A national laboratory of the U.S. Department of Energy
Office of Energy Efficiency & Renewable Energy

Photoelectrochemical Water Splitting

2004 DOE Hydrogen, Fuel Cells & Infrastructure Technologies Program Review

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Photoelectrochemical Conversion
Goals and Objectives

The goal of this research is to develop a stable, cost effective, photoelectrochemical based system that will split water using sunlight as the only energy input. Our objectives are:

1. Identify and characterize *new semiconductor materials* that have appropriate bandgaps and are stable in aqueous solutions.
2. Study *multijunction semiconductor systems* for higher efficiency water splitting.
3. Develop techniques for the *energetic control* of the semiconductor electrolyte interphase.
4. Develop techniques for the preparation of transparent *catalytic coatings* and their application to semiconductor surfaces.
5. Identify environmental factors (e.g., pH, ionic strength, solution composition, etc.) that affect the energetics of the semiconductor, the properties of the catalysts, and the stability of the semiconductor.

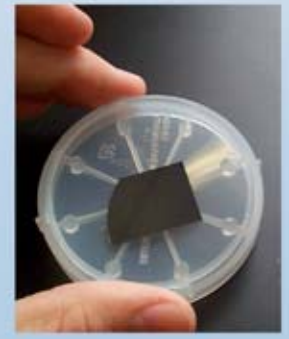
Our work this year has only been on Objective #1

Budget

Funding for FY2004 = $400k

Staff:

- Todd Deutsch, PhD Student, University of Colorado
- Jennifer Leisch, PhD Student, Colorado School of Mines



PEC Targets from Multi-Year Plan

Target Dates	2005	2010	2015
Solar-to-hydrogen efficiency (%)	7.5	9	14
Durability (hours)	1,000	10,000	20,000
Projected H_2 Cost ($/kg)	360	22	5

2010 goal: Projected Cost of PEC hydrogen within 50% of that for PV/Electrolysis.

Current NREL Status is a 12% efficiency, but only a 20-hour lifetime.

Technical Challenges *(the big three)*

Barriers for Photoelectrochemical Hydrogen Production

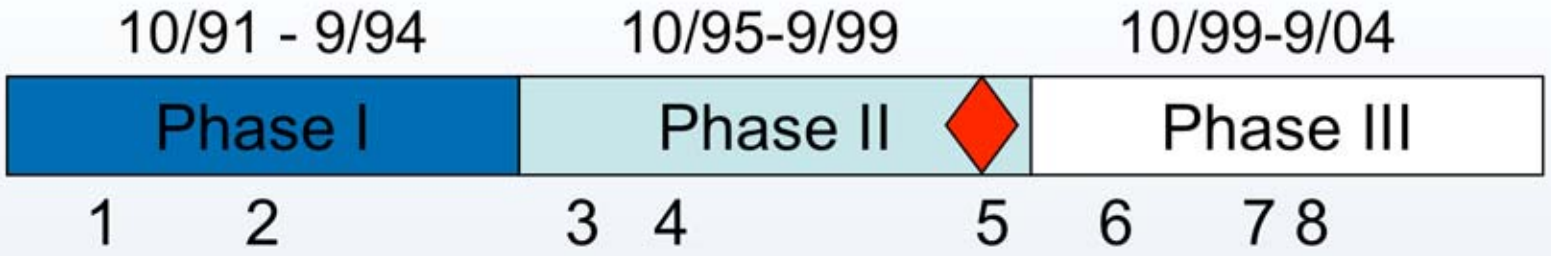
- Material Durability: Barrier M
  - The most photochemically stable semiconductors in aqueous solution are oxides, but their band gaps are either too large for efficient light absorption (~3 eV), or their semiconductor characteristics are poor.
- Efficiency (Bandgap): Barrier O
  - For reasonable solar efficiencies, the band gap must be less than about 2.2 eV, unfortunately, most useful semiconductors with bandgaps in this range are photochemically unstable in water.
- Energetics: Not Included in Multi-Year Plan
  - In contrast to metal electrodes, semiconductor electrodes in contact with liquid electrolytes have fixed energies where the charge carriers enter the solution. So even though a semiconductor electrode may generate sufficient energy to effect an electrochemical reaction, the energetic position of the band edges may prevent it from doing so. For spontaneous water splitting, the oxygen and hydrogen reactions must lie between the valence and conduction band edges, and this is almost never the case.

Summary of Approach

The primary task is to synthesize the semiconducting material or the semiconductor structure with the necessary properties. This involves material research issues (material discovery), multi-layer design and fabrication, and surface chemistry. Activities are divided into the task areas below – funded ones in *black*:

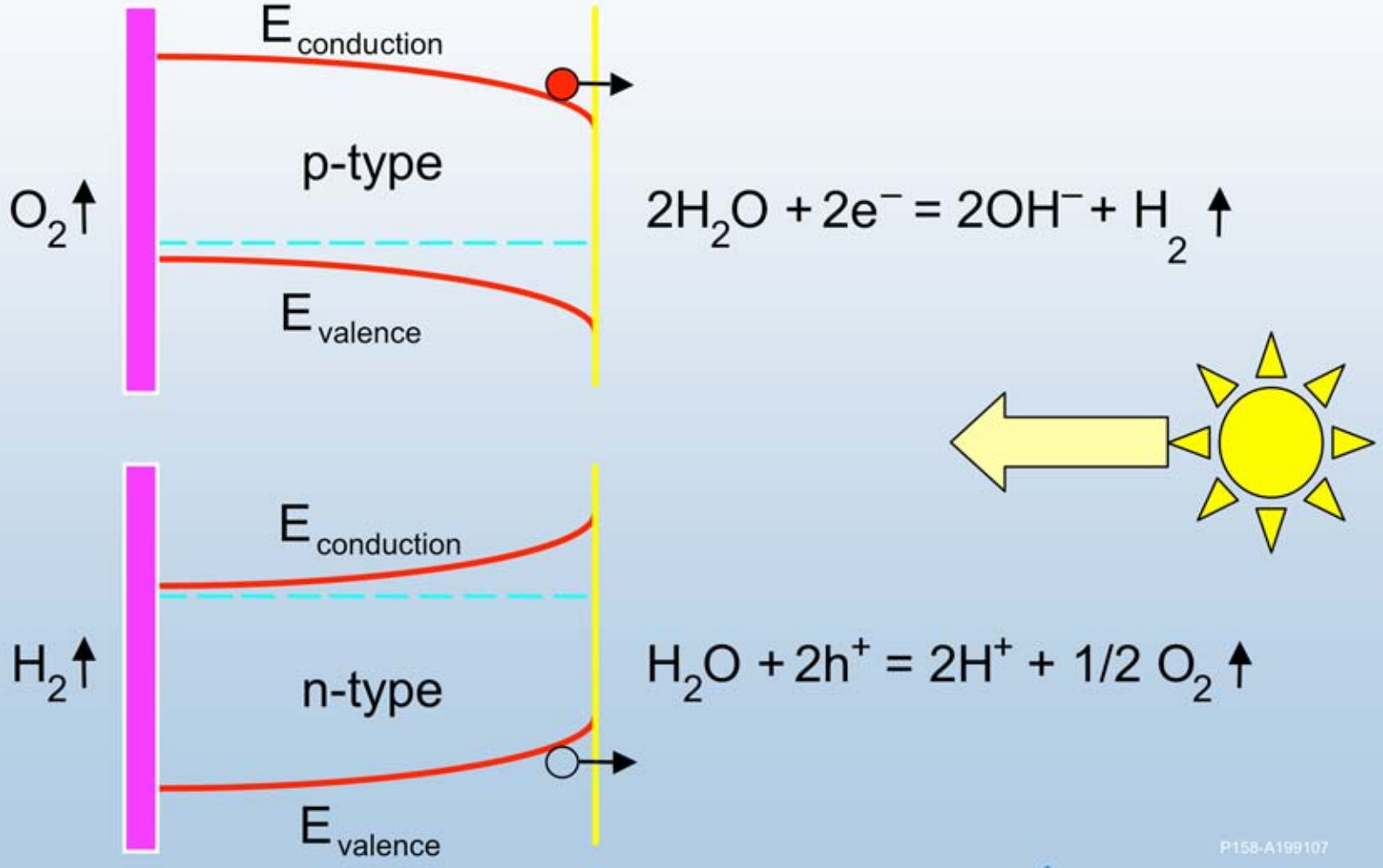
- $GaInP_2$ - NREL (fundamental materials understanding)
- *GaPN - NREL (high efficiency, stability)*
- InGaN - CSM, NREL, (high efficiency, stability)
- *$CuInGa(Se,S)_2$ - UNAM (Mexico), NREL (Low cost)*
- Multi-junction Amorphous Silicon - University of Toledo and ECD (Low cost)
- Energetics
  - Band edge control
  - Catalysis
  - Surface studies

PEC Project Timeline

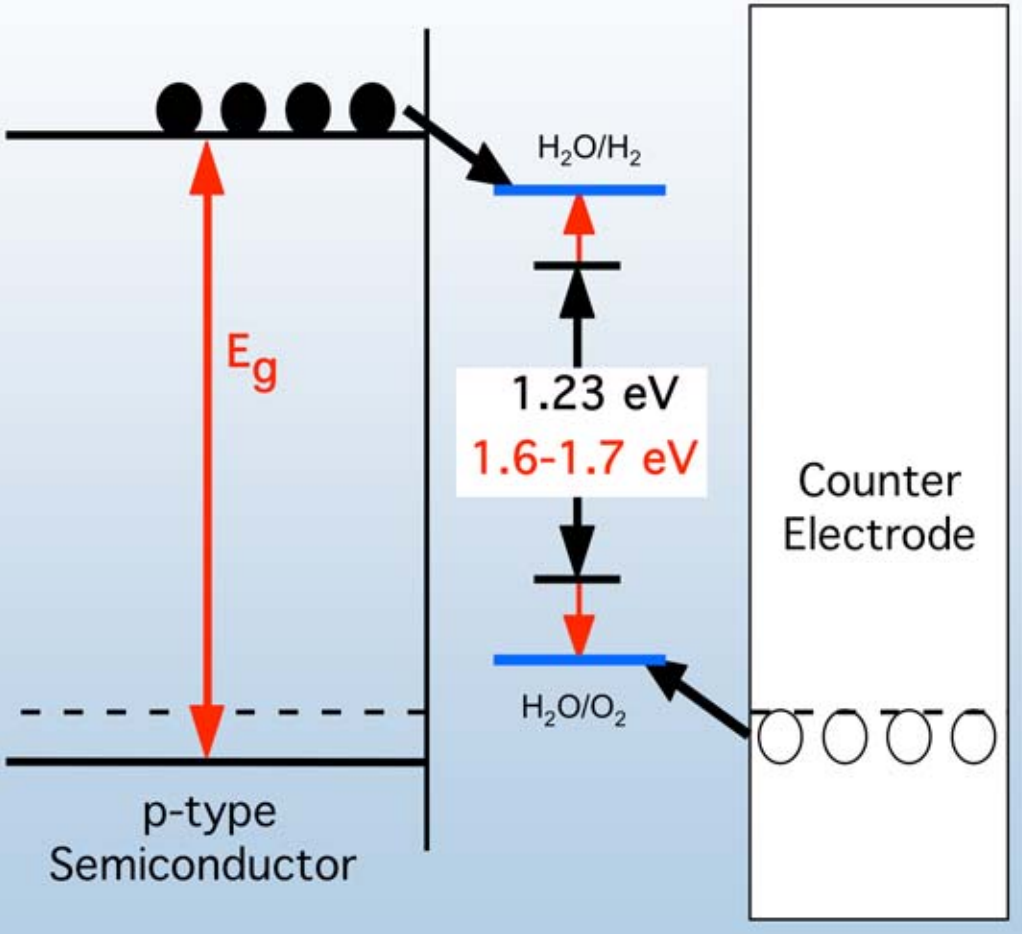


- **Phase I - Feasibility**
  - 1 Project definition and laboratory set-up
  - 2 Materials identification, experimental design and implementation.
- **Phase II – Development of High-Efficiency direct water splitting system.**
  - 3 Select materials and structure
  - 4 Structural modification and testing
  - 5 World Record result – 12.4% solar-to-hydrogen (Science)
- **Phase III – Alternative materials for longer lifetime and lower costs.**
  - 6 Studies of a-Si triple junctions
  - 7 Low cost thin-films
  - 8 Nitrides for longer lifetimes

Band Edges of p- and n-Type Semiconductors Immersed in Aqueous Electrolytes to Form Liquid Junctions



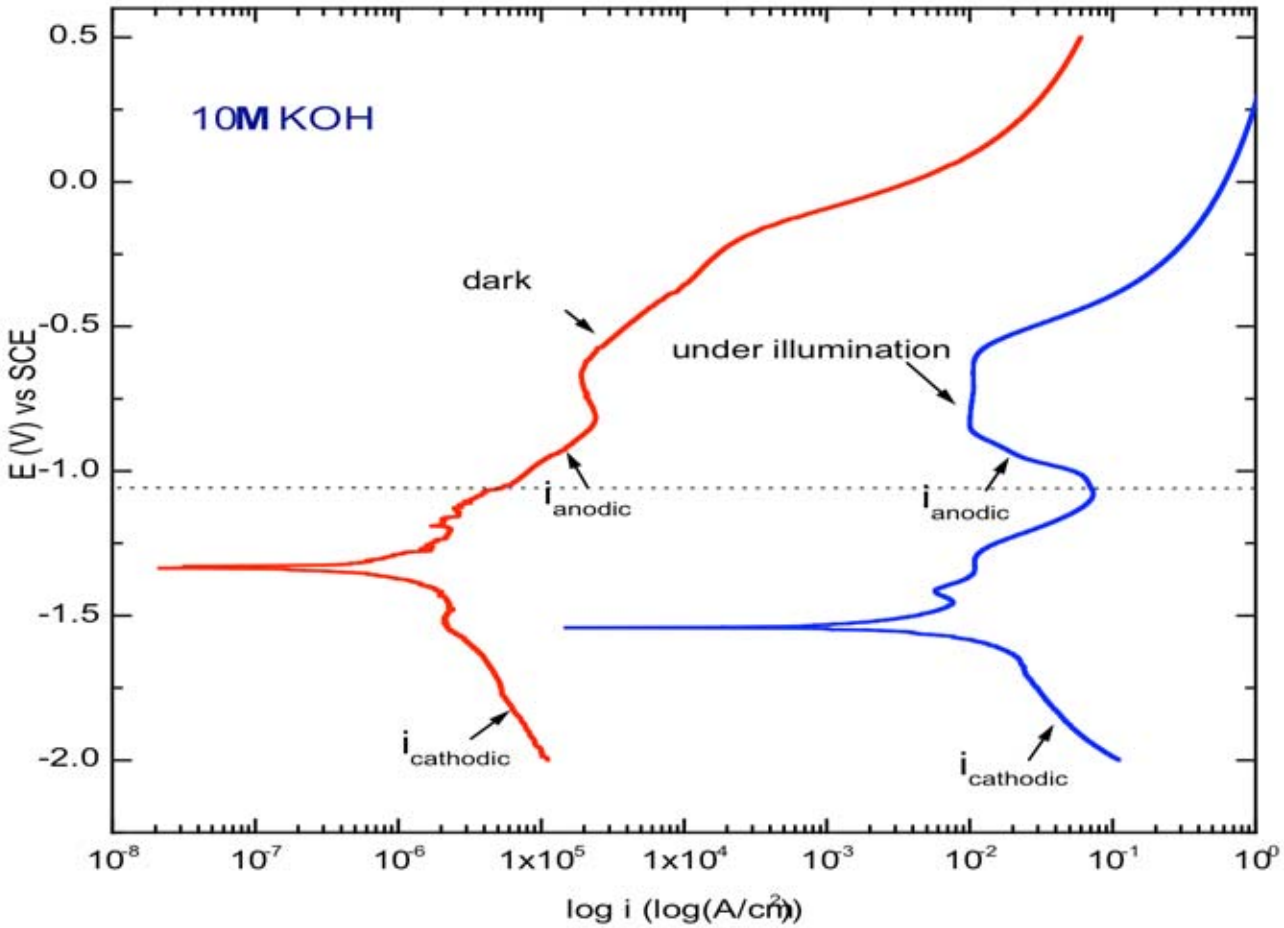
Material and Energetic Criteria



- **Band Gap** (E_g) must be at least 1.6-1.7 eV.
- **Band Edges** must straddle H_2O redox potentials
- **Rapid** charge transfer
- **Stable** in aqueous solution

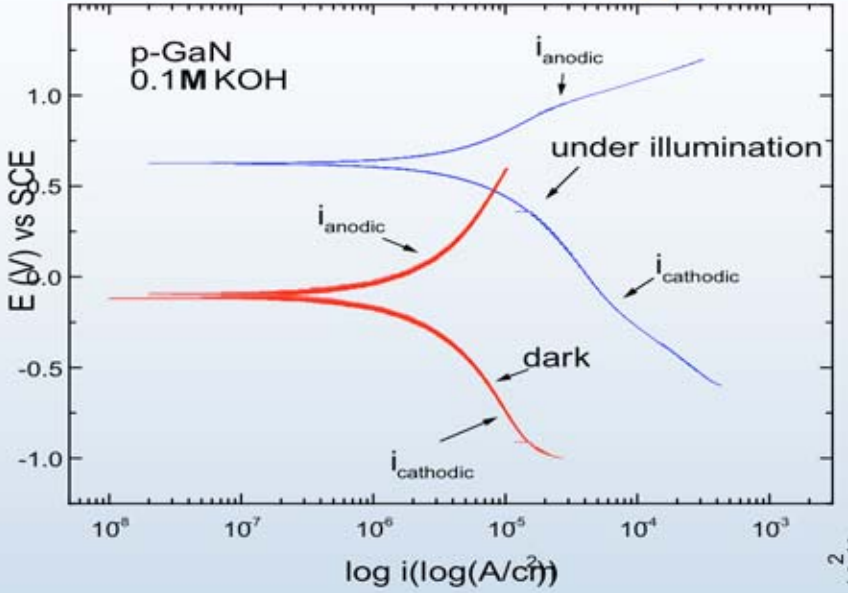
All must be satisfied simultaneously

Potentiodynamic Curves for p-GaInP$_2$ - Base



In order to meet lifetime goals we must discover materials with inherently higher stability.

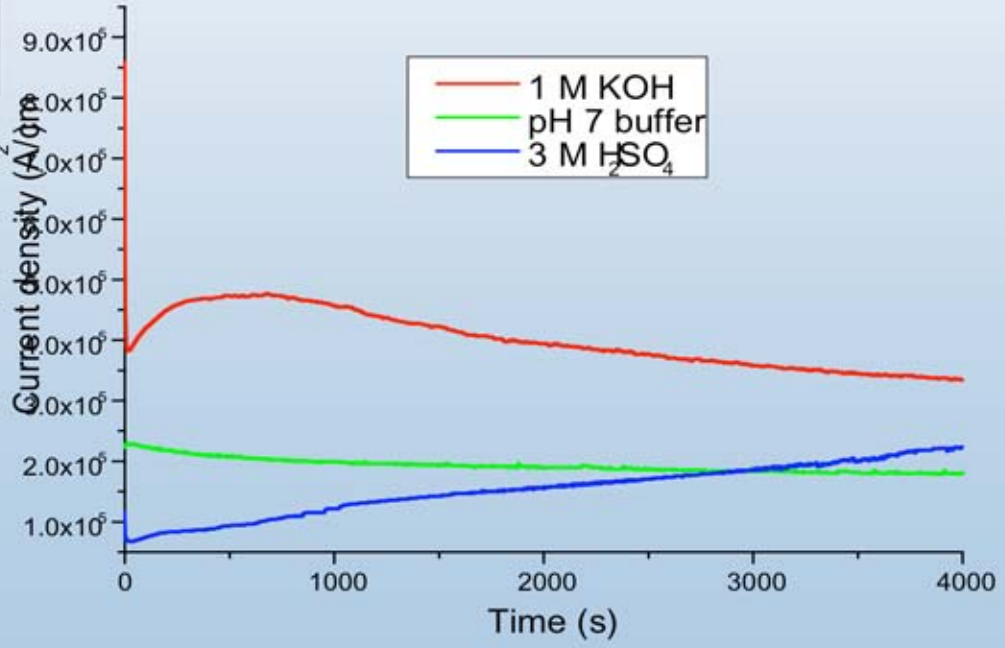
One possibility is nitride materials, an example of which is p-GaN



It shows excellent stability…

…and water splitting capability

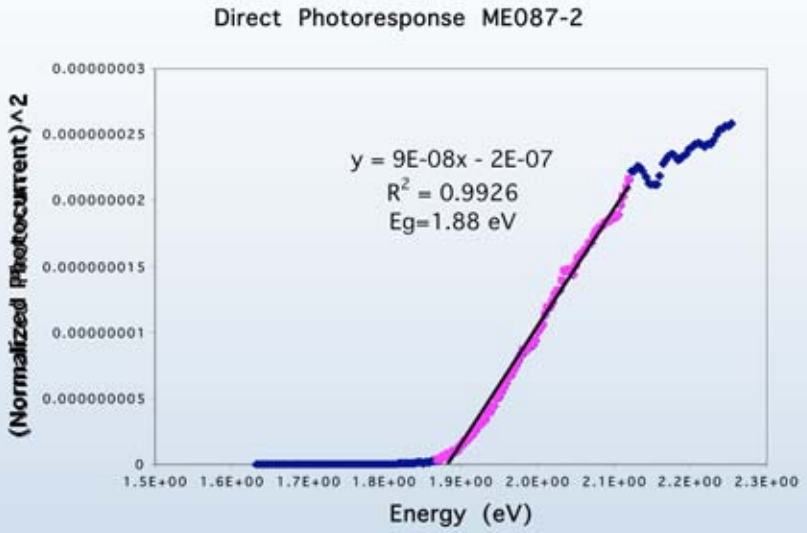
But…>3.0eV bandgap

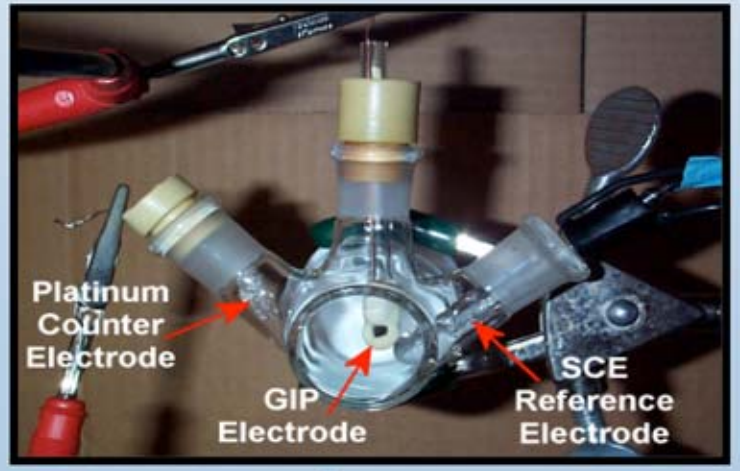


Preliminary Investigation of $GaP_xN_{(1-x)}$ for PEC Water Splitting Systems

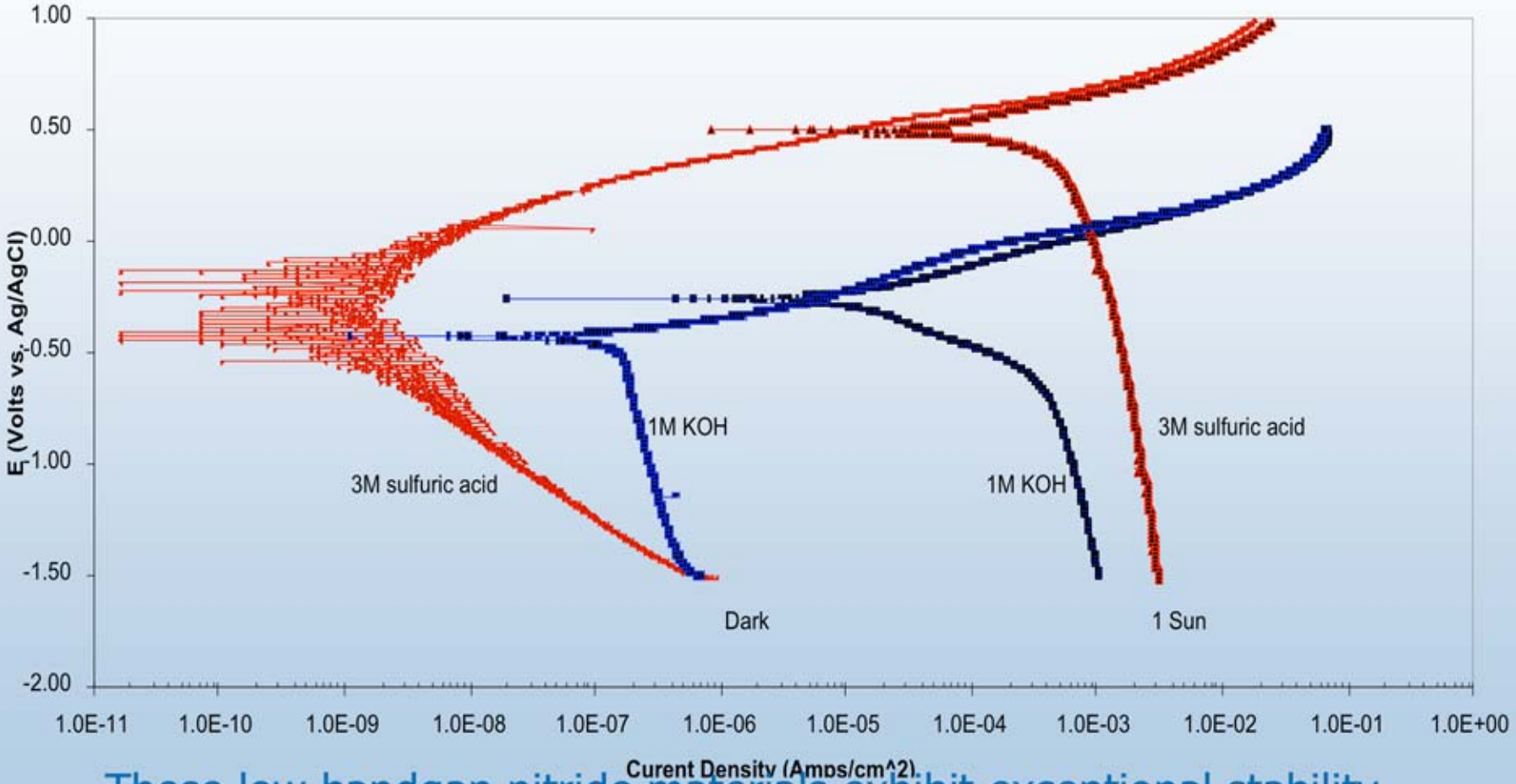
with Professor Carl Koval *University of Colorado at Boulder*

Electrode	% Nitrogen	Meas. Direct E_g
ME477-3	1.6	2.07
ME477-4	1.6	2.06
ME460-3	2.1	2.01
ME460-4	2.1	2.01
ME463-3	2.6	2
ME463-4	2.6	2
ME461-3	3.5	1.96
ME461-4	3.5	1.96





Corrosion analysis for GaPN



These low bandgap nitride materials exhibit exceptional stability.

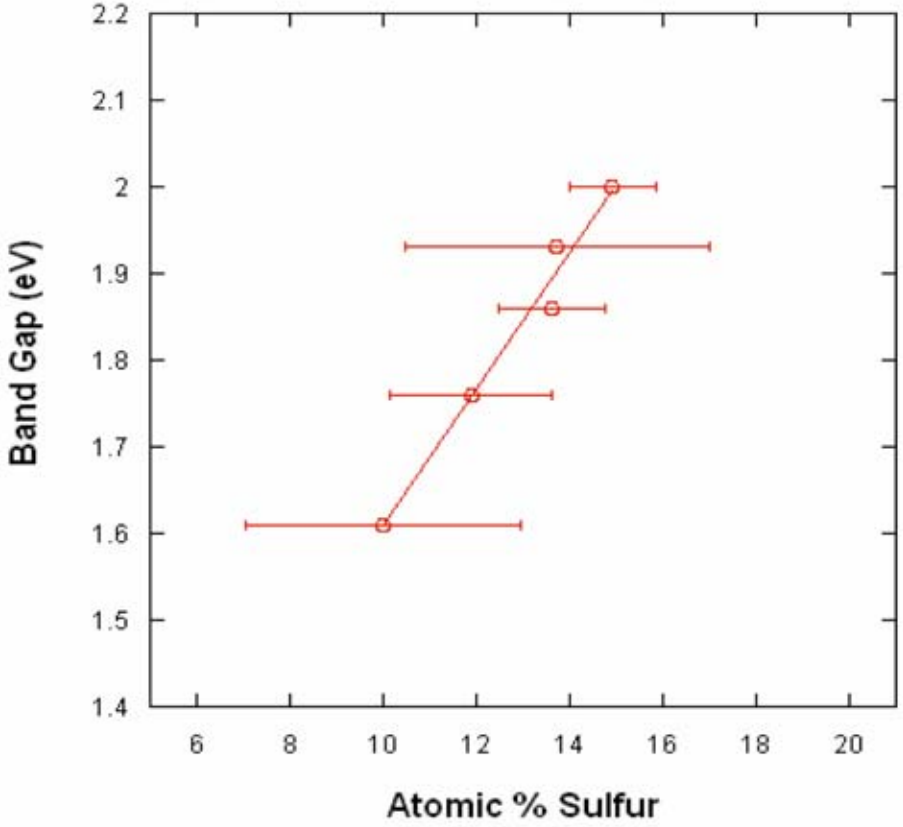
GaPN - Preliminary Results

(Preliminary two-electrode multimeter measurements in acid (in mV and microA except where noted). Pt counter electrode.)

Electrode	Dark OCP	6sun OCP	Dark SSC	6sun SSC	type
MF097-1	-28	-1.45 V	0.1	-3.5 mA	n
MF097-2	-20	-1.49 V	0.1	-5.0 mA	n
MF097-3	-7	-0.67 V	0.1	-3.0 mA	n
MF097-4	-5	-0.81 V	0.1	-1.5 mA	n
MF098-1	16	250	0.05	0.4	p
MF098-2	-201	-3	-0.3	-0.4	p
MF098-3	-230	28	-0.25	0.2	p
MF098-4	-203	3	-0.1	0.2	p

New Materials - Band Gap Requirements for Electrodeposited CIGSS

- Dependence on sulfur content noted.
- However, this is convoluted by varying concentrations of other elements (5 component system!)



Goal: Consistent synthesis of high bandgap material

Technical Challenges (Cont.)

- Catalysts:
  - Oxygen (most important -- highest energy loss).
  - Hydrogen
  - Transparency might be necessary
  - Non-precious metal (lower current density!)
- Band edge engineering
- Semiconductor hybrid designs
- Low cost system designs featuring passive controls

Project Safety

- Hydrogen generation from our samples is small (a few μl/min), so no special precautions over standard engineering controls for chemical laboratories are taken at this time.
  - Sample sizes are small (<0.5 cm^2) so hydrogen production even from the most efficient cells is low.
  - Cells are open to allow rapid diffusion of the hydrogen (no build-up).
  - Air exchanges are 6-10/hour in the lab.
  - For PEC H_2 and O_2 are produced at separated electrodes.
- For scale-up, a complete hazard identification and risk assessment will be done to identify issues relating to personnel, equipment and environmental factors.
  - Hardware and material analysis will be done to identify possible component failure modes.
  - This will be integrated into the design of the test facility and modules, and guide the write-up of the operational procedures.

Collaborations

In the US

- Colorado School of Mines
- University of Colorado
- Program Production Solicitation

Outside of the US

- Switzerland, Mexico, Armenia, Sweden, Japan

Reviewers' Comments from 2003 Poster

Comments

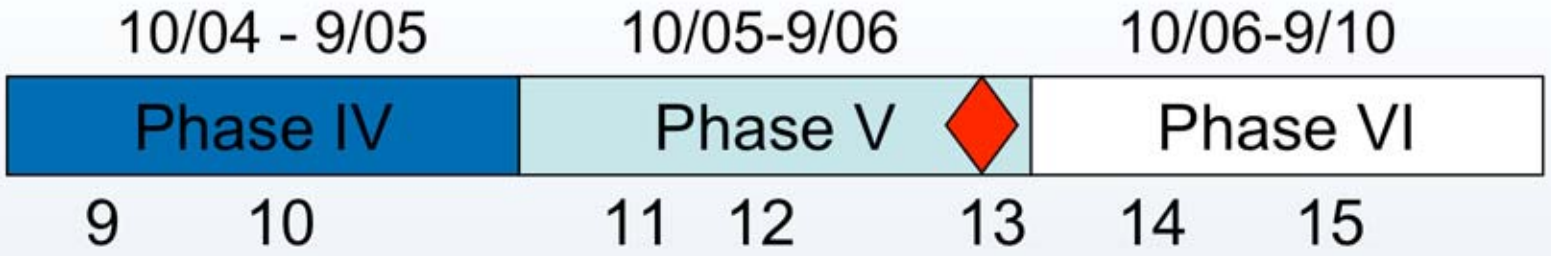
1. Focus on candidate light absorbing materials.
2. Efforts should continue to include amorphous silicon photoelectrodes as well as other newer materials.
3. Without some intermediate goals, the work will go on for 5 years without an off-ramp strategy.
4. Concentrating on the semiconductor and PEC device has left him less time for catalyst questions – developing the electrodes for the O_2 and H_2 generation.

Response

1. Focused on nitrides and thin-film CIGSSe material
2. No funding for a-Si
3. Intermediate goals concentrate on specific material studies. Materials with poor properties are discarded, e.g. the multijunction $GaInP_2$ system and GaAsPN.
4. No funding for catalysts studies.

"A great apostle of the program to a skeptical industrial world."

PEC Project Timeline - Outyears



- **Phase IV – Synthesis and characterization of Nitride materials and thin-film materials**
  - 9 GaNP and CuInSSe materials – perhaps a-Si
  - 10 GaInN materials
- **Phase V –High-Efficiency direct water splitting system based on nitrides.**
  - 11 Select materials and structure
  - 12 Structural modification and testing
  - 13 8% and 1000 hours
- **Phase VI – Module development and testing**
  - 14 Design development and safety assessment
  - 15 Build and test
  - 16 IPO and retire!

Future Plans

- Remainder of FY2004:
  - Continue evaluation of nitride material
  - Continue evaluation of thin-film CIGSSe
- For FY2005:
  - Additional materials with LBNL, CSM, …
  - Coatings: SiN, SiC, …
  - Band-edge engineering (perhaps with Office of Science.
  - Multijunction structures