeatability issues remain
  - PEC performance sensitive to small process parameter perturbations



# Progress: WO<sub>3</sub> Film Characterizations



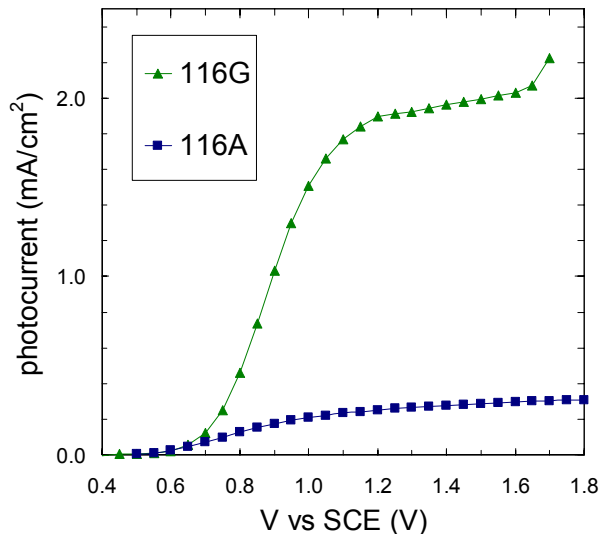
- **Correlations established between film crystallite structure and photo-activity:**
  - Higher crystallinity, indicated in better-resolved XRD peaks, results in higher photocurrent performance in many WO<sub>3</sub> sample films.....



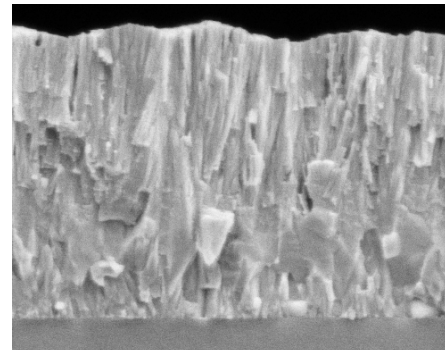


# Progress: $\text{WO}_3$ Film Characterizations

high vs. low photocurrents in two samples from same deposition



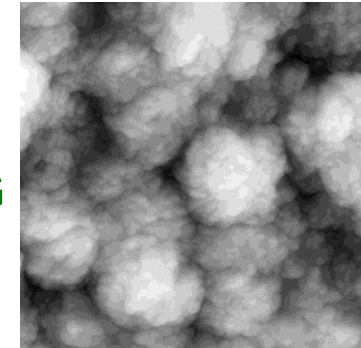
SEM cross-section



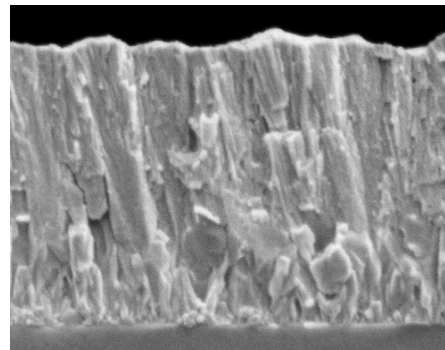
WO<sub>x</sub>116G-edge

600nm 40000X

AFM top-view

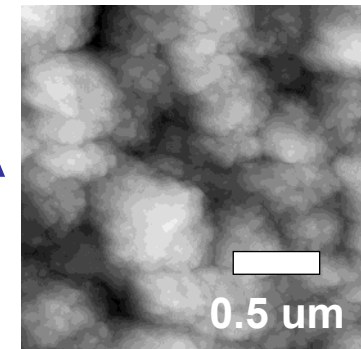


116G



WO<sub>x</sub>116A-edge

600nm 40000X



116A

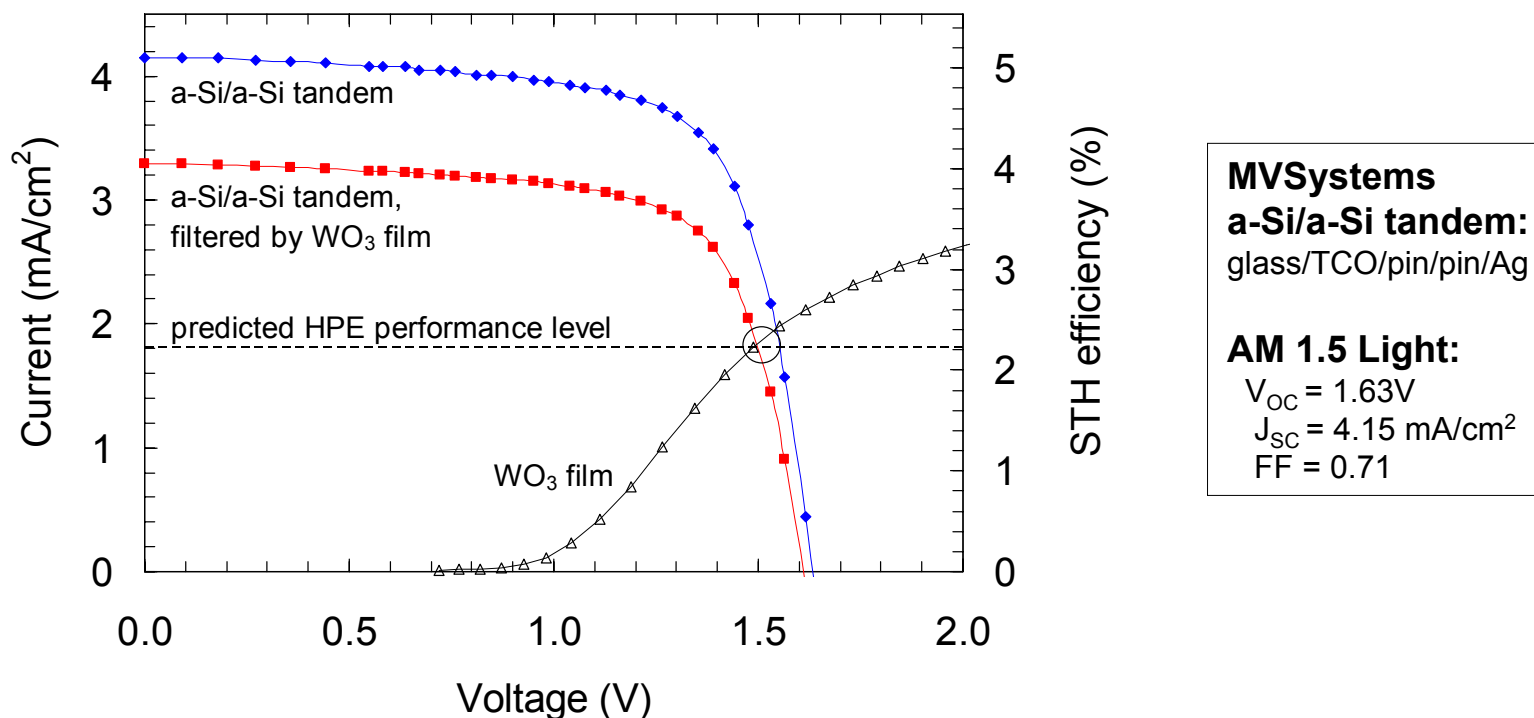
0.5 μm

➤ **Other factors at work in determining photocurrent levels:**

- Films with similar grain structure & morphology can exhibit very different photo-activity
- Quality of back contact (to tin oxide conductive layer) could play an important role
- More extensive characterizations are planned to resolve the issue



# Progress: HPE Design & Fabrication

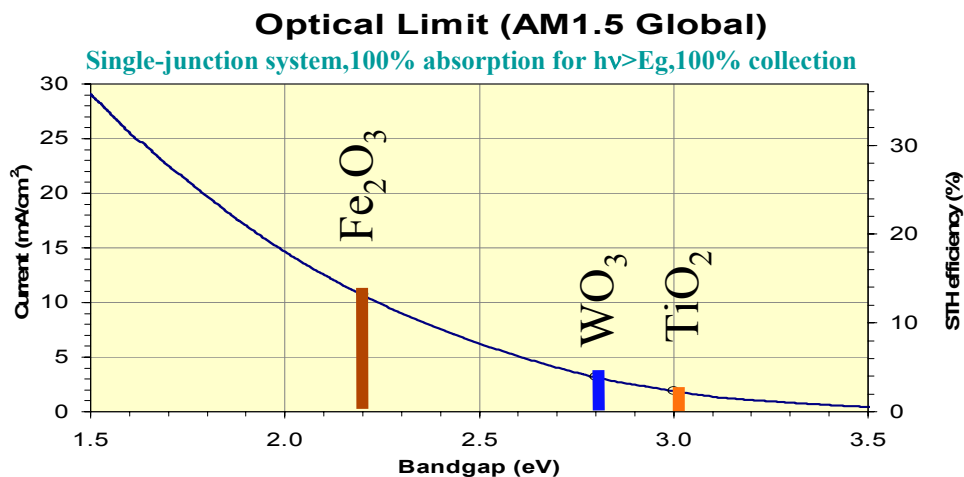


- **Materials and devices developed for new HPE prototype:**
  - a-Si tandem has sufficient current: unfiltered 4.15 mA/cm<sup>2</sup> / filtered 3.3 mA/cm<sup>2</sup>
  - Expected operating point of HPE: 1.8 mA/cm<sup>2</sup> (2.2% STH) exceeds 2% target
  - Projected fabrication/testing timetable: SS/nip/nip by 6/05, HPE by 7/05

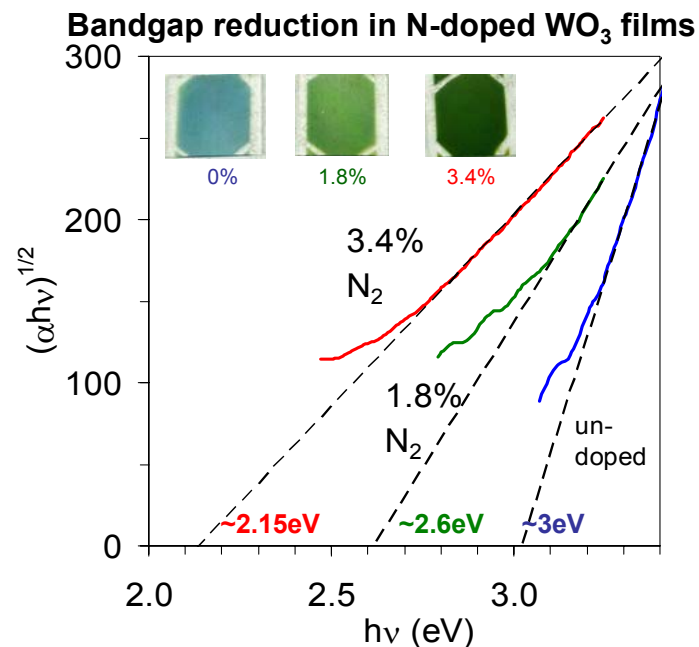


# Progress: WO<sub>3</sub> Bandgap Reduction

*Bandgap and band-edge manipulation critical to high-efficiency PEC research*



Performance limits for undoped WO<sub>3</sub>: 3.5 mA/cm<sup>2</sup>, 4% STH



- Reactive sputtering readily allows nitrogen incorporation
- Bandgap reduction verified in numerous nitrogen-doped films
- More extensive work needed to realize improved PEC photocurrents
- Other doping options to be explored through combinatorial methods



# Progress: Rapid Throughput Bandgap Screening

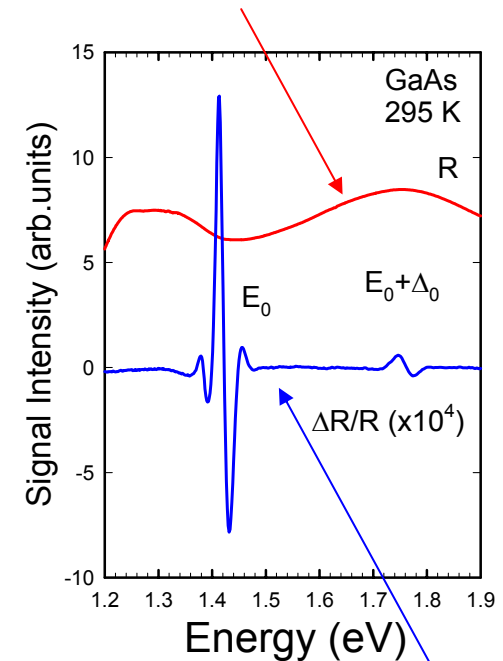
LMDS technique developed specifically for rapid-screening:



## Laser Modulation Differential Spectroscopy

- Demonstrated high sensitivity and signal-to-noise ratio
- Superior to conventional photospectroscopy and evanescent microwave probe
- Straightforward application, no need for sample preparation
- To be initially applied to doped  $\text{WO}_3$ , later applicable to other oxide materials such as  $\text{Fe}_2\text{O}_3$  and  $\text{TiO}_2$

Normal optical spectrum

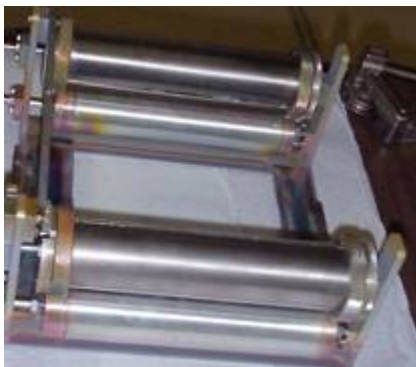


Differential spectroscopy



# Progress: Scale-up Studies

## MVSystems



- **Fabrication technology selected for initial scaled-up cost analysis :**
  - MVSystems patented reel-to-reel cassette system\* in vacuum cluster tool
  - Fully compatible with HPE device fabrication
  - 30 cm x 40 cm films and devices previously demonstrated at MVSystems
  - 30 cm x 13 meters possible using cassette

\*MVSystems patented approach for reel to reel cassette (US patent #6,258,408B1)



# Response to Reviewer Comments

**This is the first year of PEC research under SHGR funding. The work, however, grew from a DOE-funded program that was reviewed in May 04. Reviewer suggestions include:**

- Need to shift focus to new metal oxide systems.
- Integrate combinatorial approaches to development of metal oxides.

***Response:** Development of new metal oxide systems with appropriate bandgap, stability, surface activity and process compatibility with large-scale fabrication is CRITICAL to this research. Tungsten trioxide has been taken as logical starting point from which active devices can be demonstrated, and from which new lower-bandgap materials can be developed. The combinatorial approach, which needs to be applied very deliberately to screen for very specific criteria, is being implemented in this project. Initially, rapid bandgap screening will be applied to doped-metal oxide systems starting with doped  $WO_3$ , but also to  $Fe_2O_3$  and  $TiO_2$  based materials in future work. With availability of funds, additional screening techniques will need to be developed for PEC photoactivity, and other relevant properties. Moreover, the most promising materials identified through the combinatorial discovery approach will need to be transferred to a bulk-synthesis form. The film synthesis work from this project will provide invaluable experience in this effort.*

## **The May 04 review included comments regarding PEC research in general:**

“Sufficient funding in this area for long term development is lacking, however some progress was made since last year. A concern of reviewers is that this area represents a “splintered” collection of smaller projects, and that a dedicated, multi-disciplinary program that is well organized and integrated should be put in place”

***Response:** These comments are well founded and fairly accurate. The collaborative work initiated in this project is seriously intended as a first step toward a well-organized and dedicated multi-disciplinary program.*



# Future Work

- **Remaining work for FY 05**
  - Fabrication, testing and certification of HPE device using best available  $\text{WO}_3$  material with matched a-Si tandem sub-layer, with expected 2.2% STH
  - Improve repeatability of current  $\text{WO}_3$  deposition process
  - Demonstration of bandgap screening technique in doped  $\text{WO}_3$  films
  - Propose materials discovery and development plan for next step in STH efficiency (4-7%)
  - Prepare basic cost-analysis for device production based on available large-area fabrication techniques
  
- **Future work (contingent upon available funding)**
  - Implement materials discovery and development plan to reach next step in STH efficiency (4-7%)
  - Utilize lessons-learned in developing new materials & material systems
  - Continue 'team-building' efforts in PEC research community to accelerate R&D



# Hydrogen Safety

**The most significant hydrogen hazard associated with this project is:**

**The accumulation of small amounts of hydrogen over long periods of time during laboratory testing of bench-scale photoelectrode devices\***

*\*at 4% STH efficiency under 1-sun, a 3 cm<sup>2</sup> lab-scale device produces less than 0.5 milligram of H<sub>2</sub> per hour.*





# Hydrogen Safety

Our approach to deal with this hazard is as follows:

- **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<sub>2</sub> handling procedures & emergency protocols

*\*at 4% STH efficiency under 1-sun, a 3 cm<sup>2</sup> lab-scale device produces less than 0.5 milligram of H<sub>2</sub> per hour.*



# Publications and Presentations

## Journal Publications

- E. Miller, B. Marsen, D. Paluselli, R. Rocheleau, "Optimization of Hybrid Photoelectrodes for Solar Water Splitting", *Electrochemical and Solid-State Letters*, 2005, 8, A217-219.
- 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*, in press.

## Conference Presentations

### 2004 Electrochemical Society Joint International Meeting, Honolulu

- Oral Presentation: "Optimization of a Hybrid Photoelectrode for Solar Water-Splitting", B. Marsen, E. Miller, D. Paluselli, R. Rocheleau
- Poster Presentation: "Nitrogen Doping of Reactively-Sputtered Tungsten Oxide Films for Photoelectrochemical Applications", D. Paluselli, E. Miller, B. Marsen, R. Rocheleau

### 2004 International Energy Association Annex-20 Meeting, Delft, the Netherlands

- Invited Speaker: "Photoelectrochemical Hydrogen Production Research at the University of Hawaii" (via teleconference), E. Miller, B. Marsen, D. Paluselli



# Acknowledgements

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- **NREL**

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- Dr. John Turner
- Dr. Yanfa Yan
- Bobby To

- **Duquesne University**

- Dr. Shahed Khan

**MAHALO NUI LOA**

