U.S. Department of Energy
Energy Efficiency and Renewable Energy
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DOE Solar Energy Technologies Program Peer Review

Interface and Electrode Engineering for Next-Generation Organic Photovoltaic Cells

Denver, Colorado

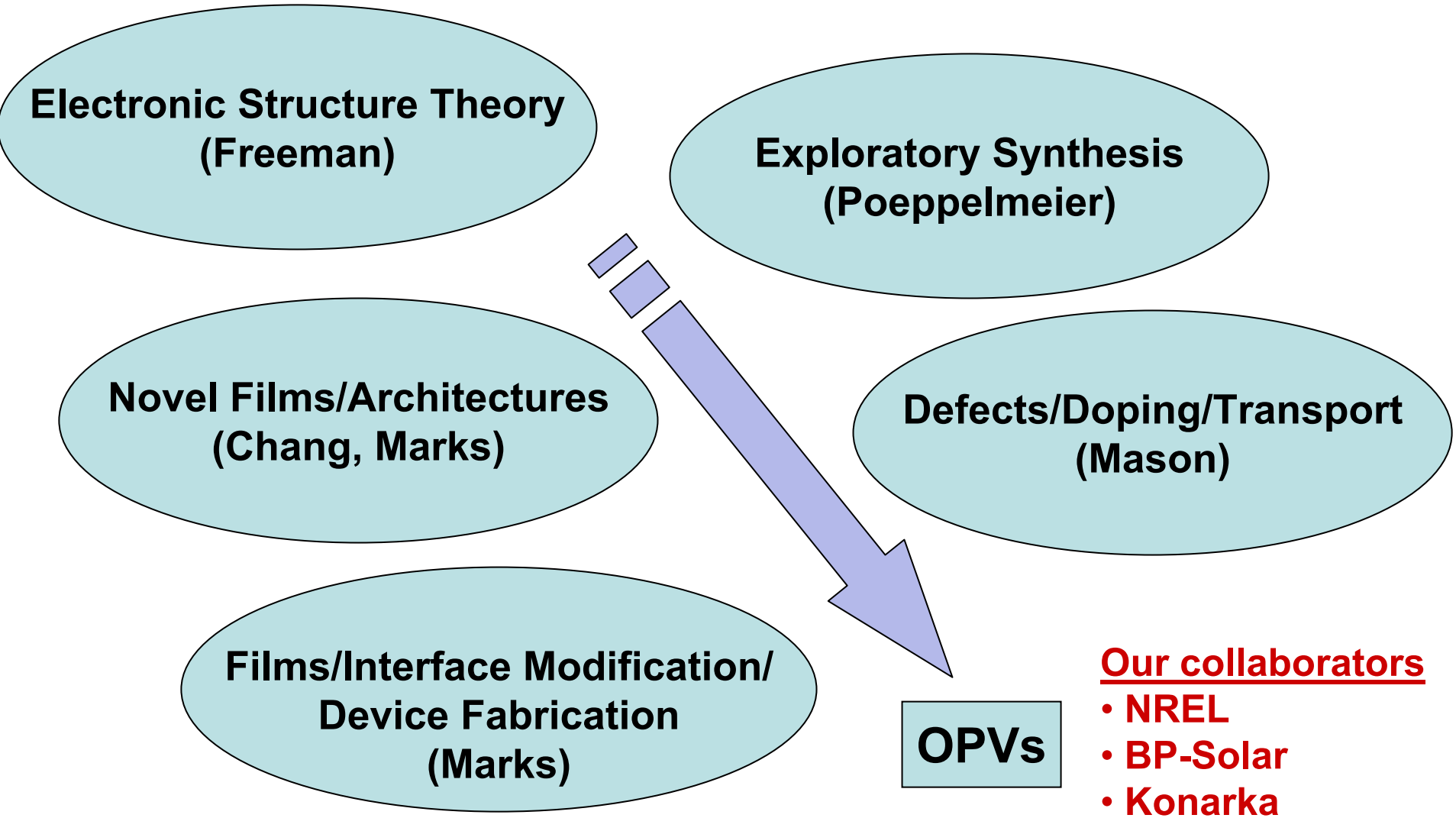
April 17-19, 2007

Research Relevance/Objective

"…to address the near term and long-term Future Generation PV goals by interface and electrode engineering to enable next-generation, efficient, easily manufacturable, and durable organic photovoltaics (OPVs)."

- **Improved transparent electrode materials (transparent conducting oxides, TCOs) for OPVs**
- **Improved electrode-organic interfaces in OPVs**

Summary Of Activities



Our collaborators

- NREL
- BP-Solar
- Konarka

Outline

- Background
- TCO Surface Electronic Structure
- CdO and Double Layer CIO/ITO Films
- Donor-Doped (?) Delafossite

Accomplishments

Parent Oxides

- CdO
- SnO_2
- In_2O_3
- ZnO
- Ga_2O_3

Binary Compounds

- Cd_2SnO_4
- $CdIn_2O_4$
- $CdSnO_3$
- $ZnSnO_3$
- Zn_2SnO_4
- $ZnGa_2O_4$
- $In_4Sn_3O_{12}$
- $Zn_kIn_2O_{k+3}$ (k=3,7-15 odd)
- $Zn_2In_2O_5$ (k=2)
- $MgIn_2O_4$
- $12CaO{\bullet}7Al_2O_3$

Binary Solid Solutions

- $Ga_{2-2x}In_{2x}O_3$

Ternary Compounds

- $Ga_{3-x}In_{5+x}Sn_2O_{16}$

Ternary Solid Solutions

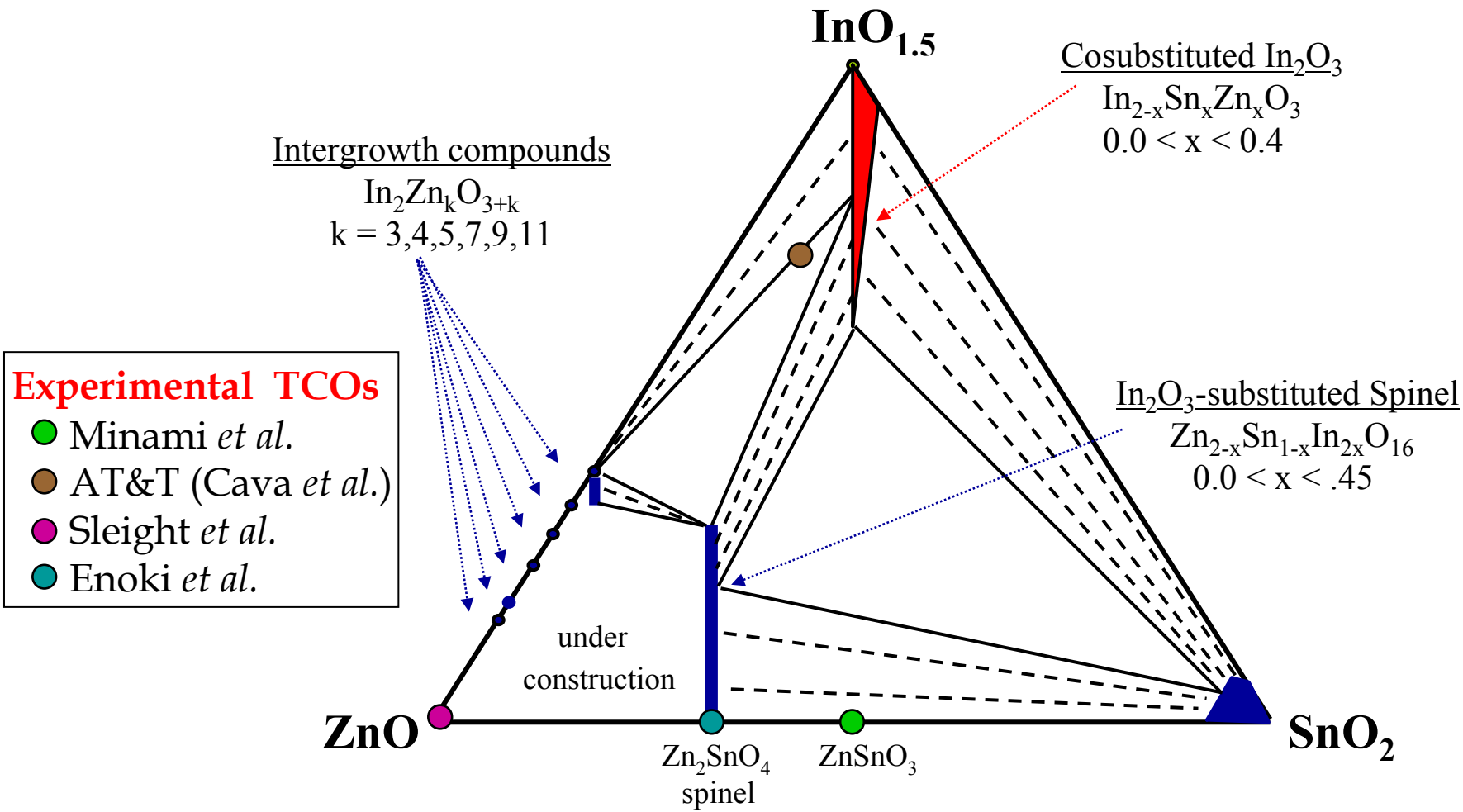
- $In_{1-x}Ga_{1+x}O_3(ZnO)_k$ (k=1,2,3)
- $Zn_{2-x}Sn_{1-x}In_{2x}O_4$
- $In_{2-2x}Sn_xZn_xO_3$
- xCd_2SnO_4-$(1-x)CdIn_2O_4$
- $In_{2-2x}Cd_xSn_xO_3$
- $Cd_{1-x}Sn_{1-x}In_{2x}O_3$
- xZn_2SnO_4-$(1-x)ZnGa_2O_4$

- New TCOs have electrical conductivities comparable to or greater than ITO making current collection more efficient

- Transparency windows broader than ITO allowing greater solar fluencty to reach the active layer

- Greater chemical stability towards corrosion.

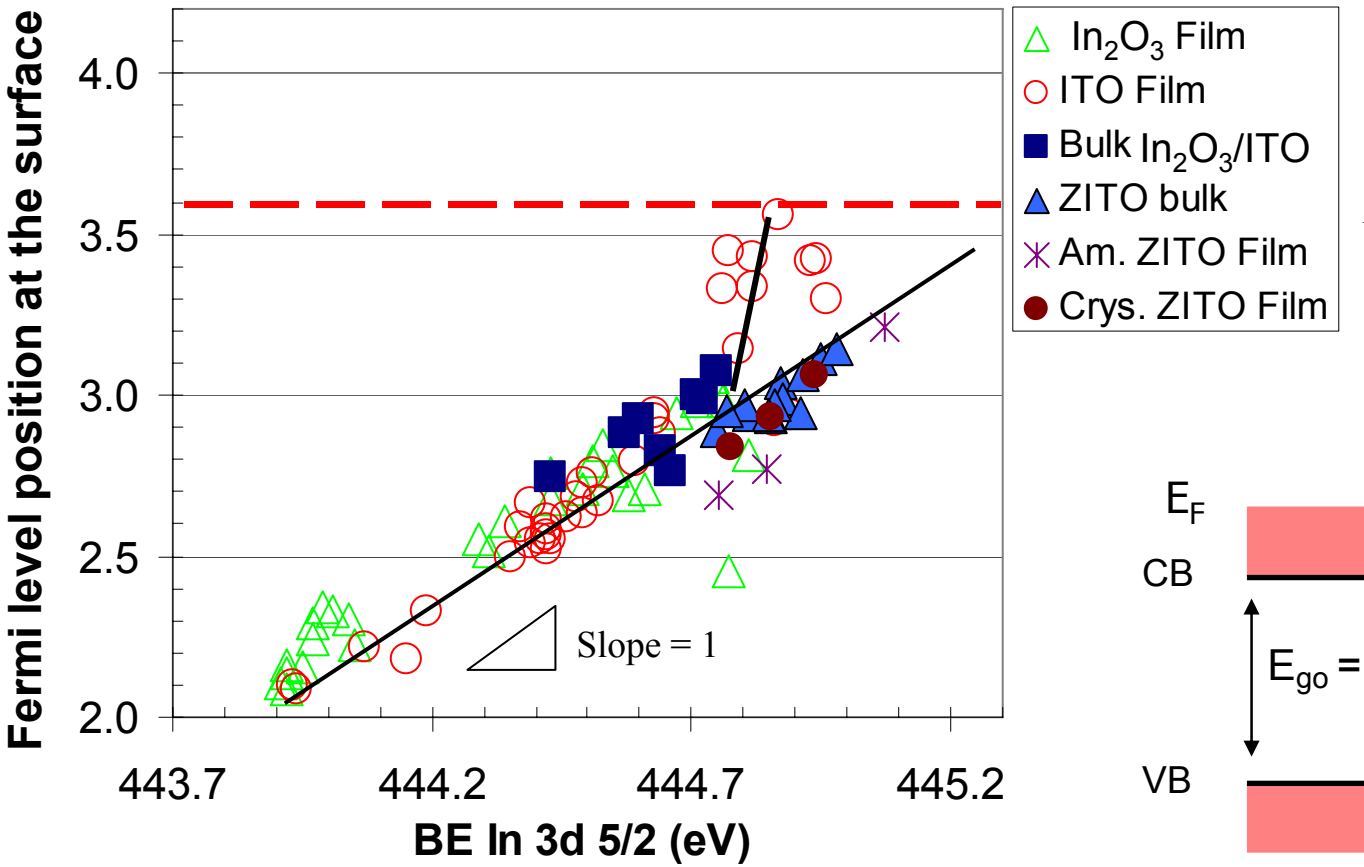
ZnO-In_2O_3-SnO_2 at 1250°C



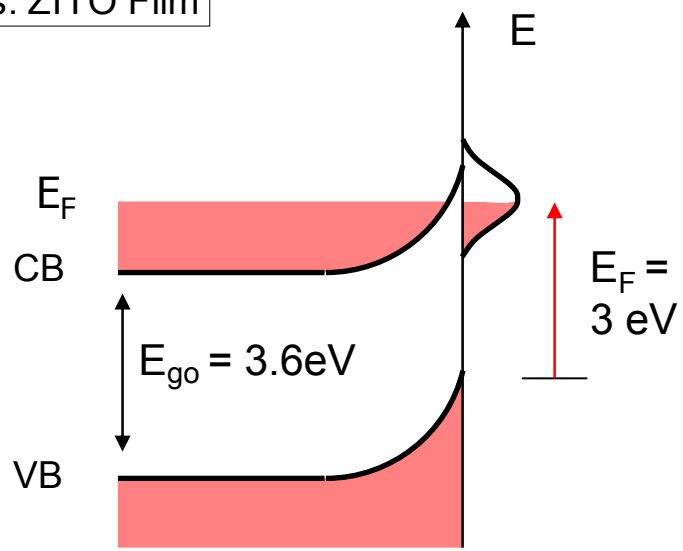
Surface Depletion in Bixbyite TCOs

• For all bixbyite materials investigated, the surface E_F position is lower than the intrinsic gap of In_2O_3 (which is 3.6 eV, shown as red line in plot below).

• This, combined with optical transmission data for films confirming a bulk band gap > 3.6 eV, is a direct indication of surface depletion effects.

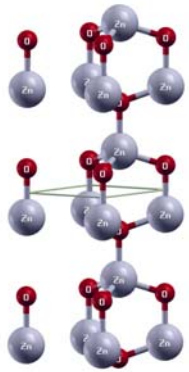


Past 3 eV and the "kink" in the diagram there is evidence for populated surface states and screening effects, shown schematically below. NOTE: ZITO differs from ITO hebavior



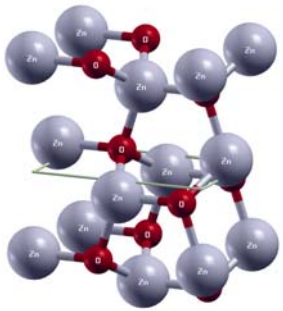
Work functions of polar and nonpolar ZnO surfaces by FLAPW

(0001)



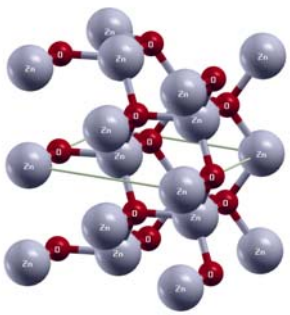
	Work Functions			
	Non-Relaxed		Relaxed	
	Cation Surface	Anion Surface	Cation Surface	Anion Surface
LDA (eV)	3.95	8.76	3.34	7.43
GGA (eV)	3.57	8.38	3.11	7.28

(10$\bar{1}$0)

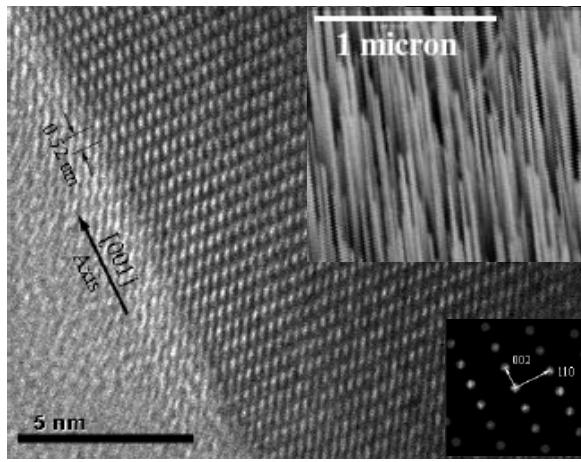


	Work Functions	
	Non-Relaxed	Relaxed
LDA (eV)	5.06	5.31
GGA (eV)	4.50	4.78

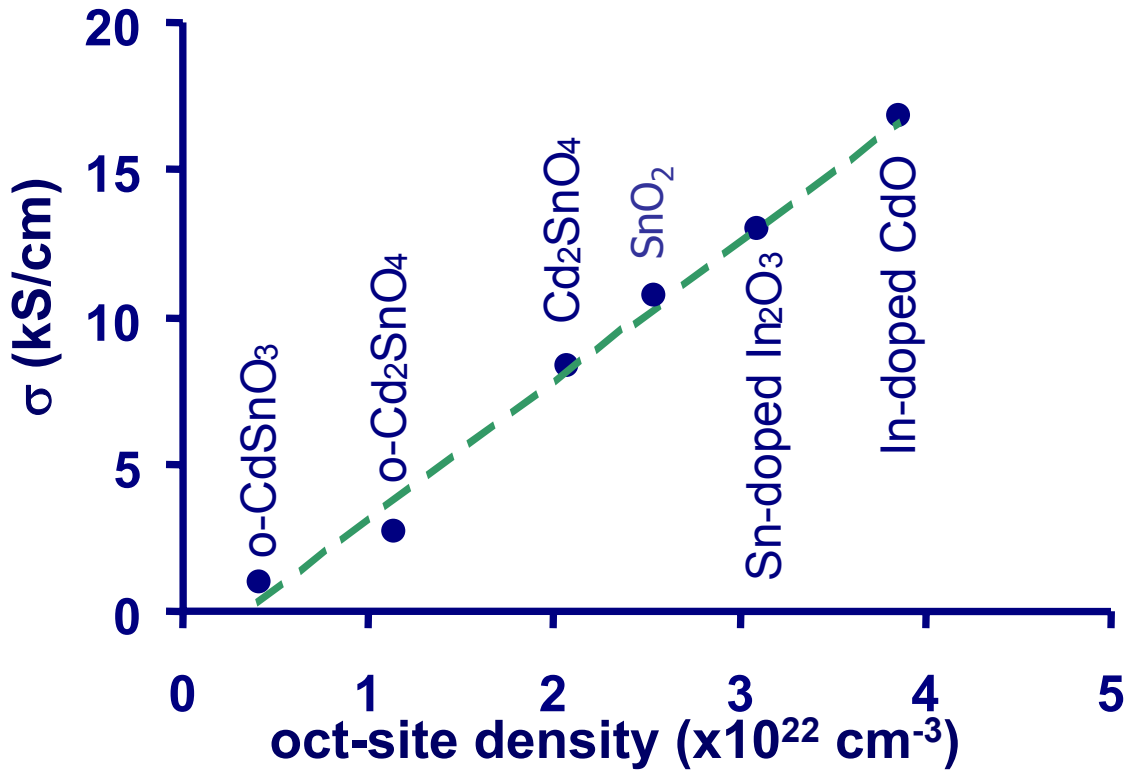
(11$\bar{2}$0)



	Work Functions	
	Non-Relaxed	Relaxed
LDA (eV)	5.14	5.19
GGA (eV)	4.58	4.76



Conductivity vs. Octahedral Site Density



$o\text{-}CdSnO_3$: R. D. Shannon, et al, J. Phys. Chem. Solids, 38, 877 (1977).
G. Haacke, Appl. Phys. Lett., 28, 622 (1976).
Cd_2SnO_4 : X. Wu, et al, J. Vac. Sci. Technol., A15, 1057 (1997).
Sn-doped In_2O_3: H. Ohta, et al, J. Appl. Phys., 91[6] 3547 (2002).
In-doped CdO: A. Wang, et al, Proc. Nat. Acad. Sci., 98, 7113 (2001).

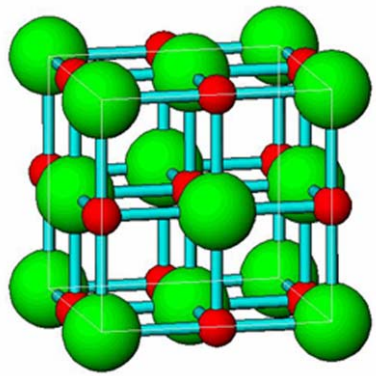
CdO Properties

CdO

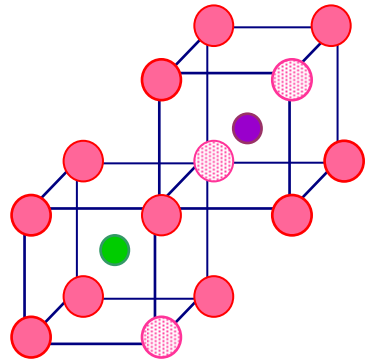
Simple Cubic Crystal Structure

Broad 5s Conduction Band

Low Carrier Effective Masses



Rock Salt



Bixbyite

$In_xCd_{1-x}O$

Simple, Homogeneously Doped Crystal Structure

Extensive Cd 5s + In 5s Mixing

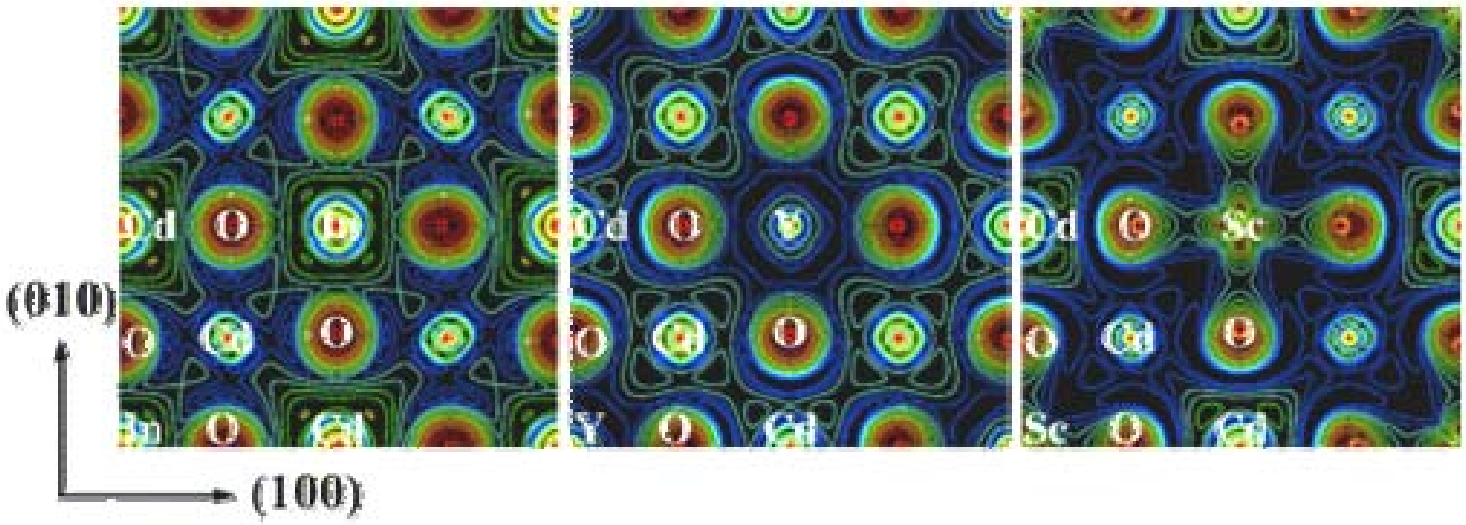
- Uniform Charge Density, Fewer Ionized and Neutral Scattering Centers
- Large Hopping Integrals, Low Effective Carrier Masses

Burstein-Moss Shift Increases Gap (Transparency Window)

Burstein-Moss Shift Compensates for Gap Shrinkage

EXPERIMENT VS. THEORY. DOPED CdO BAND STRUCTURES

Vary Dopant Ionic Radius, Electronic Structure: In^{+3}, Y^{+3}, Sc^{+3}



Calculated charge density distribution in *ab* plane within energy window of 27 meV below Fermi level for In-, Y-, and Sc-doped CdO. Only atoms within one unit cell are labeled.

- **Grain boundary scattering effects of minor importance in both epitaxial and polycrystalline CdO films**
- **Most effective dopants are those in which there is extensive hybridization of dopant and Cd^{+2} 5s states**
- **Burstein-Moss bandgap widening effects operative**
- **Small dopant ions can actually reduce Cd-O hybridization**

Amorphous Substrates/MgO(100) Template Layers

Motivation

❖CdO films on single-crystal substrates show better orientation & larger μ than on glass.

❖Single-crystal MgO is best substrate to simultaneously achieve large μ & high orientation of CdO thin films.

❖Smaller X-ray FWHM → higher mobility.

Benefits

➢MgO: Widely used as template, buffer layer to induce oriented growth

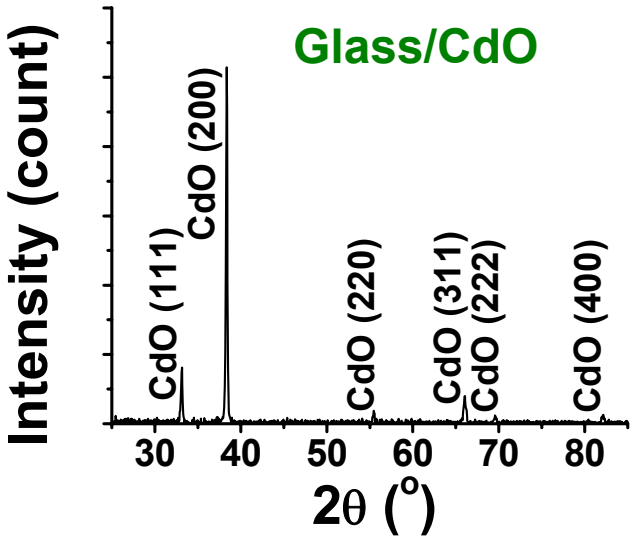
➢Reduce substrate cost vs. single-crystal substrates

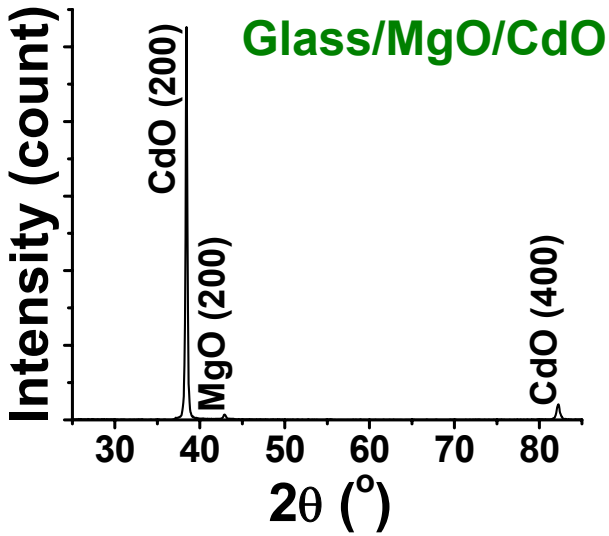
➢Negligible chemical effects on CdO films

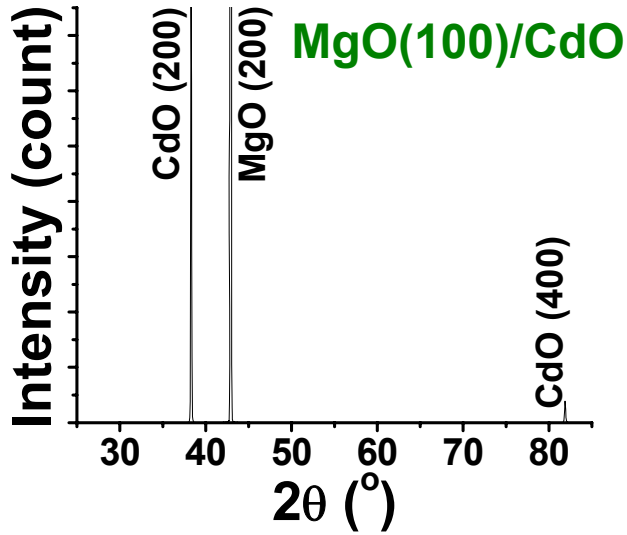
Template Strategy

Compare: CdO Growth on Three Different Substrates

Parallel CdO Growth







Substrate	CdO Thickness (nm)	Conductivity (S/cm)	Carrier Concentration ($\times 10^{20}$ cm^{-3})	Mobility (cm^2/V·s)	X-Ray FWHM (°)
Glass	290	5450±80	2.58±0.10	129±8	19
MgO Template/Glass	310	6700±210	2.65±0.15	159±5	2.1
Single-Crystal MgO(100)	690	8460±200	2.33±0.07	226±10	0.4

CdO conductivity on MgO(100) template significantly improved due to increased crystallinity and mobility.

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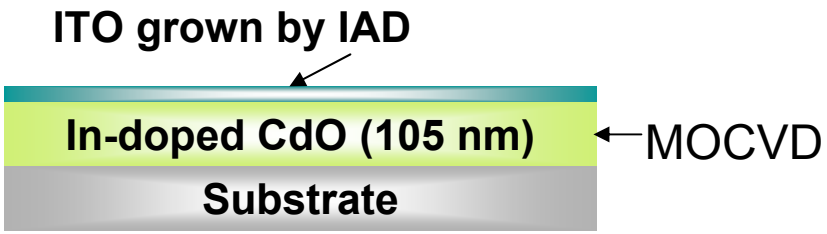
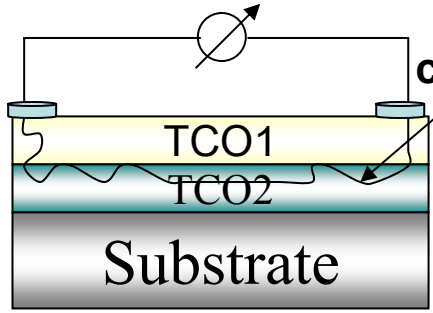
Tuning CdO Corrosion





$$\frac{1}{R_{sheet}} = \frac{1}{R_1} + \frac{1}{R_2}$$

Sample	Thickness (nm)	Sheet Resistance (Ω/□)	Transmittance (%)	Figure of Merit $\Phi = T/R_{sheet}$ ($10^{-3}\Omega^{-1}$)	In-Content (%)
CIO	167	5.6	86.4	41	4.3
CIO/ITO (23 nm)	180	5.6	87.1	45	15.8
CIO/ITO (37 nm)	194	6.1	88.0	46	21.4
ITO	130	18.0	95.1	34	90

Payoff

- ✓ Lower sheet resistance, ideal for large scale displays
- ✓ Greater optical transparency, broader band gap
- ✓ Smoother surface morphology
- ✓ Tunable work function
- ✓ Higher environment stability, e.g. reducing atmosphere.
- ✓ Lower cost, reduce In content

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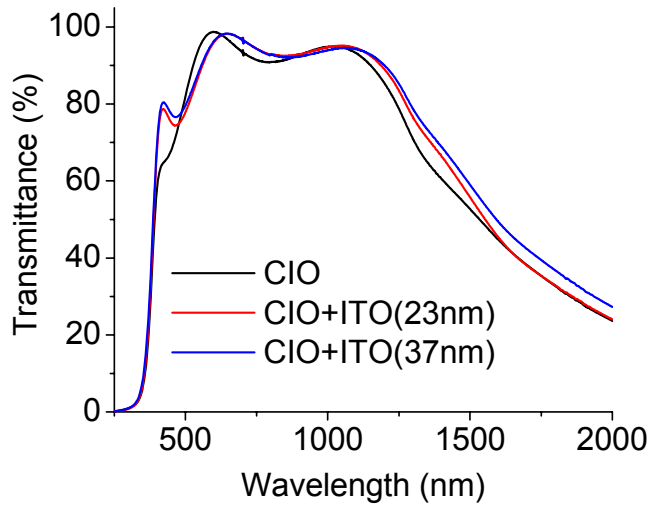
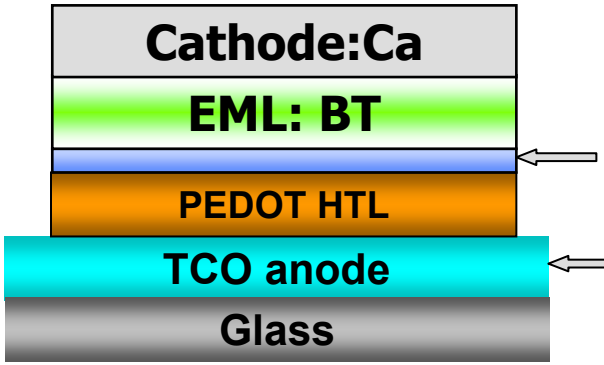
Optical Properties

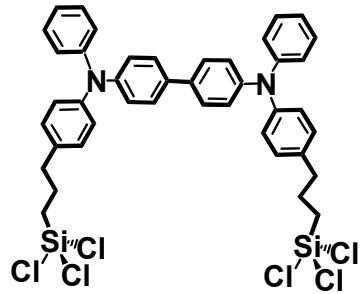


PLED Performance Using CIO/ITO Anodes

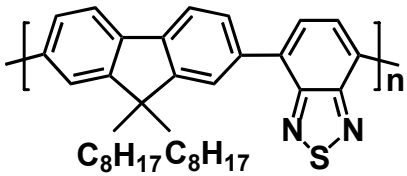


TPDSi + TFB

CIO/ITO, or ITO



$TPDSi_2$



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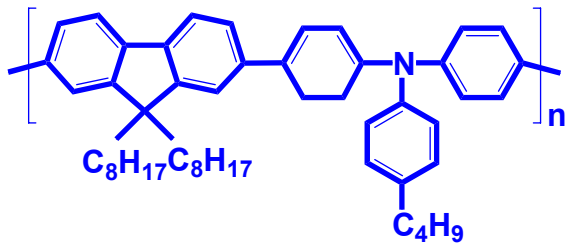
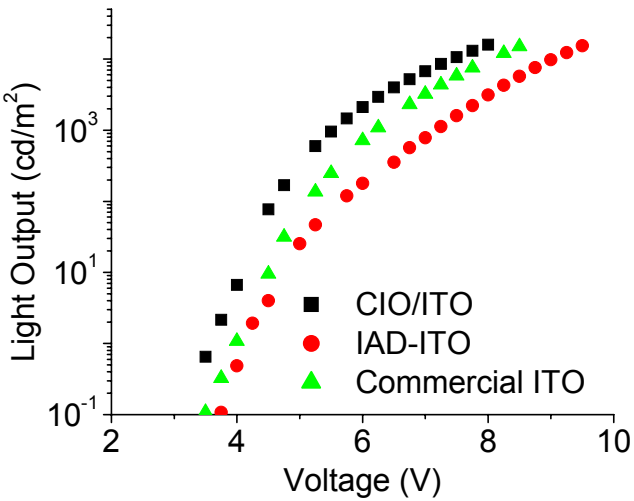
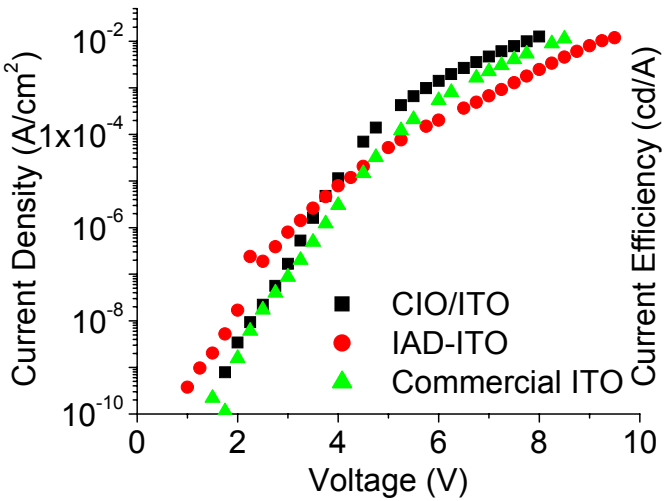
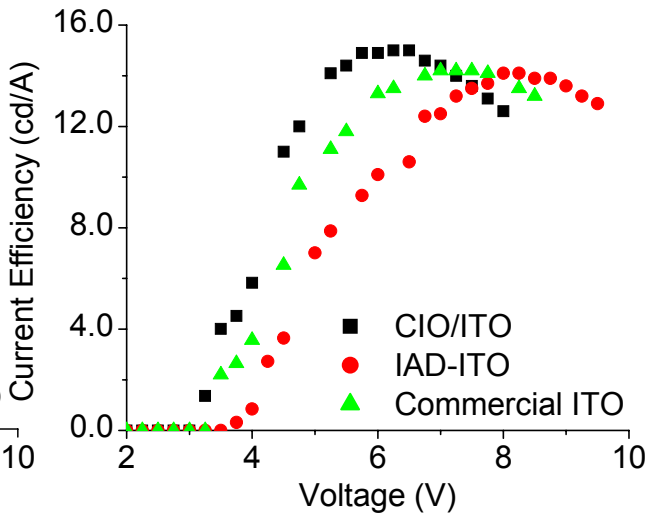


TFB







PLEDs based on double-layer TCOs exhibit lower turn-on voltage, higher light output and higher current efficiency--as high as 15 cd/A.

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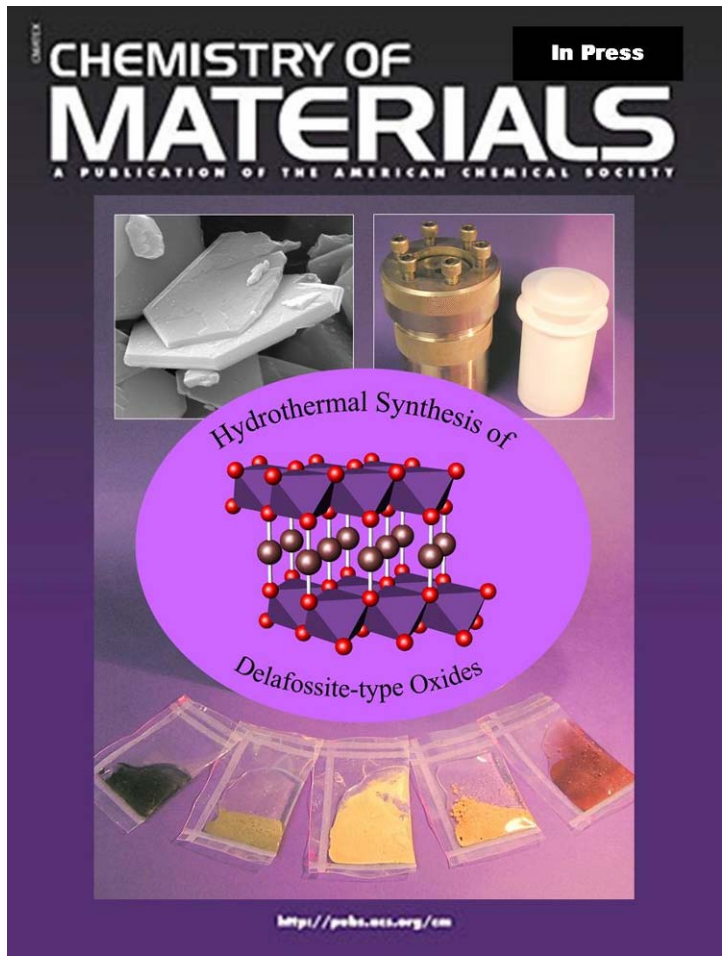
Delafossite-Type Oxides

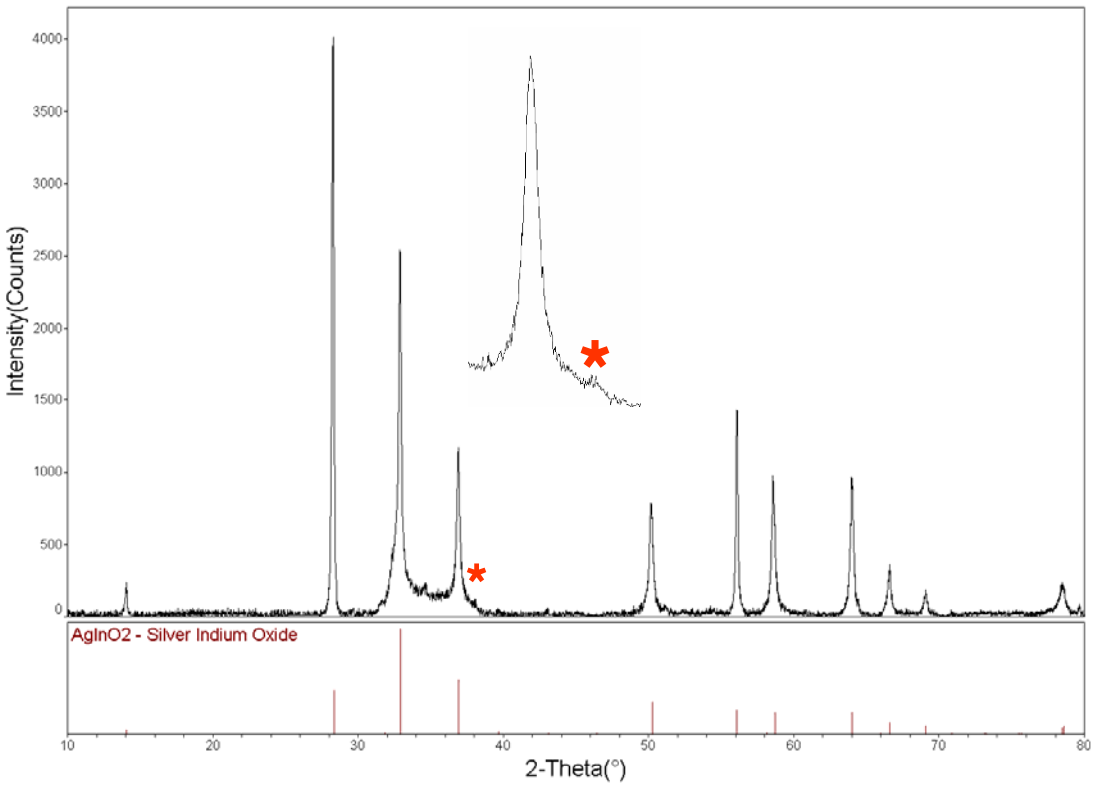
- **Hydrothermal process successfully overcomes challenges of prior synthetic methods by providing the first single step, *low temperature and pressure*, route by which delafossite-like materials can be fabricated *with phase purity*.**

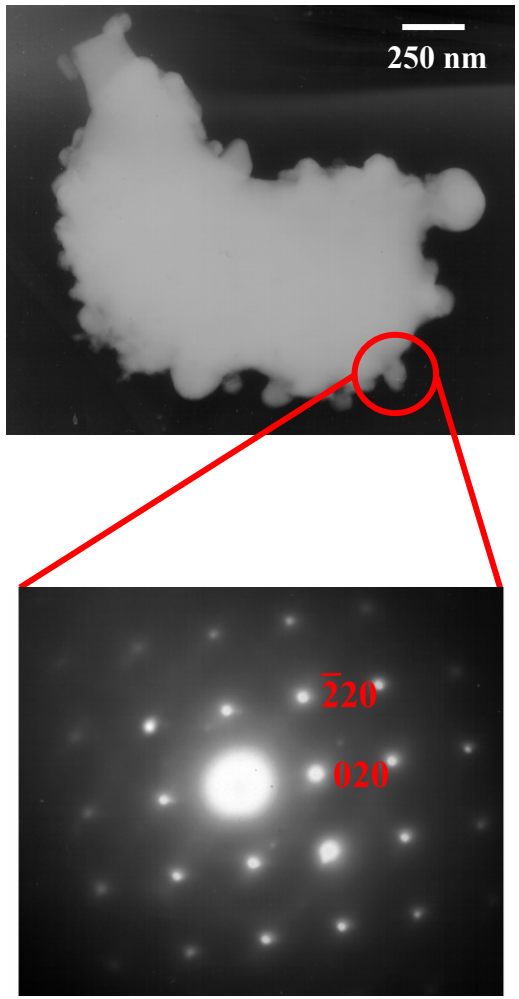
- **$CuAlO_2$, $CuGaO_2$, ($CuInO_2$ missing !), $CuScO_2$, $CuFeO_2$ (the mineral delafossite) and $AgAlO_2$, $AgGaO_2$, $AgInO_2$ (!!!), $AgScO_2$, $AgFeO_2$ have been prepared in a similar fashion.**

- **Solid solution, $CuAl_{1-x}Ga_xO_2$ (where $0 \leq x \leq 1$), which is currently not accessible by a high temperature solid state method, also synthesized.**



One-Step Synthesis of Ag-Delafossites

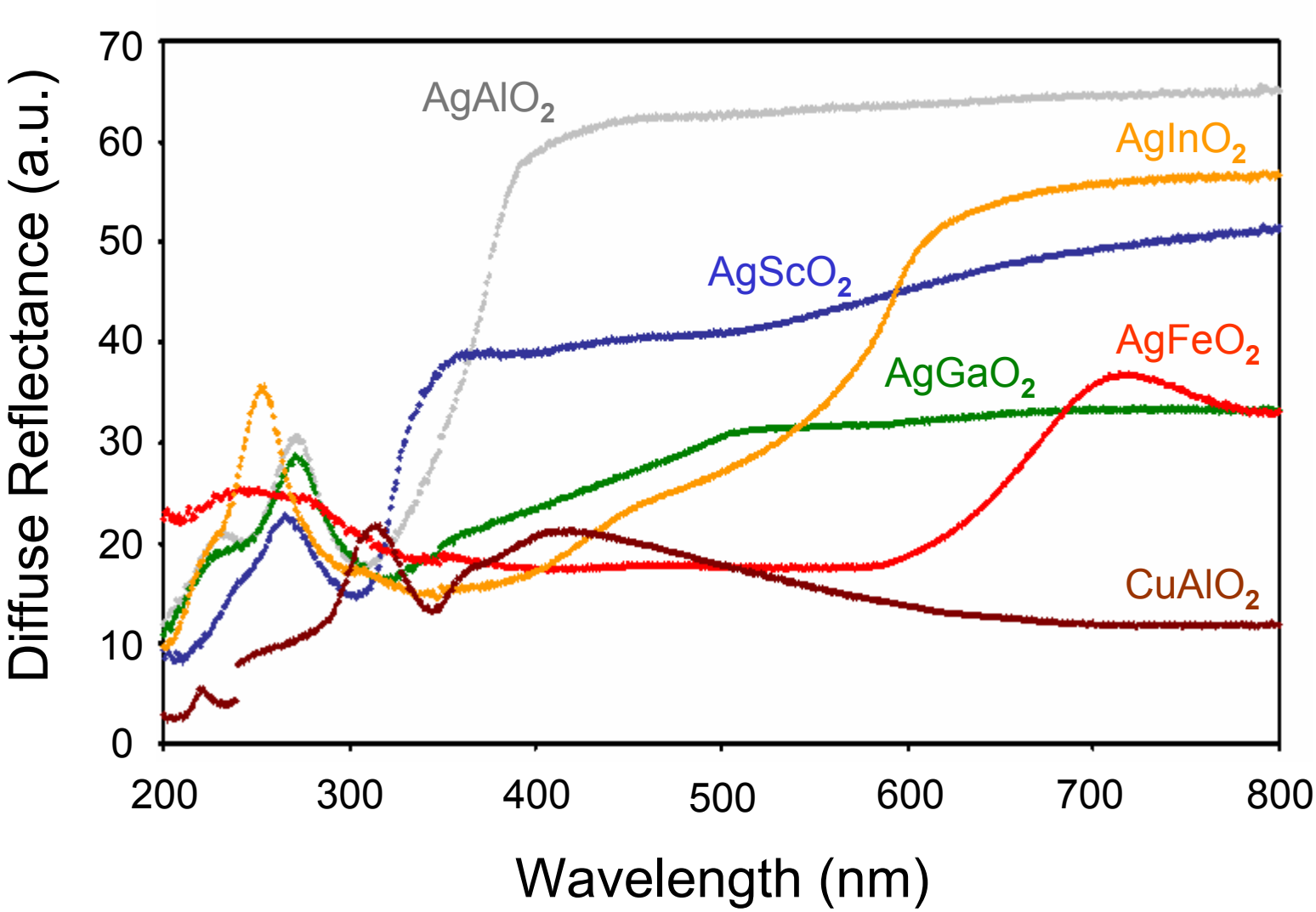




$AgInO_2$, as with all other Ag-delafossites synthesized by this technique, has a minor amount of Ag^0 present. This impurity can be traced back to the the Ag^0 impurities present in the starting Ag_2O reagent (as seen in the TEM images to the right).

Ag [001] zone axis

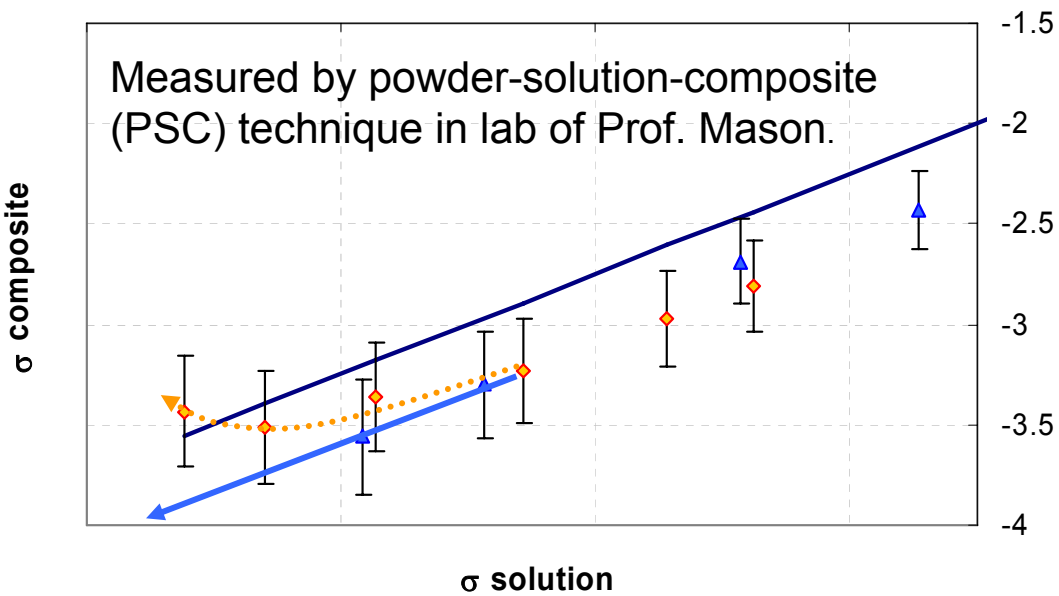
Diffuse Reflectance



Hole Doping

A^I	31 Ga 69.72	13 Al 26.98	21 Sc 44.96	49 In 114.8
[B] mol/L	1	10^{-1}	10^{-4}	10^{-5}

Compounds	Form	σ (S/cm)
$CuGaO_2$	powder	0.0056
$CuGaO_2$	film	0.006
$AgGaO_2$	crystal	2×10^{-8}
$AgGaO_2$	film	3.2×10^{-4}
$AgGaO_2$	**powder**	**$\leq 10^{-4}$**



Major Scientific Issues

- Improper chemical and electronic matching between transparent electrodes and organic active layer
- Current losses and leakage at interfaces
- Poor adhesion/interfacial stability

Broad Future Plans

- TCO electrodes which are electronically, chemically, and surface compatible with the active organic elements of OPVs.

- Efficient current extraction, interfacial stable, charge-blocking layers for OPV.

- Basic science of the electrode interface leading to improved understanding and guidance for next-generation OPV materials design.