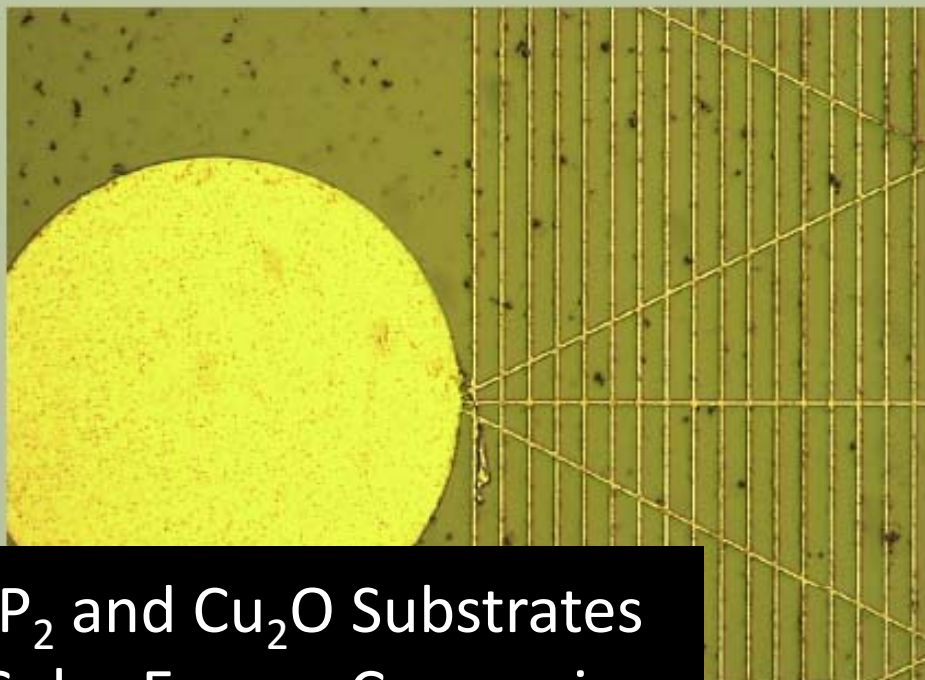
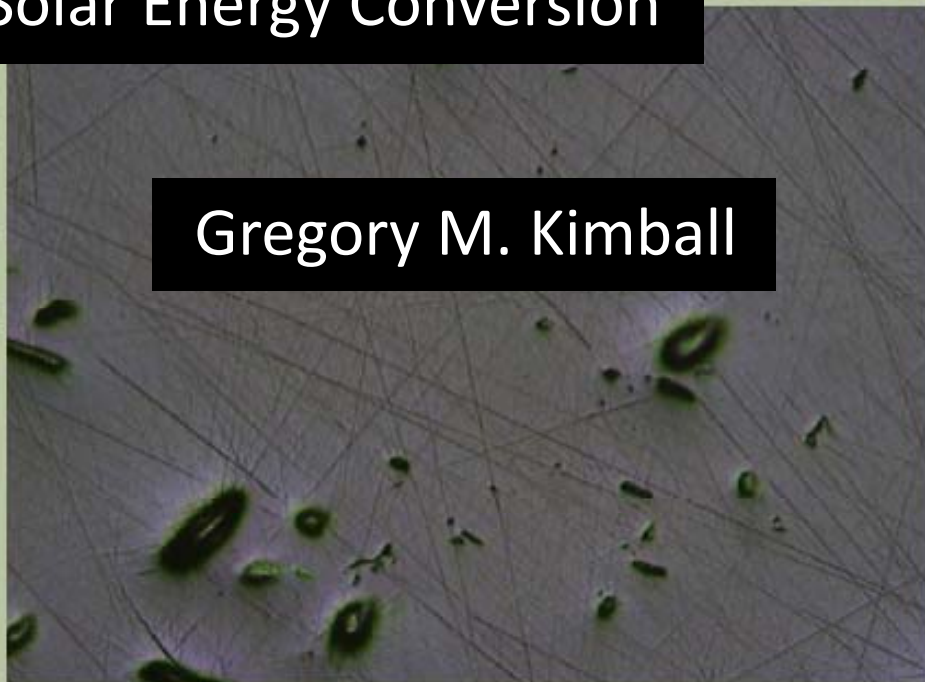
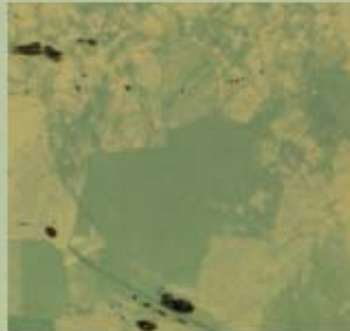
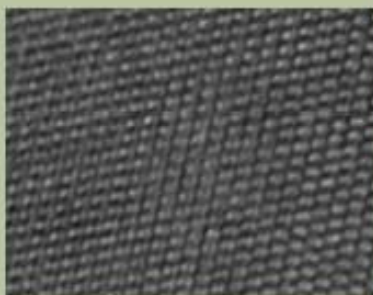
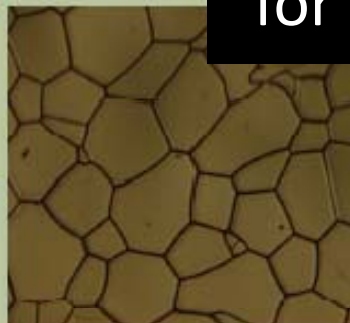
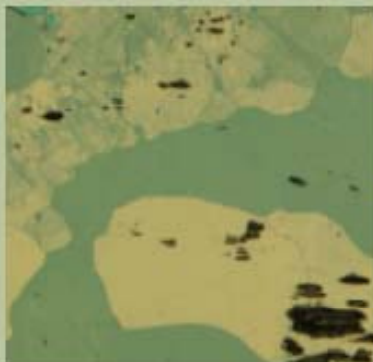




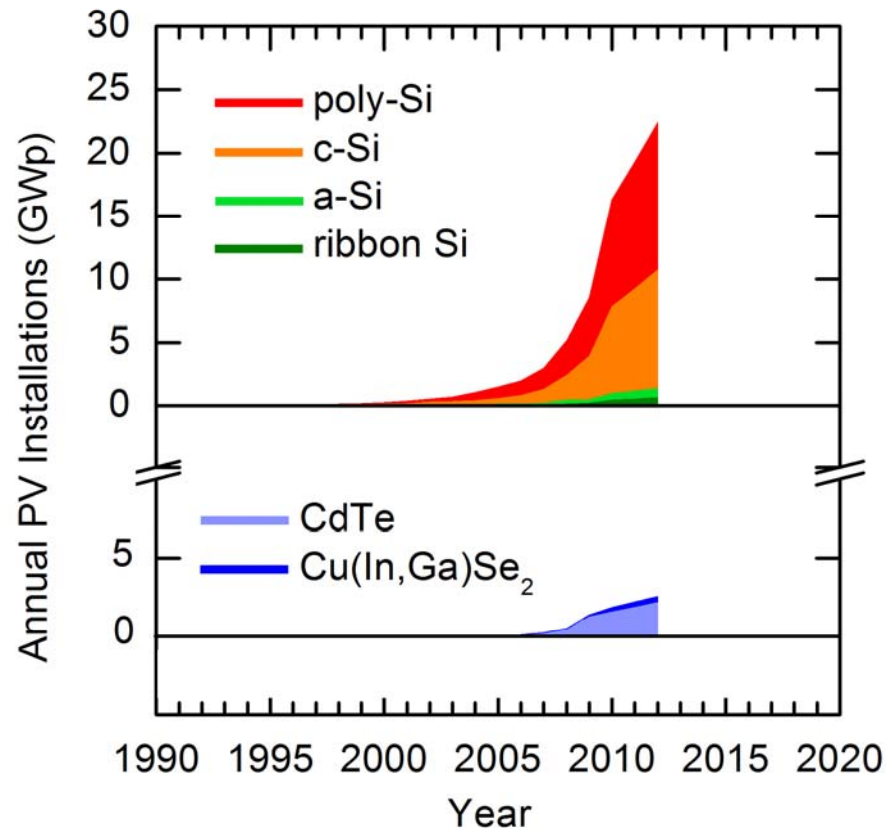
Zn_3P_2 and Cu_2O Substrates
for Solar Energy Conversion



Gregory M. Kimball

Photovoltaics market: 1990 – present

Photovoltaics market composition

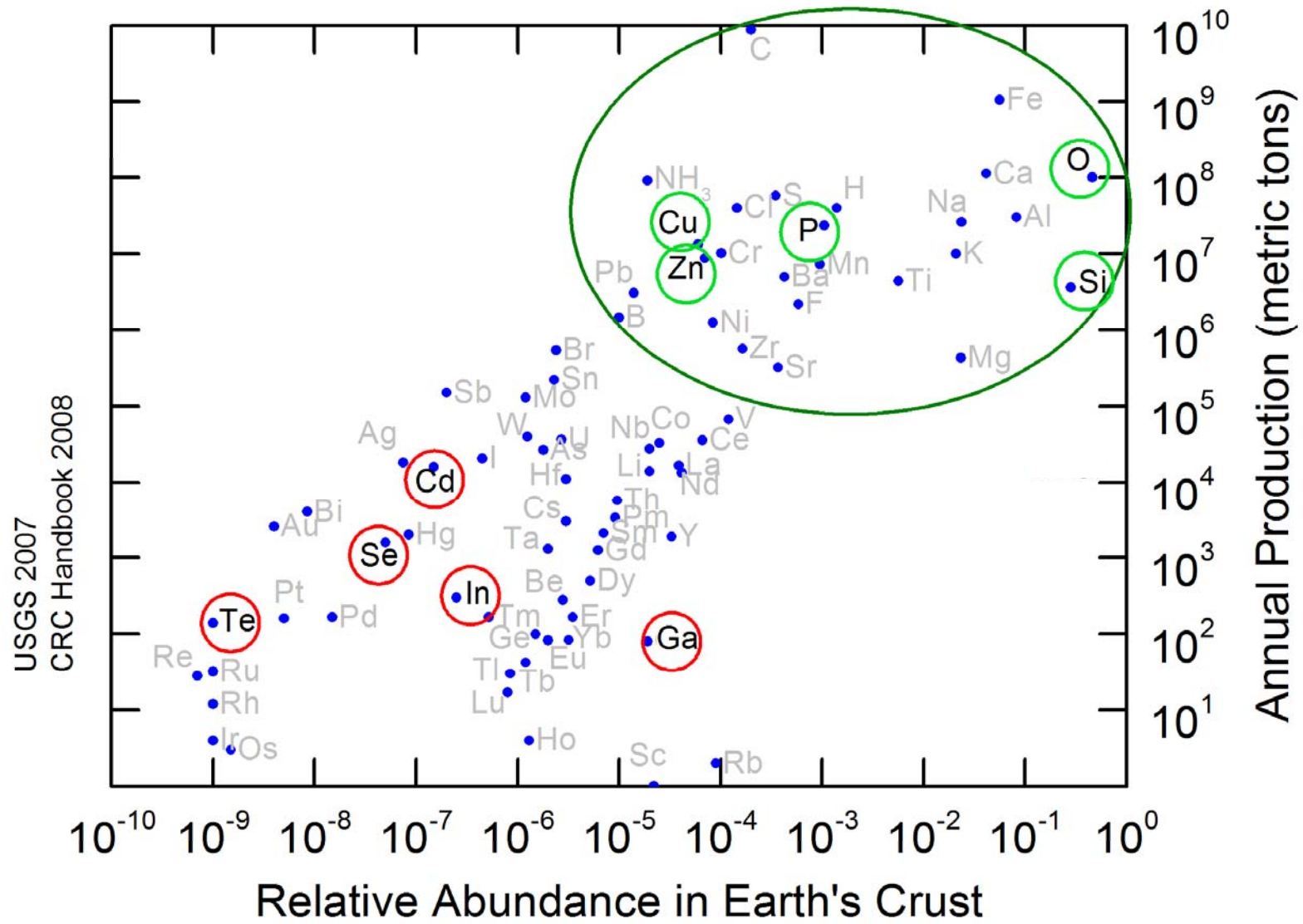


- What should we make our solar cells out of?
 - How can we make installing PV cost less than laying concrete?
- **The future is wide open for new ideas!**



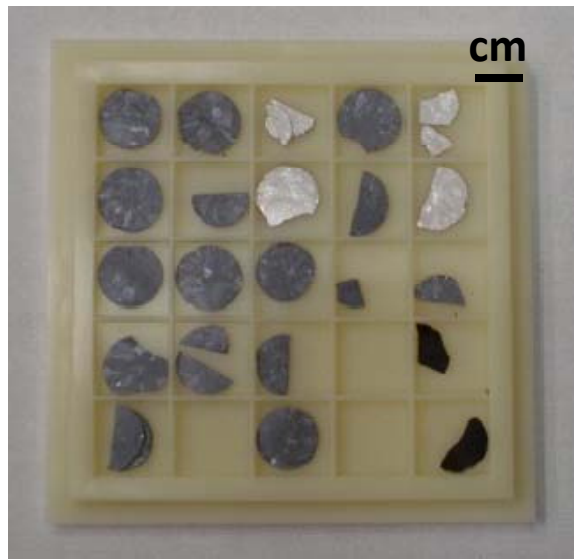
“Price, technology and the illusion of control.” Paula Mints, Navigant Consulting. 21 April 2011.
“Global PV market, 2011.” Chihheng Liang, Digitimes Research, Taipei. 11 May 2011.

Earth-abundant thin films

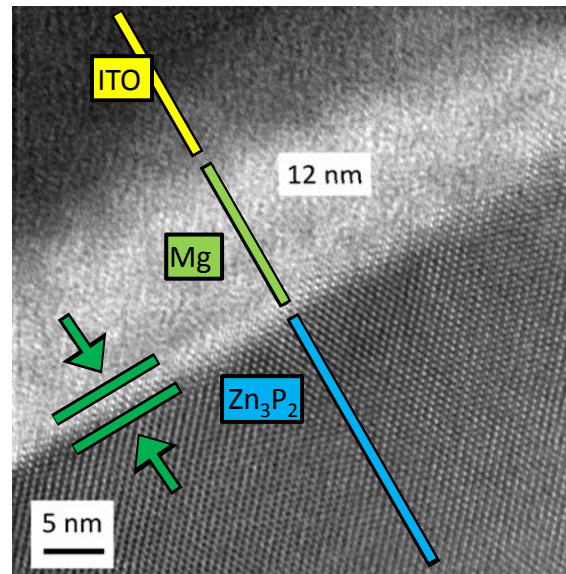


Zn_3P_2 and Cu_2O substrates for solar energy conversion

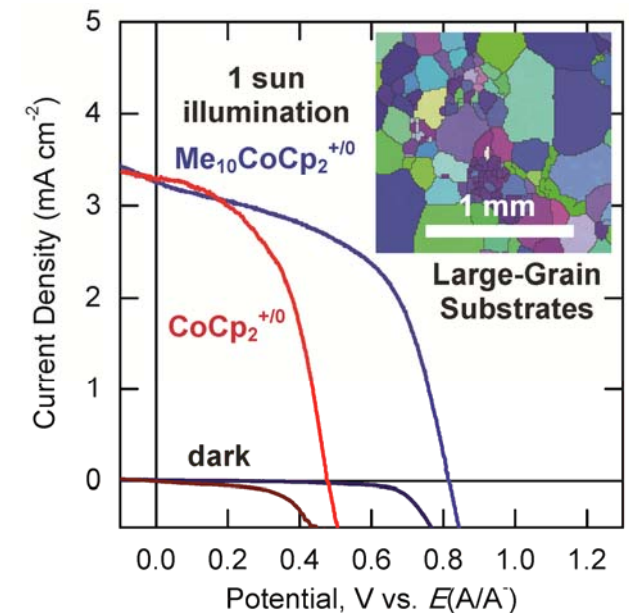
Cornering the market
for 'Solar-Grade' Zn_3P_2



Why is annealing critical
in $\text{Mg}/\text{Zn}_3\text{P}_2$ solar cells?

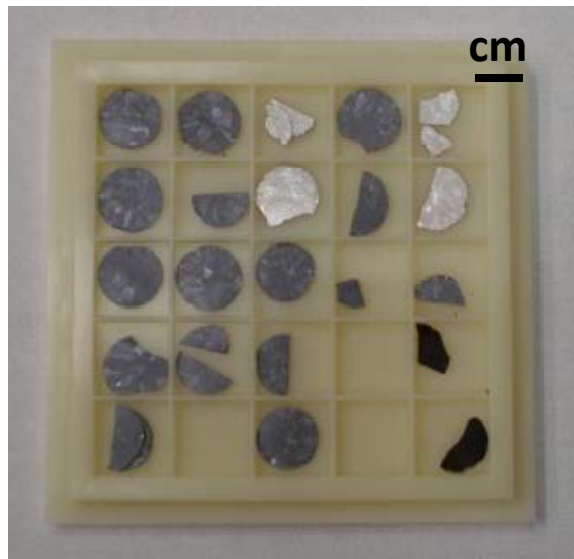


High performance
 Cu_2O /liquid junctions

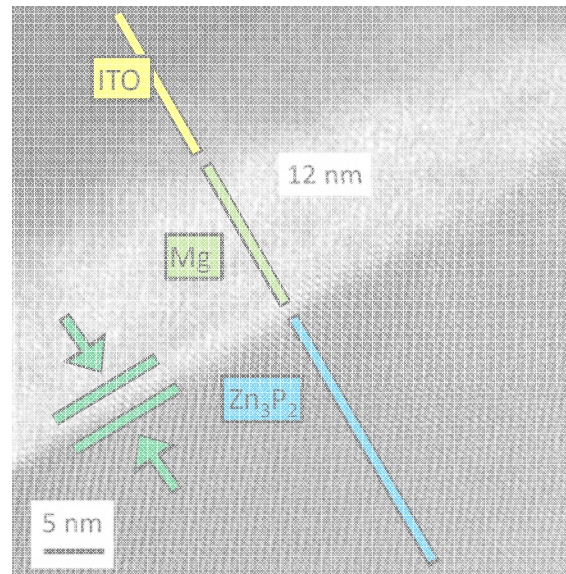


Zn_3P_2 and Cu_2O substrates for solar energy conversion

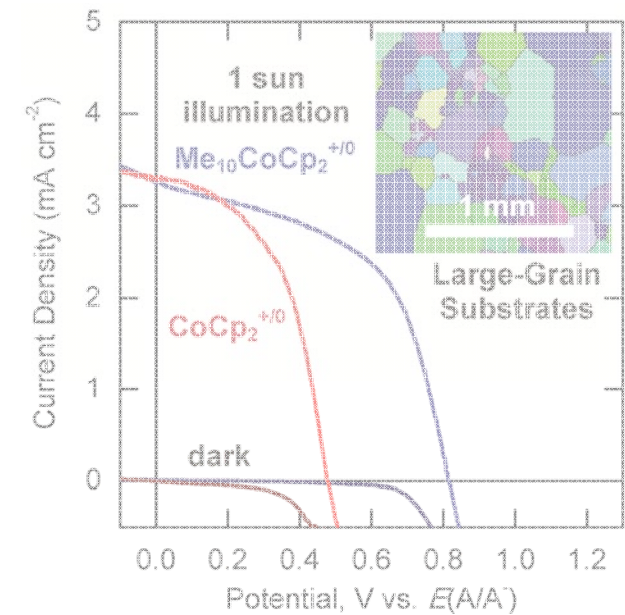
Cornering the market
for 'Solar-Grade' Zn_3P_2

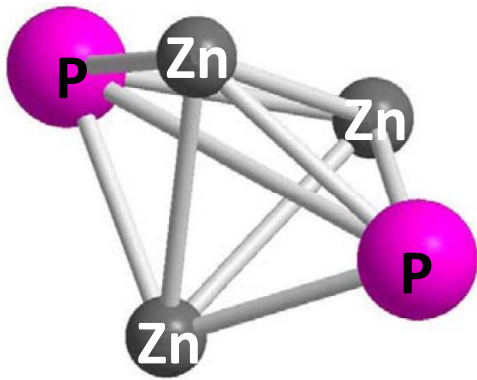


Why is annealing critical
in $\text{Mg}/\text{Zn}_3\text{P}_2$ solar cells?



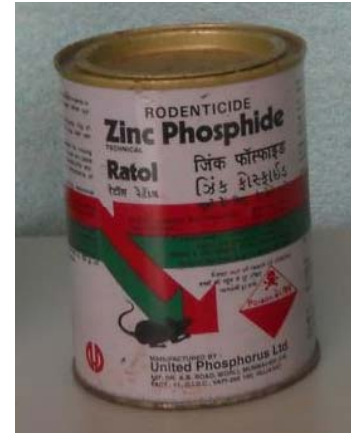
High performance
 Cu_2O /liquid junctions

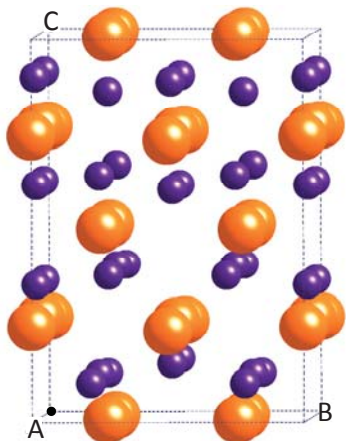




Zn₃P₂ for rodenticide

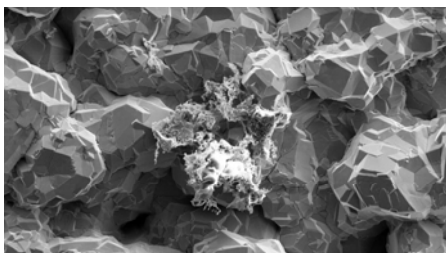
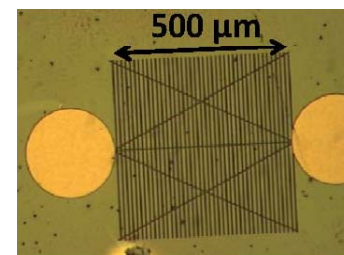
- Readily synthesized from zinc and phosphorus
- Selective for rodents, environmentally safe
- Market size: 100's of tons, 1000's of km² cropland
- Keeps rats off your roof!





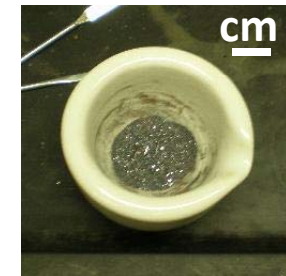
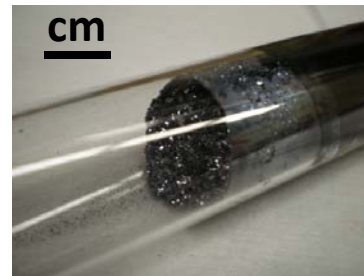
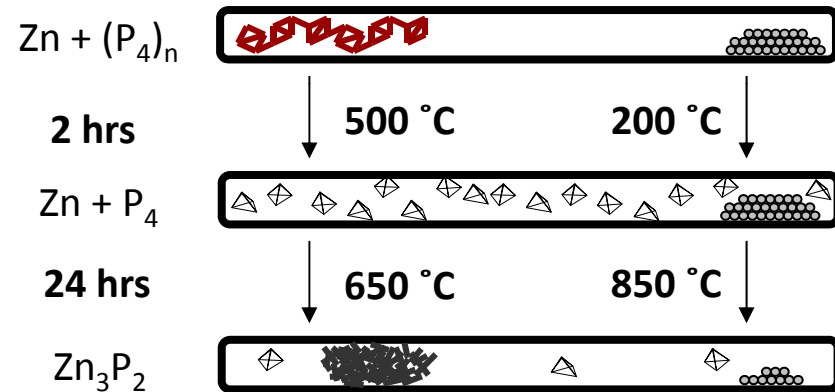
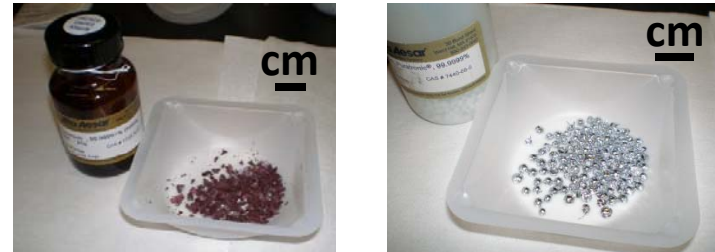
Zn₃P₂ for photovoltaics

- Readily synthesized from zinc and phosphorus
- Direct 1.5 eV band gap, environmentally safe
- Mg/Zn₃P₂ solar cells of 6% efficiency
- Keeps rats off your roof!

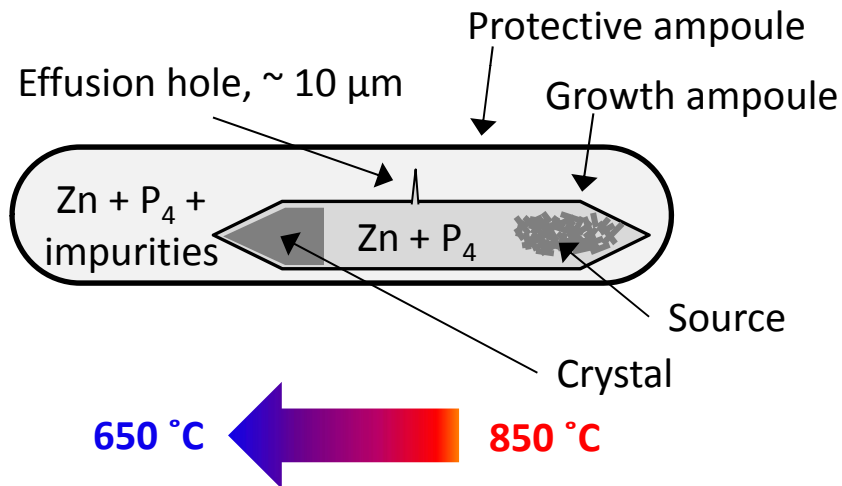
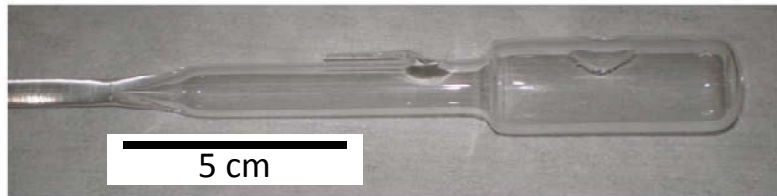


Zn_3P_2 from the elements

- High purity 99.9999% red phosphorus and zinc shot
- High temperature reaction in vacuum-sealed quartz tubes
- **Quantitative yield of 99.999+% Zn_3P_2 powders**



Preparing Zn_3P_2 substrates

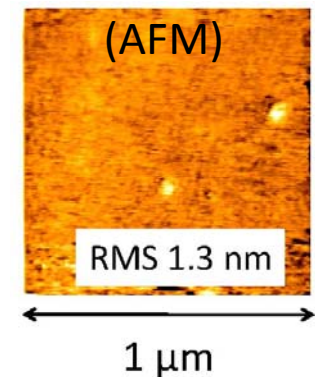


- Crystal growth by physical vapor transport (PVT) in vacuum-sealed quartz tubes
- Growth rates of $0.5 - 2.0 \text{ mm}\cdot\text{hr}^{-1}$

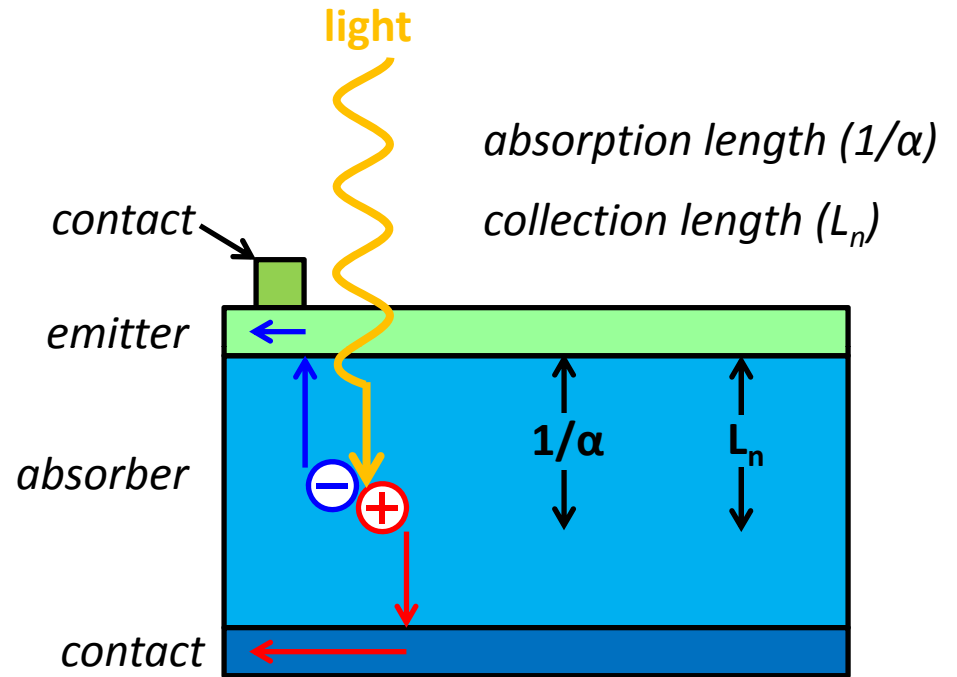
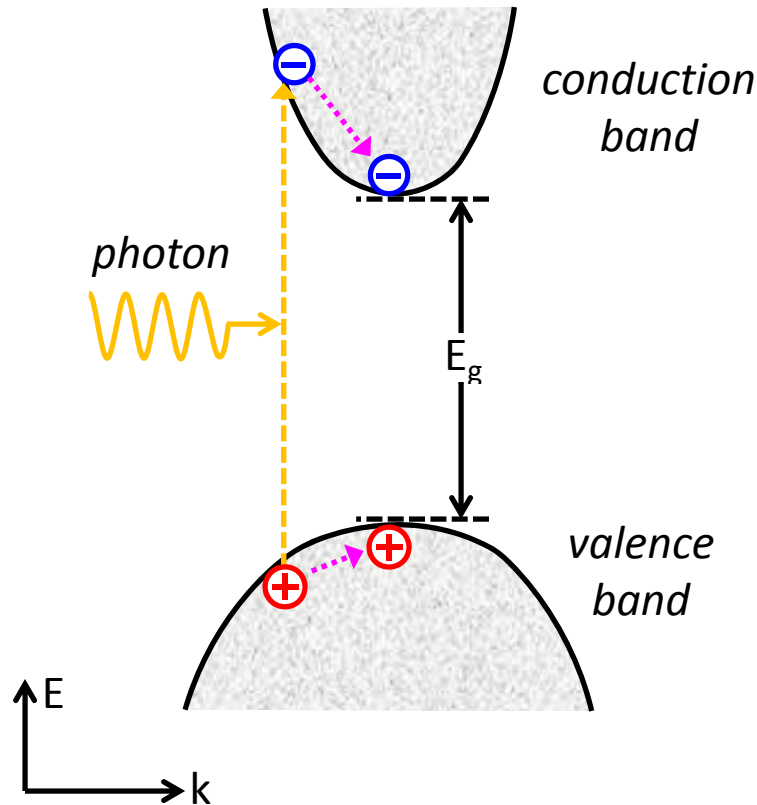
➤ **Large-grain, quasi-single crystals**



Lapping,
polishing



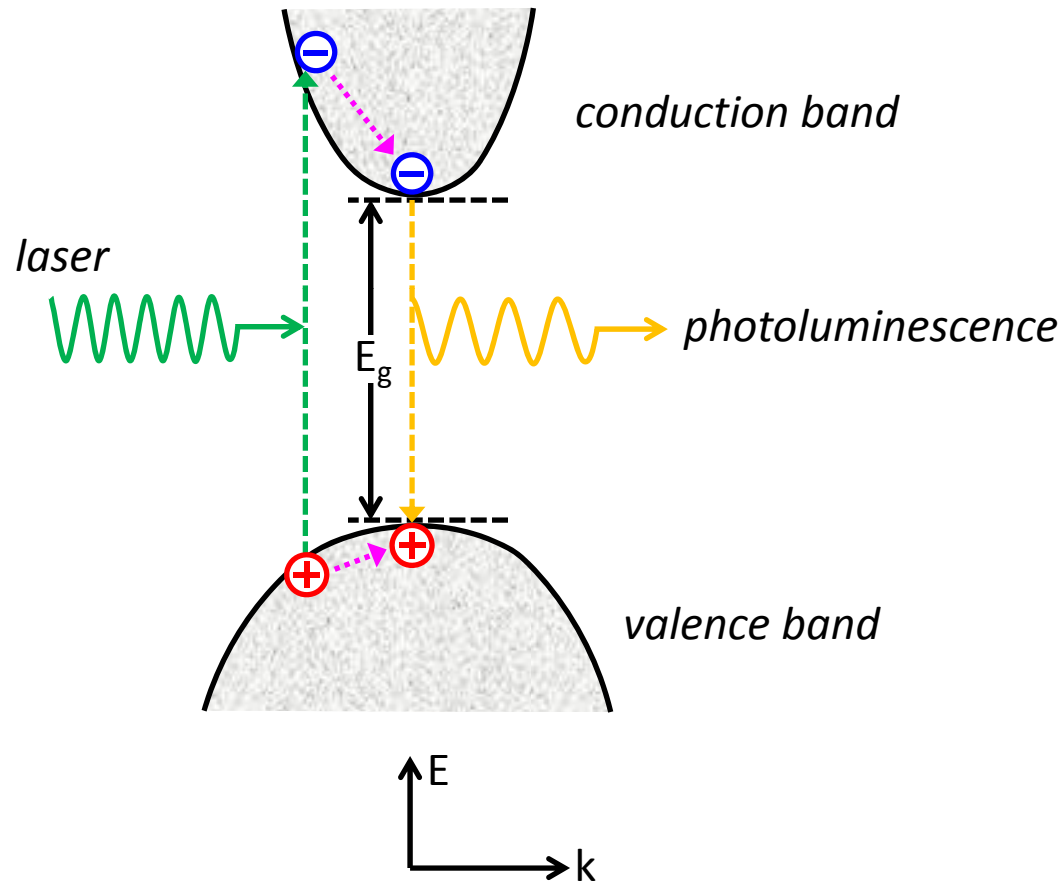
Properties of semiconductors



1. What is the fundamental band gap?
2. What is the absorption length? the collection length?
3. Can it be doped p-type? n-type?



Photoluminescence of semiconductors



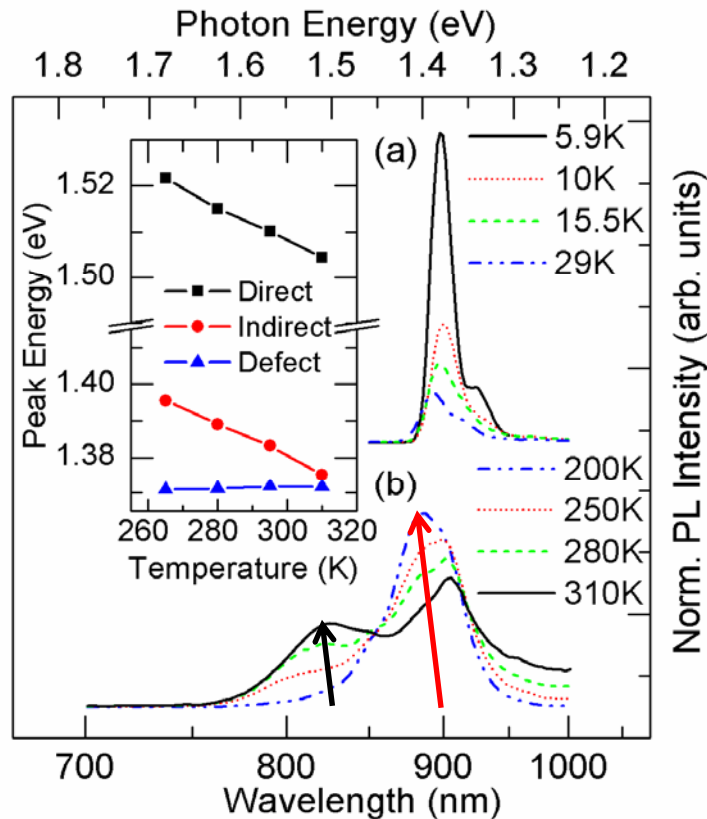
- Pump with light that is strongly absorbed
- Monitor light emission spectrum and intensity
- **Used to measure the band gap and to investigate carrier recombination**



G. M. Kimball, A. M. Müller, N. S. Lewis, H. A. Atwater, Appl. Phys. Lett. 95, 112103, 2009.

Temperature-dependent photoluminescence

Photoluminescence spectra



- Known direct transition at 1.50 eV
- At room temperature, the strongest emission is at 1.38 eV
- Is the luminescence due to defects or an indirect band gap?

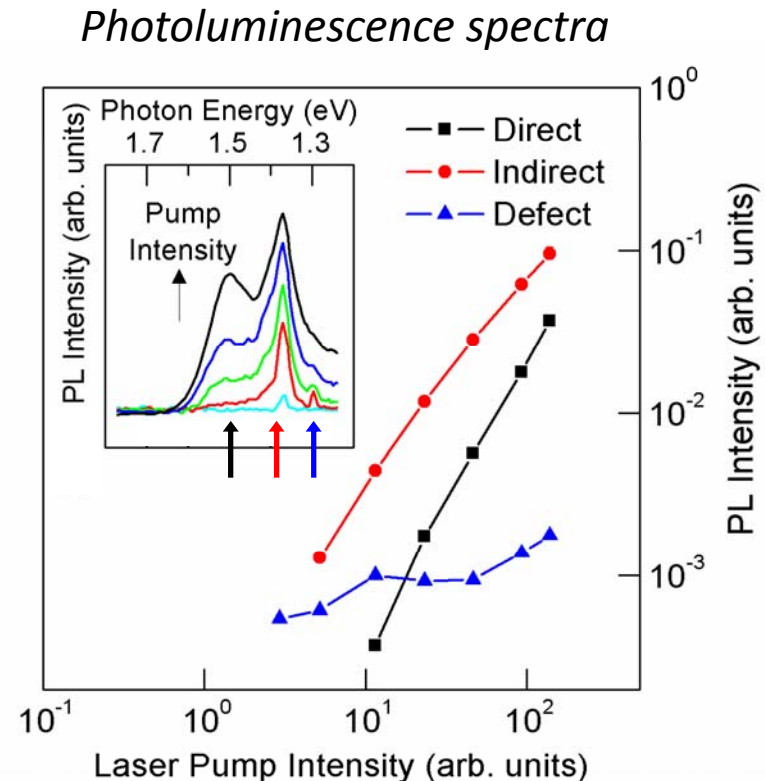
Evidence for indirect band gap at 1.38 eV



G. M. Kimball, A. M. Müller, N. S. Lewis, H. A. Atwater, Appl. Phys. Lett. 95, 112103, 2009.

Intensity-dependent photoluminescence

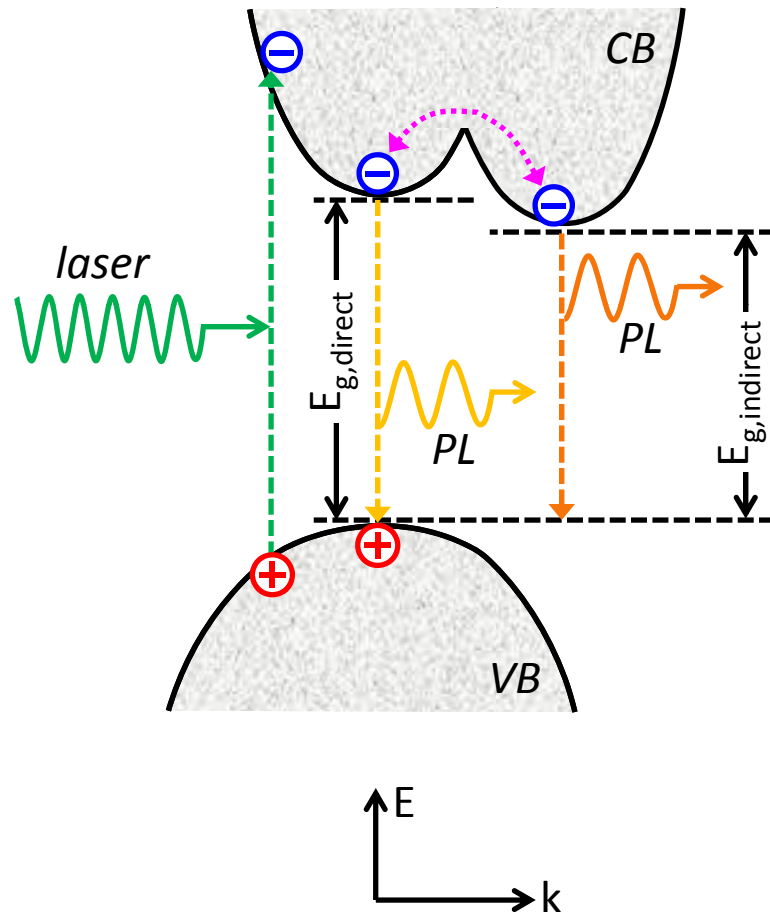
- Band edge luminescence
 - Dominates at high laser intensity
 - Constant peak positions
- Defect luminescence
 - Saturates at high laser intensity
 - Peak position blue shifts



Clear evidence for indirect band gap at 1.38 eV



Band structure of Zn_3P_2



- **$E_{g,\text{indirect}} = 1.38 \text{ eV}$ and $E_{g,\text{direct}} = 1.50 \text{ eV}$**
- Above 200 K there is thermal promotion of carriers from indirect to direct band gap
- Band gap values increase with cooling



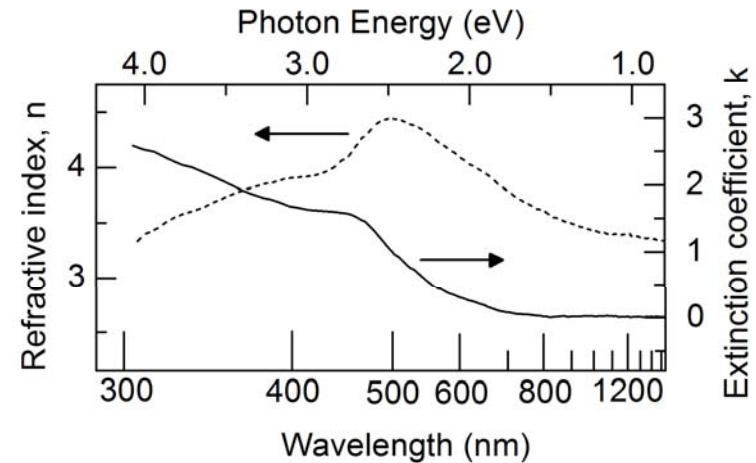
G. M. Kimball, A. M. Müller, N. S. Lewis, H. A. Atwater, Appl. Phys. Lett. 95, 112103, 2009.

Analysis by spectroscopic ellipsometry

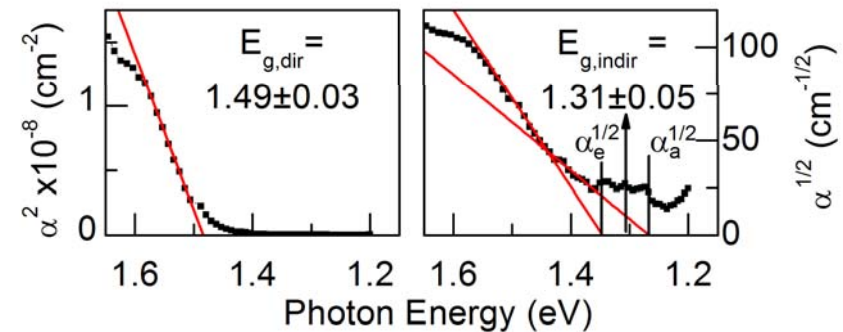
- Measured $n(\omega)$, $k(\omega)$ by spectroscopic ellipsometry
- Absorption coefficient:
$$\alpha \text{ (cm}^{-1}\text{)} = 4\pi k / \lambda$$
- Confirmed direct and indirect band gaps

➤ **Absorption length of 2 μm for 90% light absorption**

Real and imaginary refractive index

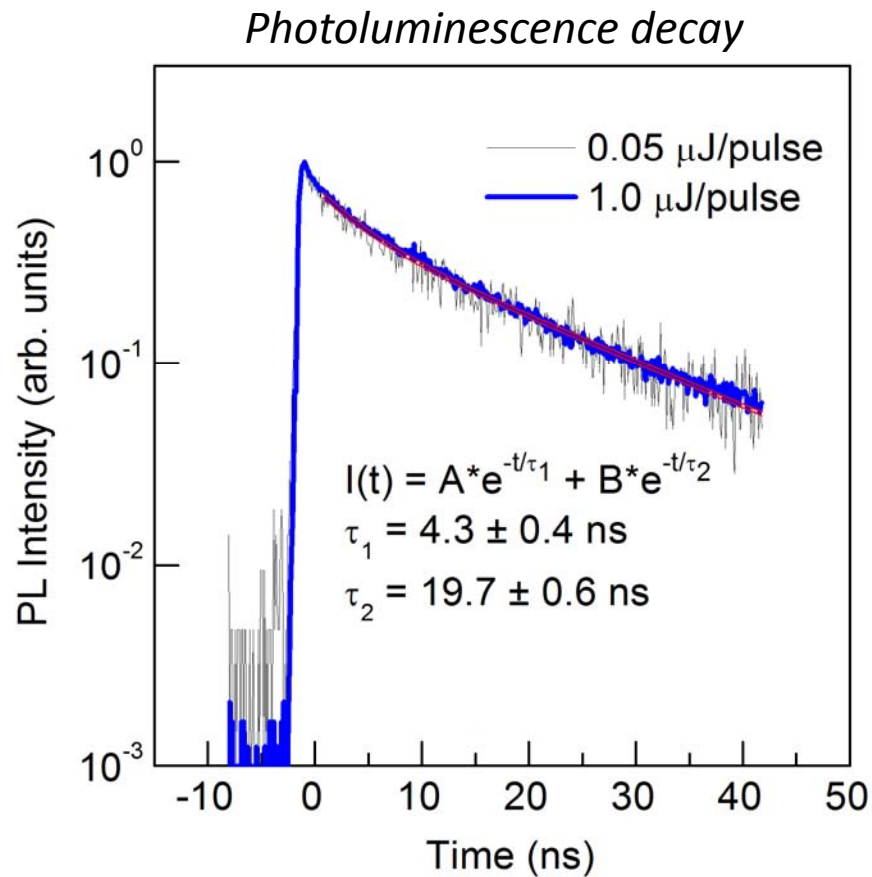


absorption spectra



G. M. Kimball, A. M. Müller, N. S. Lewis, H. A. Atwater, Appl. Phys. Lett. 95, 112103, 2009.

Time-resolved photoluminescence



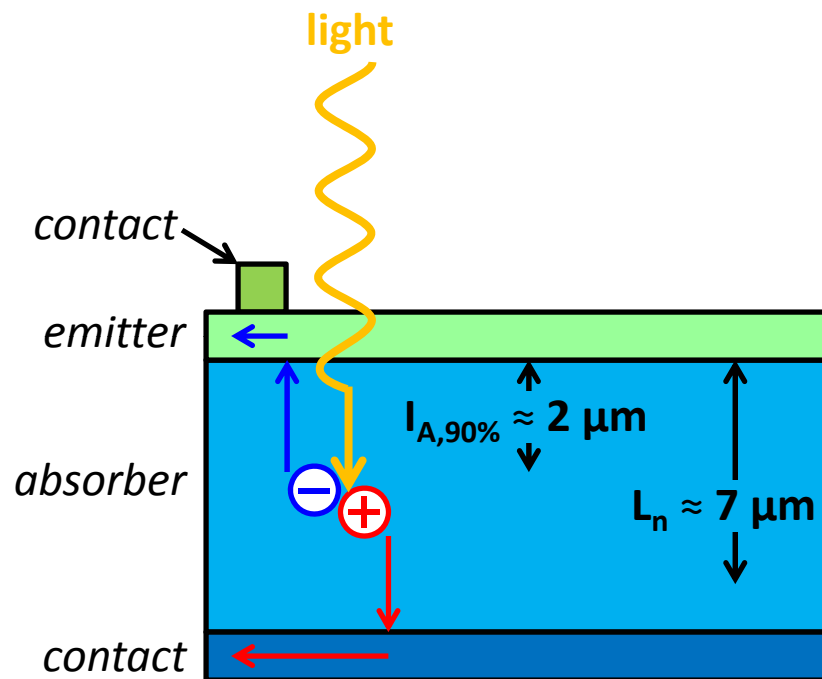
- Immediately after laser pulse, carrier recombination is surface-dominated ($\tau_{1,\text{surface}}$)
- At long times, the PL decay is limited by the bulk minority carrier lifetime ($\tau_{2,\text{bulk}}$)

Evidence for electron collection lengths $\geq 7 \mu\text{m}$



G. M. Kimball, A. M. Müller, N. S. Lewis, H. A. Atwater, Appl. Phys. Lett. 95, 112103, 2009.

Light absorption and carrier collection



- Absorption length $\approx 2 \mu\text{m}$ for 90% light absorption
- Collection length $\approx 7 \mu\text{m}$ for efficient carrier collection

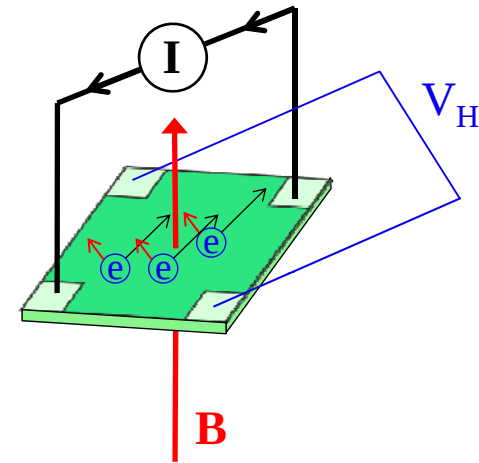
**Collection lengths ($7 \mu\text{m}$) > absorption lengths ($2 \mu\text{m}$)
for high quality Zn_3P_2 substrates**



G. M. Kimball, A. M. Müller, N. S. Lewis, H. A. Atwater, Appl. Phys. Lett. 95, 112103, 2009.

Doping experiments and the Hall effect

- Nominally undoped substrates exhibit low p-type doping
- P and Ag act as p-type dopants
- **Control of p-type doping from $10^{13} - 10^{18} \text{ holes}\cdot\text{cm}^{-3}$**



Hall effect measurements

Dopant	Anneal Ambient	$p \text{ (cm}^{-3}\text{)}$	$\mu_p \text{ (cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}\text{)}$
none	none	$10^{13} - 10^{14}$	16 ± 3
none	P ₄	$3.7 \pm 0.4 \times 10^{16}$	12 ± 1
Ag (1.3 nm)	P ₄	$3.0 \pm 0.1 \times 10^{17}$	14 ± 1
Ag (12 nm)	P ₄	$7.6 \pm 0.8 \times 10^{17}$	17 ± 2
Ag (80 nm)	P ₄	$7.5 \pm 0.4 \times 10^{17}$	17 ± 1

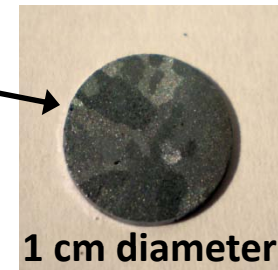
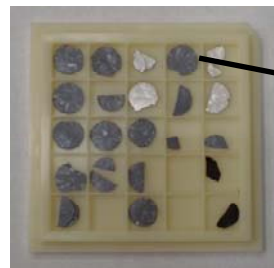
G. M. Kimball, N. S. Lewis, H. A. Atwater. Thirty-fifth IEEE PVSC, 2010.



Cornering the market for 'Solar-Grade' Zn_3P_2

- Revealed $E_{g,\text{indirect}} = 1.38 \text{ eV}$ and $E_{g,\text{direct}} = 1.50 \text{ eV}$
- Active region of $\geq 7 \mu\text{m}$ for solar energy conversion
- Control of p-type doping from $10^{13} - 10^{18} \text{ holes}\cdot\text{cm}^{-3}$

➤ **Dominating 'Solar-Grade' Zn_3P_2 Since 2008**

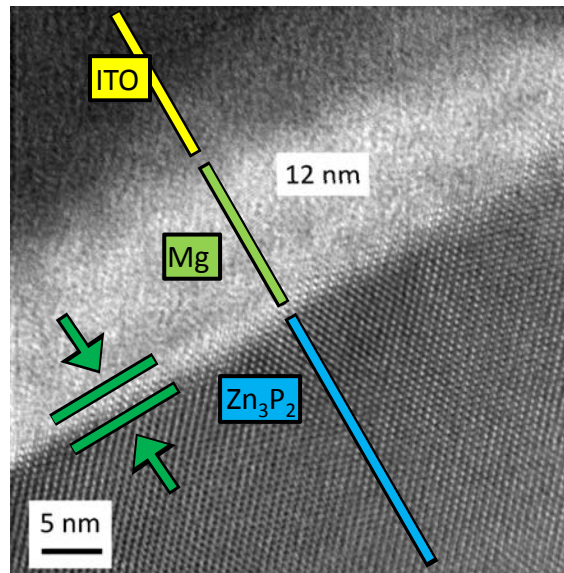


Zn_3P_2 and Cu_2O substrates for solar energy conversion

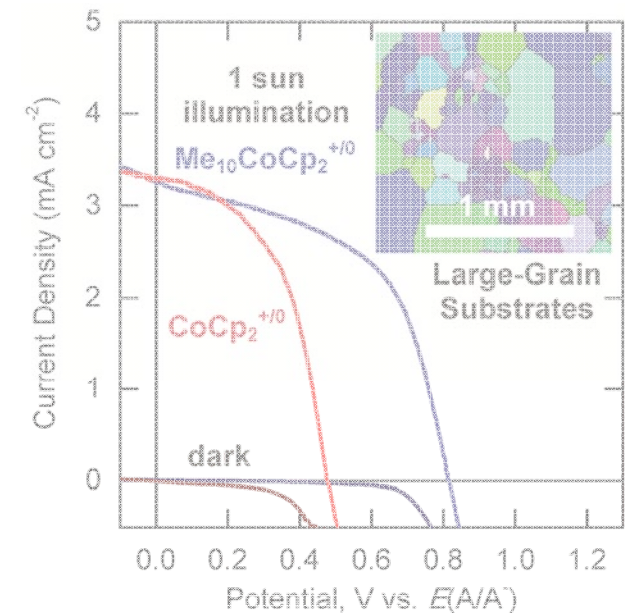
Cornering the market
for 'Solar-Grade' Zn_3P_2



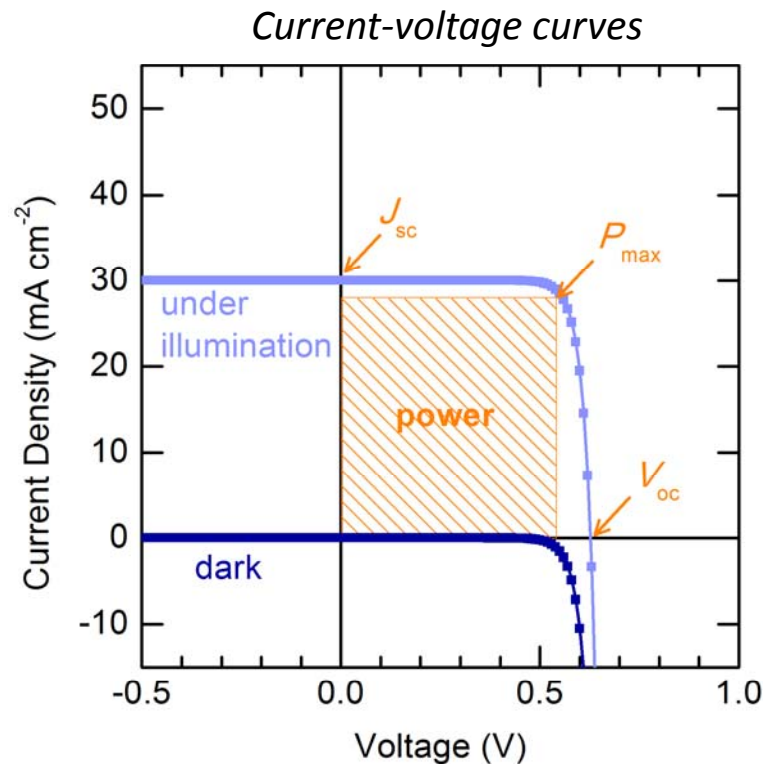
Why is annealing critical
in $\text{Mg}/\text{Zn}_3\text{P}_2$ solar cells?



High performance
 Cu_2O /liquid junctions



Ideal solar cell performance



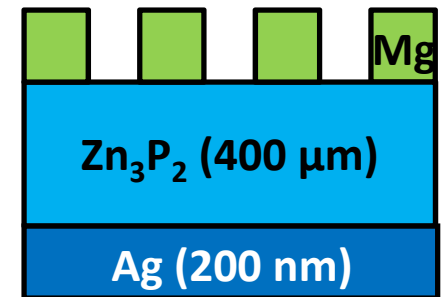
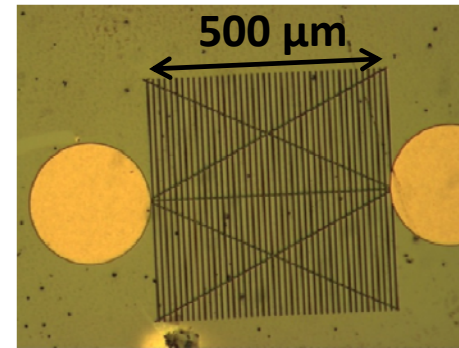
- Photons generate electron-hole pairs which are collected as current in the solar cell.
 - Higher quality junctions extract more voltage for each electron-hole pair.
- **Improve current collection and junction quality to maximize power.**



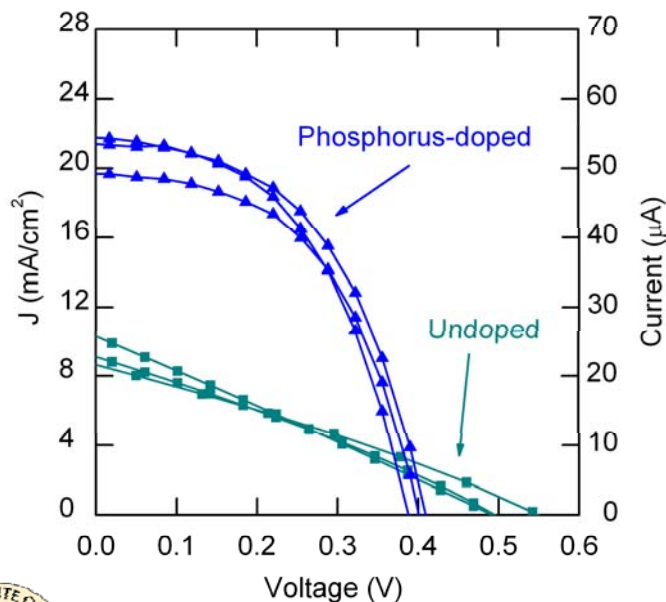
G. M. Kimball, N. S. Lewis, H. A. Atwater, *Thirty-fifth IEEE PVSC*, 2010.

Mg/Zn₃P₂ solar cell performance

**Zn₃P₂ substrates
incorporated in solar cells
reaching 4.5% efficiency**



Current-voltage curves



Solar cell parameters

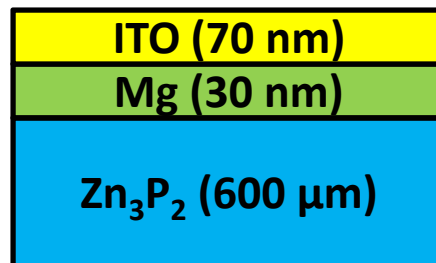
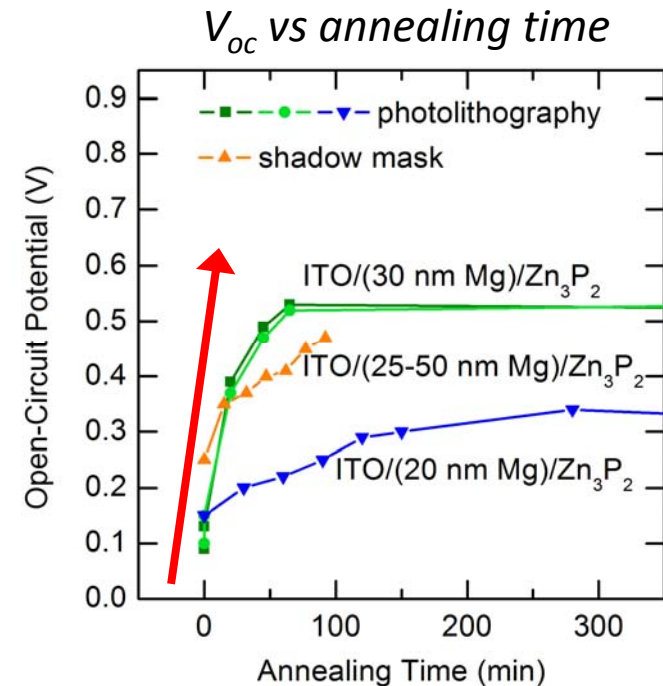
Sample	J_{sc} (mA·cm ⁻²)	V_{oc} (V)	FF	η (%)
Undoped	8.5	0.55	0.29	1.38
Undoped	10.3	0.49	0.26	1.31
Undoped	9.1	0.50	0.29	1.30
P-doped	21.8	0.39	0.50	4.20
P-doped	21.4	0.41	0.51	4.48
P-doped	19.7	0.40	0.52	4.08
Record	14.9	0.49	0.71	5.96



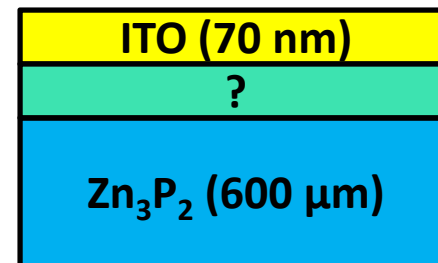
Annealing ITO/Mg/Zn₃P₂ solar cells

➤ **Zn₃P₂ solar cells show large V_{oc} improvements with annealing**

- What causes the poor initial performance?
- How does annealing change the Zn₃P₂ solar cell?

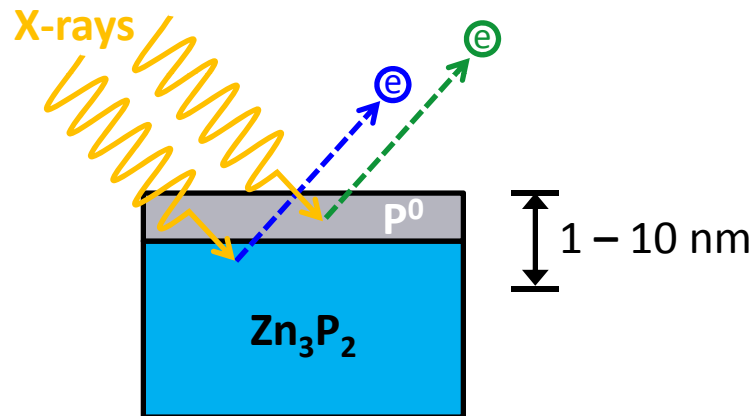


100 °C,
in air



Evaluating etched Zn_3P_2

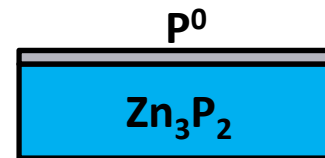
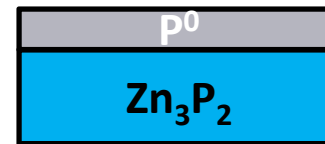
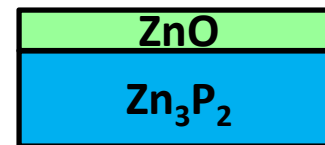
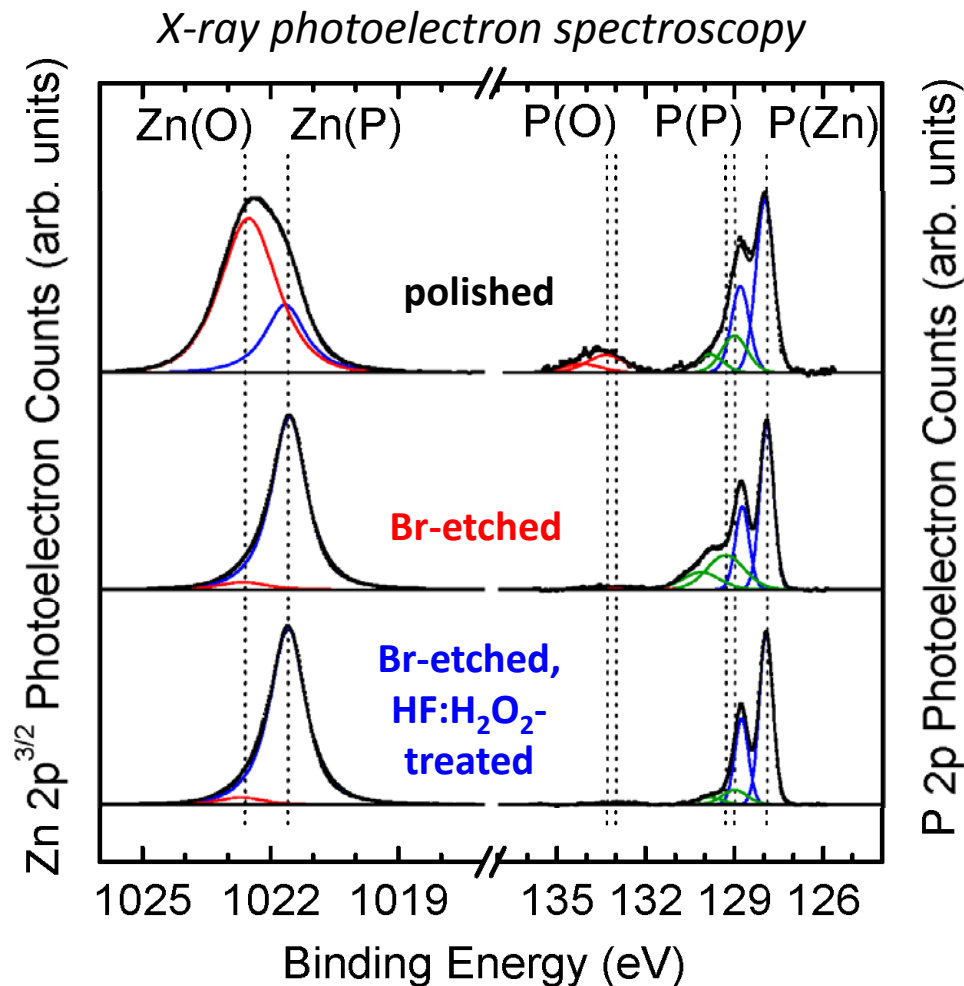
X-ray photoelectron spectroscopy



- What is the surface composition of freshly etched Zn_3P_2 ?
- Which elements are there and what are they bonded to?
- **X-ray photoelectron spectroscopy (XPS) probes the first 1 – 10 nm of surface atoms**



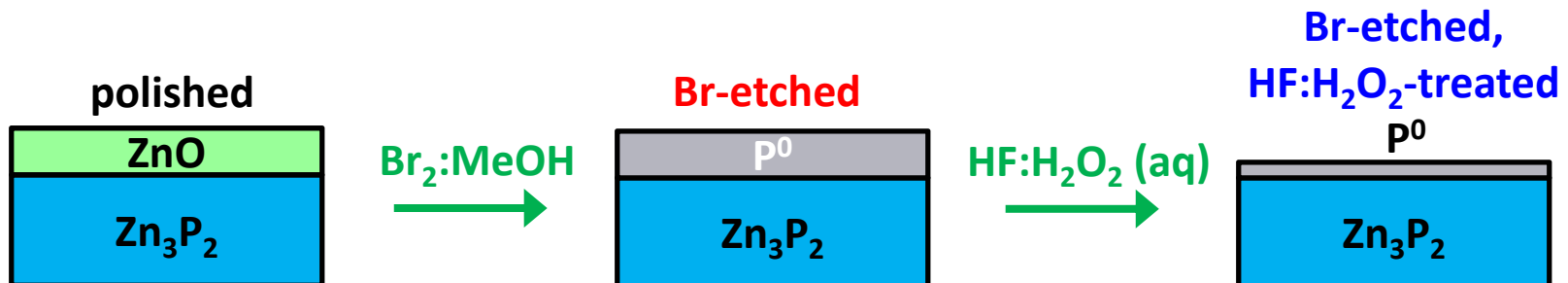
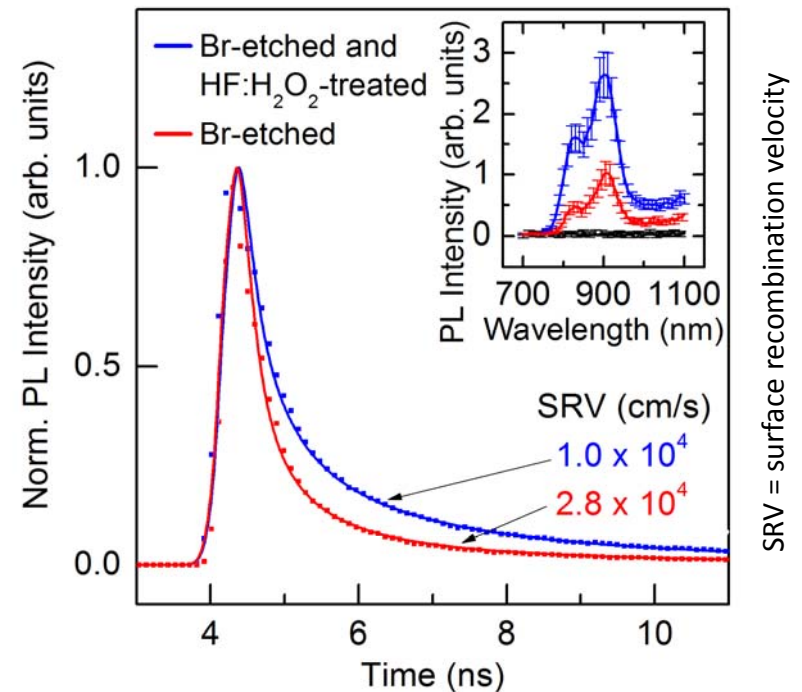
Evaluating etched Zn_3P_2



Evaluating etched Zn_3P_2

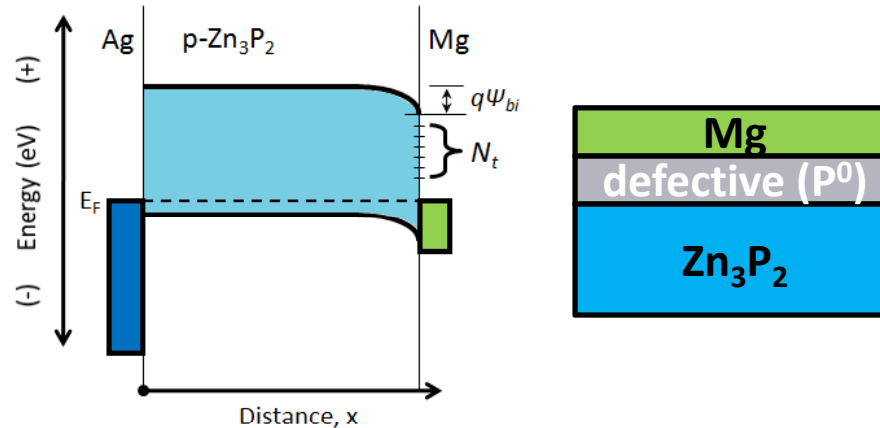
- $\text{Br}_2:\text{MeOH}$ etching enables room temperature PL measurements
- $\text{HF}:\text{H}_2\text{O}_2$ (aq) treatment enhances PL intensity
- **Removal of surface P^0 correlates with fewer surface defects**

Photoluminescence decays and spectra

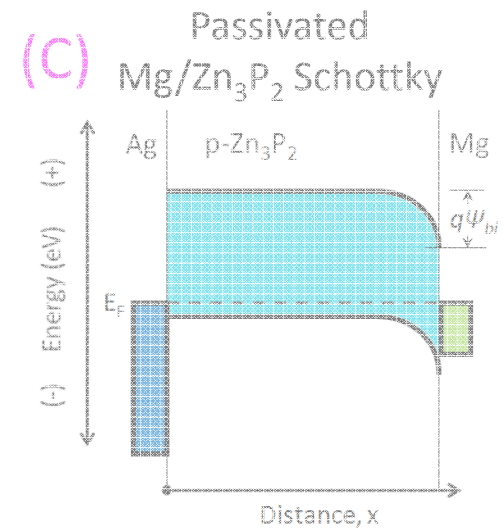
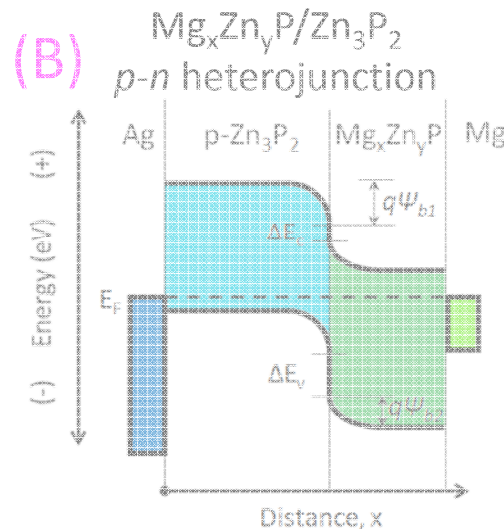
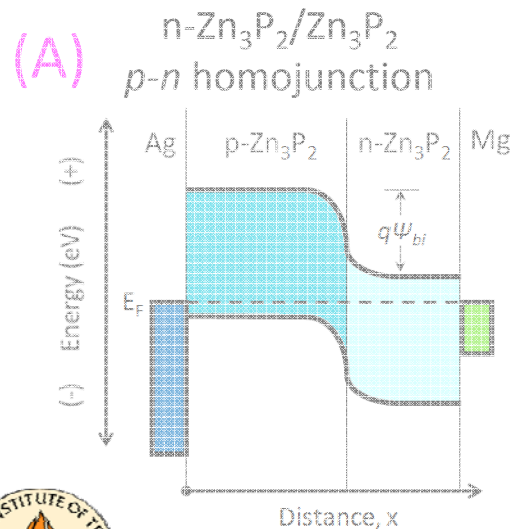


Why is annealing critical?

As-fabricated,
 V_{oc} less than 100 mV

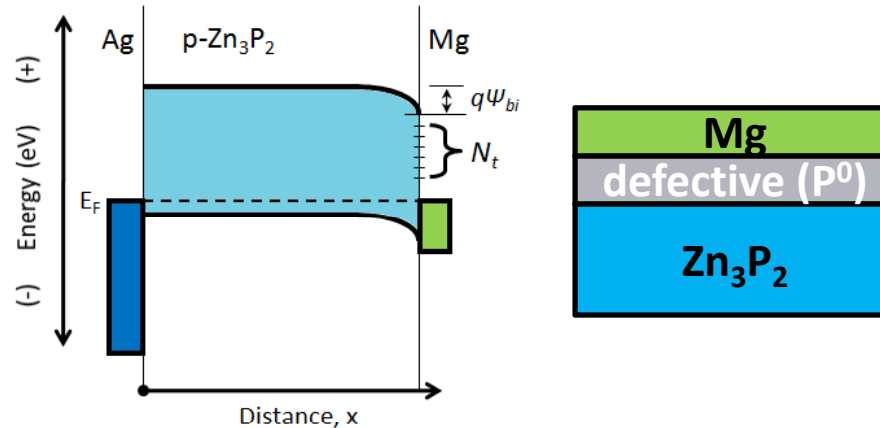


? **Anneal, 100 °C** ?

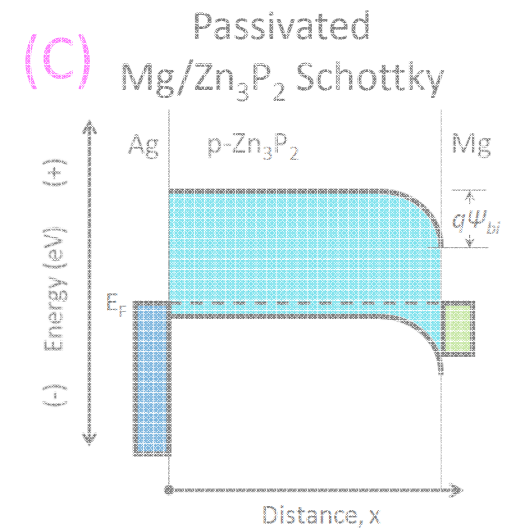
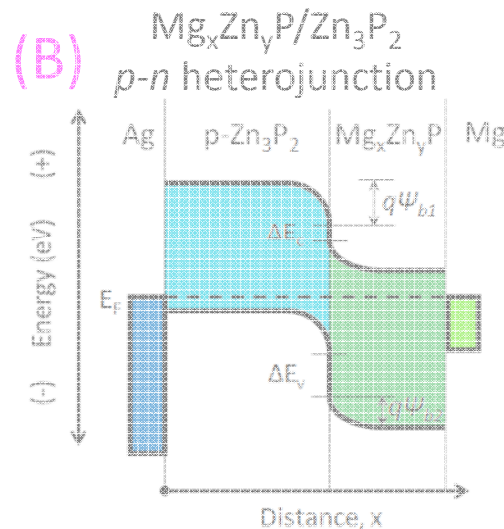
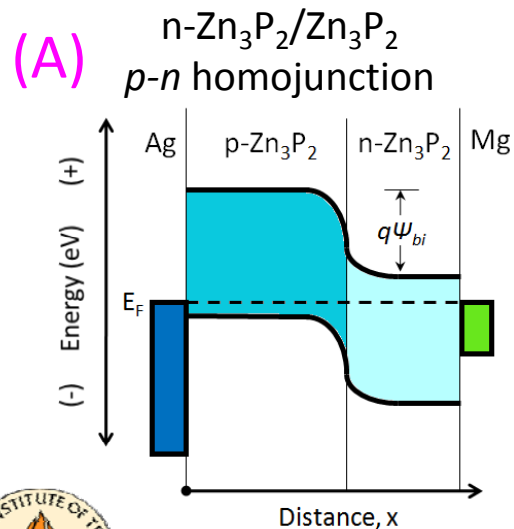


Why is annealing critical?

As-fabricated,
 V_{oc} less than 100 mV

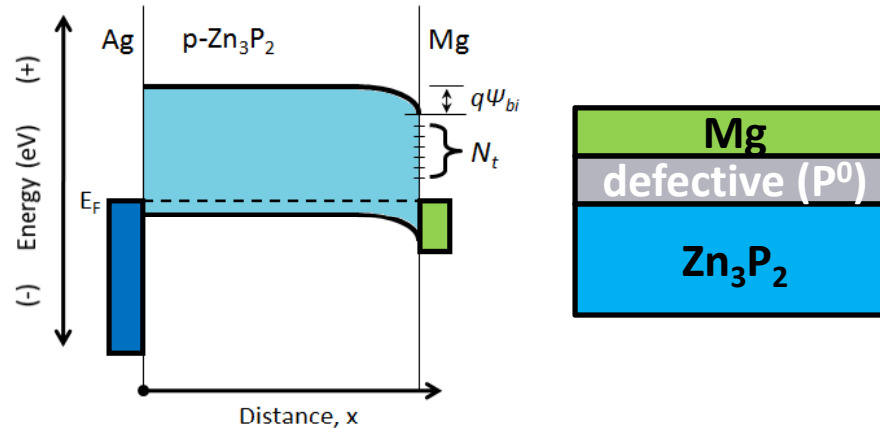


? **Anneal, 100 °C** ?

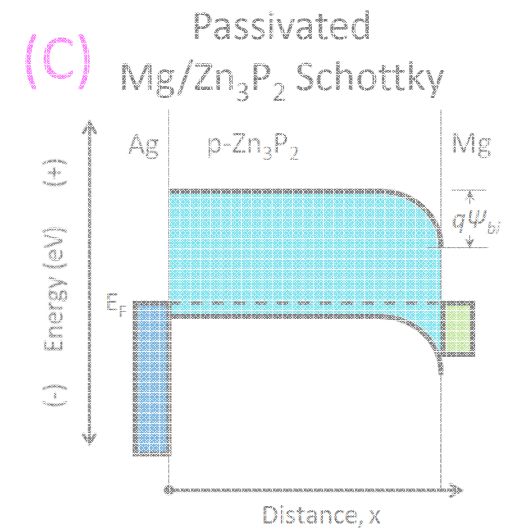
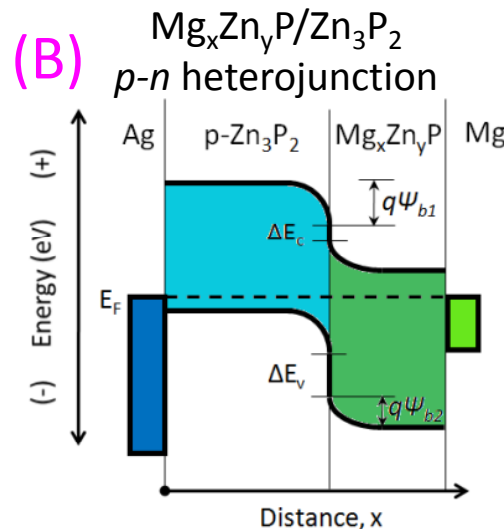
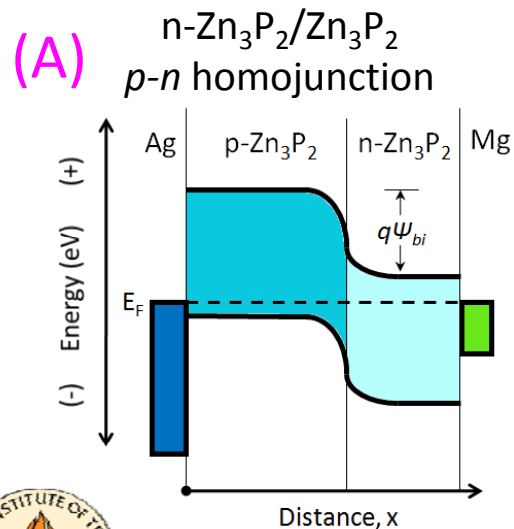


Why is annealing critical?

As-fabricated,
 V_{oc} less than 100 mV

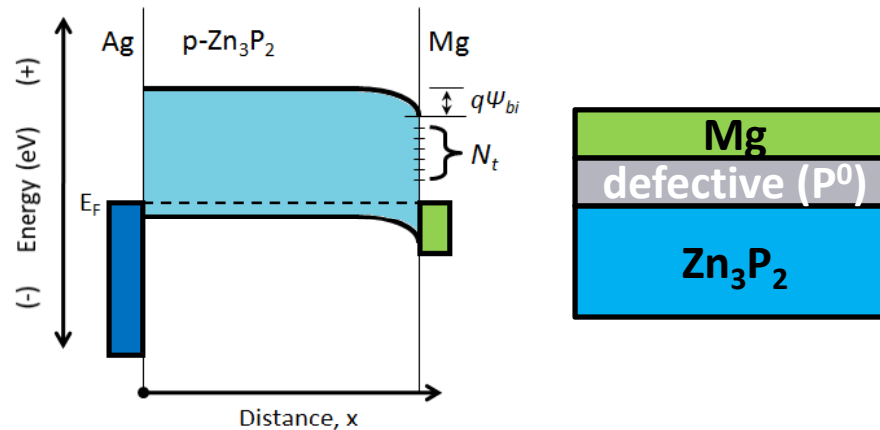


? **Anneal, 100 °C** ?

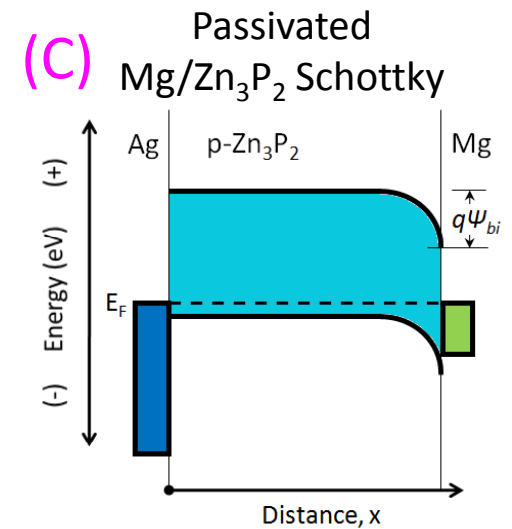
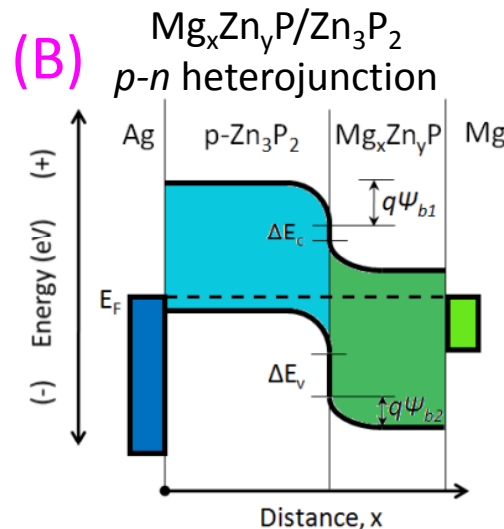
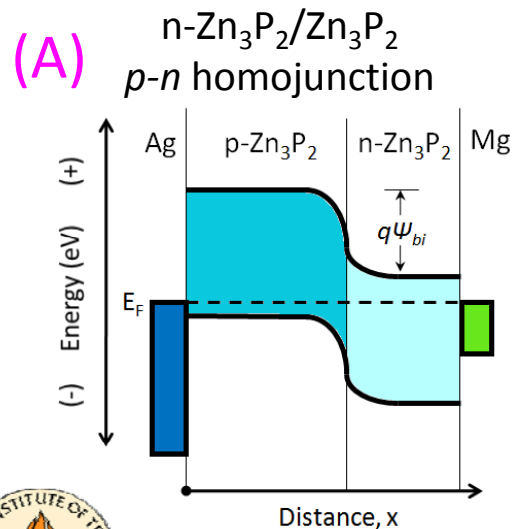


Why is annealing critical?

As-fabricated,
 V_{oc} less than 100 mV



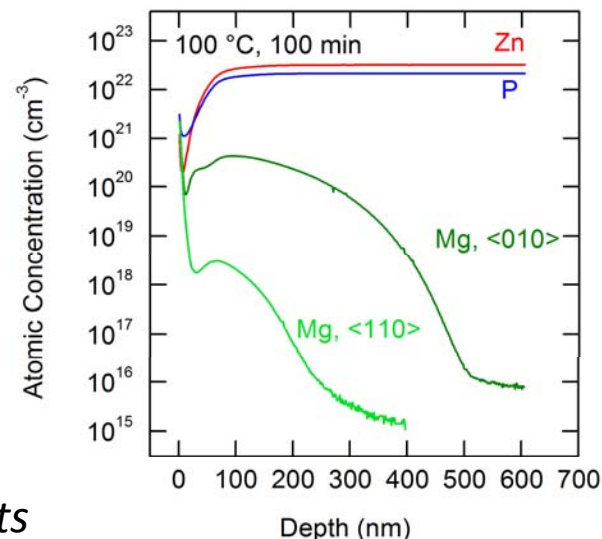
? **Anneal, 100 °C** ?



(A) Evaluating Mg-doped Zn_3P_2

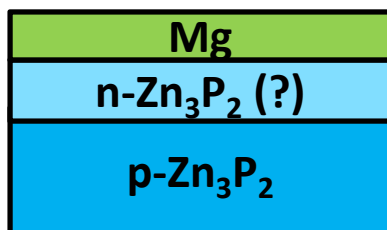
- Mg diffuses readily into Zn_3P_2
- Substrates with Mg impurities were resistive with low p-type conductivity
- **p-n homojunction formation is unlikely**

Secondary Ion Mass Spectrometry



Hall effect measurements

p-n homojunction?



Dopant	Anneal Ambient	p (cm ⁻³)	μ_p (cm ² ·V ⁻¹ ·s ⁻¹)
none	none	$10^{13} - 10^{14}$	16 ± 3
none	P ₄	$3.7 \pm 0.4 \times 10^{16}$	12 ± 1
Mg (80 nm)	P ₄	$3.8 \pm 0.8 \times 10^{13}$	19 ± 3
Mg (80 nm)	P ₄ + Mg	$5.4 \pm 0.8 \times 10^{13}$	41 ± 18
Mg (80 nm)	Vacuum	$6.0 \pm 3.2 \times 10^{12}$	48 ± 25
Mg (80 nm)	Mg	$1.5 \pm 0.4 \times 10^{14}$	9 ± 2

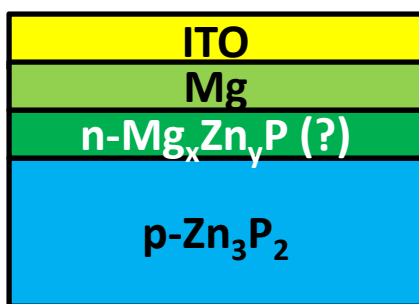
G. M. Kimball, N. S. Lewis, H. A. Atwater, *Thirty-fifth IEEE PVSC*, 2010.



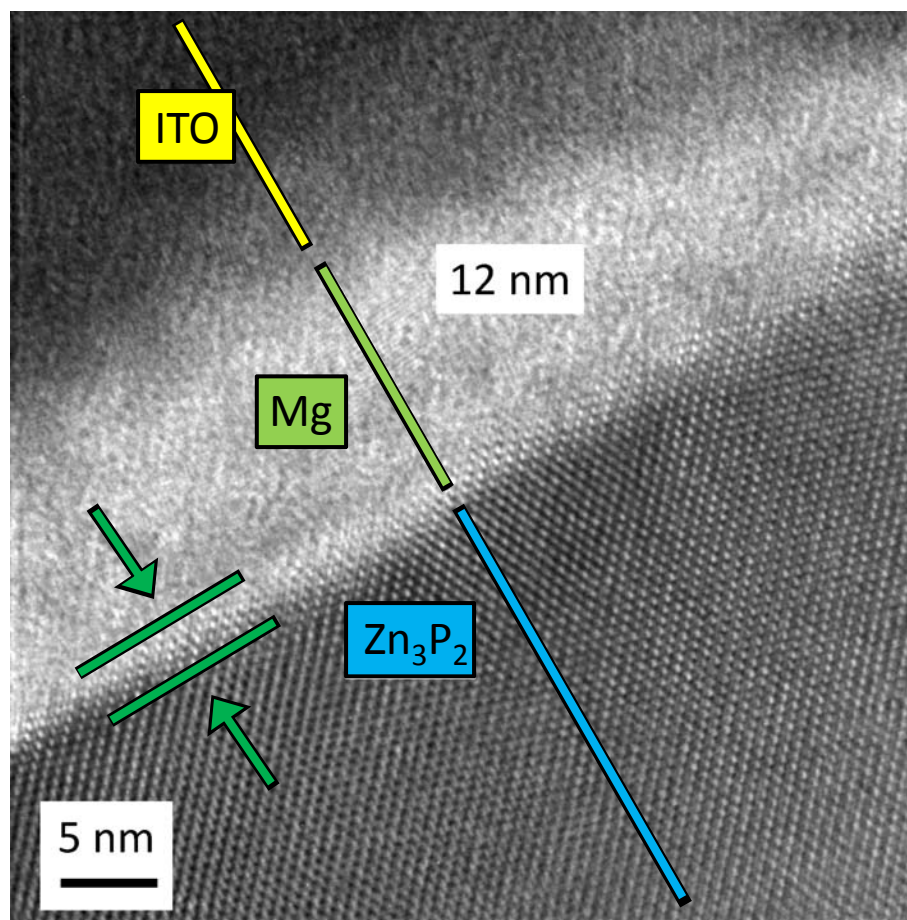
(B) Evaluating Mg-Zn-P Heterojunctions

TEM analysis shows abrupt
(< 5 nm) interface in
ITO/Mg/Zn₃P₂ solar cells

p-n heterojunction?



Transmission electron microscopy cross-section



Annealed at 100 °C in air for 100 min

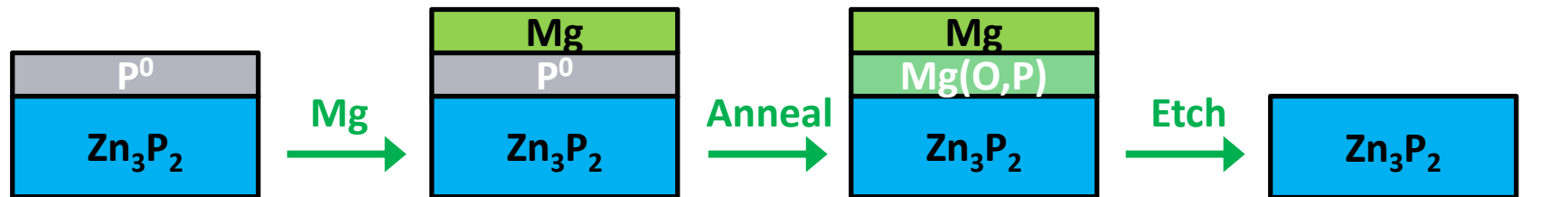
G. M. Kimball, (in preparation), 2011.



(C)

Evaluating Mg passivation

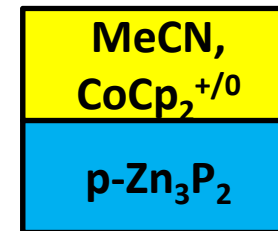
defective surface



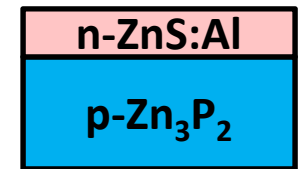
passivated surface

- Freshly etched Zn_3P_2 has a defective surface
- **Mg/ Zn_3P_2 undergoes a solid-state passivation reaction that improves V_{oc}**
- Passivated Zn_3P_2 can then be incorporated into solar cell

Make a solar cell



Liquid contact



Solid-state contact

Mg (200 nm) deposited on Br-etched Zn_3P_2 , annealed at 100 °C for 90 min, and removed in 10 mM EDTA/10% H_2O_2 (aq, pH 10).

G. M. Kimball, (in preparation), 2011.



(C)

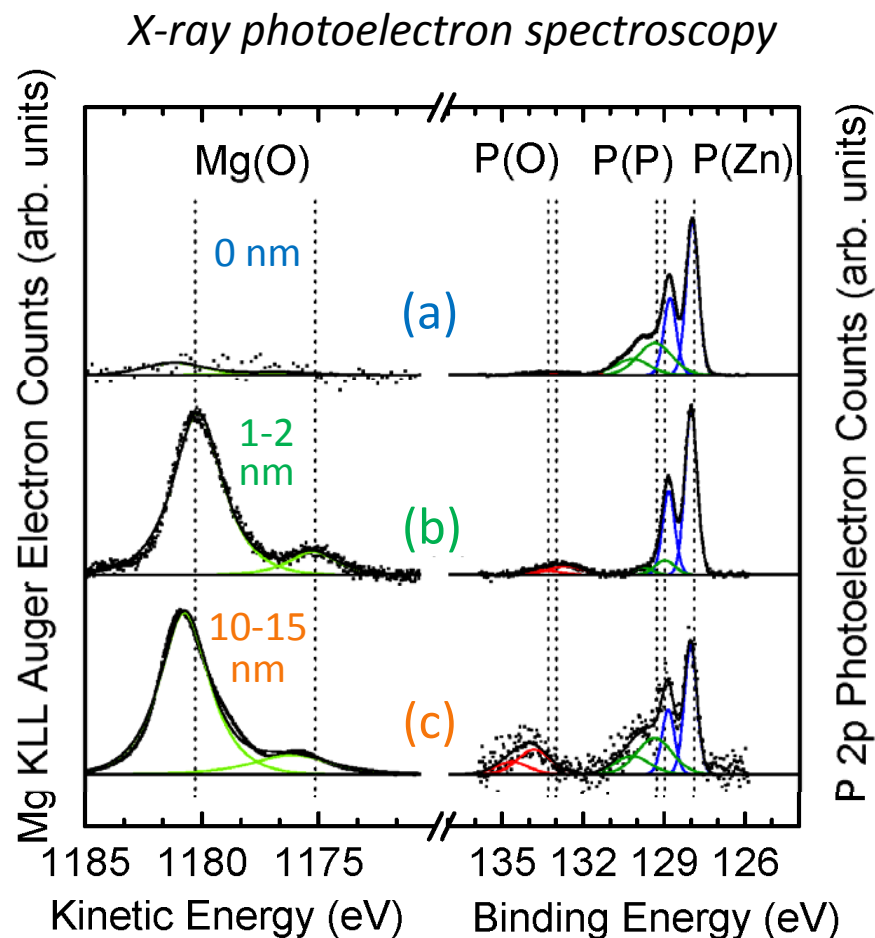
Surface analysis of Mg passivation

- (a) Etched with $\text{Br}_2:\text{MeOH}$
- (b) Mg treated, etched with EDTA (aq), 15 sec
- (c) Mg treated, etched with EDTA: H_2O_2 (aq), 60 sec

Mg treatment appears to remove (P^0) and surface defects

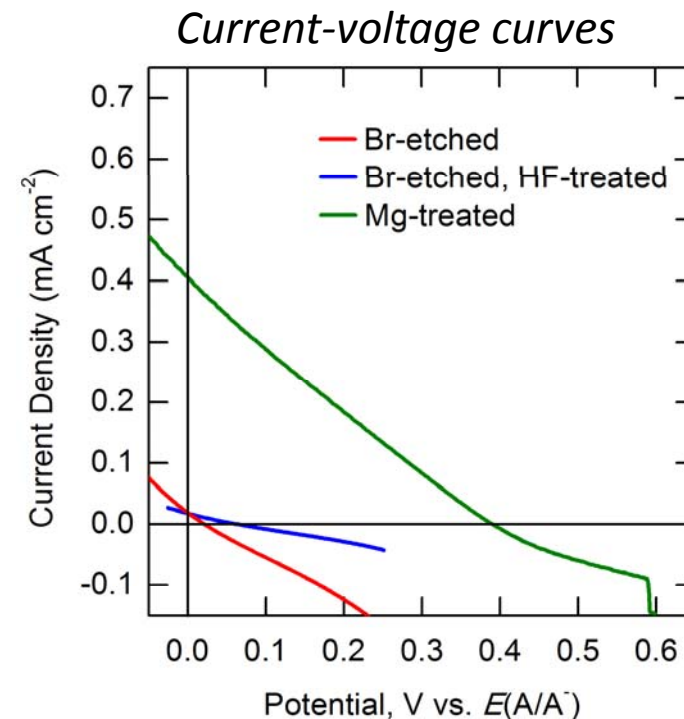
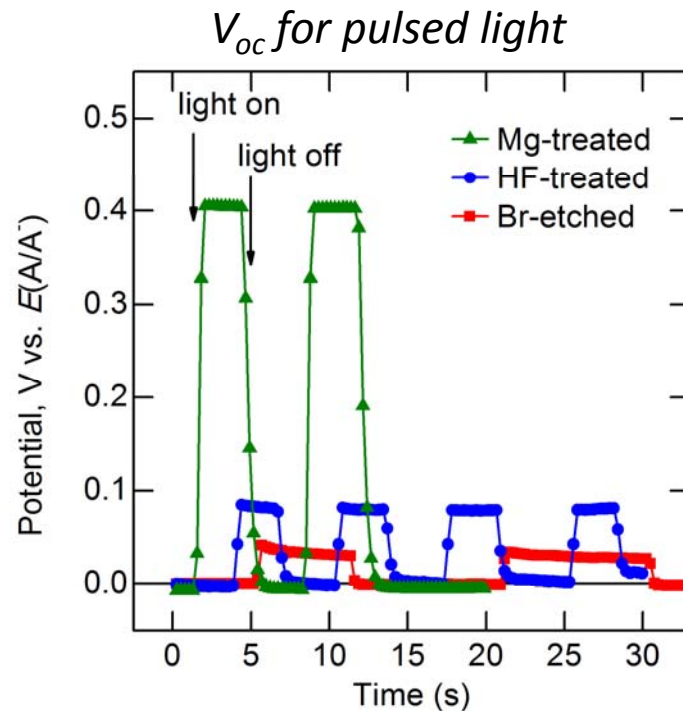
Mg treatment:

1. Br-etched Zn_3P_2 metallized with 200 nm Mg
2. Substrates annealed at 100 °C for 90 min
3. Mg removed in 10 mM EDTA/10% H_2O_2 (aq, pH 10).



(C)

Effect of Mg treatment



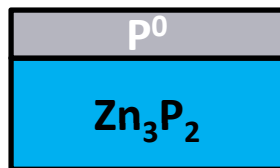
- Freshly etched Zn_3P_2 yields V_{oc} values < 100 mV
- **Mg-treatment yields V_{oc} values reaching 400 mV**
- Residual MgO introduces significant series resistance



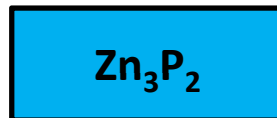
The Future of Zn_3P_2 passivation

- Nonaqueous Mg etching chemistry to reduce the formation of resistive MgO
- Reactive metals other than Mg to yield more complete passivation with fewer side effects
- **Mg passivation opens up new approaches to high performance Zn_3P_2 solar cells!**

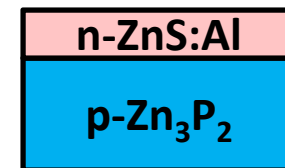
defective surface



passivated surface



solid-state contact

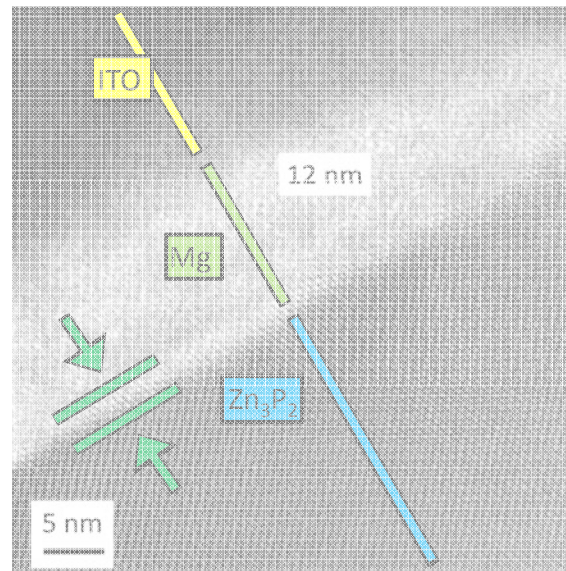


Zn_3P_2 and Cu_2O substrates for solar energy conversion

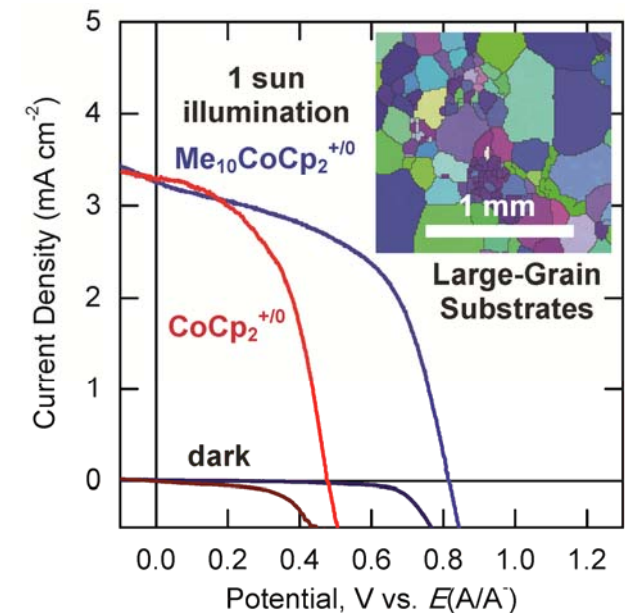
Cornering the market
for 'Solar-Grade' Zn_3P_2



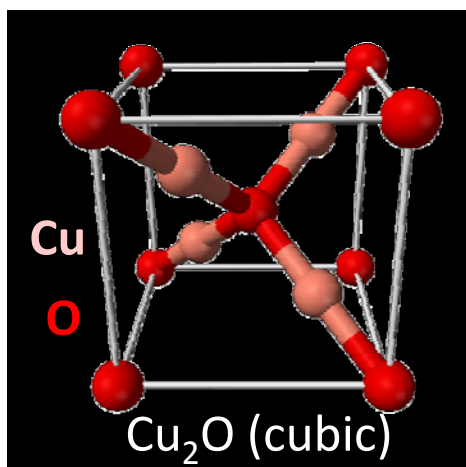
Why is annealing critical
in $\text{Mg}/\text{Zn}_3\text{P}_2$ solar cells?



High performance
 Cu_2O /liquid junctions



Cu₂O: Wide Band Gap Material

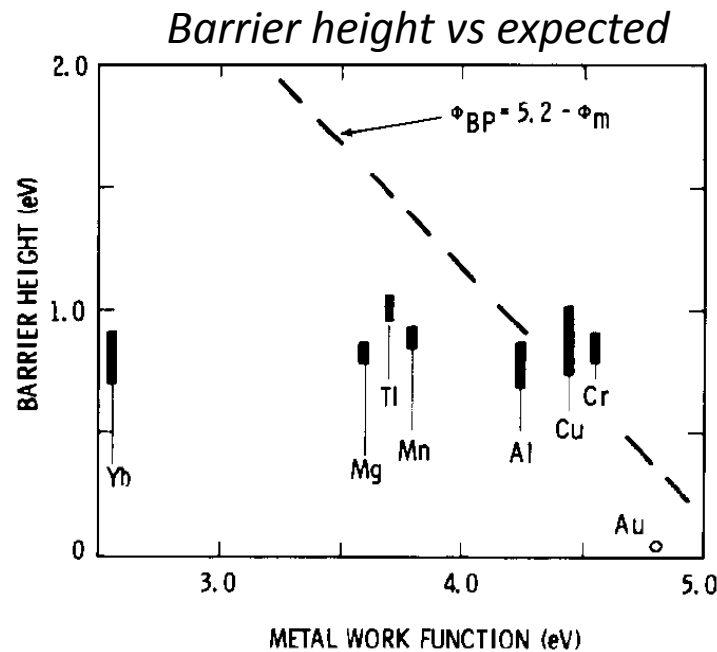


Progress from the 1980s

- Direct band gap at 2.0 eV
- Cu/Cu₂O diodes of 1.8% efficiency
- Oxidized from Cu metal
- Promising for two-junction solar cell

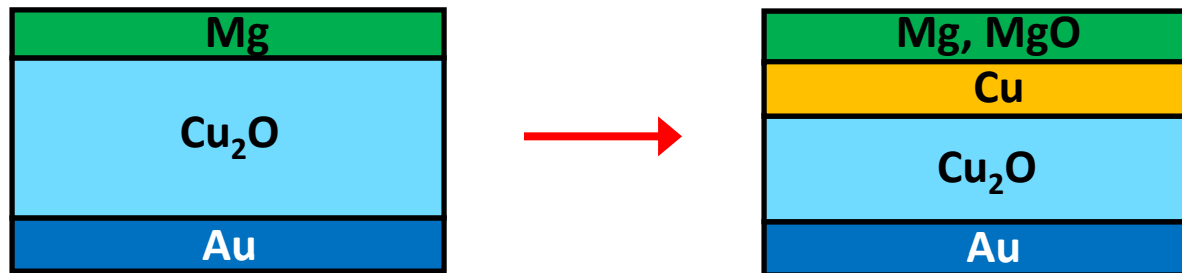


Are stable, high barrier contacts possible?



- Cu precipitation limits the V_{oc} to 300 – 400 mV in Cu_2O diodes
- Occurs spontaneously at reducing interfaces

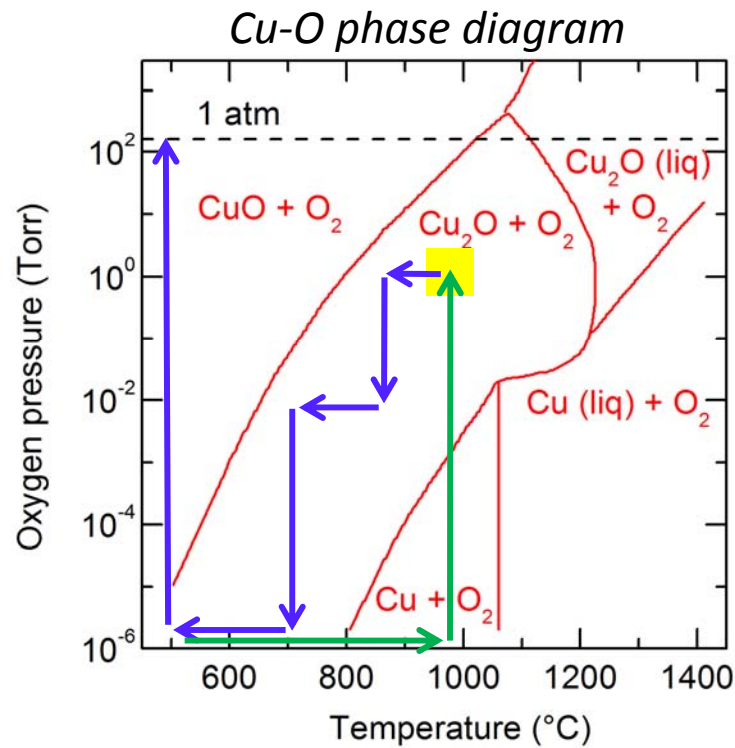
➤ **Preventing interfacial Cu would allow higher performance**



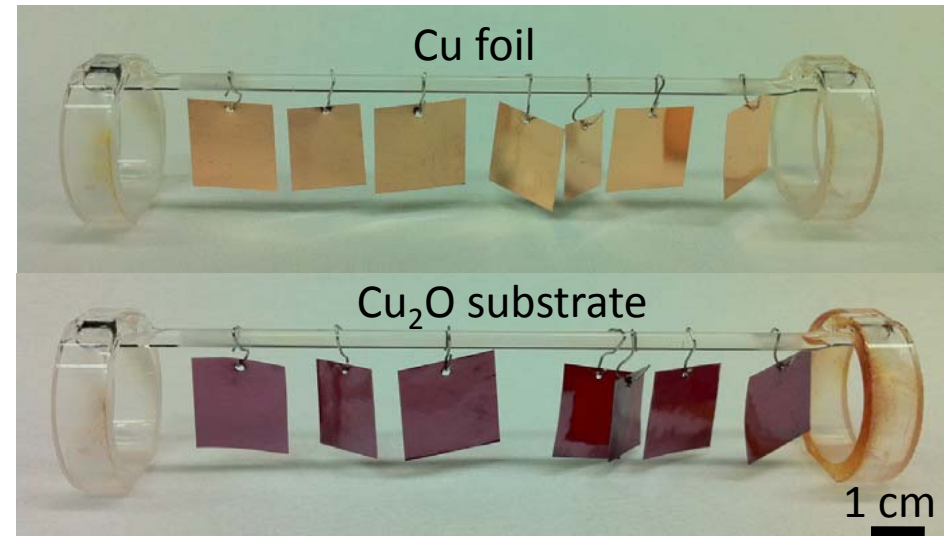
L. C. Olsen, R. C. Bohara, M. W. Urie, Appl. Phys. Lett. 34, 1, 1979.
L. C. Olsen, W. Miller, Solar Cells, 7, 247 – 279, 1982.



Cu_2O from the elements



■ 980 °C, 6 Torr O_2 for 2 hrs



Cu_2O substrates from the thermal oxidation of 99.9999% Cu foils



C. Xiang, G. M. Kimball, R. Grimm, N. S. Lewis. *En. & Env. Sci.* DOI: 10.1039/c0ee00554a, 2011.

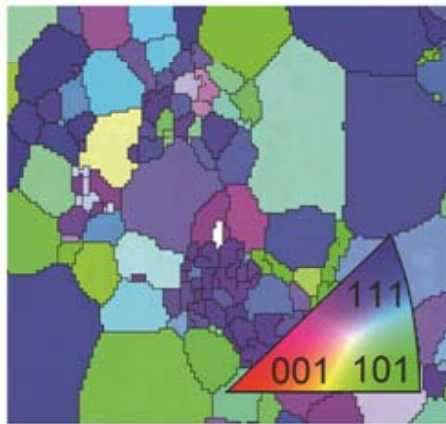
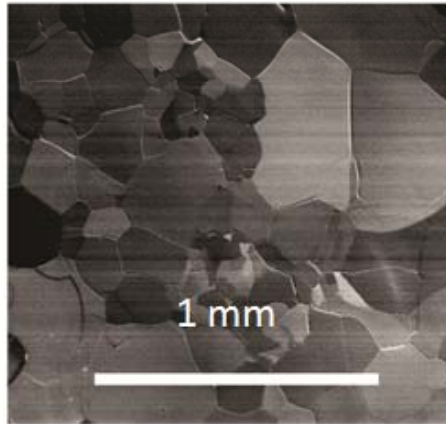
9/27/2011

Gregory Kimball – Thesis Defense

40

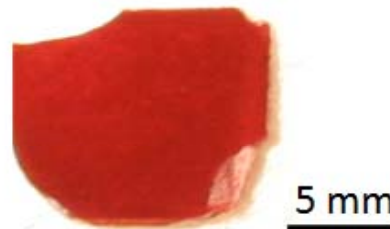
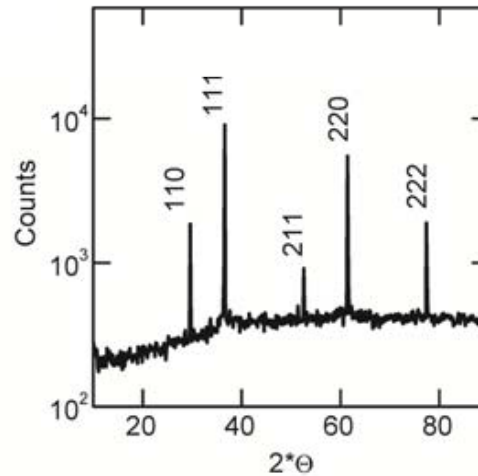
High purity Cu_2O substrates

SEM image



Crystal orientation

X-ray diffraction



Electronic properties:

$$N_A = 3.7 \times 10^{13} \text{ cm}^{-3}$$

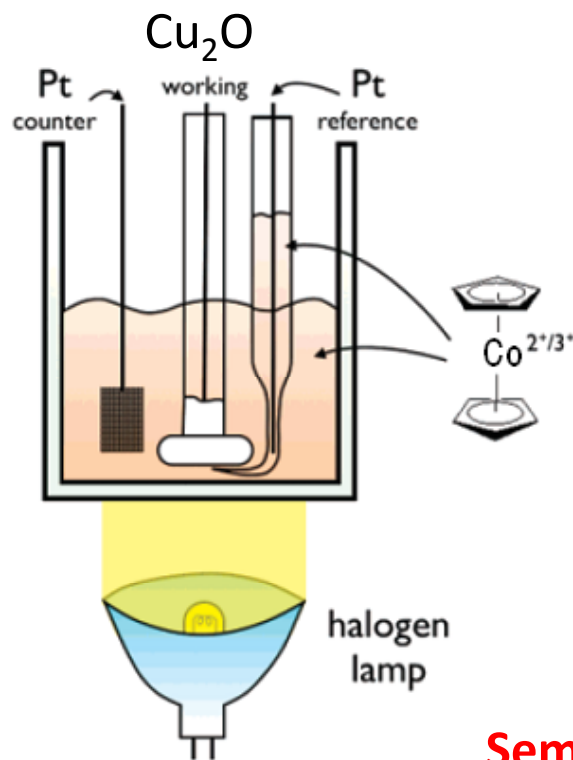
$$\mu_p = 65 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$$

**High quality, large grain
 Cu_2O substrates**

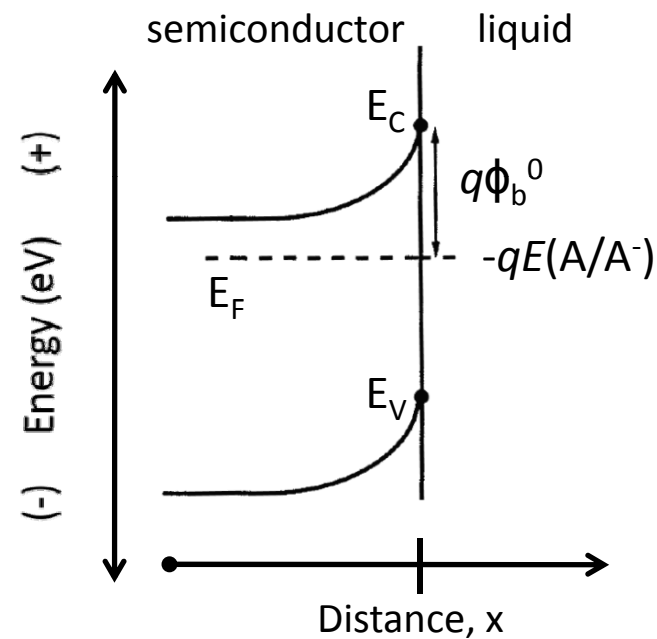


Photoelectrochemistry of semiconductors

Schematic of PEC cell



Band diagram of PEC cell



Semiconductor/liquid junctions allow noninvasive characterization of semiconductor absorbers



Image: J. R. Maiolo

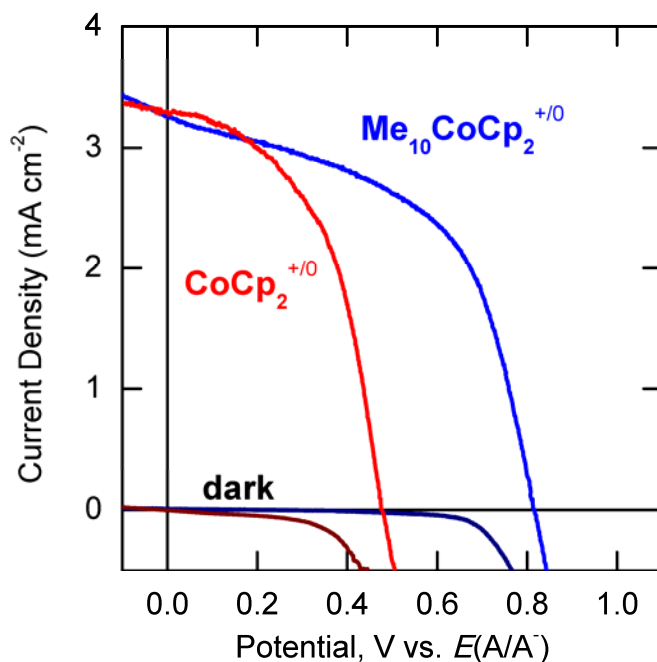
9/27/2011

Gregory Kimball – Thesis Defense

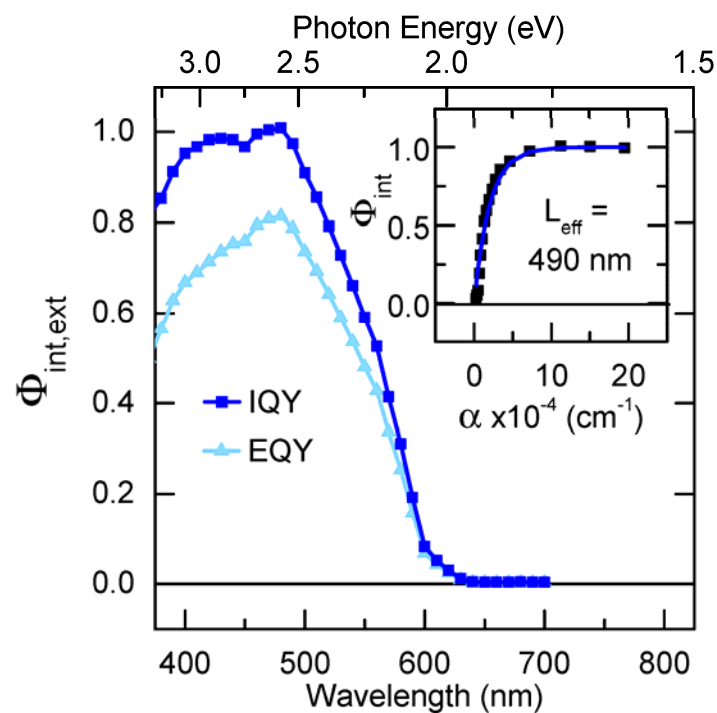
42

Performance of Cu_2O liquid junctions

Current-voltage curves



Quantum yield spectra

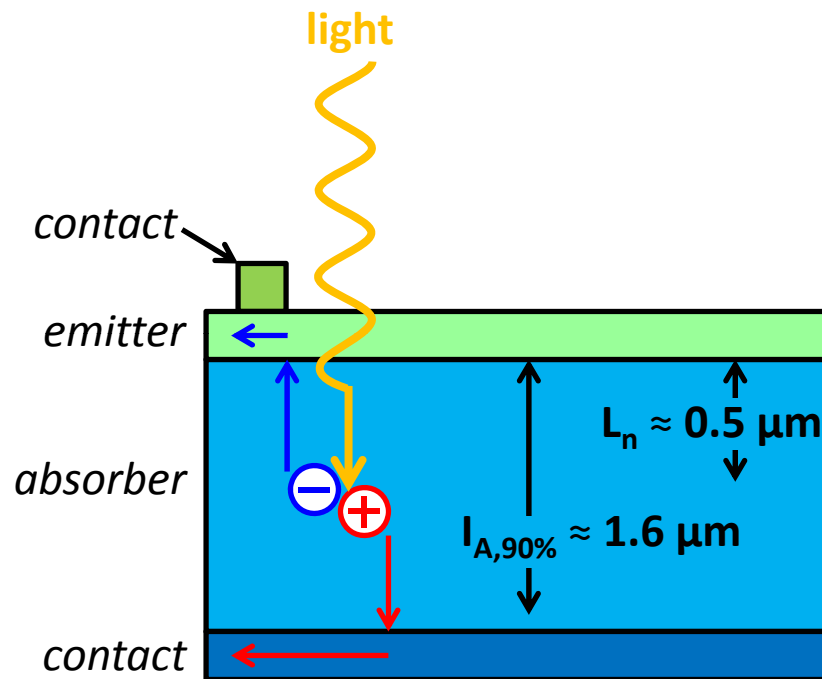


- Record open circuit potential of $> 800 \text{ mV}$ in a regenerative photoelectrochemical cell
- Internal quantum yields $\approx 100\%$ from $400 - 500 \text{ nm}$

C. Xiang, G. M. Kimball, R. Grimm, N. S. Lewis. *En. & Env. Sci.* DOI: 10.1039/c0ee00554a, 2011.



Light absorption and carrier collection



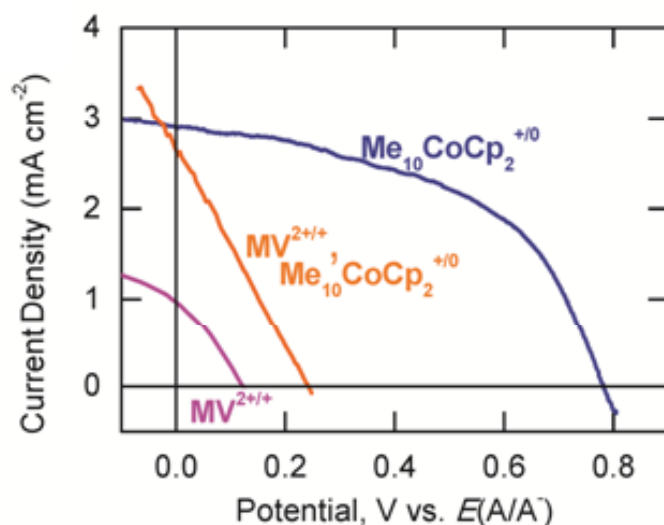
- Absorption length $\approx 1.6 \mu\text{m}$ for 90% light absorption
- Collection length $\approx 0.5 \mu\text{m}$ for incomplete carrier collection

**Improved collection lengths would enable
> 6% efficient Cu_2O solar cells**

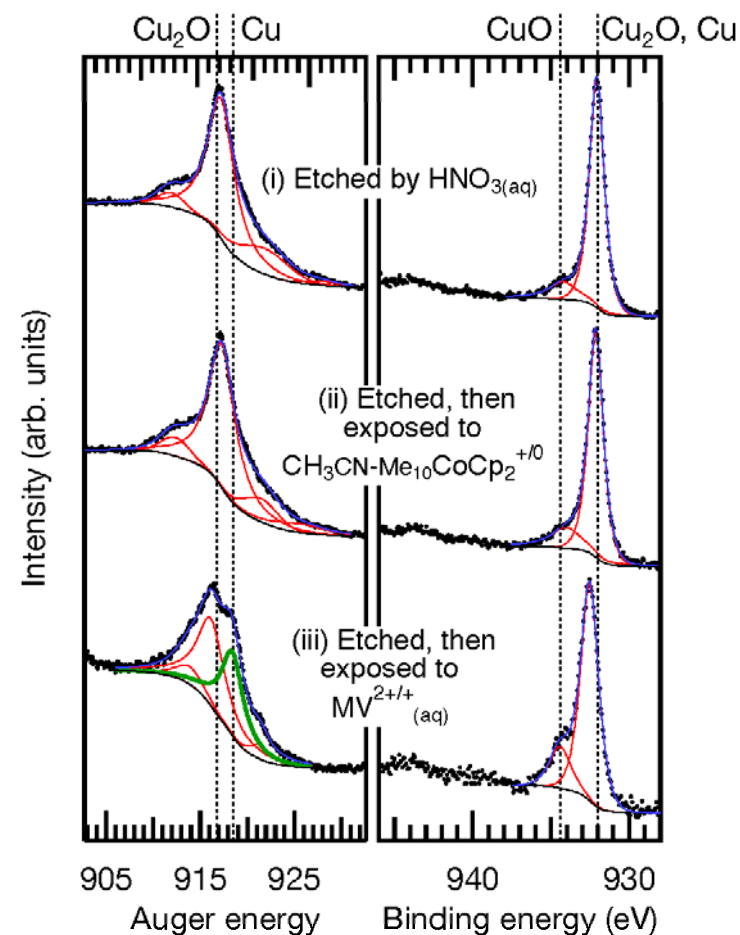


Stability of Cu_2O /liquid junctions

Current-voltage curves



X-ray photoelectron spectroscopy



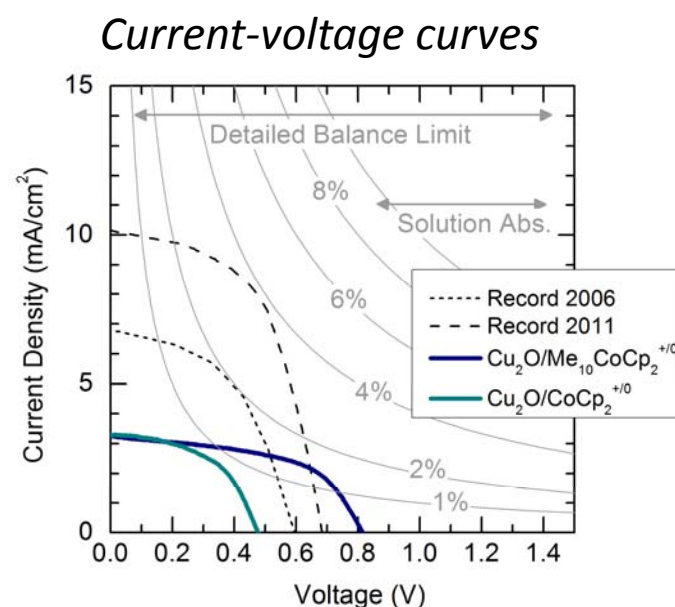
➤ **Cu_2O is stable in the nonaqueous system**

- Photocorrosion is evident in acid (aq)
- Corroded samples show greatly reduced performance



Attainable efficiency

Light source	J_{sc}^{MAX} (mA·cm ⁻²)	J_{sc}^{IQY} (mA·cm ⁻²)	J_{sc}^{PEC} (mA·cm ⁻²)	J_{sc}^{exp} (mA·cm ⁻²)
AM 1.5	14.1	9.0	5.0	n/a
100 mW·cm ⁻² ELH	13.8	7.2	4.7	3.3
10 mW·cm ⁻² ELH	1.4	0.68	0.44	0.41

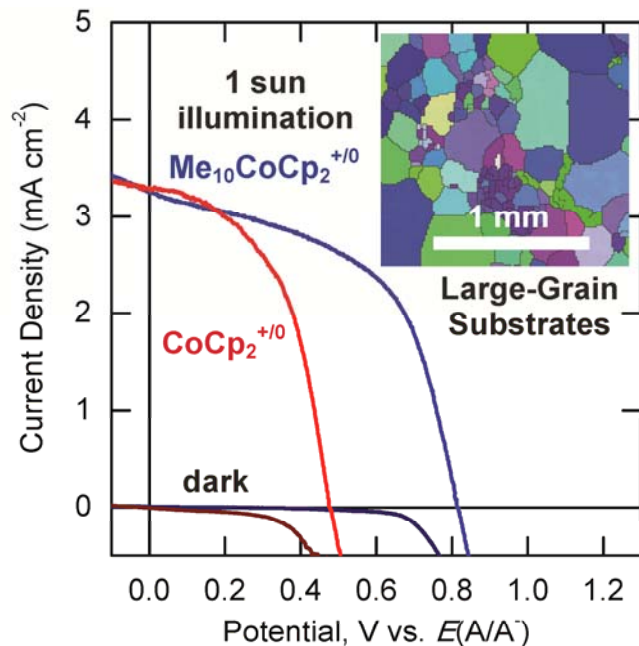


Solution absorption loss $\approx 4 \text{ mA}\cdot\text{cm}^{-2}$

Bulk recombination loss $\approx 6 \text{ mA}\cdot\text{cm}^{-2}$



High performance Cu_2O /liquid junctions



- Achieved open-circuit potential record of 820 mV using a Cu_2O absorber
- Demonstrated internal quantum yields $\approx 100\%$ from 400 – 500 nm illumination
- Showed stable performance of high barrier semiconductor/liquid contacts to Cu_2O



Conclusions

- Prepared high purity substrates of Zn_3P_2 and Cu_2O to investigate their potential for solar energy conversion.
- Revealed $E_{g,\text{indirect}} = 1.38 \text{ eV}$, $E_{g,\text{direct}} = 1.50 \text{ eV}$ and collection lengths $\geq 7 \text{ }\mu\text{m}$ by PL measurements of Zn_3P_2 substrates.
- Examined 4.5% efficient $\text{Mg}/\text{Zn}_3\text{P}_2$ solar cells to elucidate the passivation reaction of Mg metal with Zn_3P_2 surfaces.
- Demonstrated $V_{\text{oc}} > 800 \text{ mV}$ and internal quantum yields $\approx 100\%$ from 400 – 500 nm for Cu_2O substrates.



Acknowledgements



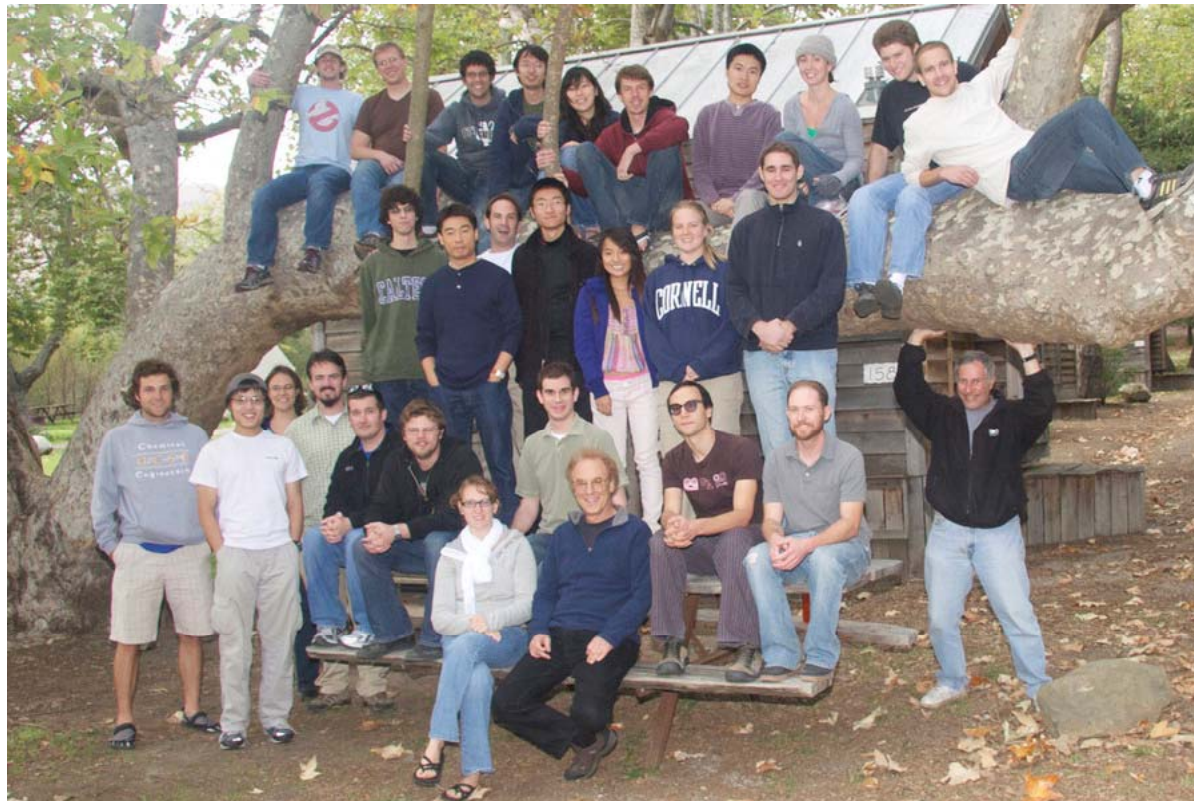
- Professor Harry Atwater
- Committee: Professors Harry Gray, Mitchio Okomura, Tom Miller, Rick Flagan
- Jeff Bosco, S. Faisal Tajdar, Davis Darvish, Samantha Wilson, Gerald Miller, Michael Deceglie, Michael Kelzenberg, Adele Tamboli, Marina Leite, Vivian Ferry, Krista Langeland, Imogen Pryce, Ryan Briggs, Robert Walters, Seokmin Jeon, Mike Filler
- Alireza Ghaffari, Carol Garland, Steve Rozeveld, Marty DeGroot, Rebekah Feist





Acknowledgements

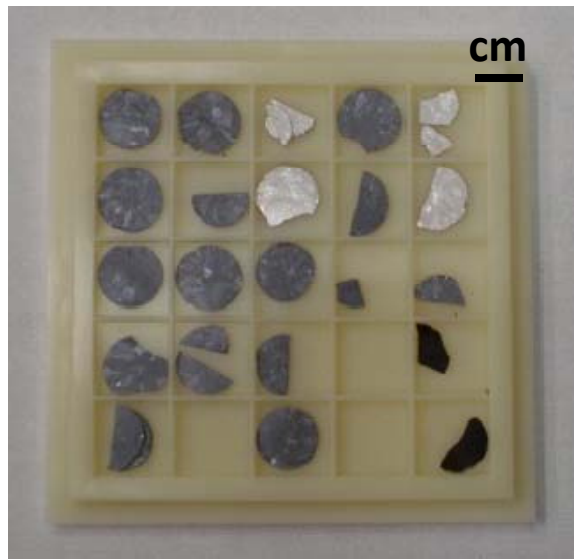
- Professor Nathan Lewis
- Chengxiang Xiang, Ron Grimm, Astrid Müller, James McKone, Shannon Boettcher, Nick Strandwitz, Liz Santori, Emily Warren, Leslie O'Leary, Steven Maldonado, Matt Traub, David Gleason-Rohrer, David Knapp, Matt Traub
- Brave Undergraduates: Jeanne Peng, Jared Sacco, Charlie Jaramillo, Andrew Gong
- Bruce S. Brunschwig, Jay Winkler, Richard Gerhart, Yunbin Guan, Chi Ma



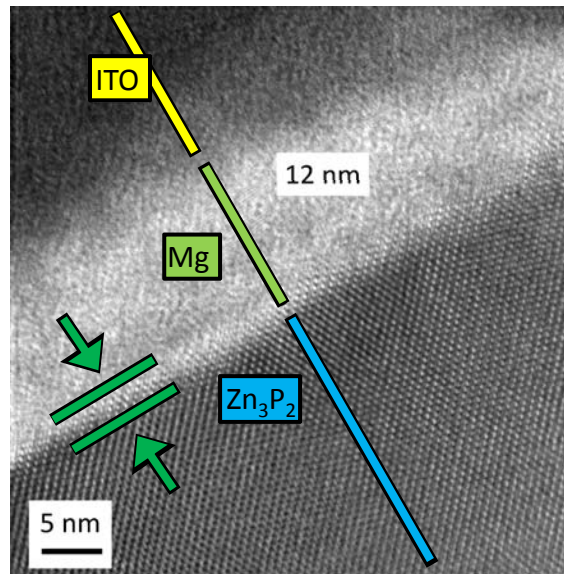


Zn_3P_2 and Cu_2O substrates for solar energy conversion

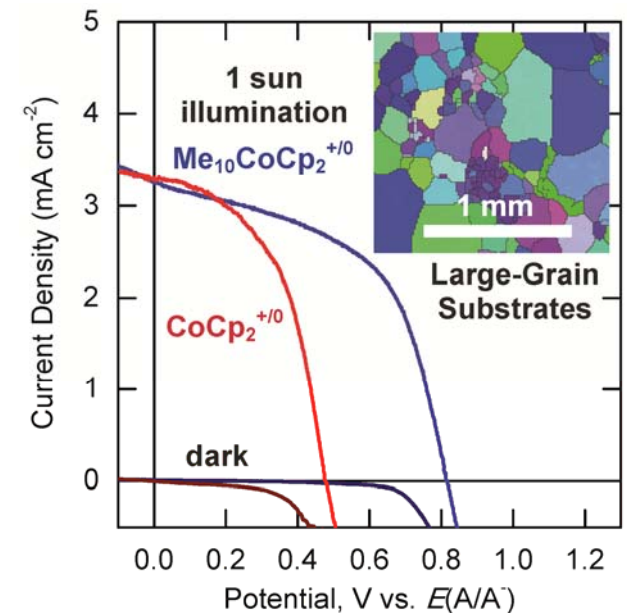
Cornering the market
for 'Solar-Grade' Zn_3P_2



Why is annealing critical
in $\text{Mg}/\text{Zn}_3\text{P}_2$ solar cells?



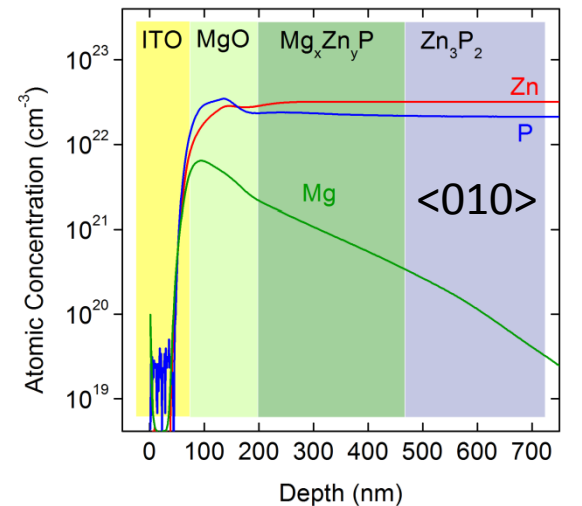
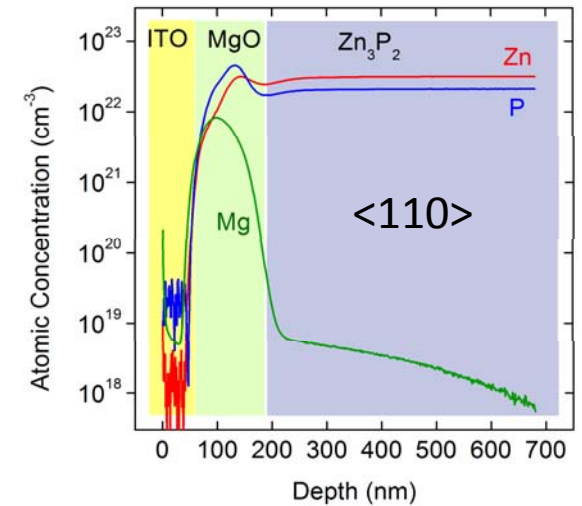
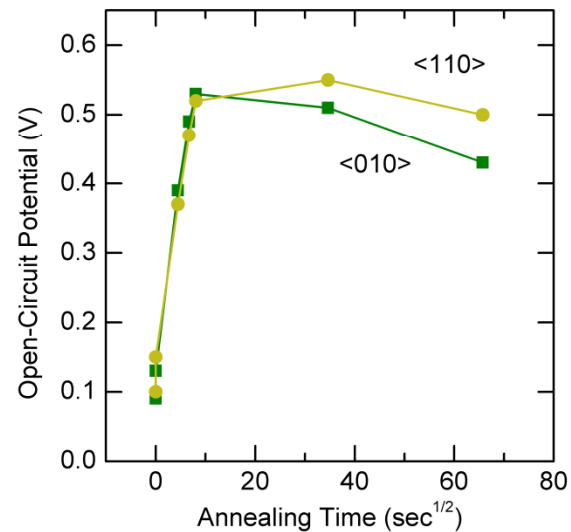
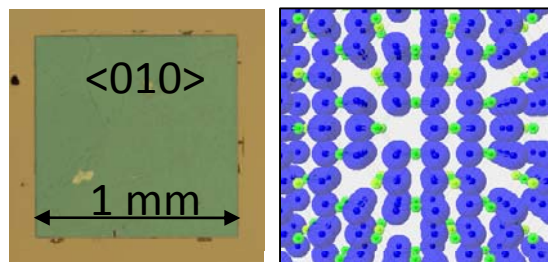
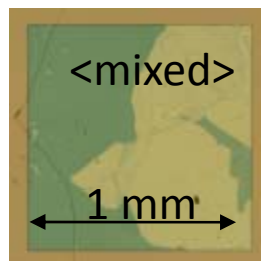
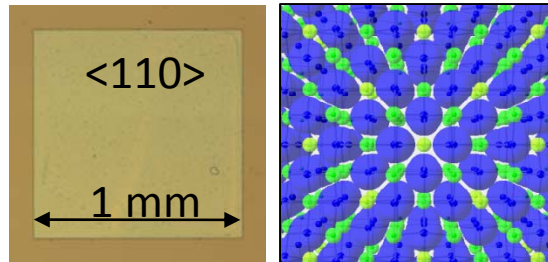
High performance
 Cu_2O /liquid junctions







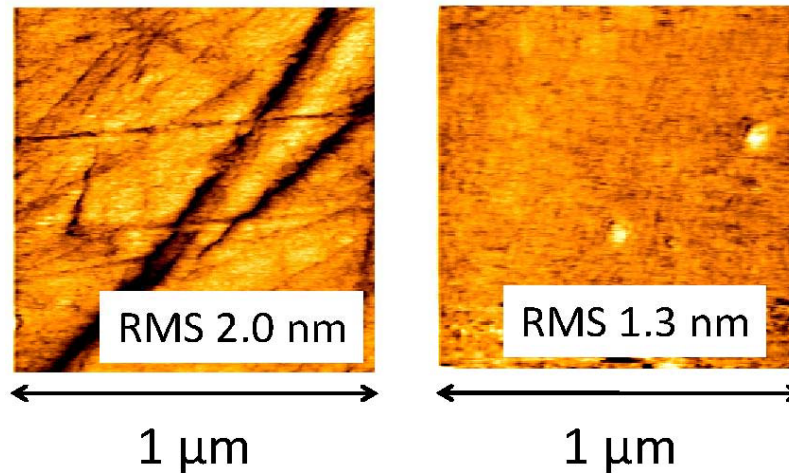
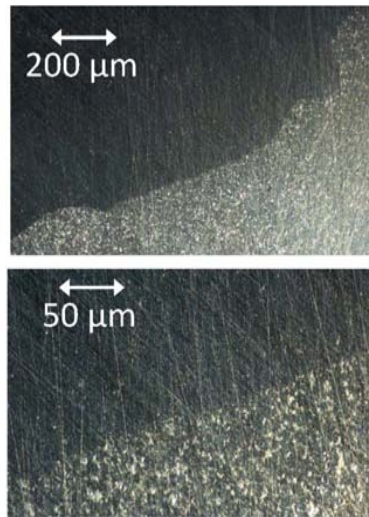
Evaluating Mg-Zn-P Heterojunctions



- Mg alloying and doping are orientation-dependent
- V_{oc} increase is independent of orientation



Rough Wafers to Substrates

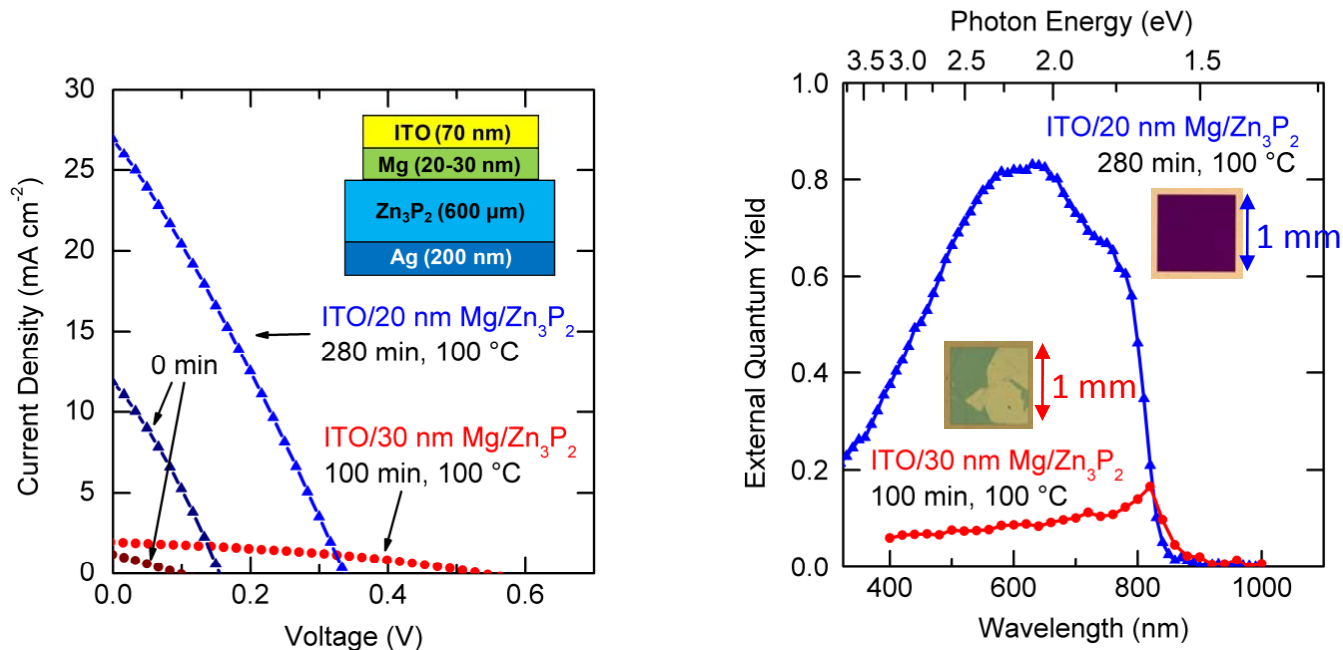


Atomic force
microscopy
(AFM) images

- Microfracturing for certain grains
- Diamond abrasive pad, diamond slurries and chemical polish
- **Specular, 1 – 2 nm RMS roughness Zn_3P_2 substrates**



ITO/Mg/Zn₃P₂ Device Results



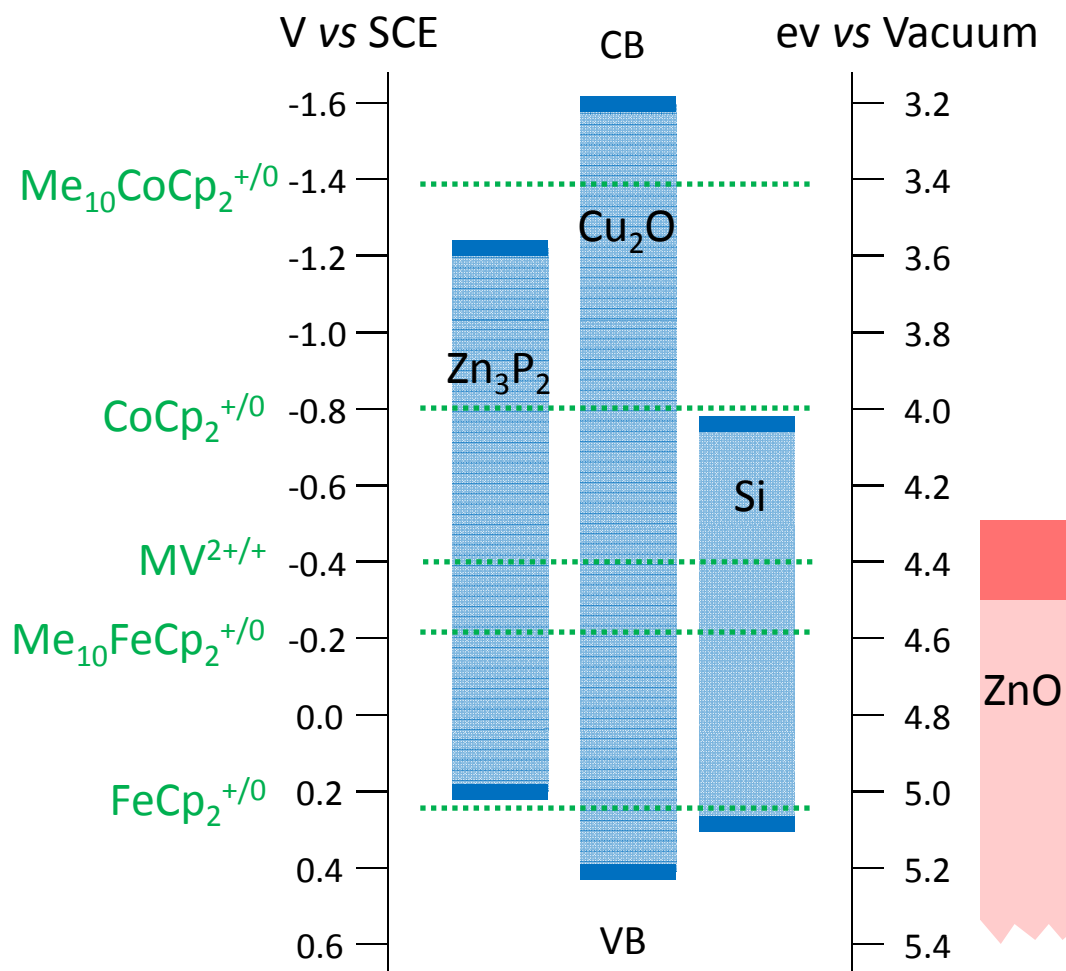
- ITO/Mg/Zn₃P₂ devices show large V_{oc} improvement upon annealing
- Thin Mg layers cause shunting, thick Mg layers increase reflection
- **Mg enables high V_{oc} but limits J_{sc} and FF**



G. M. Kimball, N. S. Lewis, H. A. Atwater, *Thirty-seventh IEEE PVSC*, 2011.

Photoelectrochemistry of semiconductors

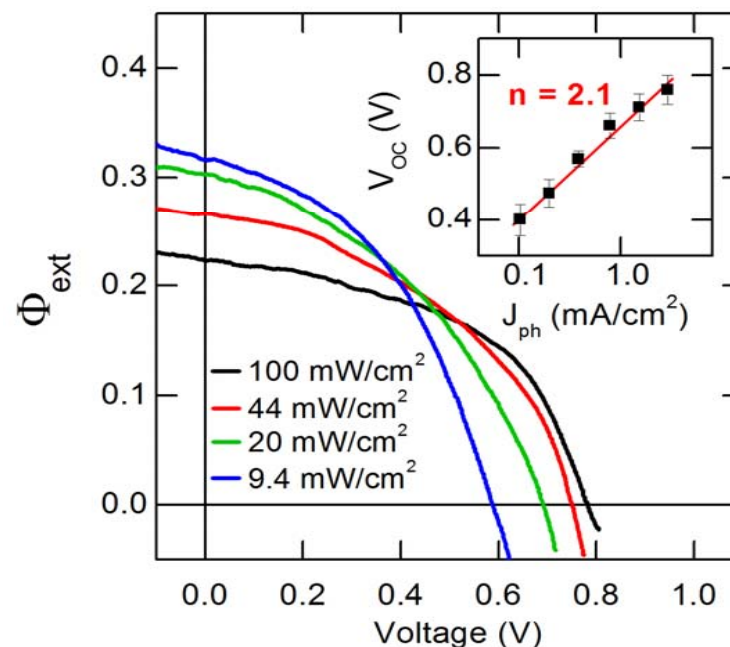
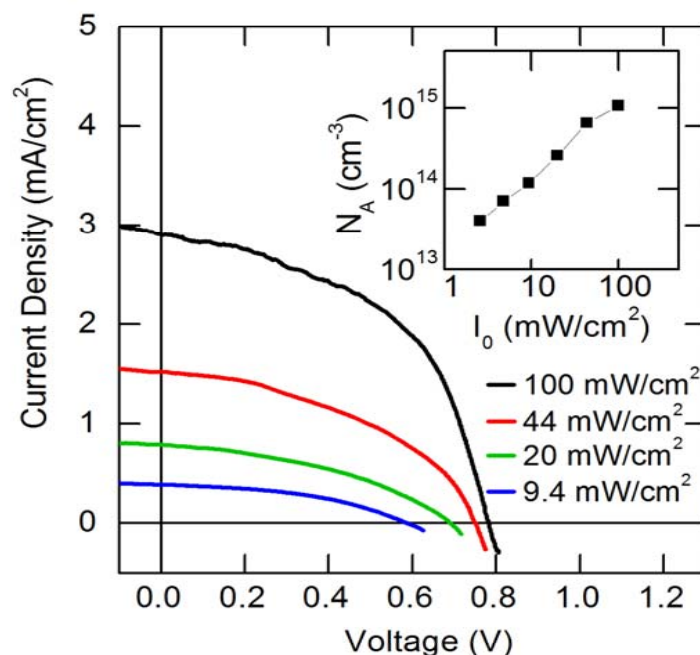
- Solution potential tunable over a wide energy range
- Control of barrier height for both p- and n-type materials
- **Characterize absorber layers without the confounding effects of solid-state junctions**



Light intensity dependence behavior

Increased light intensity causes:

- Lower series resistance due to photoconductivity
- Reduced Φ_{ext} due to higher solution absorption



C. Xiang, G. M. Kimball, R. Grimm, N. S. Lewis. *En. & Env. Sci.* DOI: 10.1039/c0ee00554a, 2011.