Photoelectrochemical Water Systems for H_2 Production

2005 DOE Hydrogen, Fuel Cells & Infrastructure Technologies Program Review

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This presentation does not contain any proprietary or confidential information.

Overview

Timeline

- Project start date: 1991
- Project end date: tbd
- Percent complete: tbd

Budget

- Total project funding
  - DOE share: $5M (~0.75 FTE + postdoc average)
- Funding received in FY04: $400k
- Funding for FY05: $800k ($650k for PEC, $150k for Database task).

Barriers

- Barriers addressed
  - ✓ **M. Materials Durability**
  - ✓ **O. Materials Efficiency.**
  - ✓ **N. Device Configuration Designs.**

Partners

- Interactions/ collaborations
  - Colorado School of Mines
  - University of Colorado
  - Program Production Solicitation
    - MVSystems, Inc
    - Midwest Optoelectronics

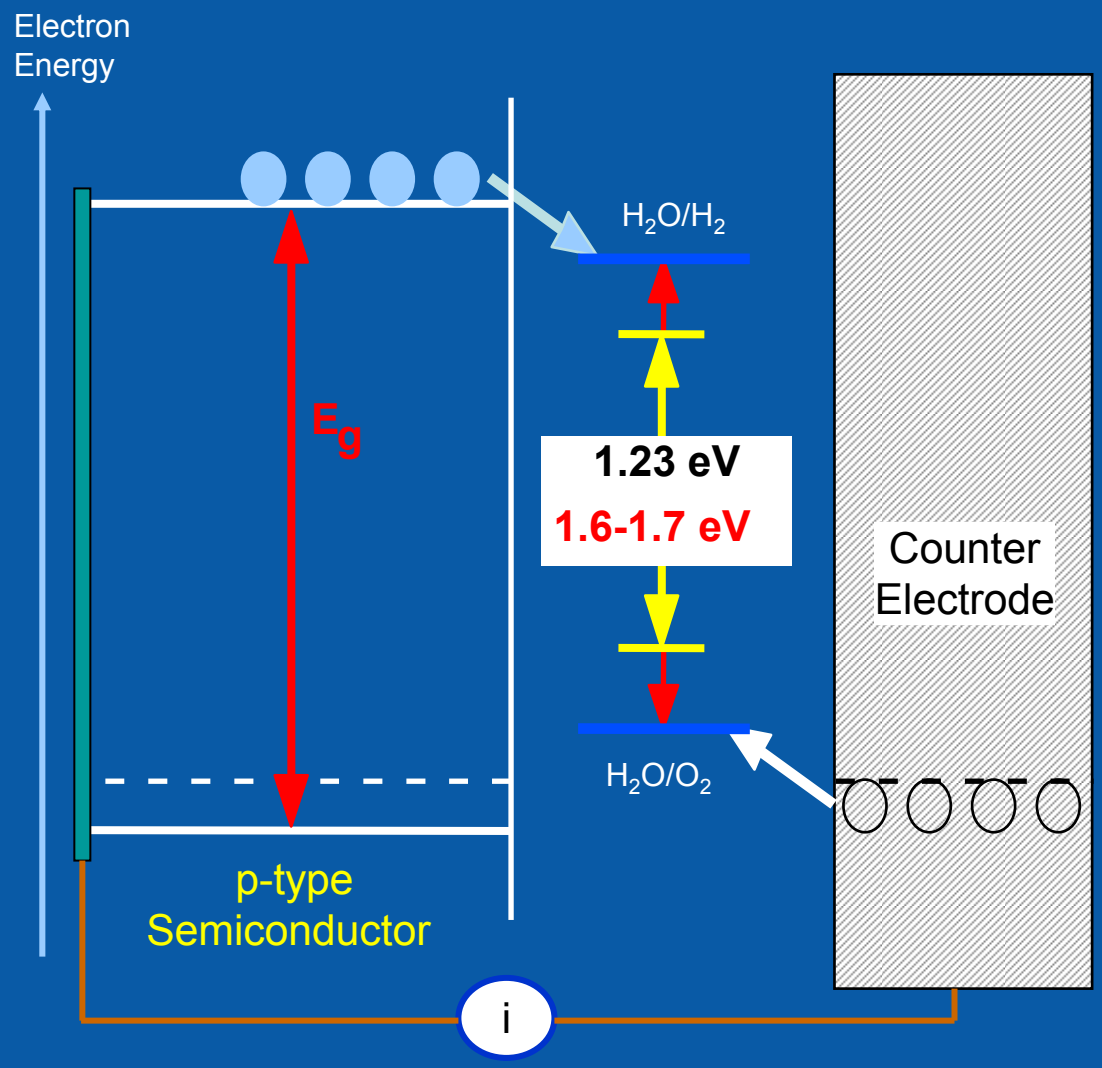
Photoelectrochemical Conversion
Goals and Objectives

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 interface, and for the preparation of transparent catalytic coatings and their application to semiconductor surfaces.
4. 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.
5. Develop database to house a library of the material properties being discovered by the DOE program.

Technical Challenges *(the big three)*

Material Characteristics for Photoelectrochemical Hydrogen Production



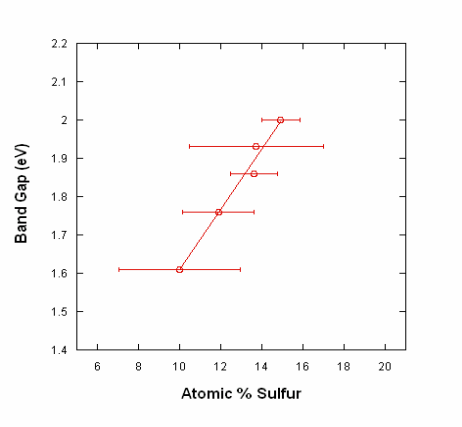
- **Efficiency –** the band gap (E_g) must be at least 1.6-1.7 eV, but not over 2.2 eV
- **Material Durability –** semiconductor must be stable in aqueous solution
- **Energetics –** the band edges must straddle H_2O redox potentials (Grand Challenge)

All must be satisfied simultaneously

Approach: High Efficiency Materials and Low-cost Manufacturing.

- III-V materials have the highest solar conversion efficiency of any semiconductor material.
  - Largest range of available bandgaps
  - ….but
    - Stability an issue – nitrides may be the answer
    - Band-edge mismatch with known materials – tandems an answer

- I-III-VI materials offer low-cost manufacturing.
  - Synthesis procedures for desired bandgap unknown.
  - ….but
    - Stability in aqueous solution?
    - Band-edge mismatch?



Approach: Materials Summary

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 – focus areas in *black*:

- *GaPN - NREL (high efficiency, stability)*
- *$CuInGa(Se,S)_2$ - UNAM (Mexico), NREL (Low cost)*
- *Silicon Nitride – NREL (protective coating and new material)*
- $GaInP_2$ - NREL (fundamental materials understanding)
- Energetics
  - Band edge control
  - Catalysis
  - Surface studies

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

with Professor Carl Koval *University of Colorado at Boulder*

GaPN:GaP

Sample	% P	% N	Direct Eg (eV)
ME477	98.4	1.6	2.07
ME460	97.9	2.1	2.01
ME463	97.4	2.6	2
ME461	96.5	3.5	1.96

GaPN:Si

Sample	% P	% N	Direct Eg (eV)
MF098	98.2	1.8	2.01
MF097	98.1	1.9	1.94

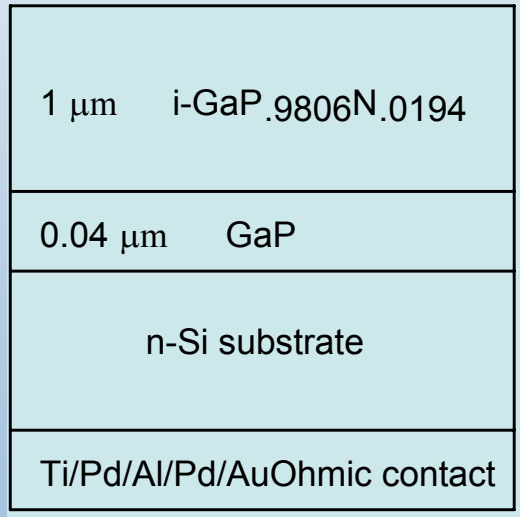
- Control band gap energy by varying nitrogen composition, Goal: < 2.0 eV
- Direct band gap in nitrogen composition range of interest, <5% N.

Approach: Two configurations

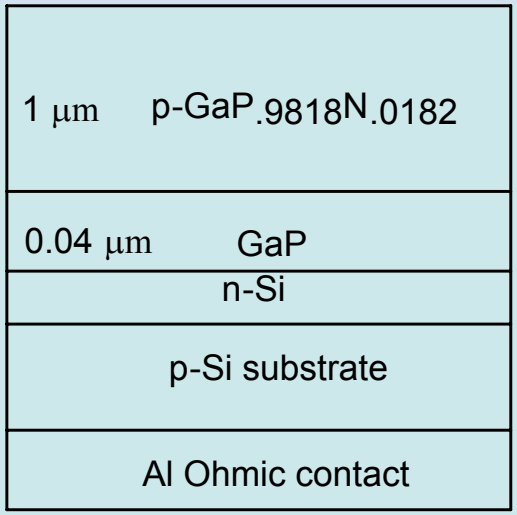
One for material study and one for possible high-efficiency tandem cell.

- GaPN/tj/ p-GaP or n-silicon substrate
  - Undoped
  - No low energy transition expected

- GaPN/tj/ p/n silicon substrate (tandem)
  - Undoped
  - Low energy transition expected



MF097



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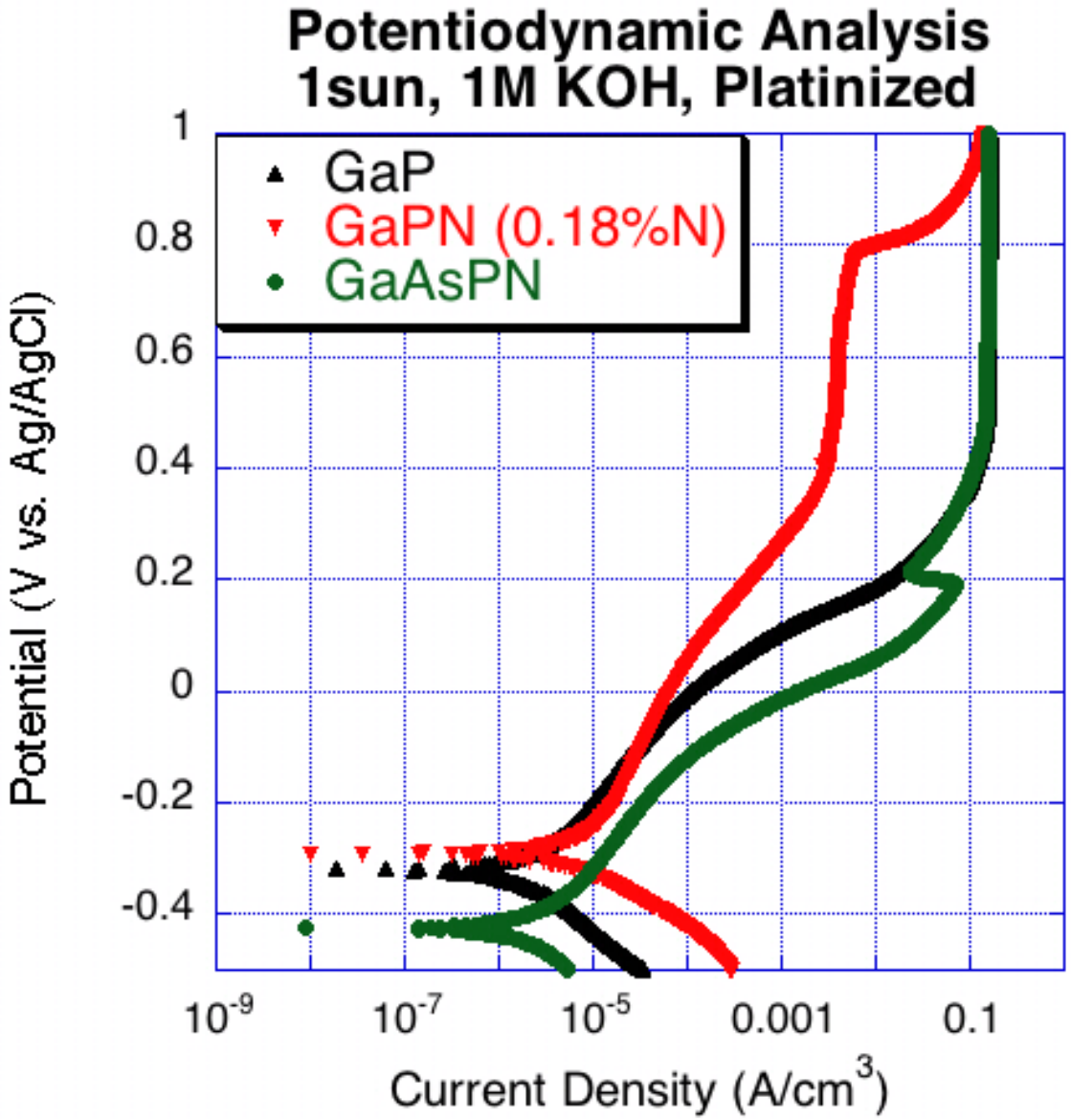
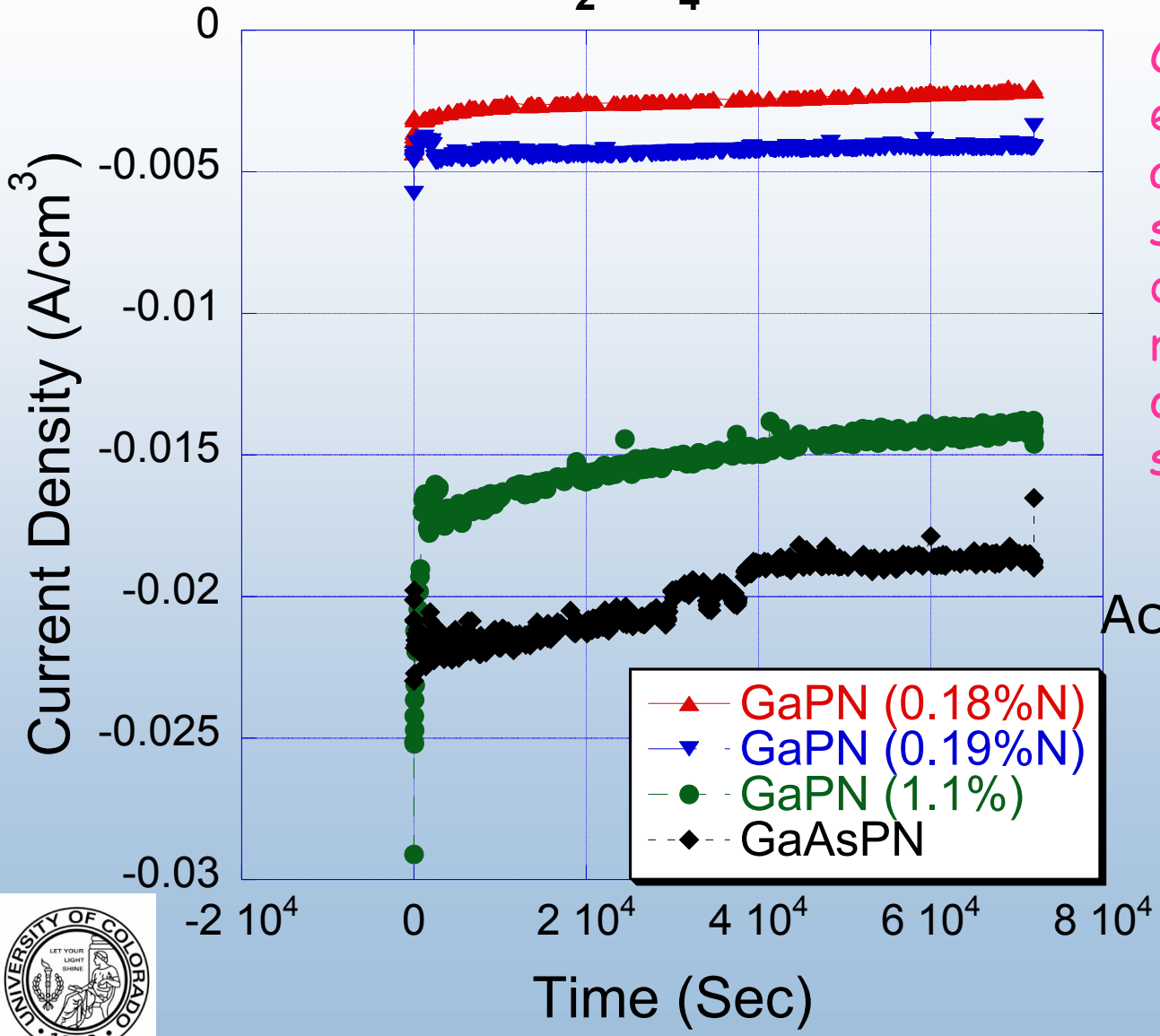


Corrosion experiments on GaP substrate clearly show the enhanced corrosion resistance from nitrogen addition.

J-t Durability Testing
-2V, 3M H_2SO_4, 13 sun, Pt



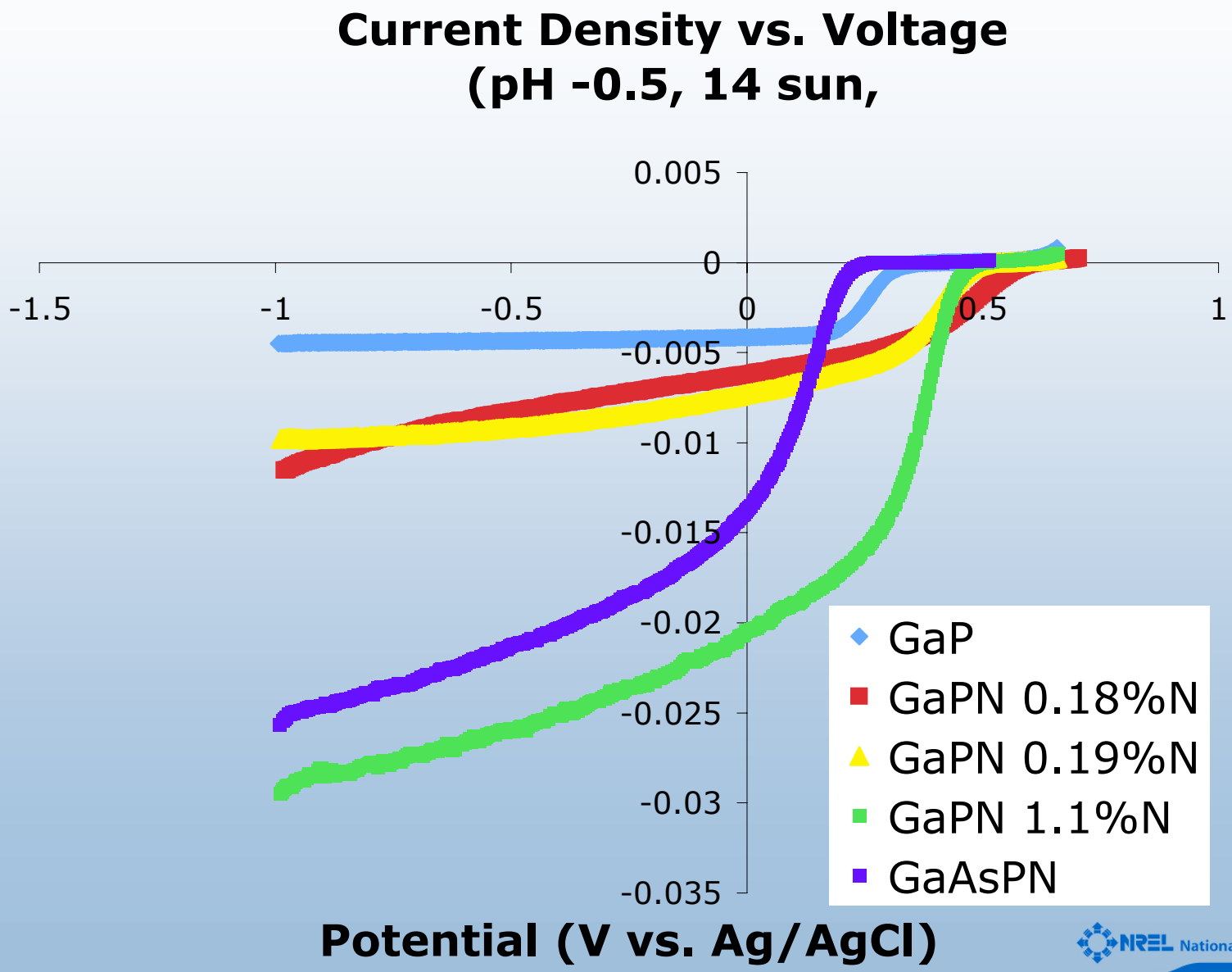
Current-time experiments under accelerated conditions show some degradation in response, but analysis of the solutions do not show any Ga.

Acid Lifetime
72 Hrs
242 Hrs
98 Hrs
110 Hrs

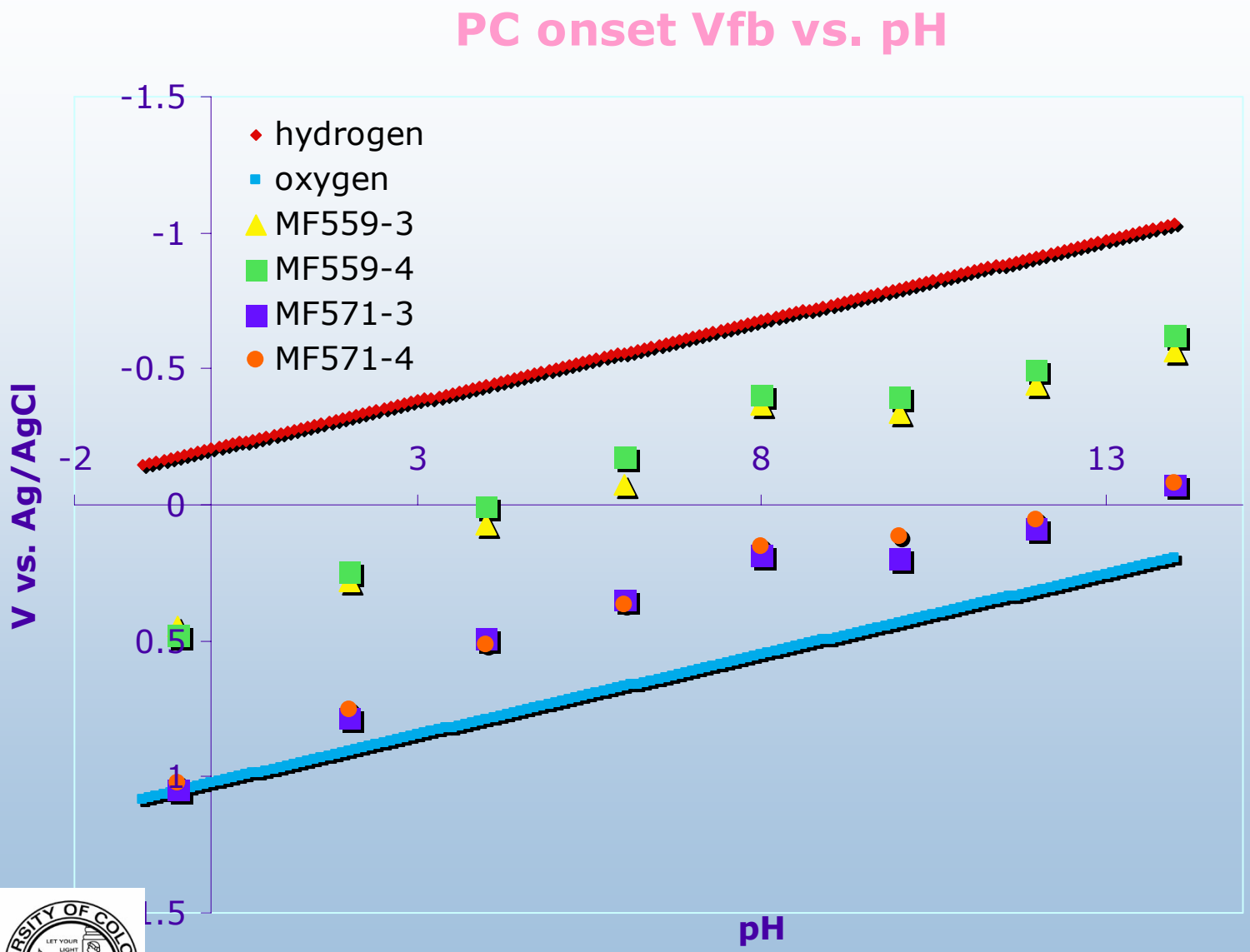
Durability Summary

- No obvious etching, no Ga in solution.
- Some have ridges (up to 1 μm) that circumscribe perimeter (may be due to epoxy)
- Longer duration needed to establish optimal composition and stability.

Photocurrent onset is used to evaluate band edge energetics



Band Edge Energetics



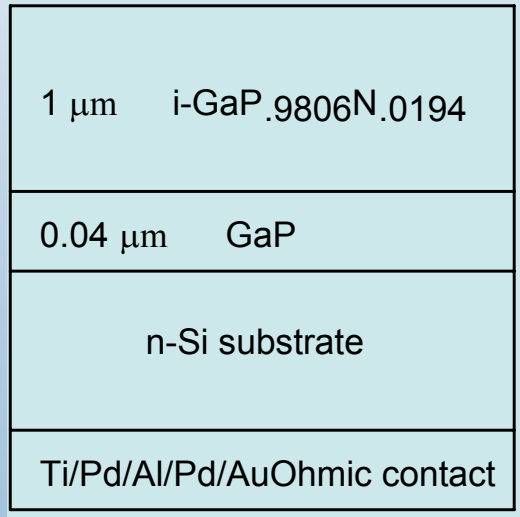
Results from the band edge energy experiments show that the band edges of these materials are too negative for spontaneous water-splitting.

Approach: Two configurations

One for material study and one for possible high-efficiency tandem cell.

- GaPN/tj/ p-GaP or n-silicon substrate
  - Undoped
  - No low energy transition expected

- GaPN/tj/ p/n silicon substrate (tandem)
  - Undoped
  - Low energy transition expected



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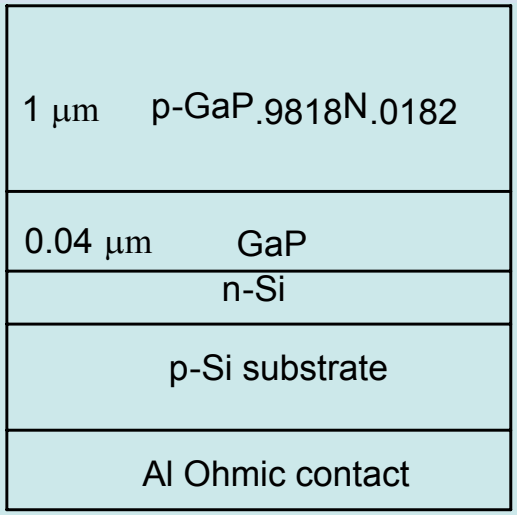
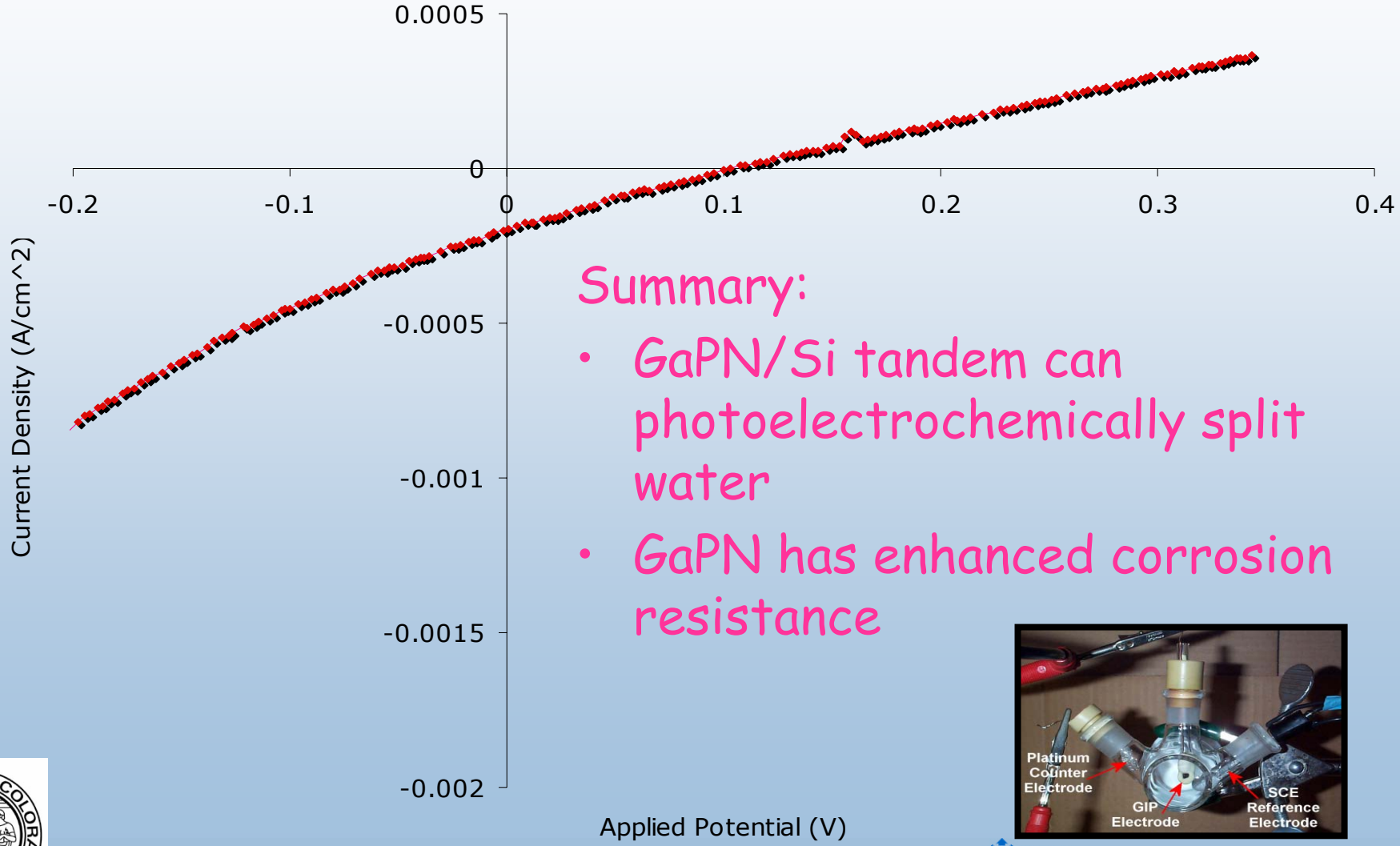


MF098

Light-Driven Water Splitting

MF771-4 2-electrode J-V in acid 1 sun illumination

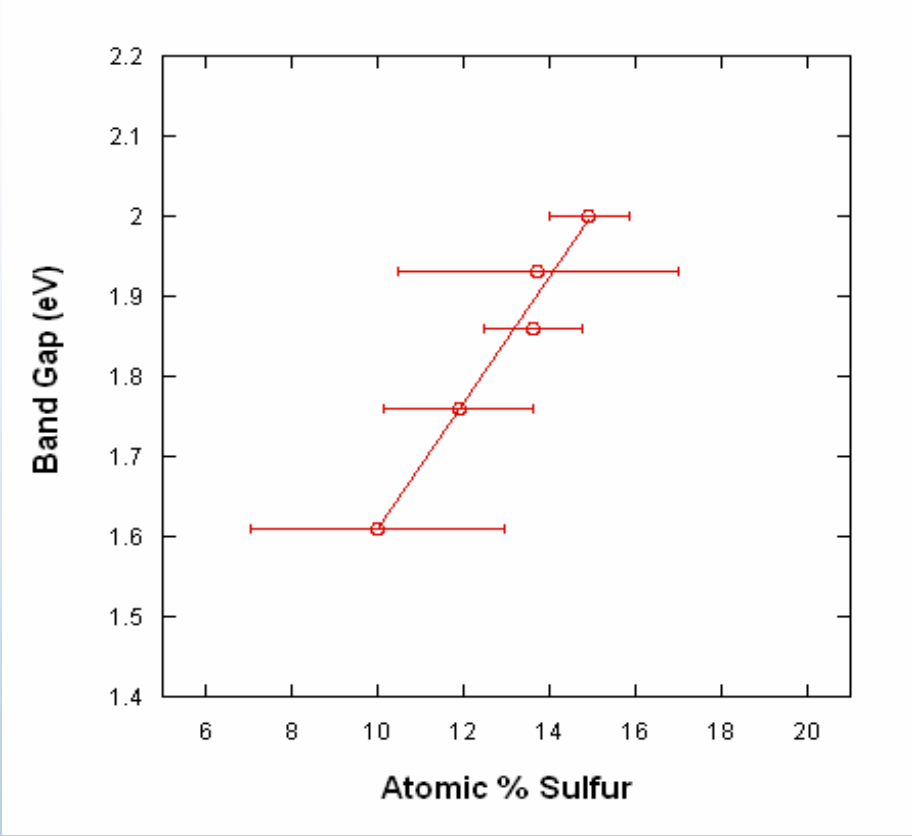


Summary:

- GaPN/Si tandem can photoelectrochemically split water
- GaPN has enhanced corrosion resistance

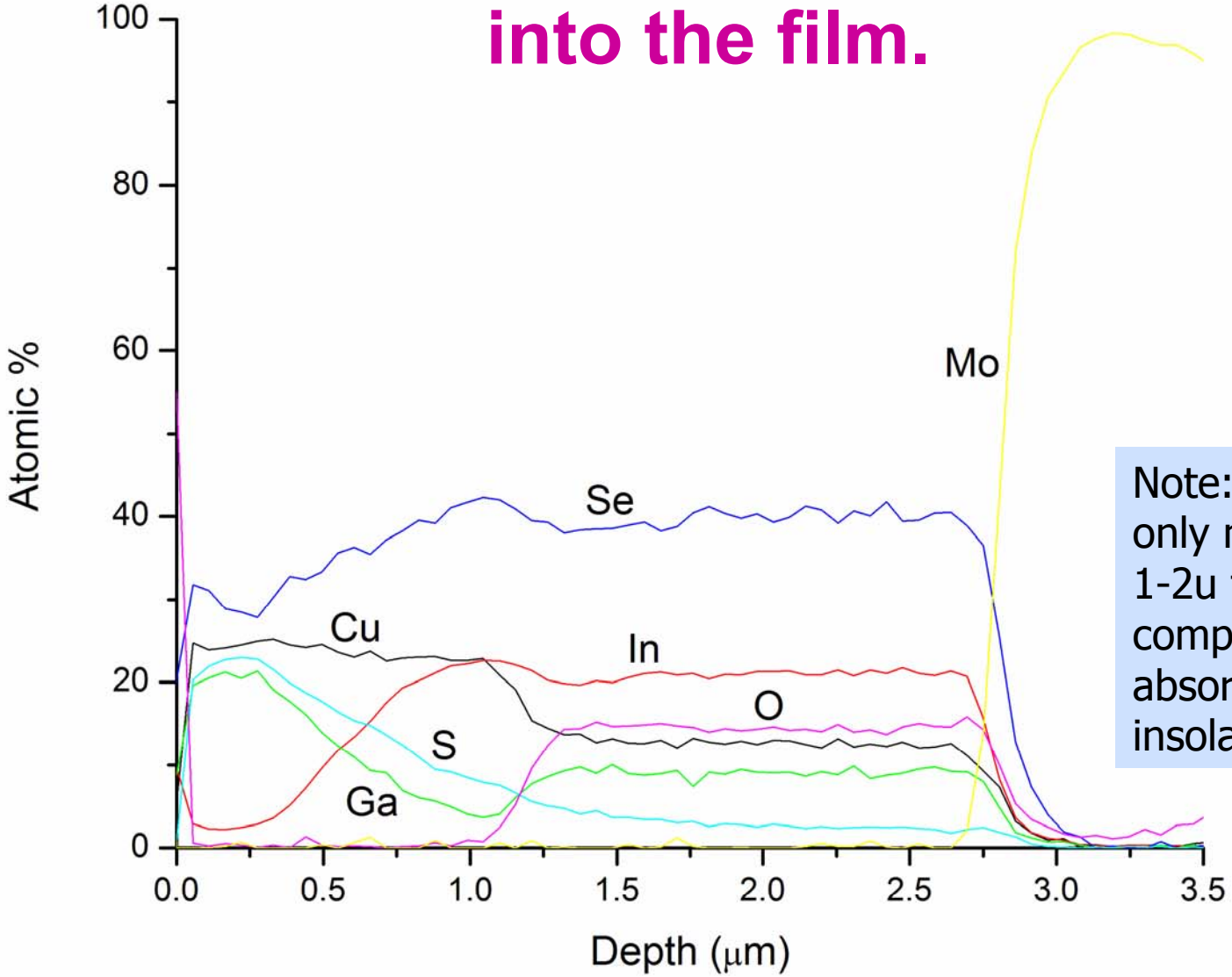
Electrodeposited CIGSS (with Colorado School of Mines)

- $Cu(In,Ga)Se_2$ (CIGS) materials offer the possibility for large-area, high-speed fabrication and low-cost materials
- High efficiencies (>18%) have been realized as PV devices, but there has not been an concerted study as to the applicability for PEC water splitting.
- Electrodeposition provides a low-cost, scalable technique for the production of large area thin film materials
- Previously we have shown that it is possible to increase the band gap beyond 1.6 eV, but a number of material and synthesis issues remain.



Goal: Consistent synthesis of high bandgap thin-film material

Depth profile showing sulfur diffusion into the film.



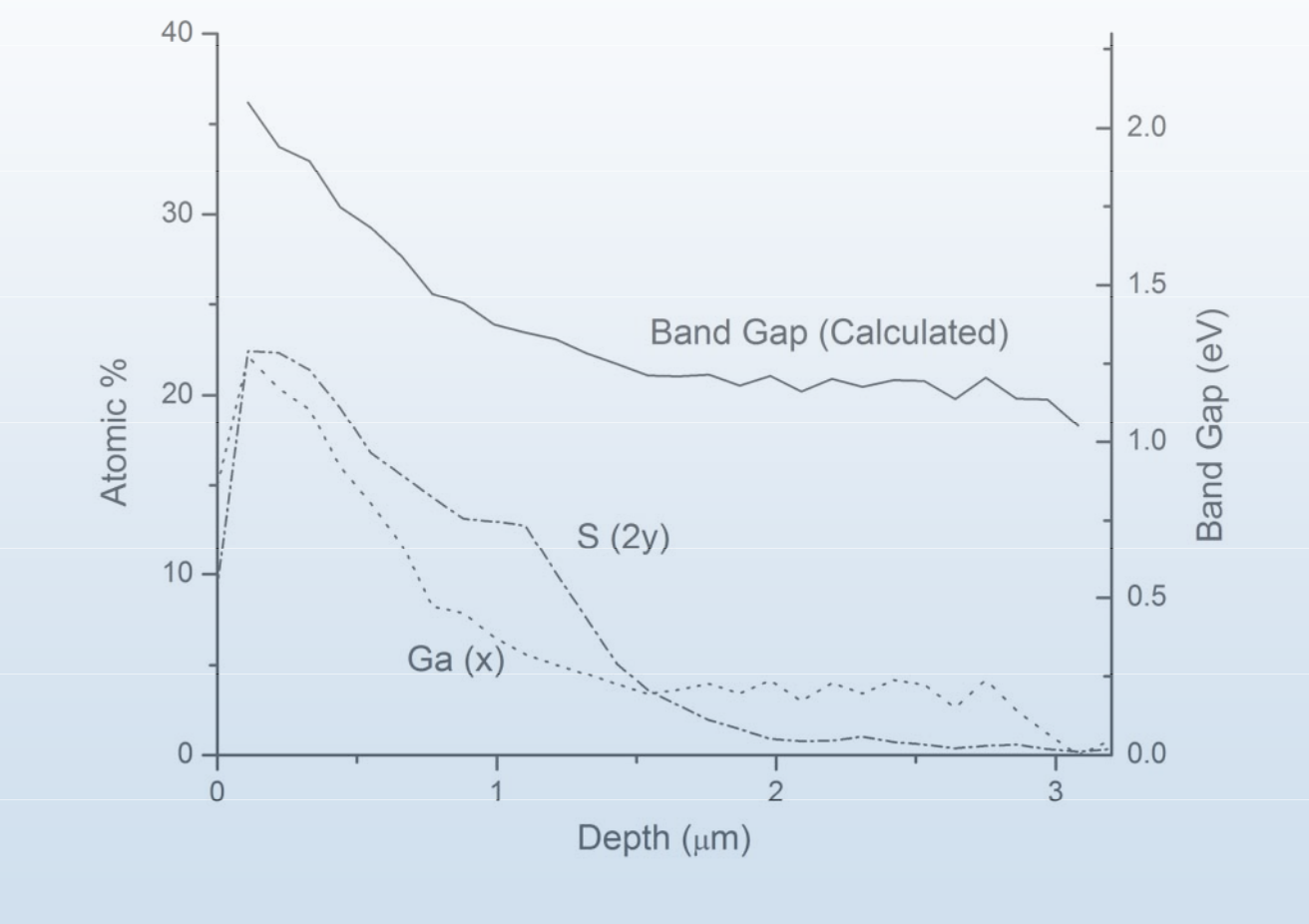
Note: These film only need to be 1-2u thick to completely absorb the solar insolation

Bandgap Grading

Semiconductor Alloy Bandgap Calculation

The bandgap dependence of Cu(Ga,In)(S,Se) can be determined from:

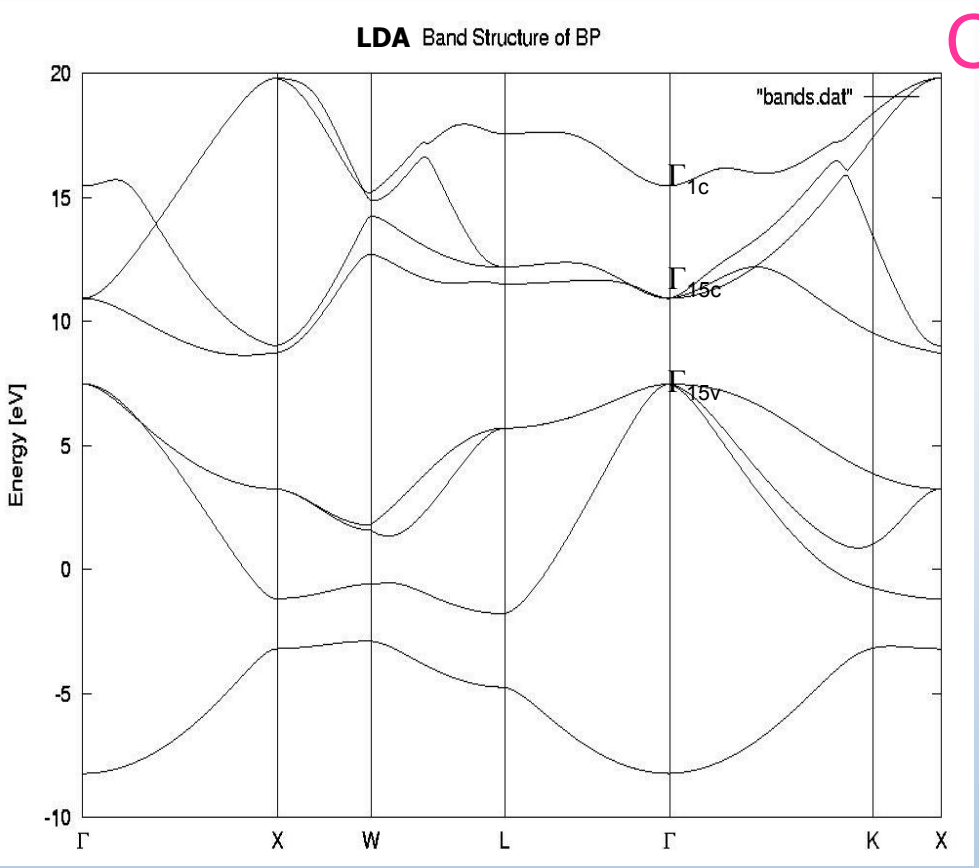
$$E_g(Cu(In_{1-x}Ga_x)(Se_{1-y}S_y)_2 = 1.00 + 0.53x + 0.54y + .15xy + .15x^2 + 0.06x^2y$$



Thin-film CIGSS Summary

- Copper and selenium in the film are seen to be highly dependent on solution concentration of copper.
- Annealing these precursor materials in a sulfur-containing atmosphere enriches them to a depth of only about 1um.
- Phase separation is evident in many of these materials, most likely due to this compositional gradient.
- Some materials show variable band gap characteristics due to this effect.

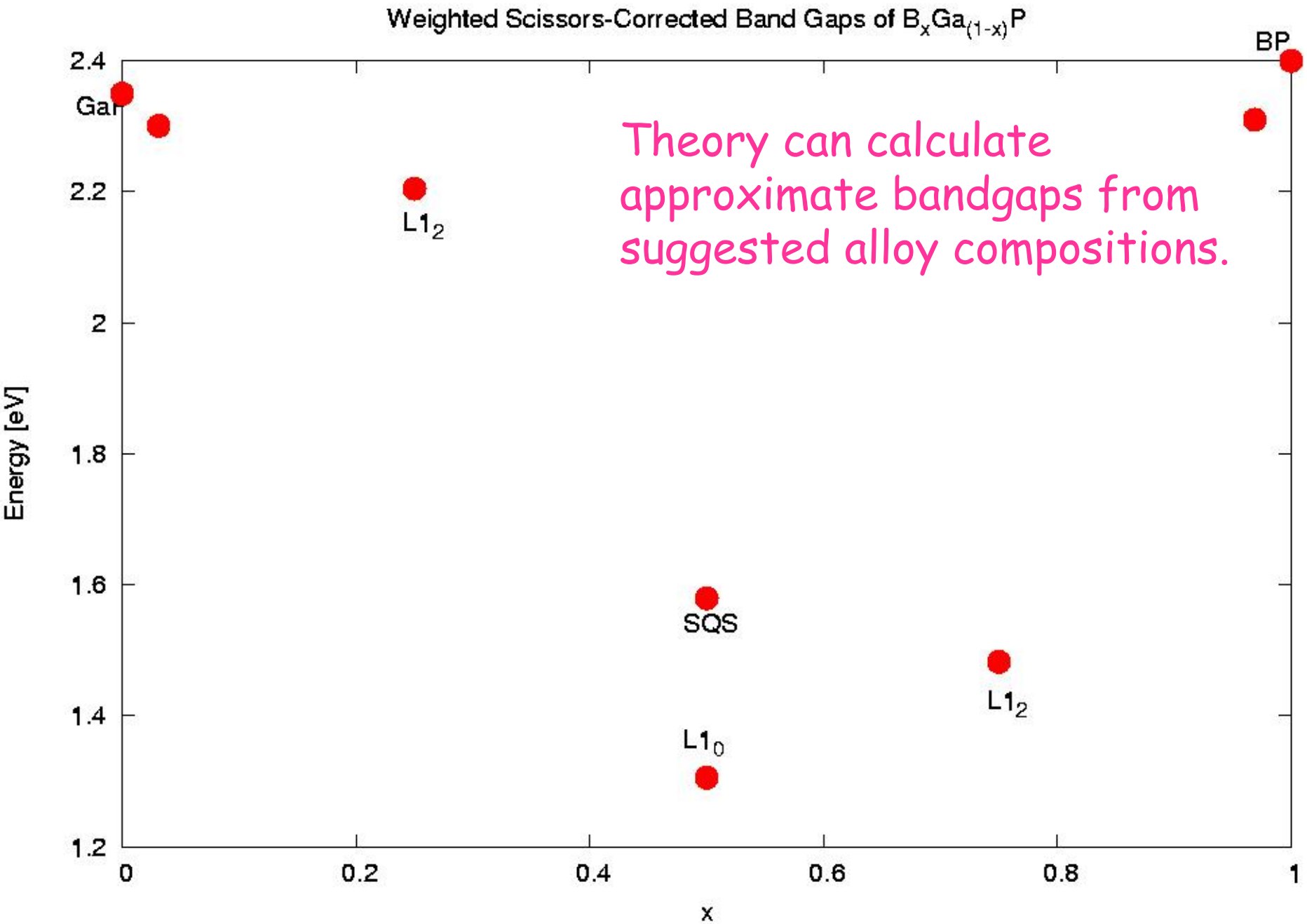
Future Direction for Materials Discovery



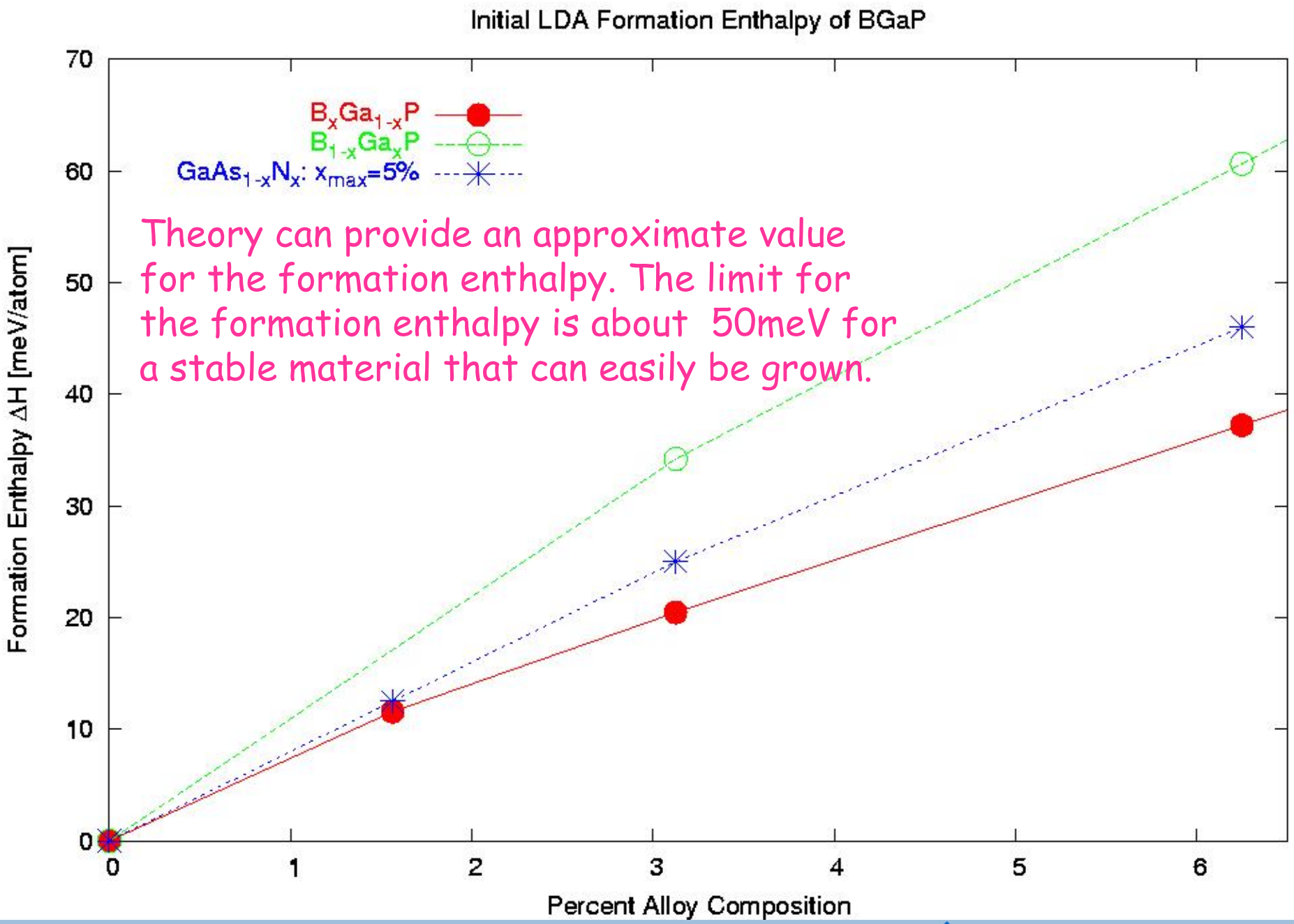
Computational-combinatorial materials discovery.

- Inverse band-structure calculations can be used to calculate semiconductor bandgap and band energies from the alloy composition.
- Can be combined with calculation of corrosion resistance.

Choice of alloys for theoretical calculations is based on PI's experience in PEC, corrosion, and other material considerations (no Cd, Hg, …)



Theory can calculate approximate bandgaps from suggested alloy compositions.



Theory can provide an approximate value for the formation enthalpy. The limit for the formation enthalpy is about 50meV for a stable material that can easily be grown.

Computational approach for combinatorial design of semiconductor chemistry for bandgap engineering.

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Combinatorial design of semiconductor chemistry for bandgap engineering: "virtual" combinatorial experimentation

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Abstract

The objective of this paper is to show how one may design combinatorial libraries a priori by integrating data mining techniques with physically robust multivariate data. It is shown that large datasets can be developed from relatively small amounts of experimental and theoretically based information. This involves a process of strategically selecting appropriate physical based parameters that can be analyzed in a multivariate manner. In this paper we identify for the first time the bandgap and lattice parameters of nearly 200 stoichiometries of new and yet to be synthesized compound chalcopyrite semiconductors. The robustness of this "virtual" combinatorial experimentation approach is demonstrated by comparison to band gap predictions from theoretical studies on a range of compositions for a selected quaternary compound semiconductor.
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JEL classification: 71.55.Cn; 71.55.Eq; 71.55.Gs

Keywords: Semiconductor compounds; Crystallographic databases; Crystal stoichiometry

1. Introduction

The field of "bandgap engineering" is in fact one of the earliest examples of combinatorial design of materials. The recognition that by matching lattice parameters of different covalently bonded semiconductors, one can engineer the bandgap of epitaxial heterostructures has been one of the success stories in integrating fundamental physics into device engineering. However, the strategy of what materials one may work with is limited to relatively few and the "discovery" of new materials with more complex chemistries is still a slow process. Clearly high throughput experimentation techniques offer some exciting possibilities for developing such new materials. In this paper we wish to outline the use of a statistically based strategy combined with the appropriate understanding of key physical parameters to show how we can develop a computational screening tool prior to conducting combinatorial experiments. We propose the idea of "virtual" combinatorial libraries, which lay a map of suggested chemical combinations, likely to give the desired properties one is seeking. Using chalcopyrite semiconductors as a testbed, we show how such a library can be built. The formalisms of the mathematical foundations are described in Appendix A but suffice it to say that a judicious use of multivariate statistics tools serves as the means to manipulate and process the incoming data.

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URL: http://www.rpi.edu/~rajank/materialsdiscovery.

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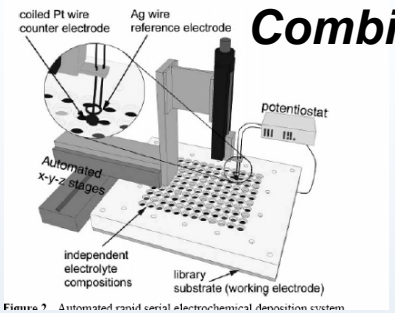
doi:10.1016/S0169-4332(03)00918-8

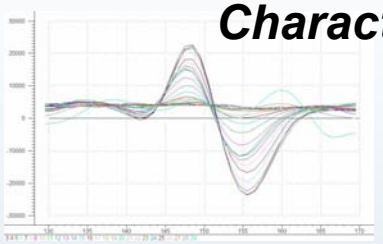
Table 4 (*Continued*)

Compound	Predicted band gap energy (eV) by PLS	Theoretical band gap energy (eV)	Nature of band gap[a]	Predicted lattice constant by PLS	Lattice constant (Å)	*c*/*a* ratio	Reference
$Zn_{0.5}Si_{0.5}P$	2.3591	1.56 (GW)	d	5.3759	5.262		[9]
$Zn_{0.5}Si_{0.5}As$	1.5299	0.68 (GW)	md	5.571	5.483		[8]
$ZnStSb_2$	−0.055	0.9		5.6125	6.077		[2]
$Zn_{0.5}Si_{0.5}Sb$	−0.055			5.6123	5.962		[8]
$ZnSiBi_2$	−1.6445			5.9063			
$ZnGeN_2$	4.9757			5.7709			
$Zn_{0.5}Ge_{0.5}P$	1.8692	1.15 (GW)	I	5.4837	5.382		[9]
$Zn_{0.5}Ge_{0.5}As$	1.04	0.23 (GW)	md	5.6789	5.597		[9]
$ZnGeSb_2$	−0.5449	0.5		5.7202	6.111		[2]
$ZnGeBi_2$	−2.1344			6.0141			
$ZnSnN_2$	4.4468			5.8719			
$ZnSnP_2$	1.3403			5.5847	5.651	2	[1,2]
$Zn_{0.5}Sn_{0.5}P$	1.3404	1.70 (GW)	I	5.5847	5.688		[9]
$ZnSnAs_2$	0.5112			5.7799	5.851	2	[1,2]
$Zn_{0.5}Sn_{0.5}As$	0.5112	0.79 (GW)	md	5.7799	5.87		[9]
$ZnSnSb_2$	−1.0738			5.8212	6.275	2	[1]
$ZnSnBi_2$	−2.6633			6.1151			
$ZnPbN_2$	3.7358			6.0915			
$ZnPbP_2$	0.6293			5.8043			
$ZnPbAs_2$	−0.1998			5.9994			
$ZnPbSb_2$	−1.7848			6.0407			
$ZnPbBi_2$	−3.3743			6.3347			
$CdCN_2$	5.8097			5.9651			
$CdCP_2$	2.7032			5.6779			
$Cd_{0.5}C_{0.5}P$	2.7032			5.6779	4.973		[8]
$CdCAs_2$	1.8741			5.8731			
$Cd_{0.5}C_{0.5}As$	1.8741			5.8731	5.201		[8]
$CdCSb_2$	0.2891			5.9143			
$Cd_{0.5}C_{0.5}Sb$	0.2891			5.9143	5.62		[8]
$CdCBi_2$	−1.3004			6.2083			
$CdSiN_2$	5.2692			5.9568			
$Cd_{0.5}Si_{0.5}P$	2.1627	1.22 (GW)		5.6696	5.378		[9]
$Cd_{0.5}Si_{0.5}As$	1.336			5.8648	5.61		[8]
$CdSiSb_2$	−0.2514	0.8		5.9061	6.344		[2]
$CdSiBi_2$	−1.18409			6.2			
$CdGeN_2$	4.7793			6.0646			
$Cd_{0.5}Ge_{0.5}P$	1.6729	0.33 (GW)	d	5.7774	5.523		[9]
$Cd_{0.5}Ge_{0.5}As$	0.8437		Metallic	5.9726	5.755		[8]
$CdGeSb_2$	−0.7412	0.2		6.0139	6.383		[2]
$CdGeBi_2$	−2.3308			6.3078			
$CdSnN_2$	4.2504			6.1657			
$Cd_{0.5}Sn_{0.5}P$	1.144			5.8785	5.797		[8]
$CdSnSb_2$	−1.2701	−0.80 (FLAPW)		6.1149	6.479		[6]
$CdSnBi_2$	−2.8596			6.4089			
$CdPbN_2$	3.5394			6.3852			
$CdPbP_2$	0.433			6.098			
$CdPbAs_2$	−0.3962			6.2931			
$CdPbSb_2$	−1.9811			6.3344			
$CdPbBi_2$	−3.5706			6.6284			
$HgCN_2$	4.5586			6.2613			
$HgCP_2$	1.4522			5.9741			
$HgCAs_2$	0.623			6.1693			

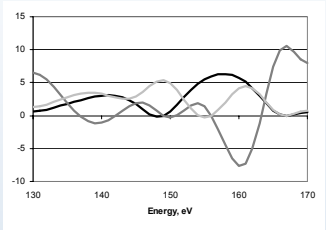
PEC Materials Informatics



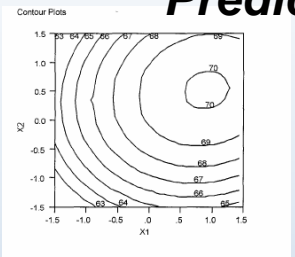
Combinatorial synthesis



Characterization



Multivariate Analysis



Prediction

Experiments
Synthesis
Characterization
Performance

Design of Experiment

Target Assessment
Response Surfaces

Management
Quality
Format
Access
Hardware
Software

Analysis
Processing
Statistical
Factor Analysis
Empirical Modeling
Neural Networks

Data Mining
Visualization
Mechanistic Modeling

Collaborative work with the DOE PEC Team members

Responses to Previous Year Reviewers' Comments

- Specific recommendations and additions or deletions to the work scope
  - Recommend a collaboration with computational groups (not necessarily only at NREL) which could provide guidance on the search for more effective semiconductor.
    - Instituted funded collaboration with NREL's Computational Sciences Center.
    - Others to be added as funding allows.
  - Recommend the addition of an industry partner even at this early stage to help set goals and objectives and define a product configuration.
    - Program solicitation awards provides for interaction with two separate companies.
- Strengths
  - Excellent understanding of scientific challenges and approaches to overcoming them to meet PEC goals.
  - Good progress. Enthusiastic, well-versed in topic.
- Weaknesses
  - Despite lack of funding for catalyst development, should be aware of any progress that could impact their ultimate goal of a system demo.
    - Some crosscutting work under a funded DOE fuel cell project.

MYPP PEC Targets and NREL status

Target, Dates ->	2005	NREL:2005 (GIP Tandem)	NREL:2005 (GaNP & CuInGaSSe)	2010	2015
Semiconductor Bandgap (eV)	2.8	<2.0eV	<2.0eV	2.3	2.0
Chemical conversion process efficiency (%)	4	12	<5	10	12
Solar-to-hydrogen efficiency (%)	NA	12	<1	8	10
Durability (hours)		20	240+	1000	5,000

MYPP Goal: Develop advanced renewable photoelectrochemical and biological hydrogen generation technologies. By 2015, verify the feasibility of these technologies to be competitive in the long term.

Future Plans

- Remainder of FY2005:
  - Continue understanding and improvement of nitride-based material.
  - Develop new electrosynthesis approaches to incorporate sulfur into the CIGSSe films.
  - Initiate tandem cell design with thin-film CIGSSe.
  - Develop computational work.
  - Finalize plans for computational library.

- For FY2006:
  - Look at possible new materials with LBNL, CSM, …
  - Coatings: SiN, SiC, …
  - Band-edge engineering (Office of Science proposal).
  - Multijunction structures

Presentations and Publications

- Papers:
- John A. Turner, “The Sustainable Hydrogen Economy”, Science, 305, p 972, (2004)
- A.M. Fernandez, N. Dhere, J.A. Turner, A.M. Martýnez, L.G. Arriaga, and U. Cano “Photoelectrochemical characterization of the Cu(In,Ga)S2 thin-film prepared by evaporation”, Solar Energy Materials (in press – available on-line).

- Presentations:
- Presentation (at NREL) to representatives from 3M Corporate Research who were visiting NREL to look at possible collaborative projects.
- Invited talk at the workshop on Photosynthesis that was organized at LBNL as part of their energy initiative workshop series.
- Invited talk at the Gordon Conference on Catalysis entitled “Photoelectrochemical Water Splitting”.
- Plenary lecture at the opening of the Renewable Energy Center in Trondheim, Norway.
- J. Leisch taught a class on hydrogen for Solar Energy International at their Alternative Fuels Workshop.
- Participated in the National Science Foundation’s workshop on Hydrogen Energy presenting a talk on electrolysis and PEC water splitting.
- Invited talk at University of Denver entitled “Materials and Band-Edge Engineering Approaches to Photoelectrochemical Water Splitting”.
- Heiland Lecture entitled “The Hydrogen Economy”, sponsored by the Department of Geophysics at the Colorado School of Mines, Golden, CO, September 3, 2004
- Presentation at the LERDWG meeting on “Progress in photoelectric reduction of water”, Washington DC, September 21, 2004
- Participated in National Public Radio’s “Talk of the Nation – Science Friday”, July, 2004.
- Todd Deutsch gave a talk at the International Electrochemical Society meeting in Honolulu, Hawaii, entitled “Preliminary Investigation of GaP1-xNx Semiconductor Materials for Photoelectrochemical Hydrogen Production.”
- Jennifer Leisch presented a poster at the International Electrochemical Society meeting in Honolulu, Hawaii, entitled “Photoelectrochemical Hydrogen Production: Graded Bandgap Structures from Electrodeposited CIS-based Precursors.”
- J. Turner, Todd Deutsch, & Jennifer Leisch participated in the DOE PEC workshop held in conjunction with the International Electrochemical Society meeting in Honolulu, Hawaii.
- J. Turner gave a talk as part of the NREL Visitor’s Center’s VC Powerlunch series entitled “The Sustainable Hydrogen Economy.”

Presentations (2)

- J. Turner gave a presentation on “The Sustainable Hydrogen Economy” as part of a Web Conference for DOE Regional Office staff and state energy offices.
- J. Turner participated in the U.S. Department of Energy's Solar - H2 workshop. This was a joint workshop between the DOE Solar and Hydrogen programs. J. Turner gave a talk entitled “Direct Photoelectrochemical Production of Hydrogen”.
- J. Turner gave an invited talk at the Stanford Linear Accelerator (SLAC) entitled “The Sustainable Hydrogen Economy”, as well as meet with staff members there to discuss possible collaborative projects.
- J. Turner gave an invited talk at the Colorado Chapter of ASM meeting entitled “Fuel Cell Technology and the Sustainable Hydrogen Economy”.
- J. Turner was an invited lecturer for a Sustainable Development class at the University of Colorado, Boulder. He presented an overview on the hydrogen economy and fuel cell technologies.
- J. Turner gave an invited talk entitled “Direct Photoelectrochemical Production of Hydrogen” as part of the seminar series for the University of California , Berkeley (and LBNL).
- J. Turner gave a presentation on “The Sustainable Hydrogen Economy” as part of a Mensa Colloquium on energy.
- J. Turner gave a presentation at the GE Whitney Symposium of Science and Technology entitled ”Photoelectrochemical Water Splitting”.
- J. Turner participated in the U.S. Department of Energy's BES Solar energy workshop.
- J. Turner was honored as the 2005 Sverdrup Visiting Scientist at Augsburg College and gave a lecture entitled “The Sustainable Hydrogen Economy”

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.