Transparent Conductors Part II

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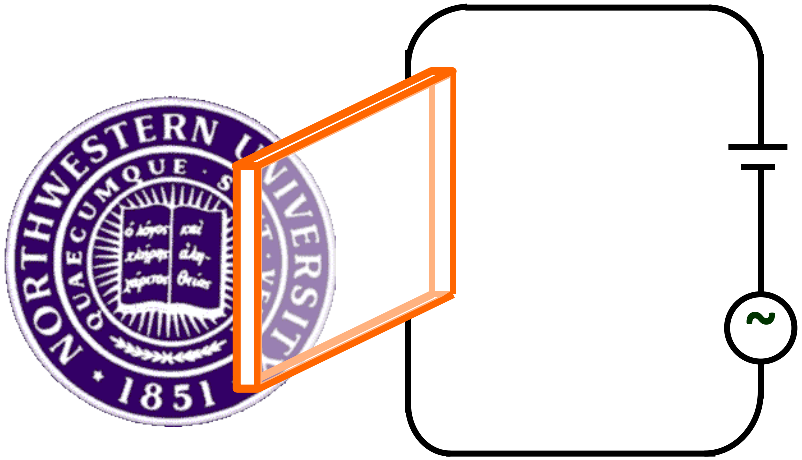
Conclusions

- With the exception of ZnO, the best TCOs are high octahedral site density crystal structures
- They are n-type only
- The “basis” cations are In, Sn, Zn, Cd and Ga
- Their defect chemistries can be complicated (not just oxygen vacancies)
- Phase diagrams play an important role
- If you can make a comparable p-type TCO…

An Introduction to TCOs



Transparency
(> 80% through visible spectrum for
typical 1 μm thin film)

Conductivity (> 10^3 S/cm)

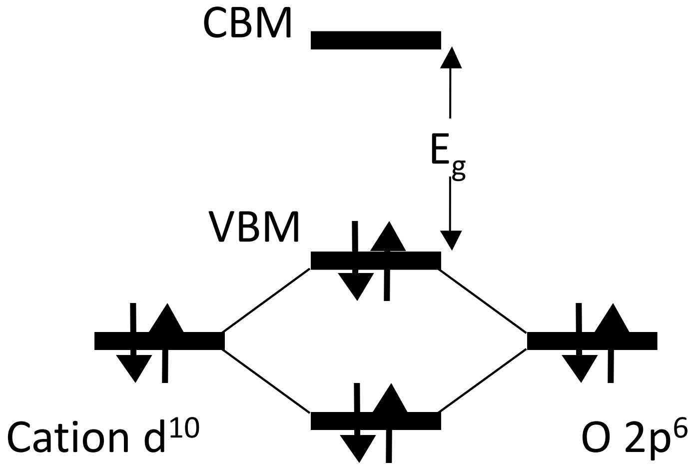
- What About p-Type TCOs
- The Importance of Work Functions
- The What and How of Work Functions
- Surface Science Definitions
- Work Function “Myths”
- Manipulating Work Functions
- Motivation for New TCOs
- Amorphous TCOs
- What the Future Holds

What About p-Type TCOs?

The Strategy of Kawazoe et al.

- Delocalize O-2p levels at the VBM through enhanced covalency
  - Quasi-tetrahedral coordination of oxygen by cations
  - Linear coordination of cations
- Chose d^{10} cations with energy levels close to that of O-2p

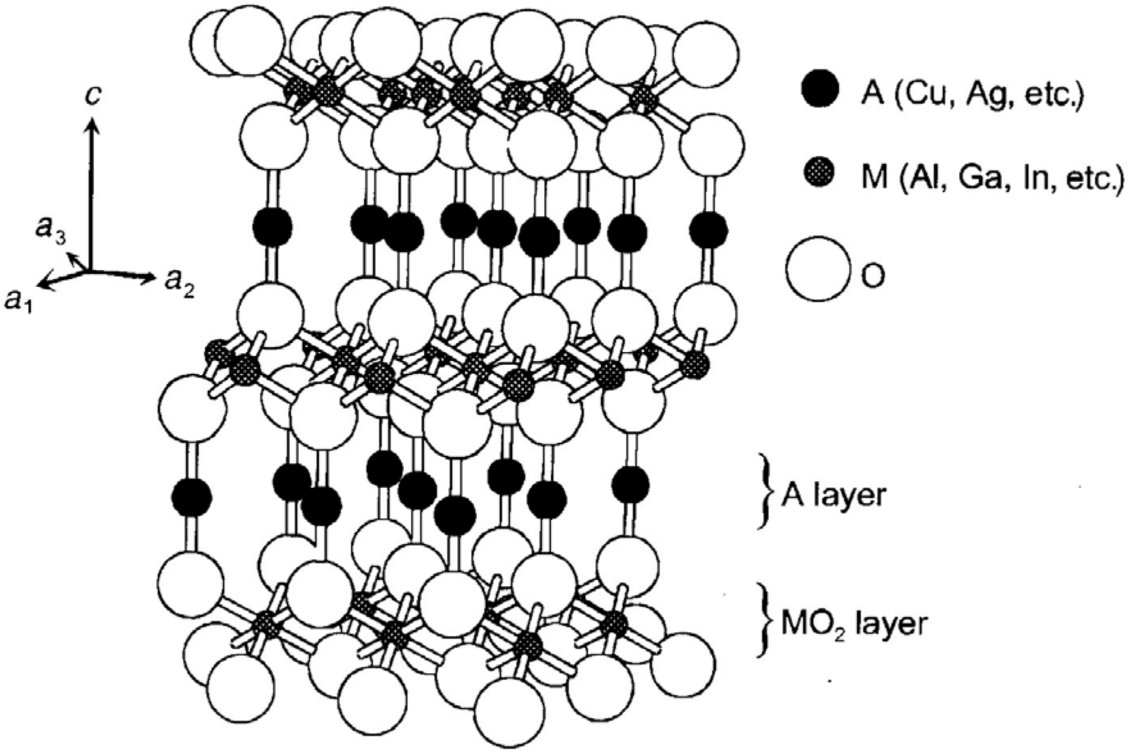
p-type TCOs



H. Kawazoe, H. Yanagi, K. Ueda, and H. Hosono. MRS Bull. **25**(8)28 (2000).

Linear cation TCO family

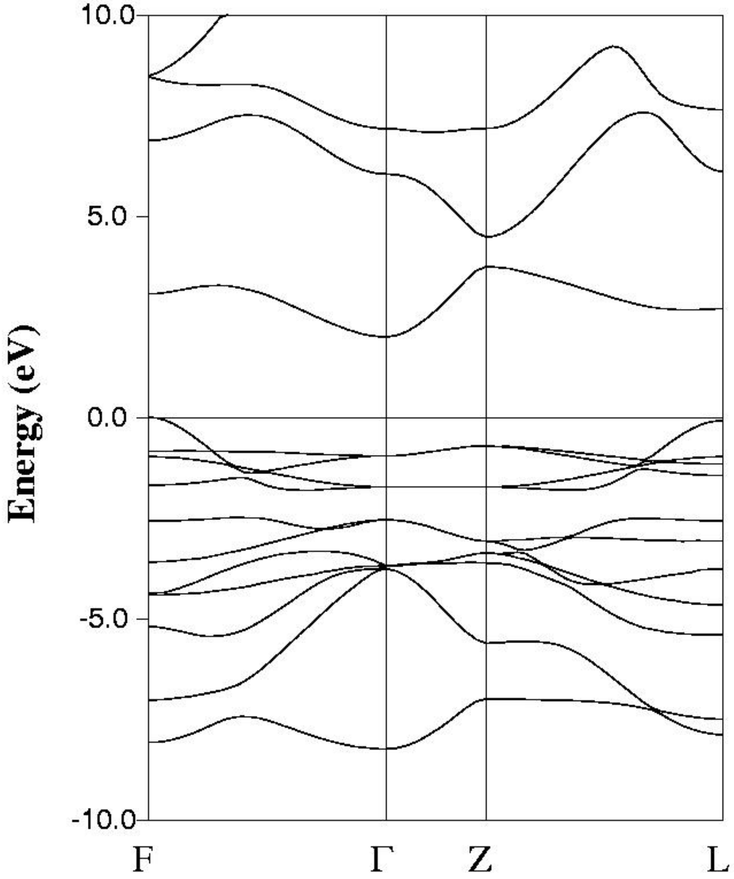
"delafossite" **AMO_2**



- Alternating layers of octahedra and Cu in linear coordination
- Two stacking sequences: rhombohedral and hexagonal
- p-type!

H. Kawazoe, H. Yanagi, K. Ueda, and H. Hosono. MRS Bull. **25**(8)28 (2000).

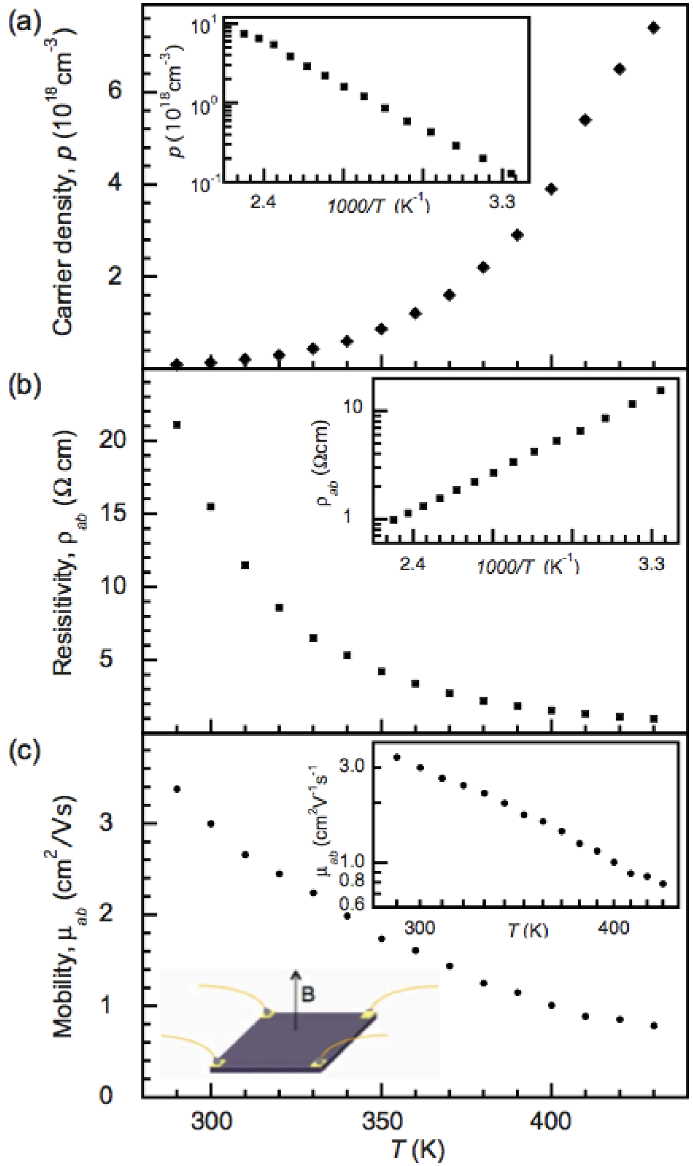
Band structure of $CuAlO_2$



B.J. Ingram, T.O. Mason, R. Asahi, K.T. Park, and A.J. Freeman Phys. Rev. B. **64**, 155114, (2001).

$CuAlO_2$ Single Crystal Electrical Results

- Band Conductor
- Relatively low, anisotropic mobilities
  - *ab*-plane: 3.0 $cm^2\,V^{-1}\,s^{-1}$
  - *c*-direction: 0.12 $cm^2\,V^{-1}\,s^{-1}$
- Tough to dope!



Tate, J. *et al*. Phys. Rev. B. **80**, 165206, (2009).

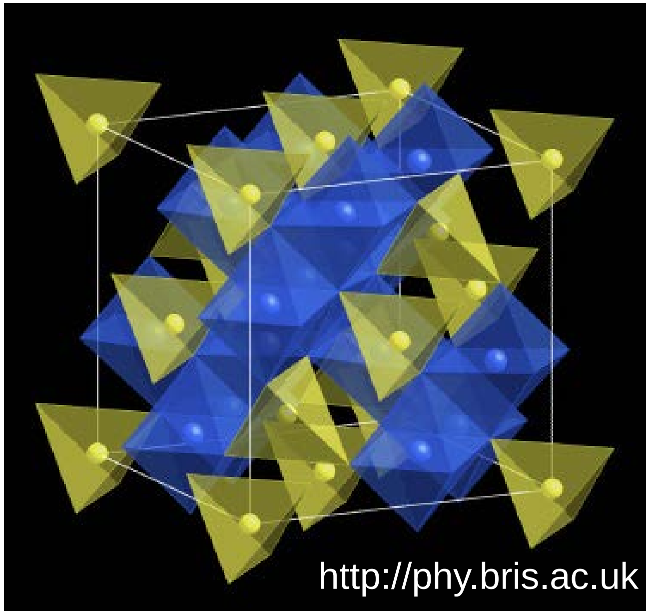
Review of literature data for delafossites

	σ (S/cm)	%T (visible) (film thickness)	E_g (eV)
$CuYO_2$:Ca(1)	1.0	40-50 (250 nm)	3.5
$CuScO_2$ (2)	15-30	40 (110 nm)	
$CuGaO_2$ (3)	6.3×10^{-2}	80 (500 nm)	3.6
$CuInO_2$:Ca (4)	2.8×10^{-3} (p)		3.9
$CuInO_2$:Sn	3.8×10^{-3} (n)		
$CuAlO_2$ (5)	16	32-52 (120 nm)	3.6

1. M. K. Jayaraj, et al. *Thin Solid Films*. **397**, 244 (2001).
2. N. Duan, et al. *Appl. Phys. Lett.* **77**(9), 1 (2000).
3. K. Ueda, et al. *J. Appl. Phys.* **89**(3), 1790 (2001).
4. H. Yanagi, et al. *Appl. Phys. Lett.* **78**(11), 1583 (2001).
5. Y. Wang, et al. *Chem. Vap. Deposition.* **6**(6), 285 (2000).

A New Approach:
Non-d^{10} Cations

d^6 p-TCOs: Spinels

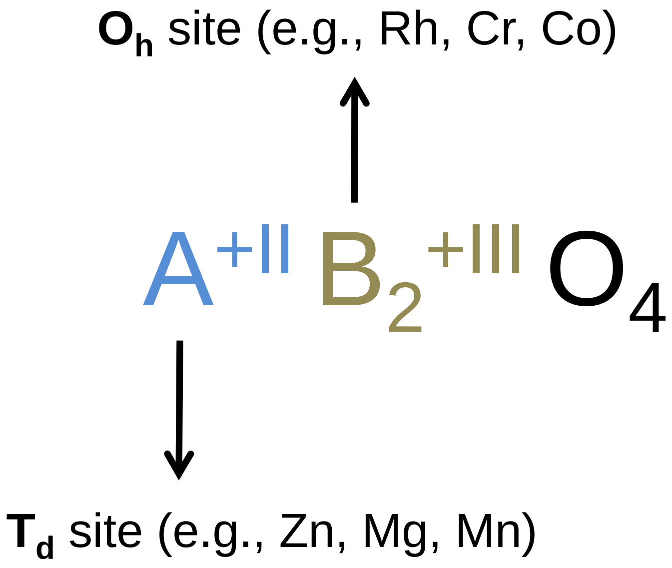


Yellow: Tetrahedral (T_d)

Blue: Octahedral (O_h)

Vertices of each polyhedron are oxygen anions.

Normal II-III Spinels:

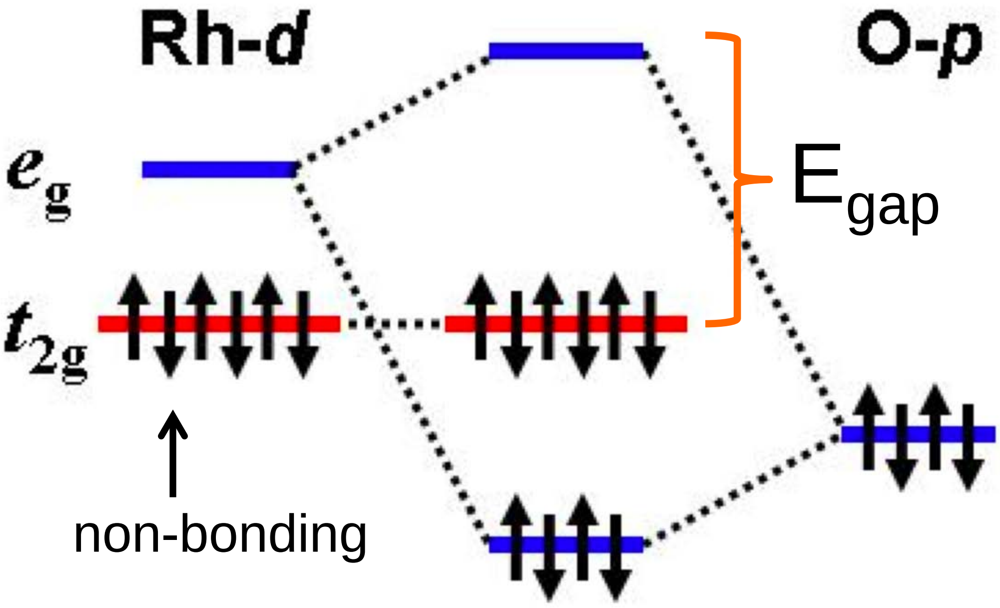


O_h site (e.g., Rh, Cr, Co)

$$A^{+II} B_2^{+III} O_4$$

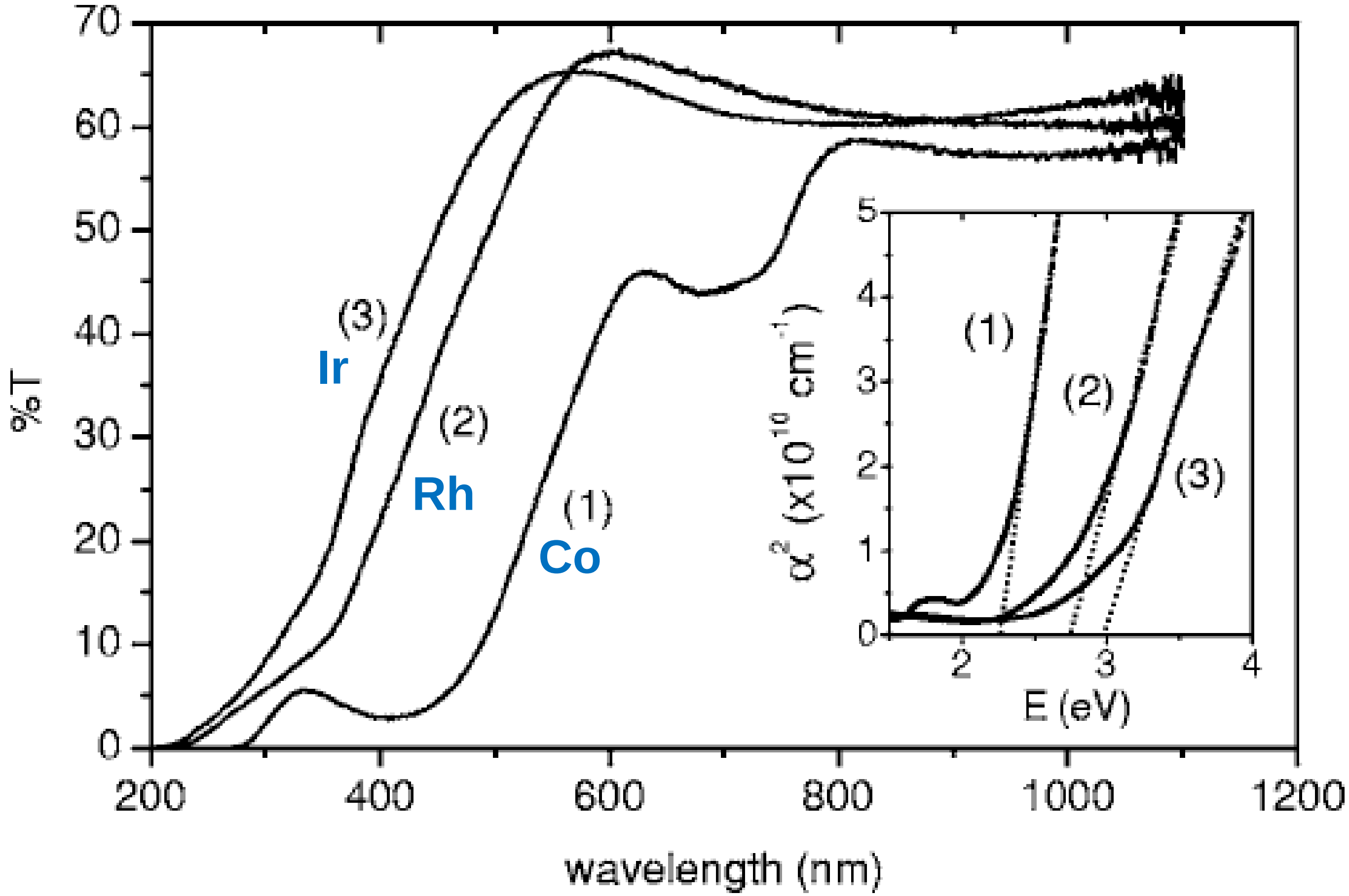
T_d site (e.g., Zn, Mg, Mn)

d^6 p-TCOs: Spinels



Crystal field splitting gives rise to transparency.

Transmission Data for ZnM_2O_4 (M = Ir, Rh, Co)



M. Dekkers *et al.*, Appl Phys. Lett. **90**, 021903, (2007).

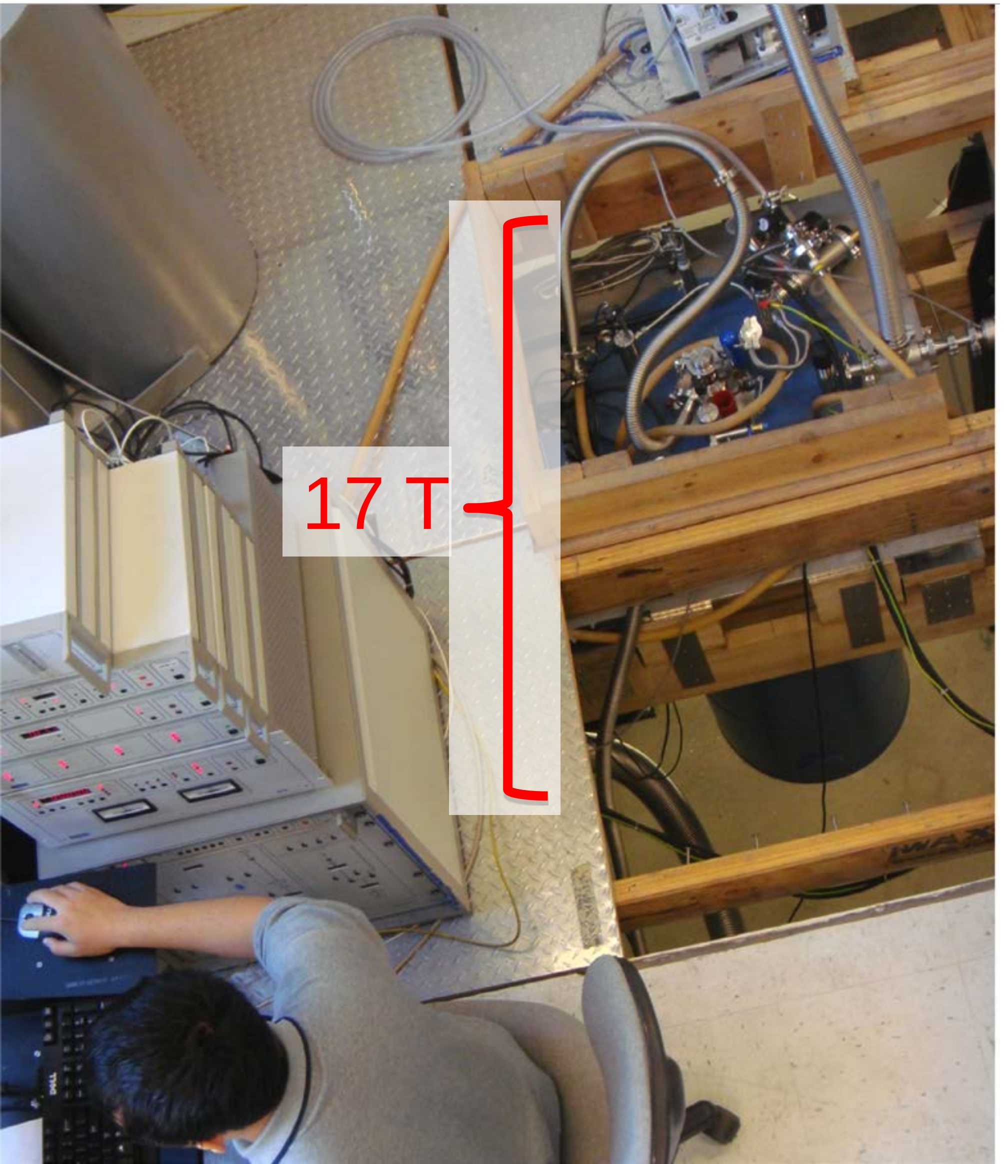
Electrical Data for d^6 Spinels

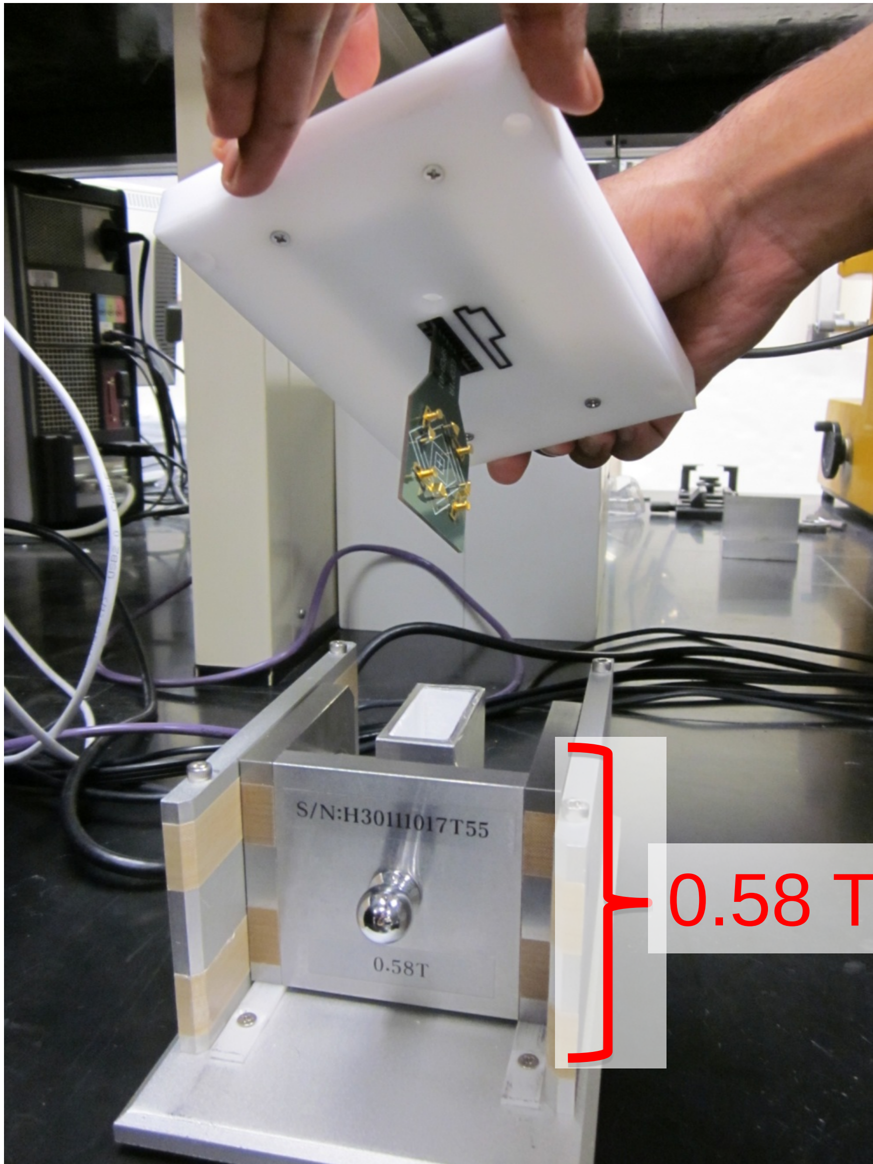
Composition	**σ (S/cm)**	**E_g**
$ZnIr_2O_4$	3.39	2.97
$ZnRh_2O_4$(1)	2.75	2.74
$ZnCo_2O_4$(1)	0.39	2.26
$ZnCo_2O_4$:Mg(2) (bulk)	0.9	

Low conductivities attributed to small hole mobilities!

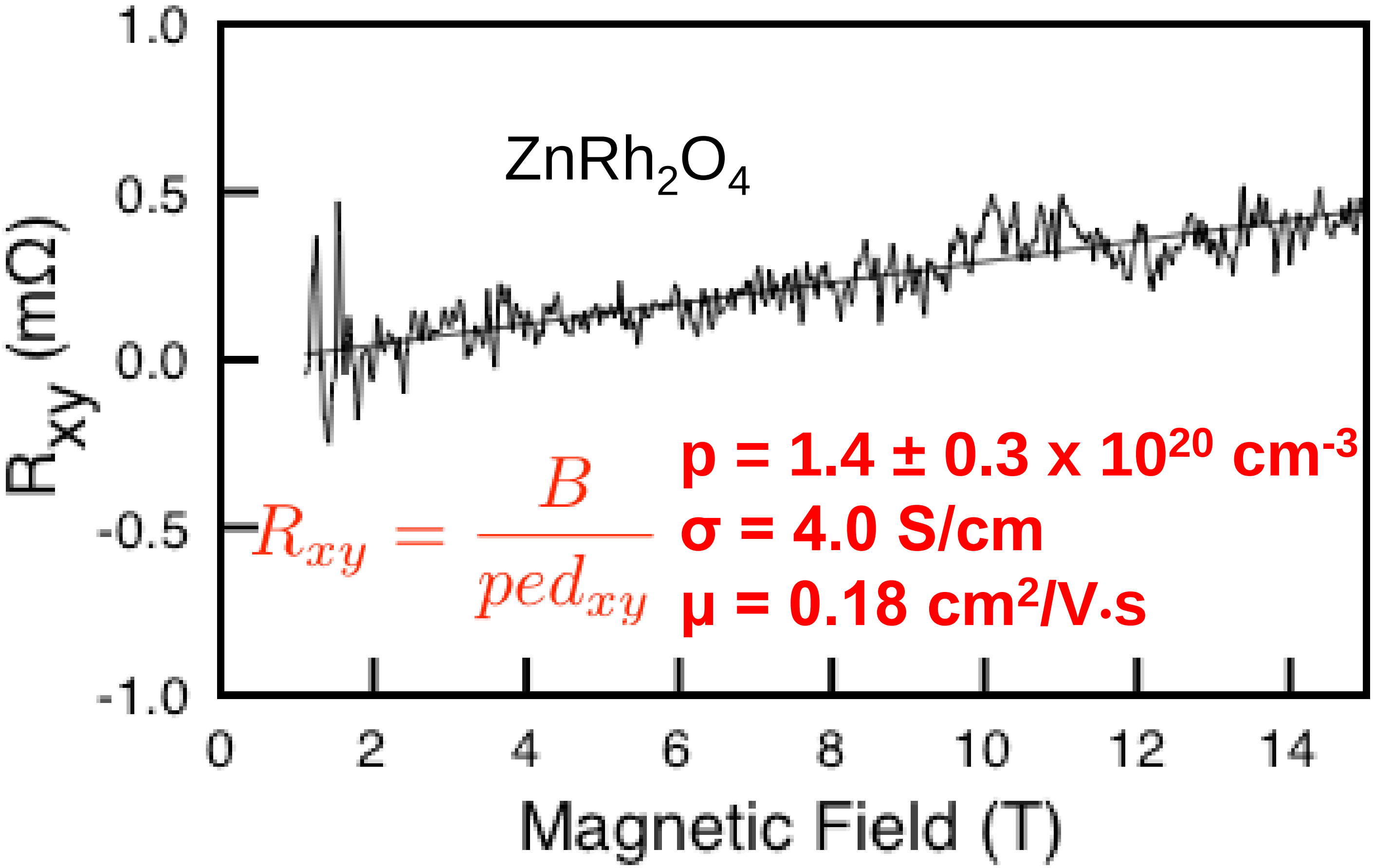
(1) M. Dekkers *et al.*, Appl Phys. Lett. **90**, 021903, (2007).
(2) J. Perkins *et al.*, Phys. Rev. B. **84**, 205207, (2011).

Hall Effect: 17 T and 0.58 T





Hall mobility at room temperature

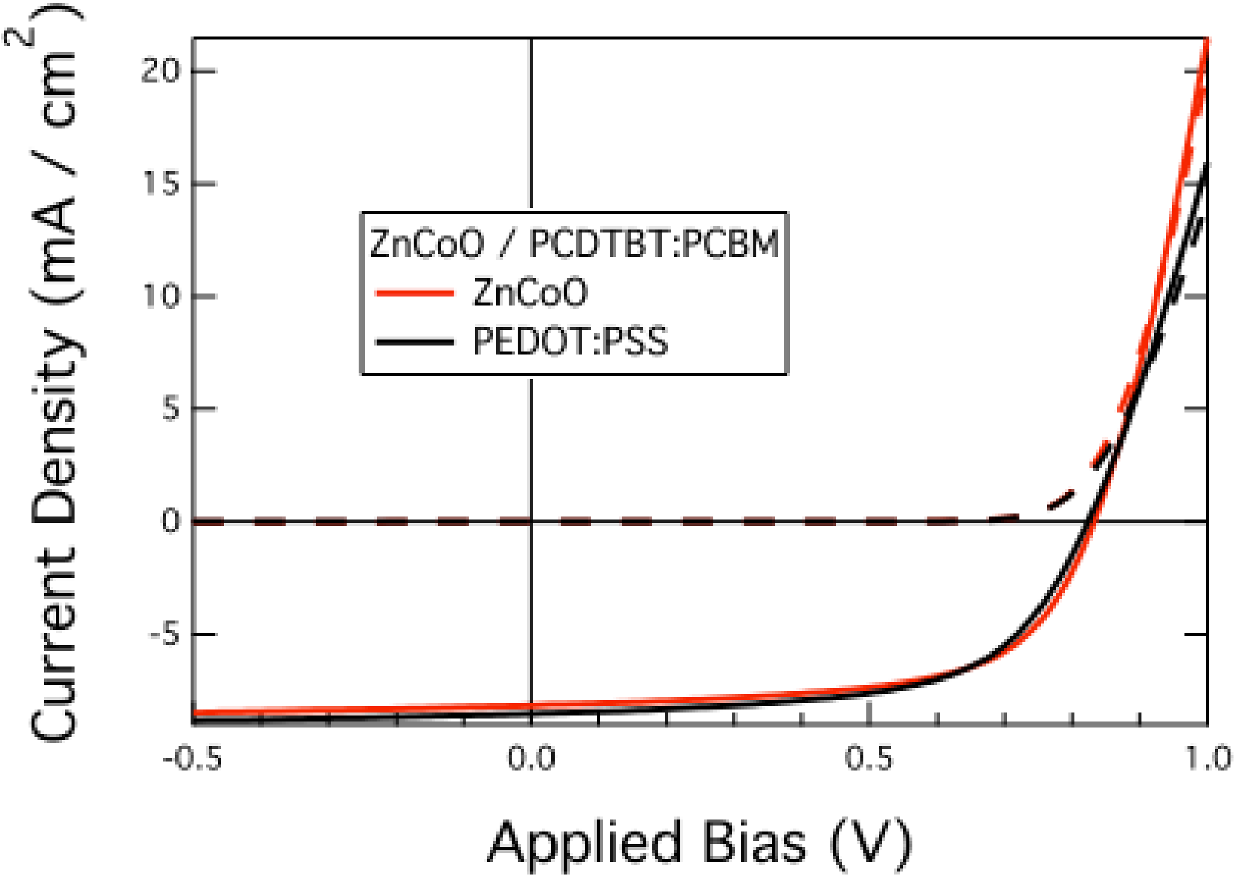


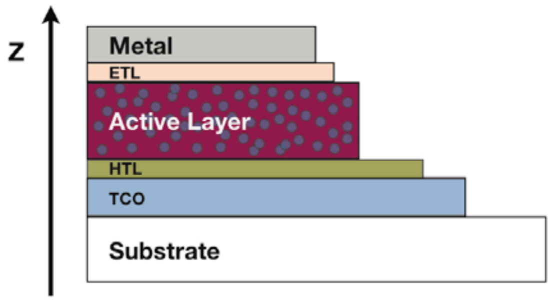
$$R_{xy} = \frac{B}{ped_{xy}}$$

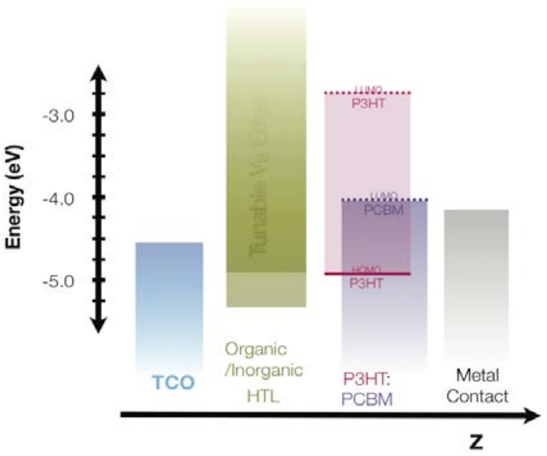
$p = 1.4 \pm 0.3 \times 10^{20}$ cm^{-3}
$\sigma = 4.0$ S/cm
$\mu = 0.18$ cm^2/V·s

A. Nagaraja *et al*., J. Am. Ceram. Soc. (2011) doi: 10.1111/j.1551-2916.2011.04771.x

Zn-Co-O is a Good Hole Transport Layer (HTL) for OPV







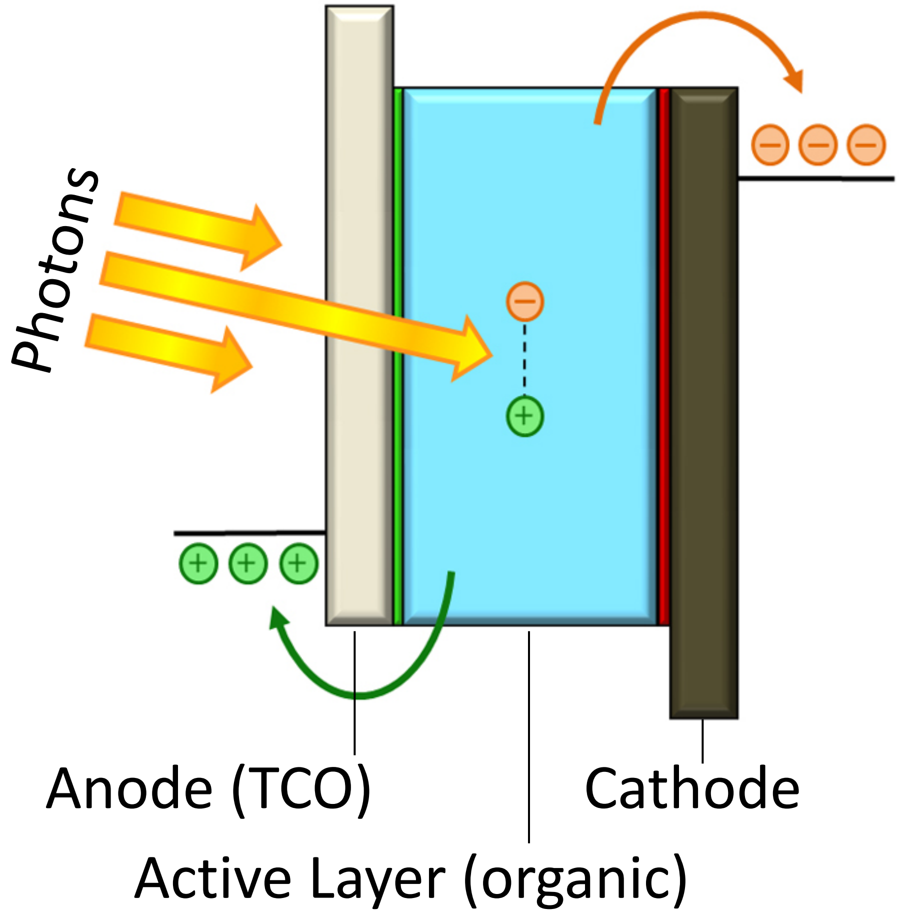
In collaboration with A. Sigdel, N.E. Widjonarko and J.J. Berry – CIS:SEM EFRC

Performance comparable to PEDOT:PSS **on the first try!**

Back to n-Type TCOs: The Importance of Work Functions

The Need for Ohmic Contacts

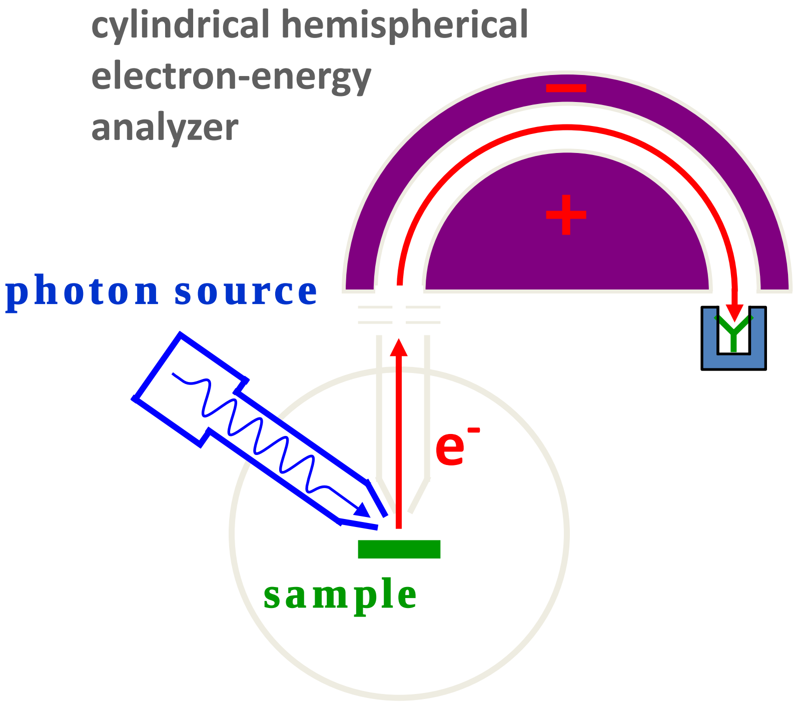
Organic Photovoltaic (OPV)



- TCOs play an integral role as electrically transparent contacts in solar cells
- Device performance depends on Ohmic contacts with electrodes
- Contact type depends on band alignment between layers

What is the Work Function?
How is it Measured?

Photoelectron Spectroscopy



cylindrical hemispherical
electron-energy
analyzer

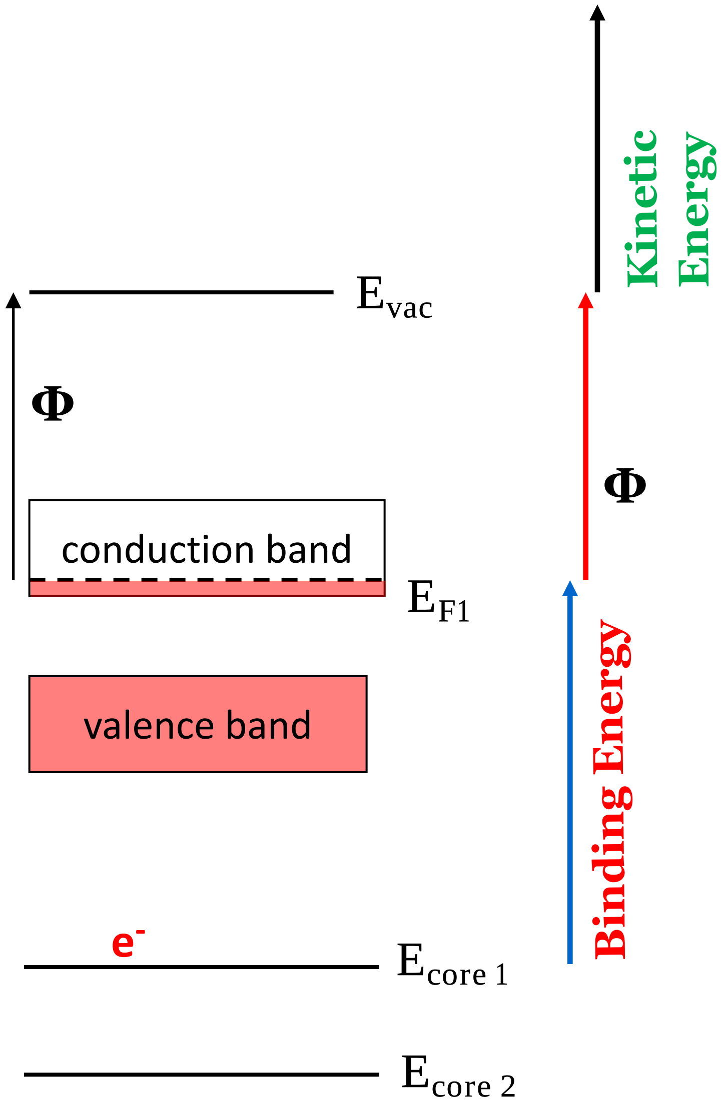
−

+

photon source

e^-

sample



E_{vac}

Φ

conduction band

E_{F1}

valence band

e^-

$E_{core\ 1}$

$E_{core\ 2}$

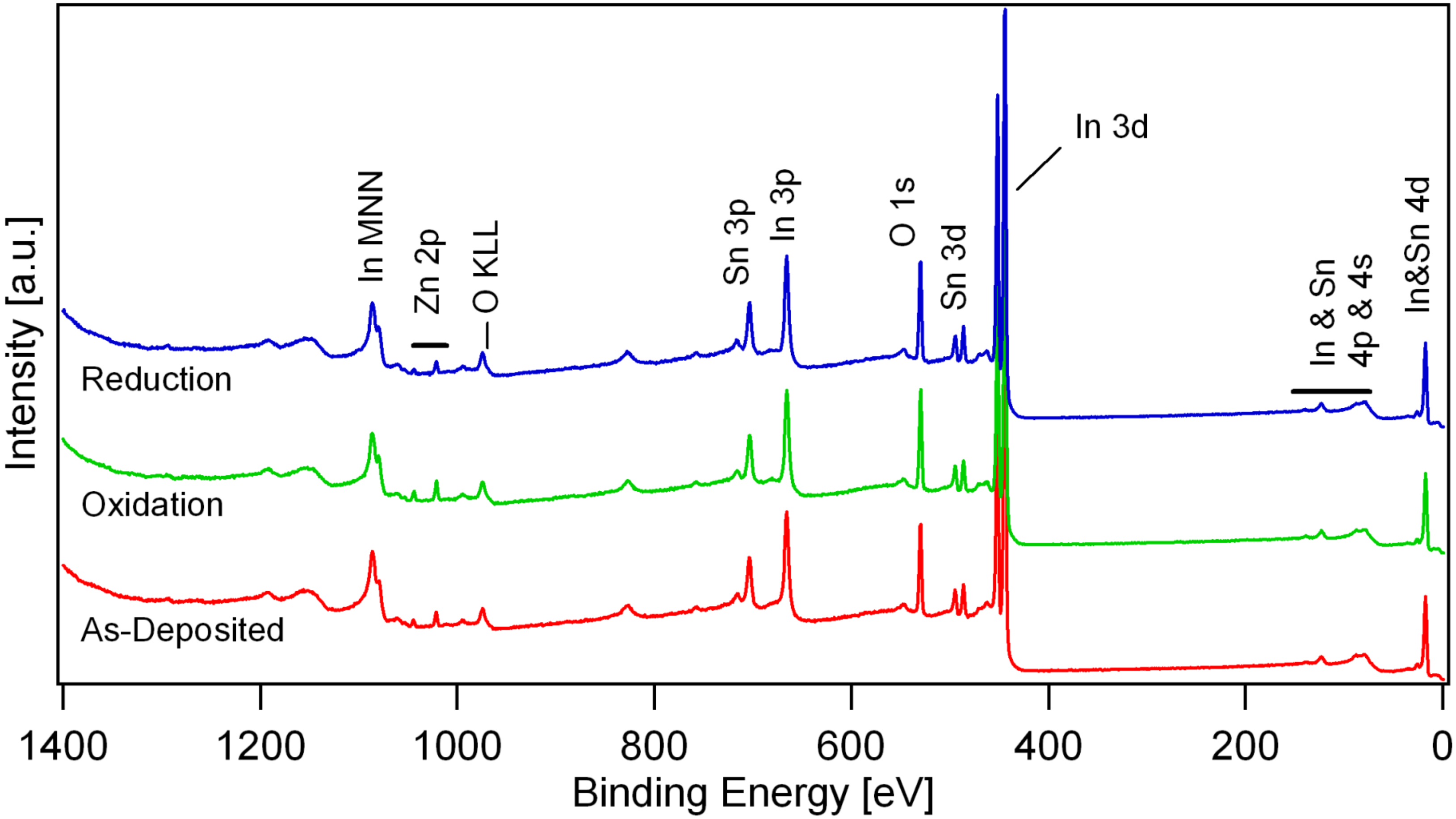
Kinetic Energy

Φ

Binding Energy

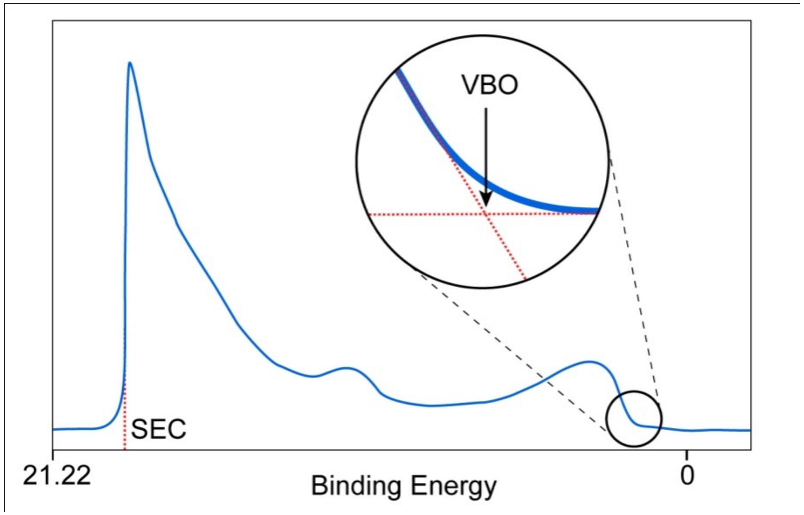
$$E_{BE} = h\upsilon_{source} - E_{kinetic} - \Phi_{analyzer}$$

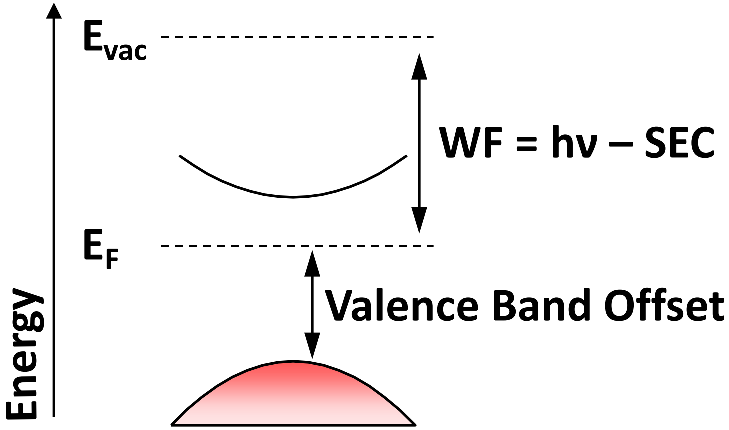
XPS Survey Spectra



c-ZITO-10

UV Photoelectron Spectroscopy



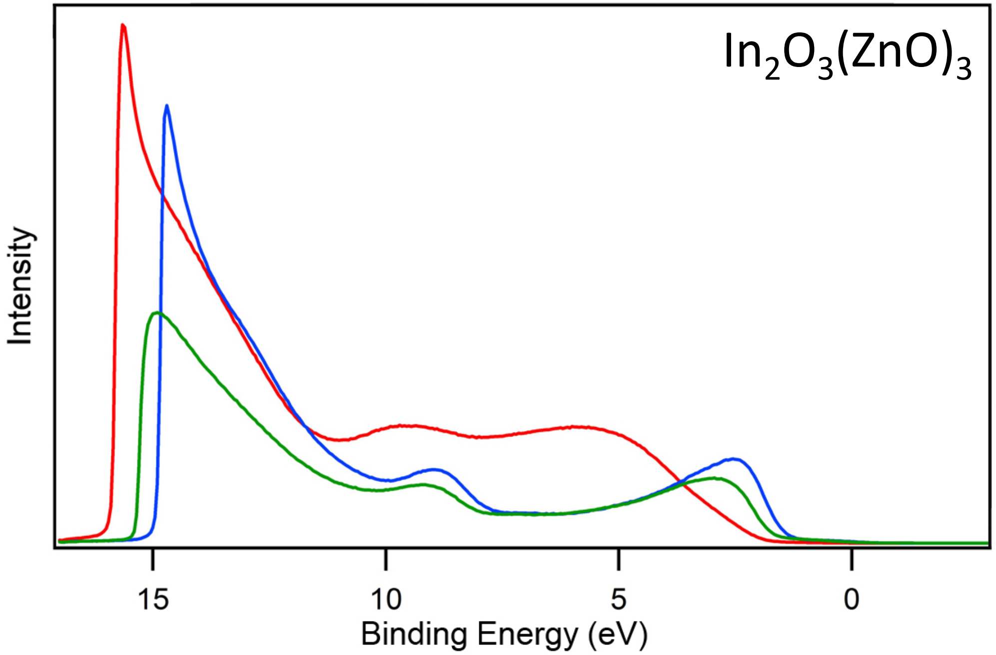

E_{vac}

WF = hν – SEC

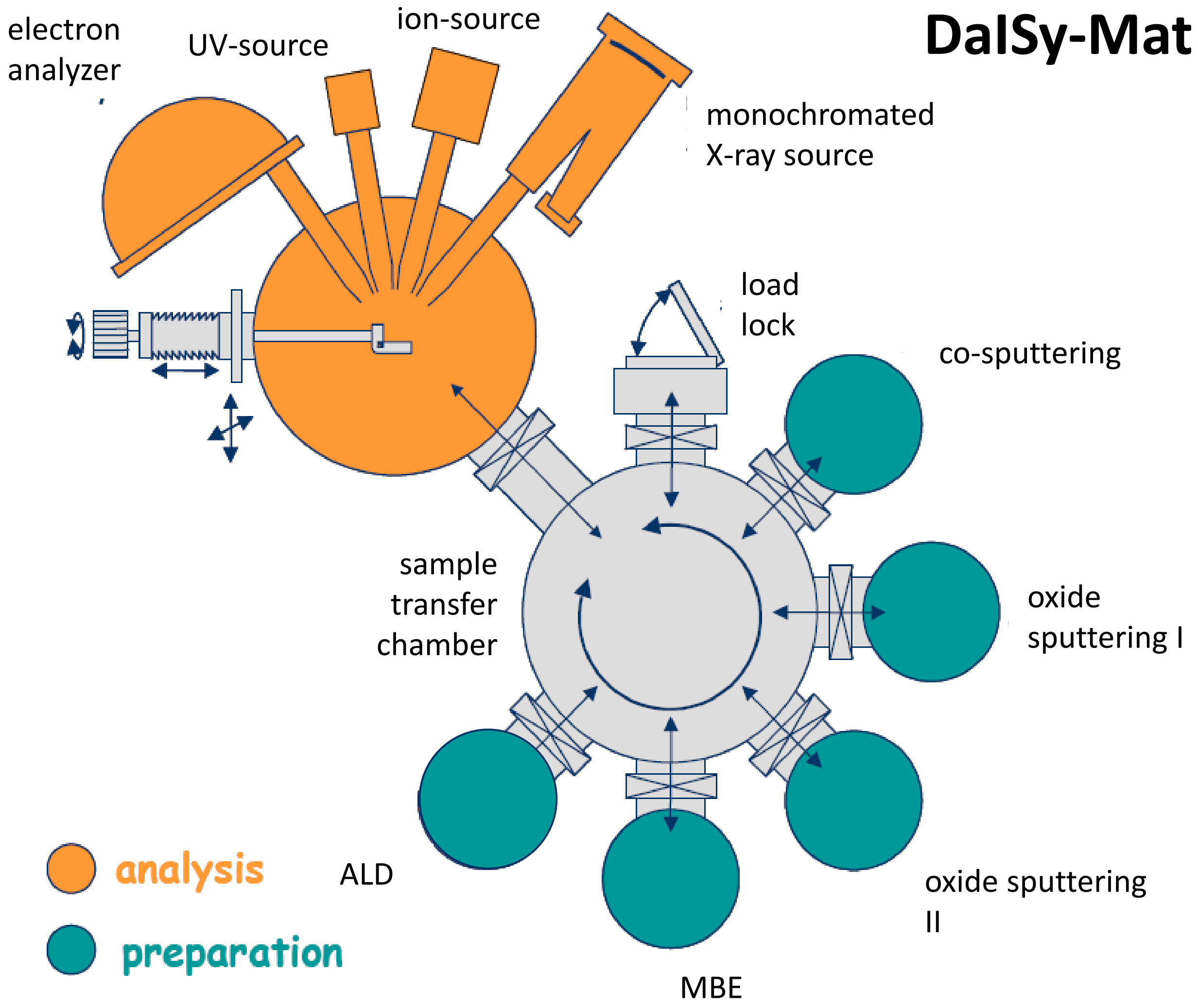
E_F

Valence Band Offset

Energy



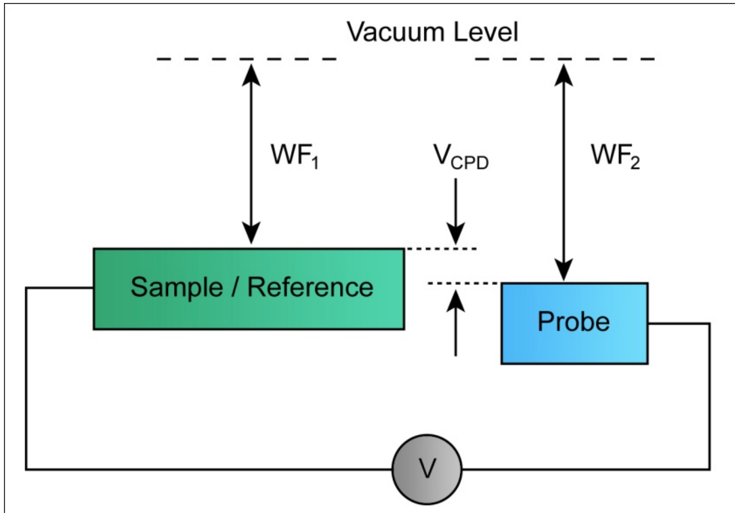
In Situ Photoelectron Spectroscopy



Technical University of Darmstadt (Darmstadt, Germany)

Kelvin Probe WF Measurements

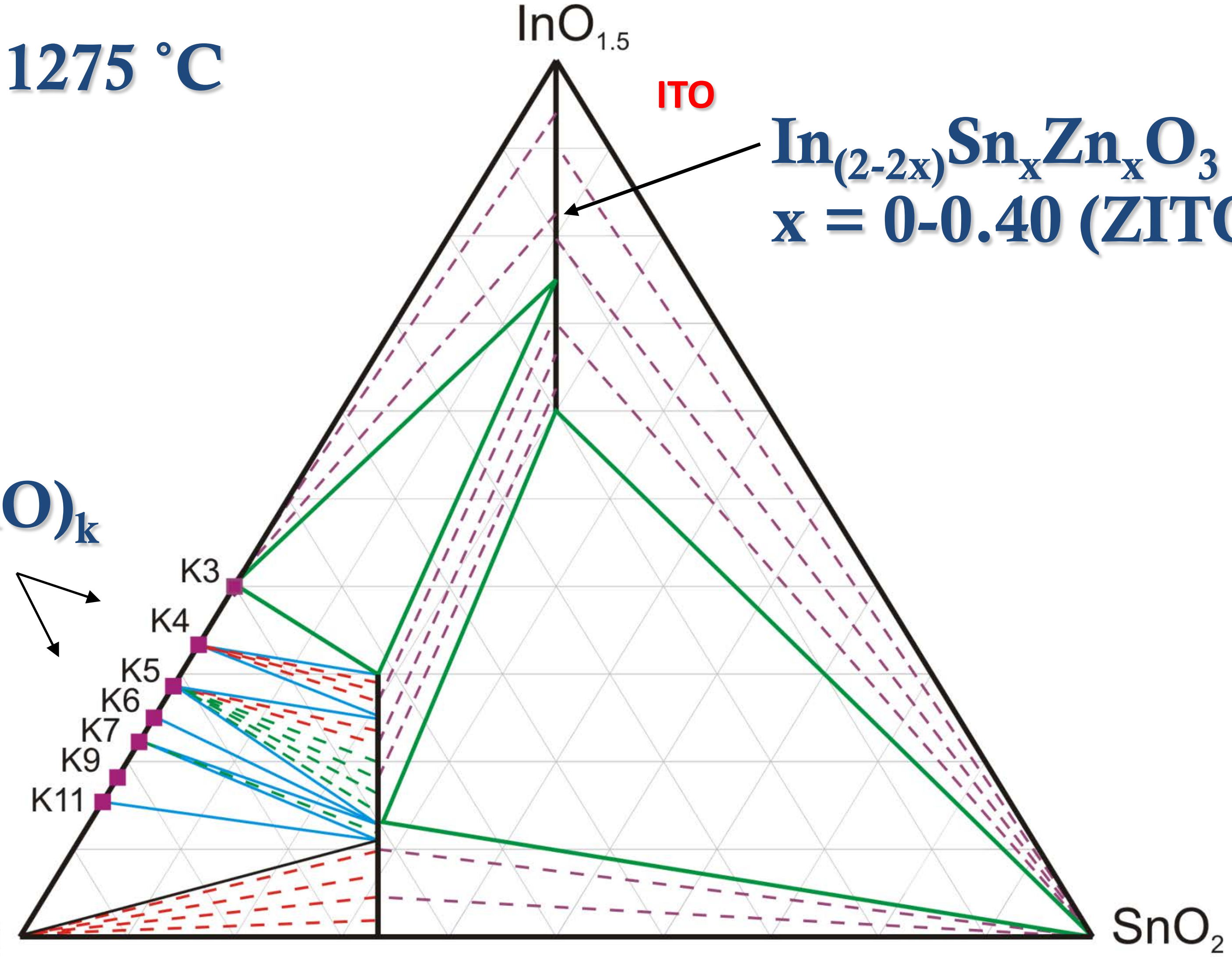
Kelvin Probe Method



Under ambient conditions!

Zn-In-Sn-O System

$T = 1275\ ^{\circ}C$



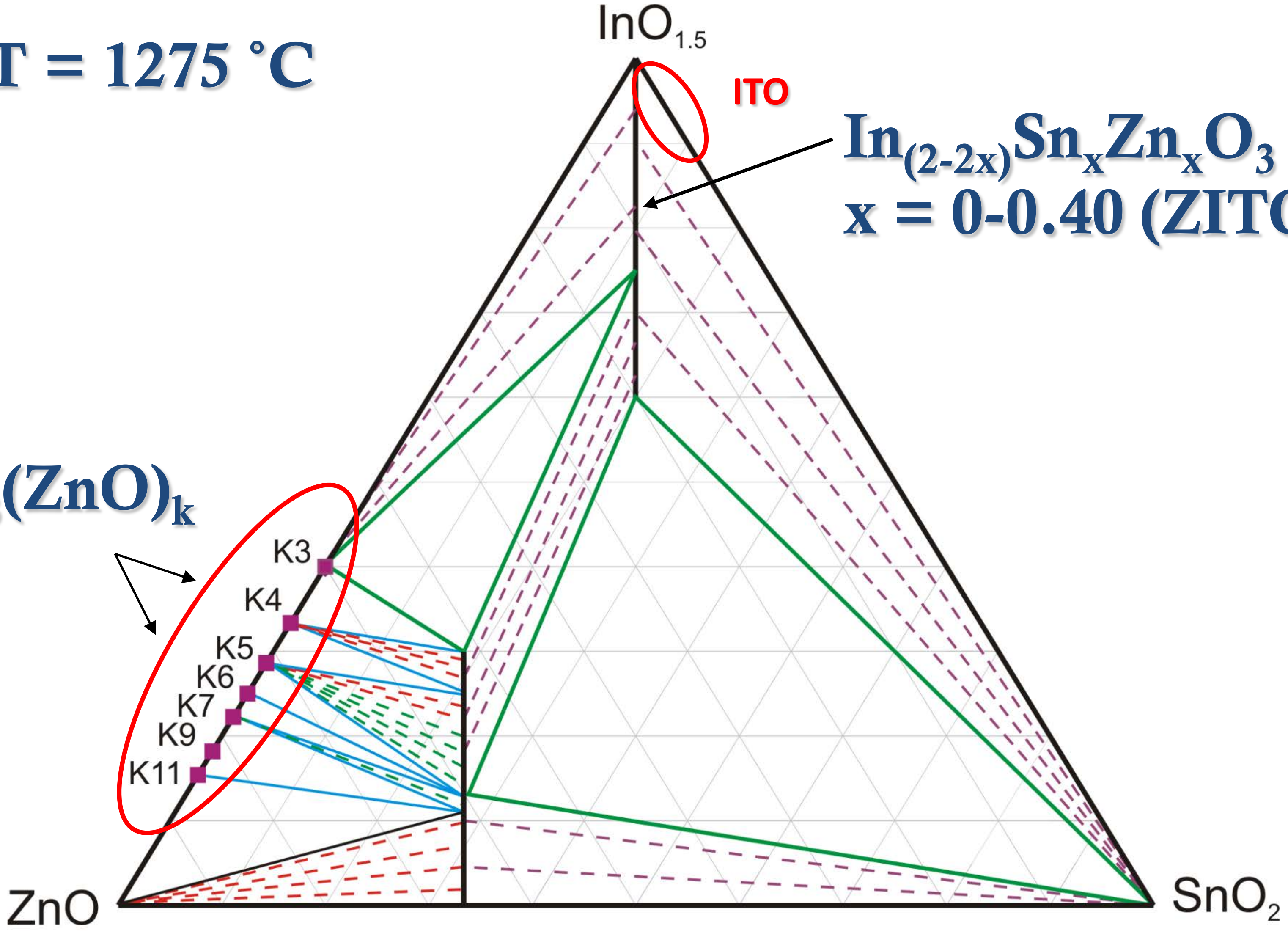
$In_{(2-2x)}Sn_xZn_xO_3$
$x = 0\text{-}0.40$ (ZITO)

$In_2O_3(ZnO)_k$

Harvey et al., J. Am. Ceram. Soc. **91** 11 (2008)

Zn-In-Sn-O System

T = 1275 °C

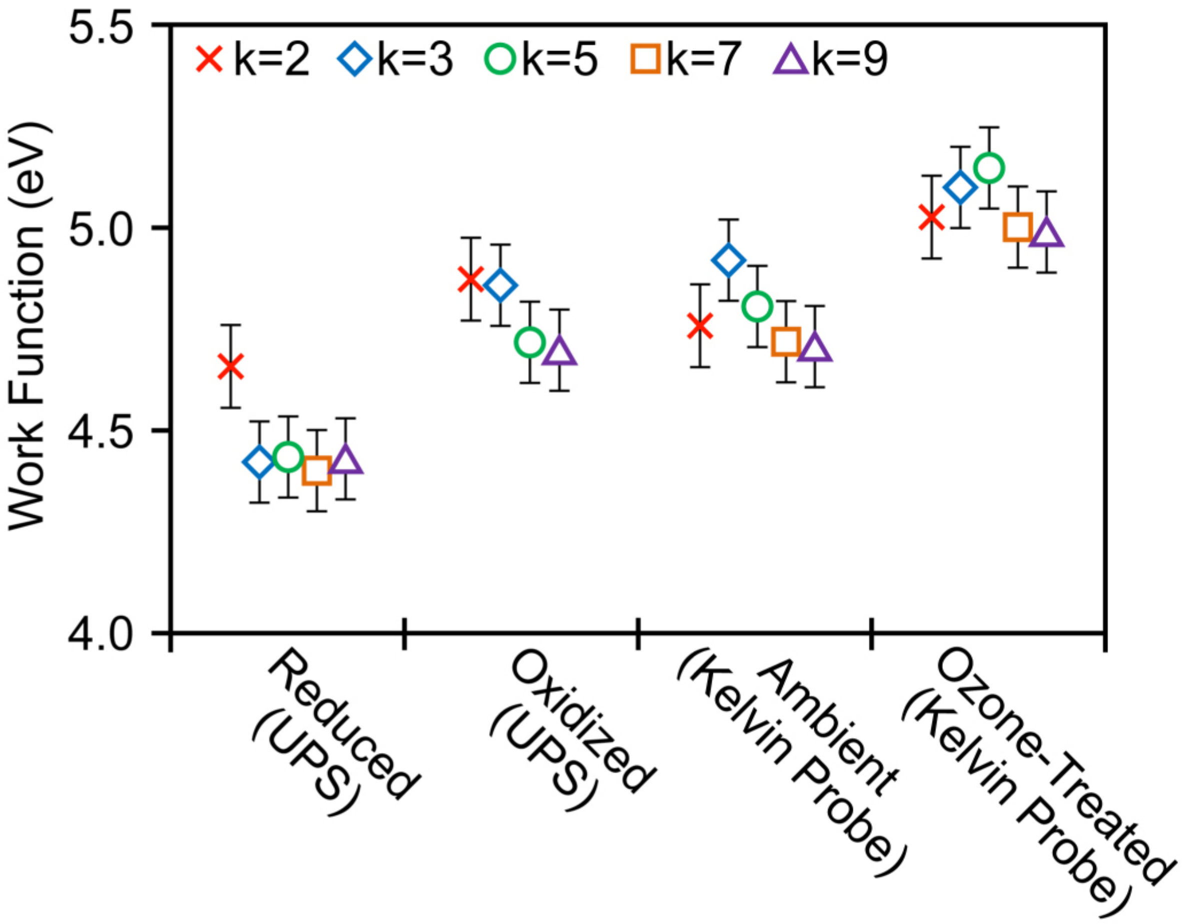


$In_{(2-2x)}Sn_xZn_xO_3$
x = 0-0.40 (ZITO)

$In_2O_3(ZnO)_k$

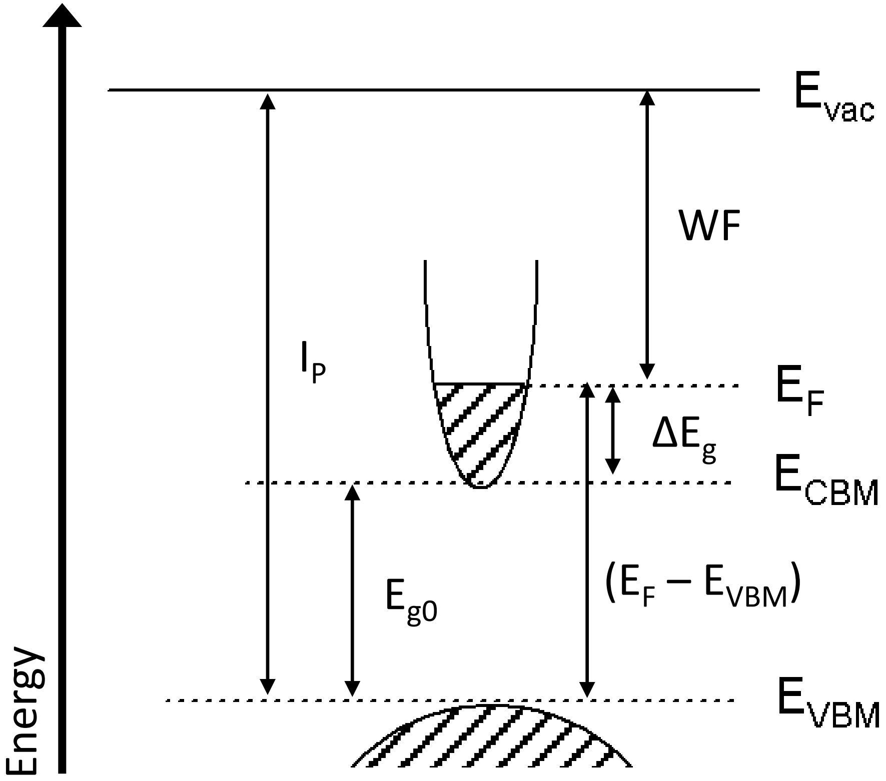
Harvey et al., J. Am. Ceram. Soc. **91** 11 (2008)

Comparison of KP and UPS



Some Surface Science Definitions

Some Basic Definitions



E_{vac} = vacuum level

E_F = Fermi level

E_{CBM} = conduction band minimum

E_{VBM} = valence band maximum

E_{g0} = fundamental band gap

ΔE_g = Burstein-Moss shift

I_p = ionization potential

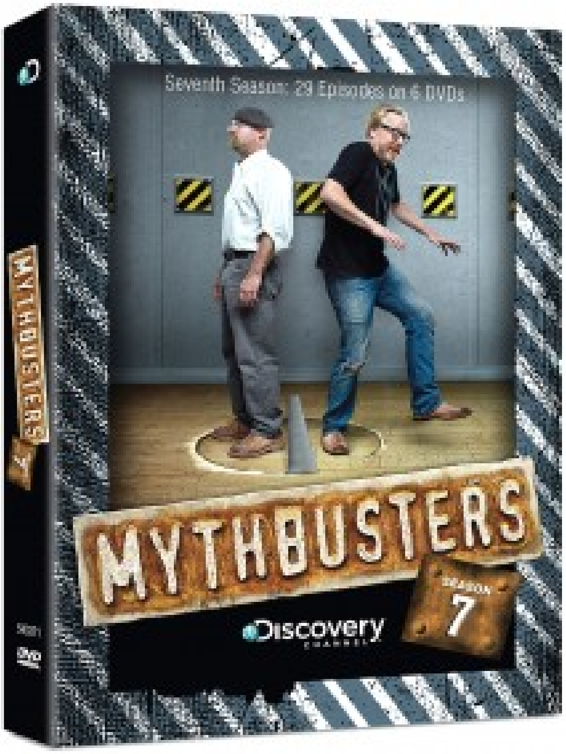
$(E_F - E_{VBM})$ = Fermi level position

WF = work function (Φ)

Debunking Work Function Myths

TCO Work Function Myths

- Every material has a unique work function
- The work function of a given oxide's surface is a constant
- The only way to change the work function of an oxide surface is "extrinsically" (e.g., by surface adsorbates)*

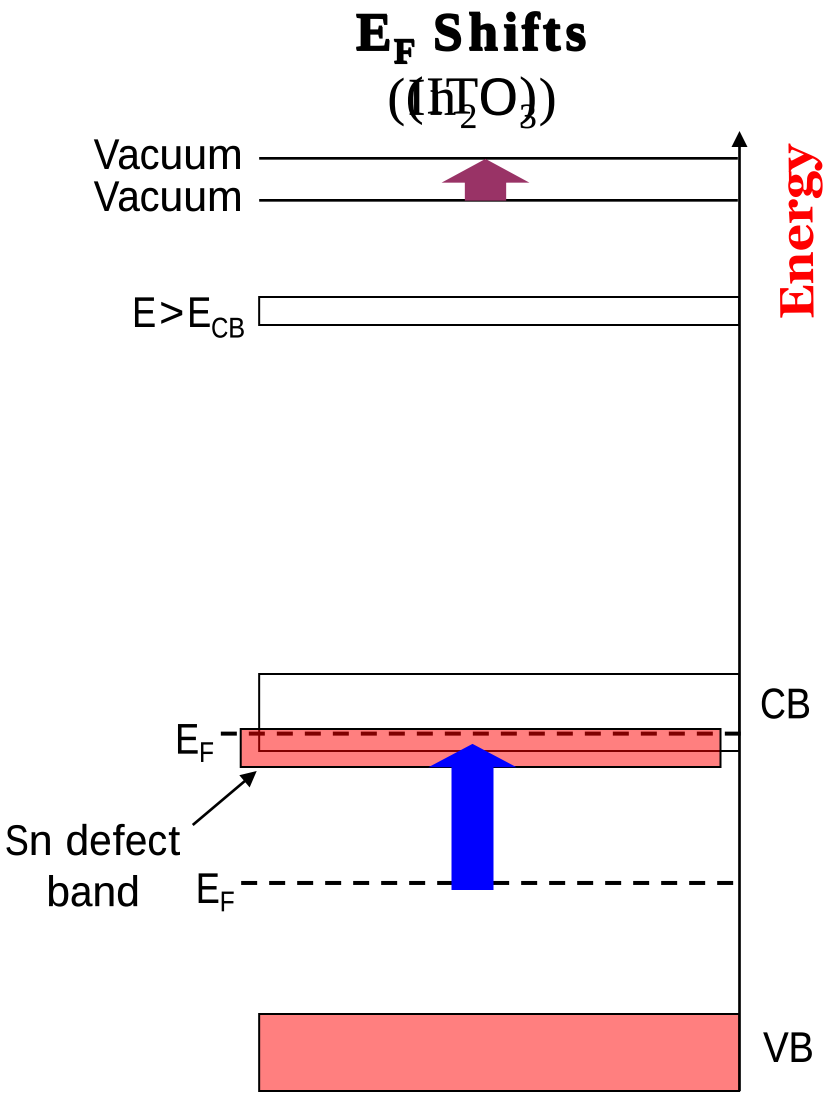


** For example, Neal Armstrong et al., Accts. Chem. Res., 42 (11) 1748 (2009).*

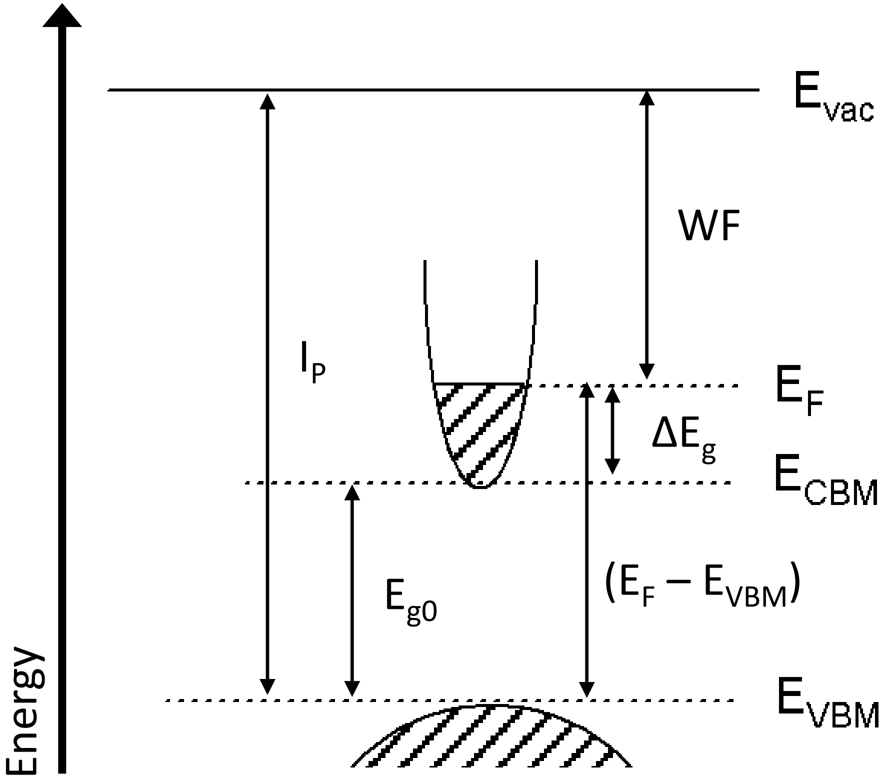
Manipulating Work Functions

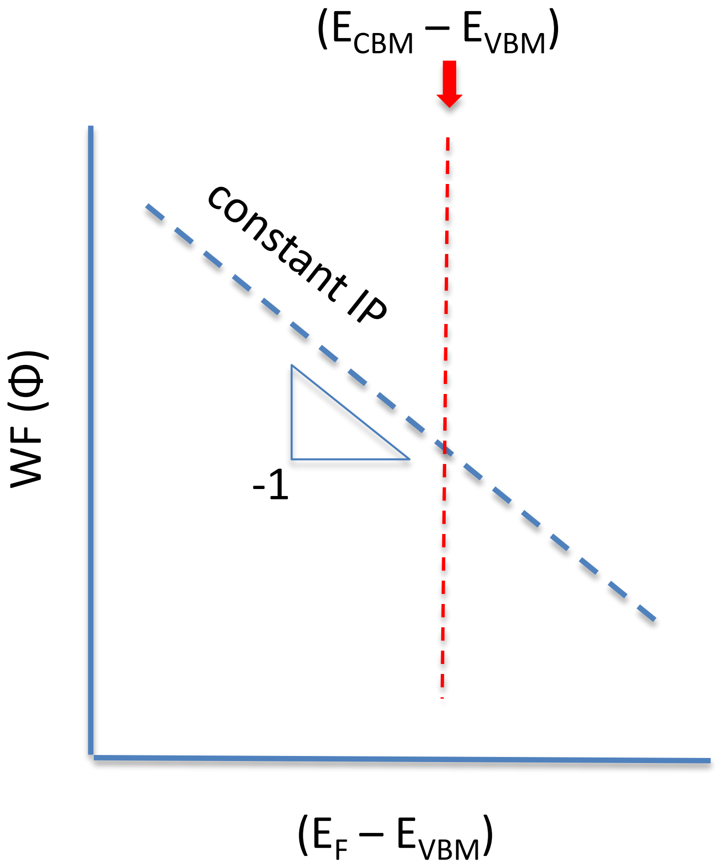
How to Modify Work Function?

- Two ways:
  - Shift the Fermi level position
    ($E_F – E_{VBM}$)
    can change independently with doping
  - Change the Ionization potential
    (E_{vac}-E_{VBM})
    can change independently with surface dipole changes (assuming E_g is constant)



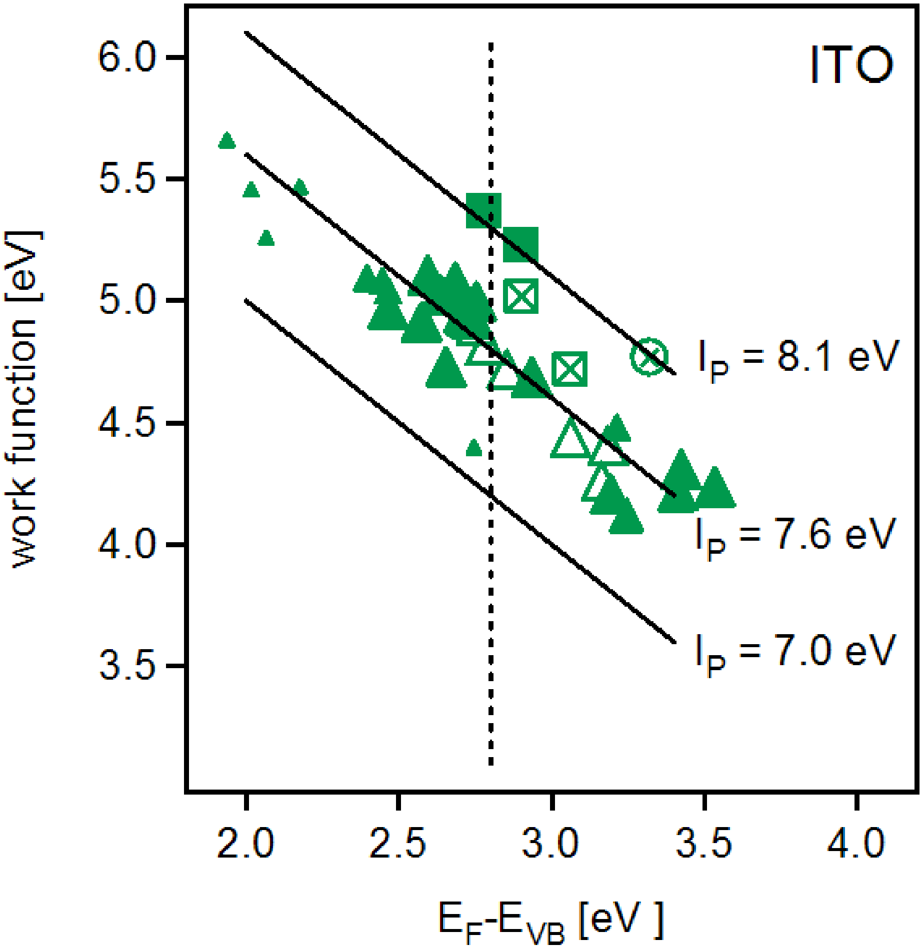
Ionization Potential Plots





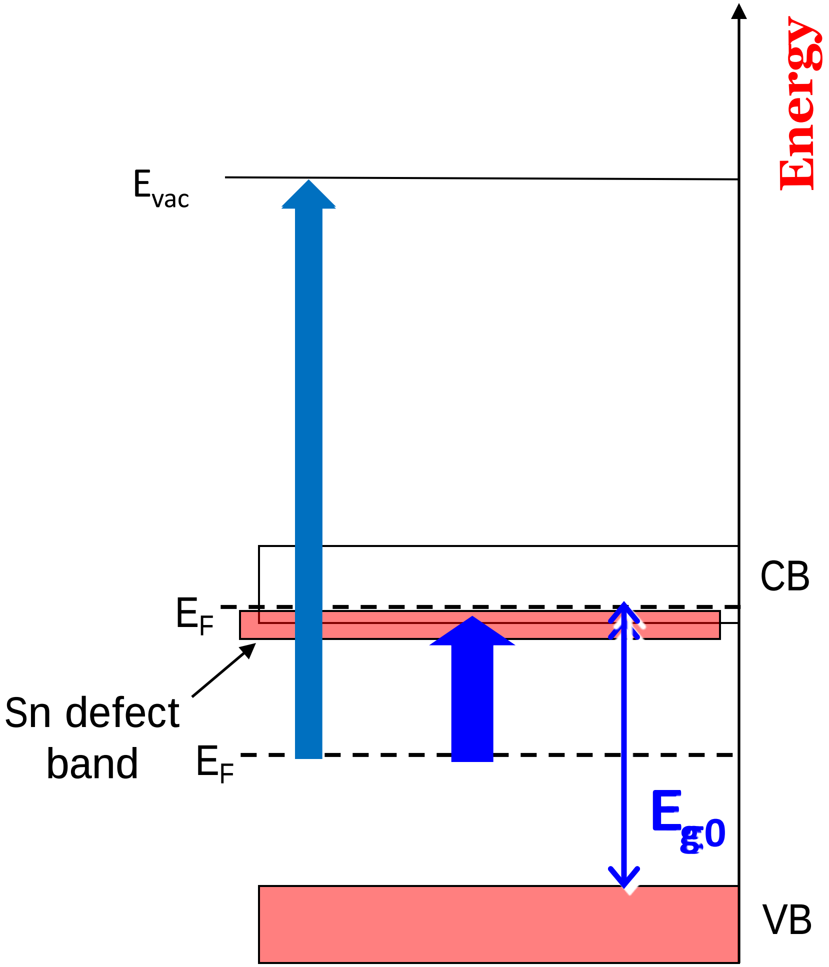
$$I_p = (E_F – E_{VBM}) + WF\ (\Phi) \rightarrow WF\ (\Phi) = I_p - (E_F – E_{VBM})$$

Changing Fermi Level Position



Burstein-Moss Shift

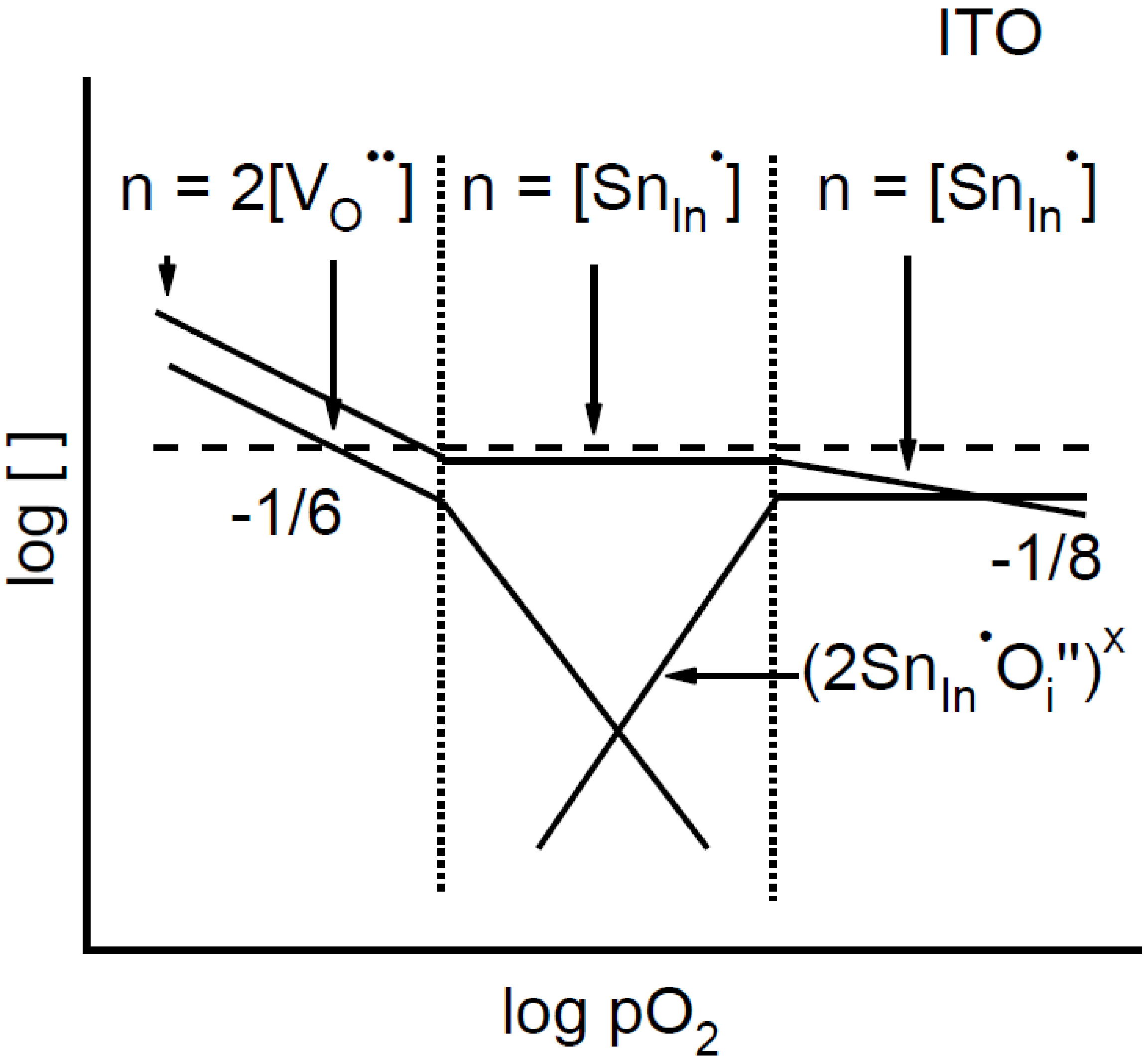
(ITO)



A. Klein et al., Materials, 3 (2010) 4892

$$IP = (E_F - E_{VB}) + WF$$

ITO Defect Chemistry



How to Modify Work Function?

- Two ways:
  - Shift the Fermi level position

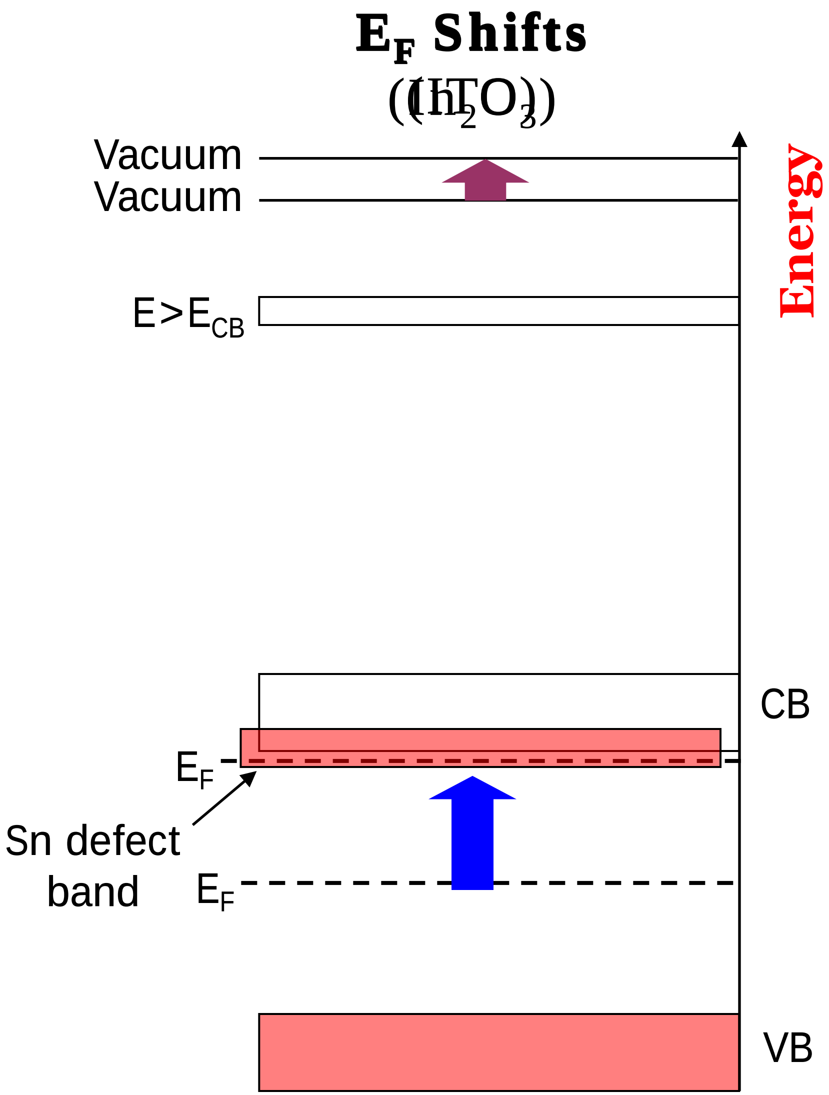
    ($E_F – E_{VBM}$)

    can change independently with doping

  - Change the Ionization potential

    (E_{vac}-E_{VBM})

    can change independently with surface dipole changes (assuming E_g is constant)



Surface Orientation Effects

Silver

Surface	Work Function	Polycrystalline Work Function
Ag (111)	4.74 eV	
Ag (100)	4.64 eV	
Ag (110)	4.52 eV	
Au(poly)		4.26 eV

Gold

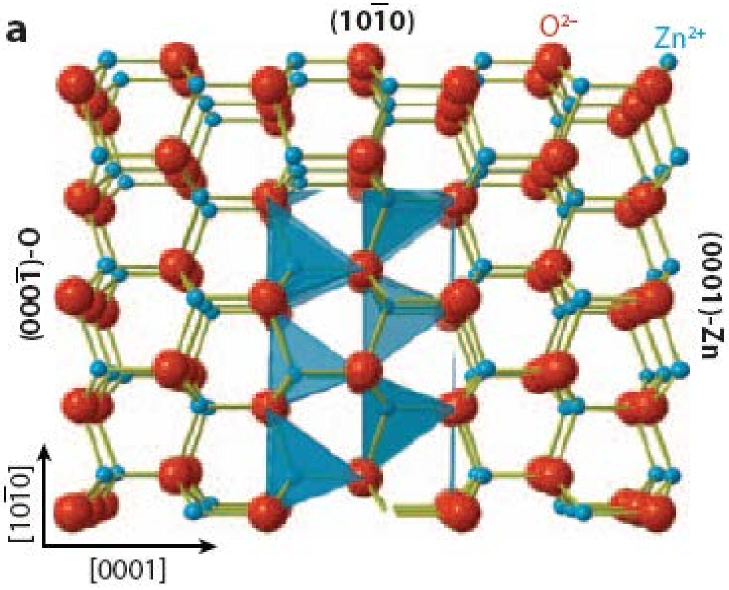
Surface	Work Function	Polycrystalline Work Function
Au (111)	5.31 eV	
Au (100)	5.47 eV	
Au (110)	5.37 eV	
Au(poly)		5.10 eV

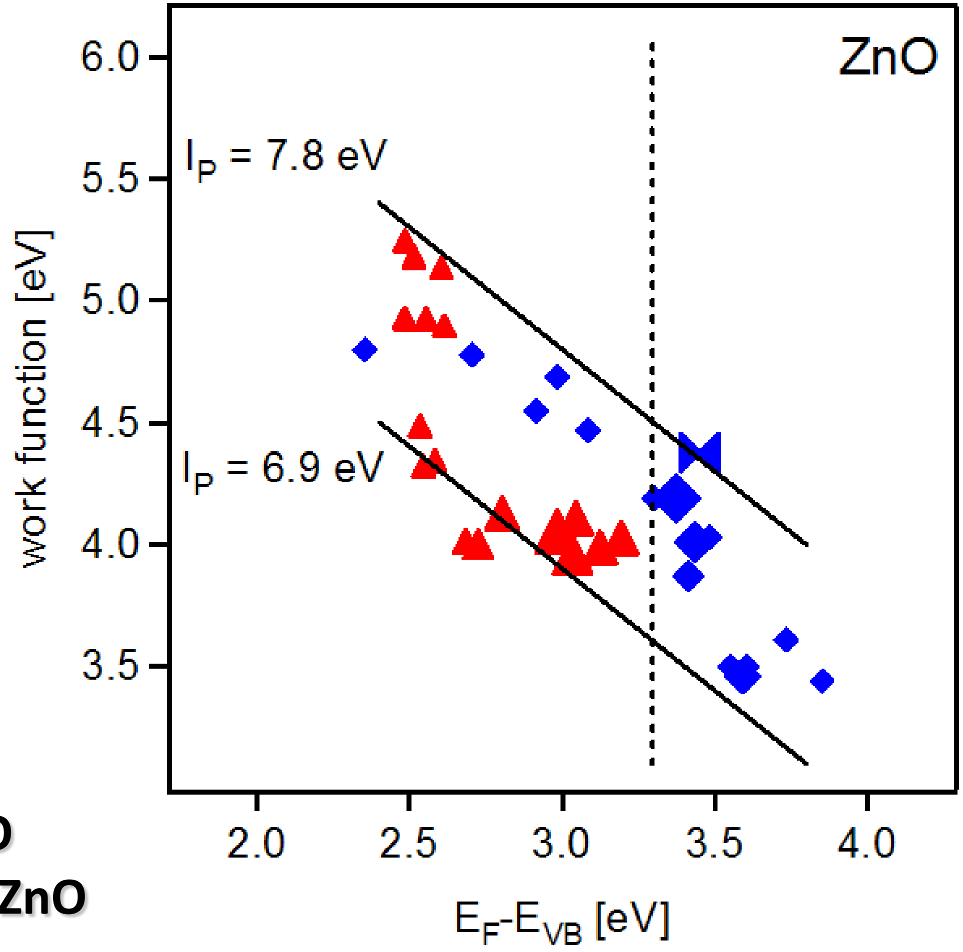
Note: close-packed surfaces have high work functions; polycrystalline specimens represent averages with low-work function orientations.

H. B. Michaelson, The Work Function of the Elements and Its Periodicity,
J. Appl. Phys. 48 (1977) 4729.

ZnO-Surface Orientations

ZnO has polar and non-polar surface terminations

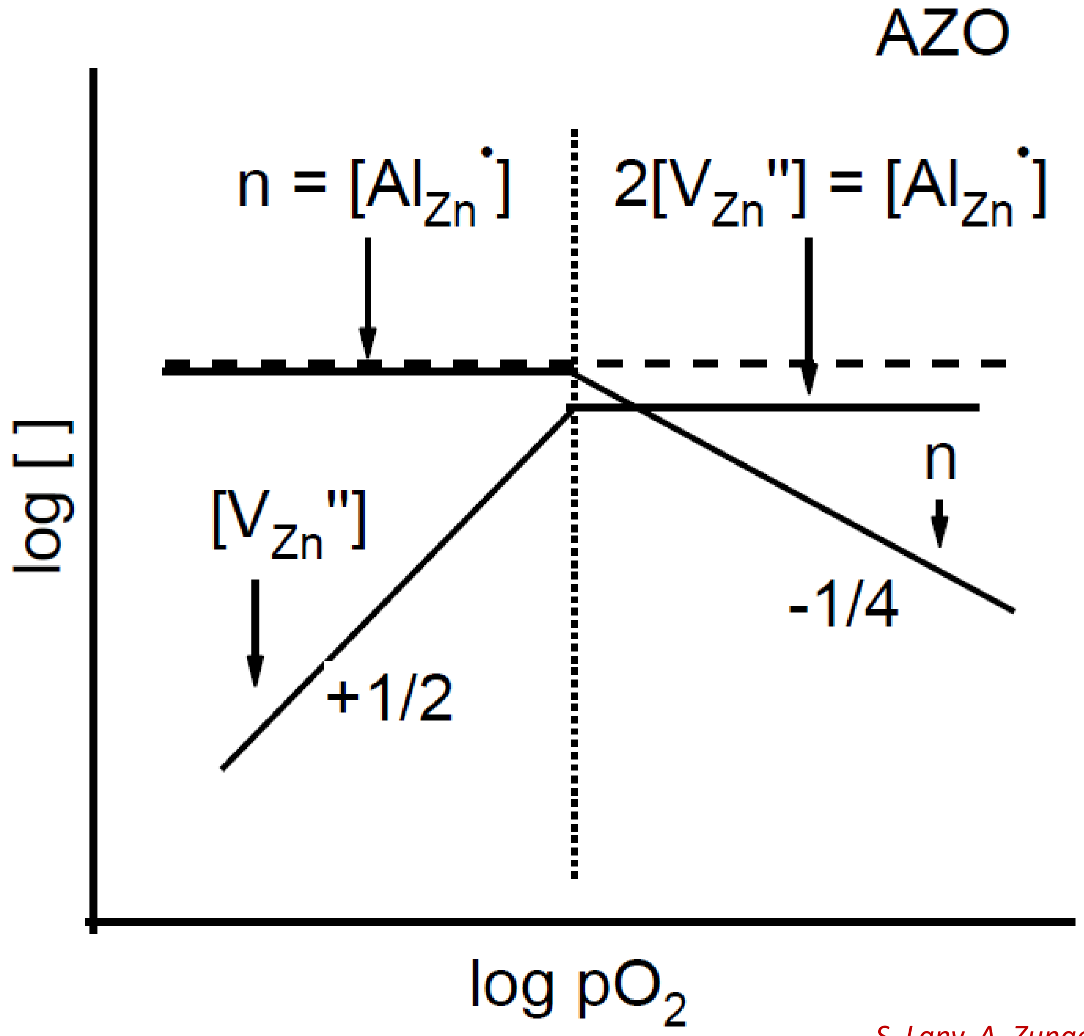




Red = ZnO
Blue = Al:ZnO

U. Diebold et al., Annu. Rev. Phys. Chem., 61 (2010) 129

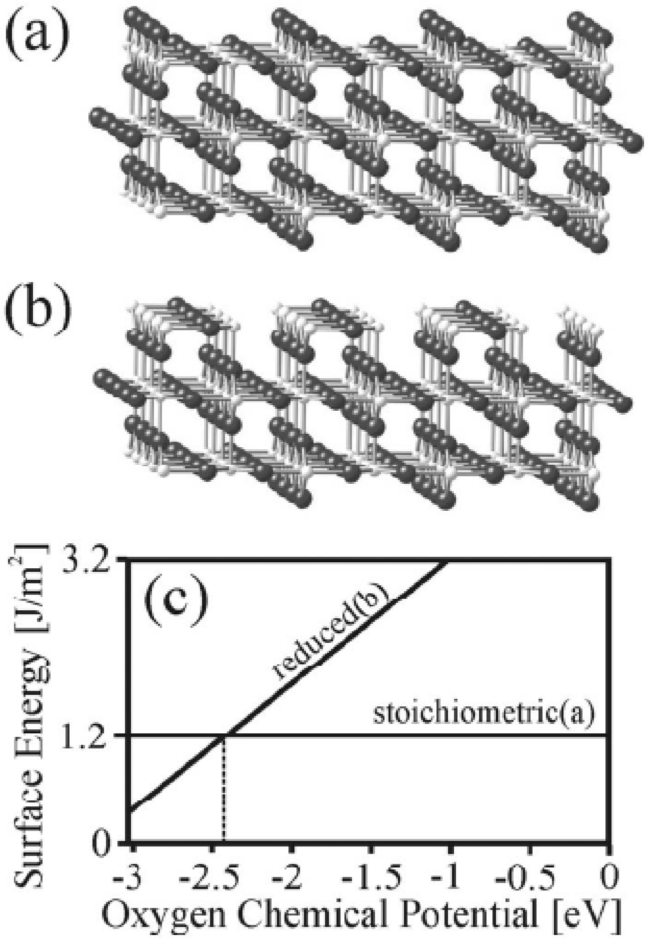
ZnO:Al Defect Chemistry

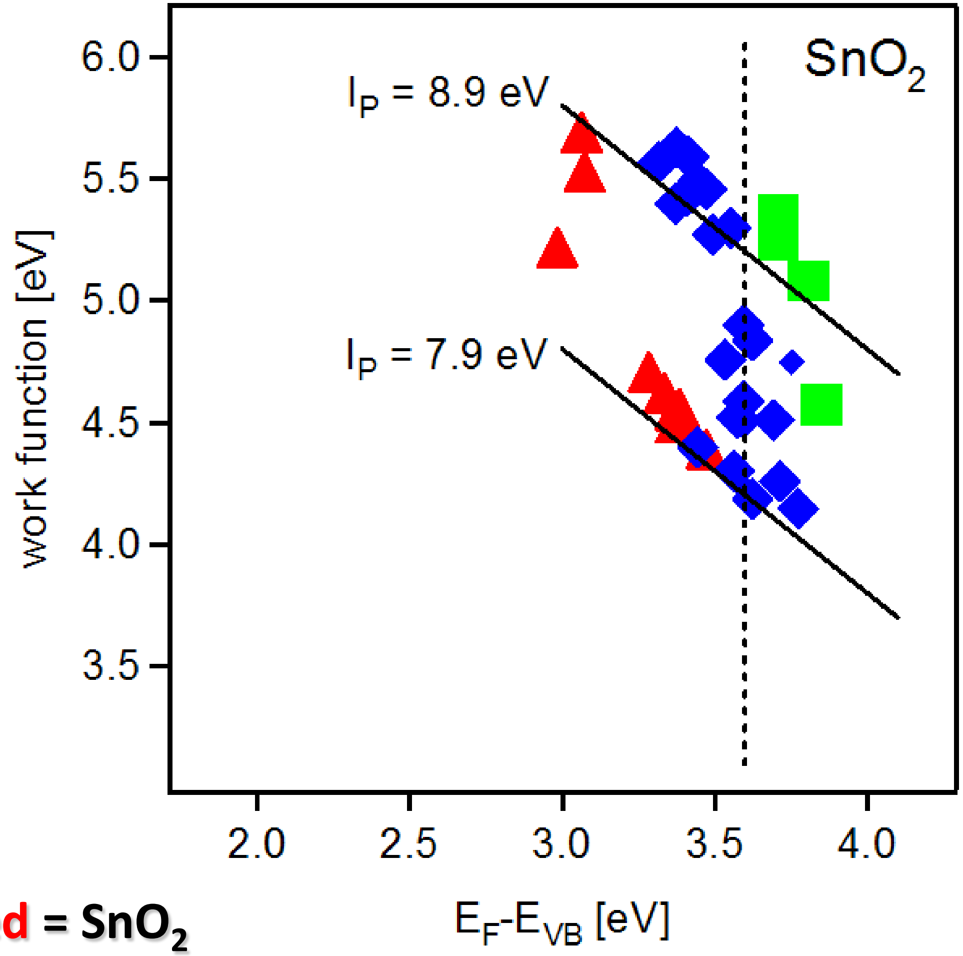


S. Lany, A. Zunger, PRL, 98, 045501 (2007)

SnO_2 Surface Terminations

(110) Surface

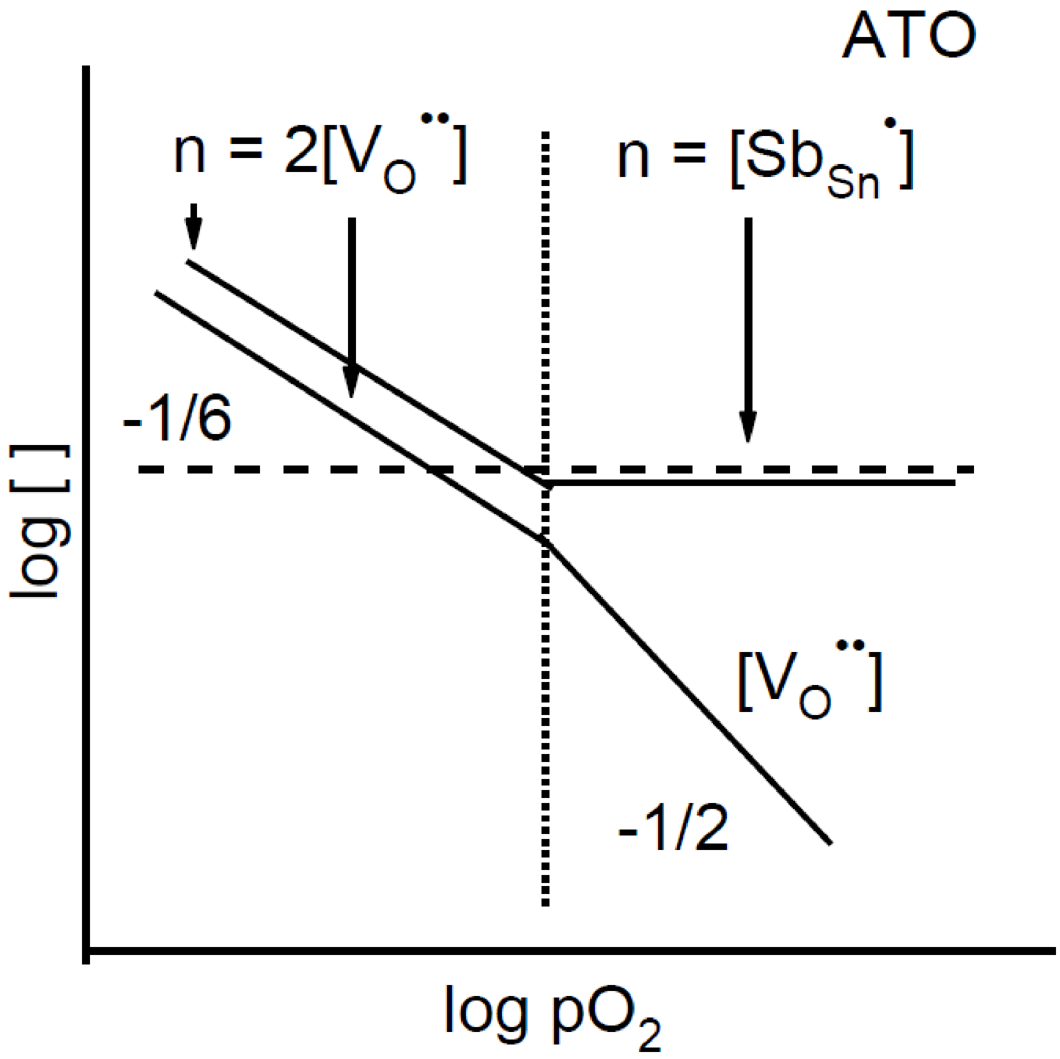




Red = SnO_2
Blue = $Sb{:}SnO_2$
Green = Bulk $Sb{:}SnO_2$

M. Batzill et al., Phys. Rev. B, ***72*** *(2005) 165414*

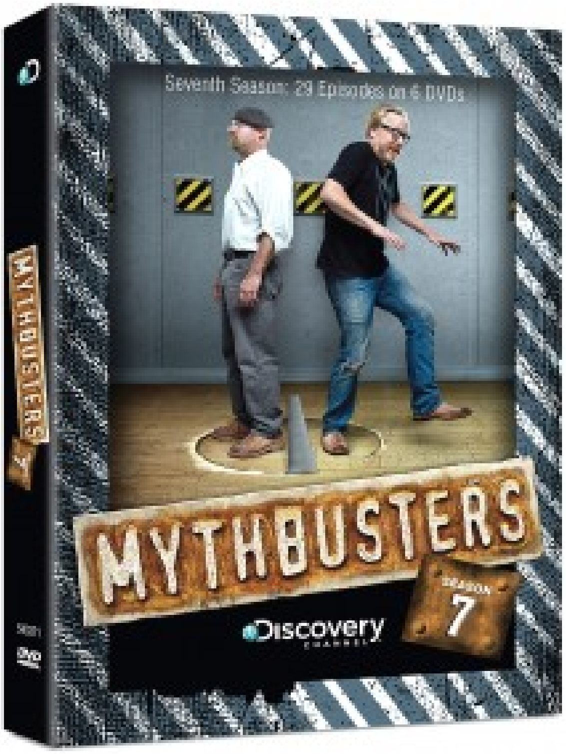
SnO_2:Sb Defect Chemistry



TCO Work Function Truths

$IP = (E_F - E_{VBM}) + WF$

- The WF of an oxide surface decreases linearly as Fermi level increases (if IP remains constant)
- The IP (WF) of an oxide surface can be changed by dipole modifications—surface orientation, surface termination, surface stoichiometry—(if Fermi level remains constant)
- We can therefore change oxide surface work functions both “intrinsically” and “extrinsically”*



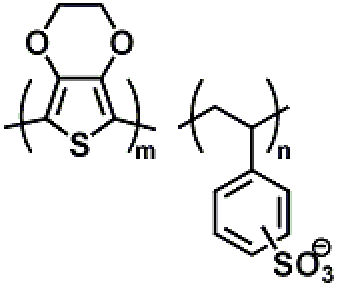
** For example, Neal Armstrong et al., Accts. Chem. Res., 42 (11) 1748 (2009).*

Motivation for New TCOs

Why Do We Need New TCOs?

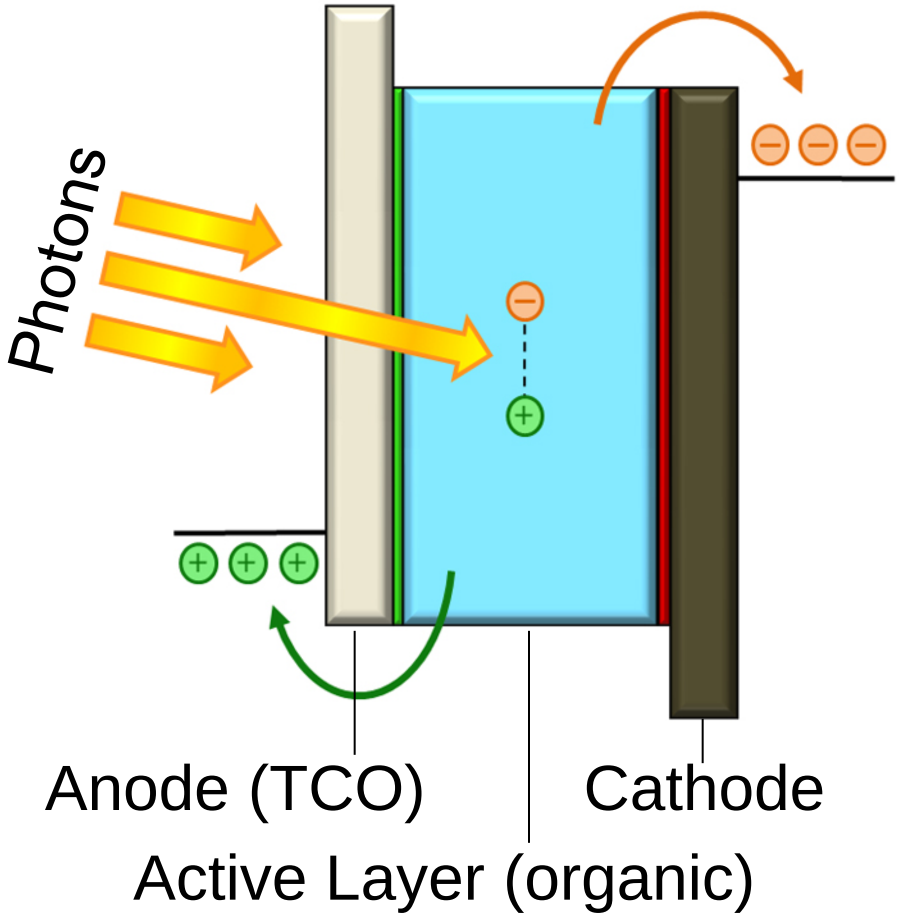
- Why do people use ITO?
  - Available
  - Good TCO (up to 10,000 S/cm conductivity, good transparency)

- Drawbacks to ITO
  - COST
    - In costs are volatile
  - STABILITY
    - ITO is etched by common barrier layer PEDOT:PSS
  - WORK FUNCTION
    - ITO work function is generally < 5eV



The Importance of TCOs in OPVs

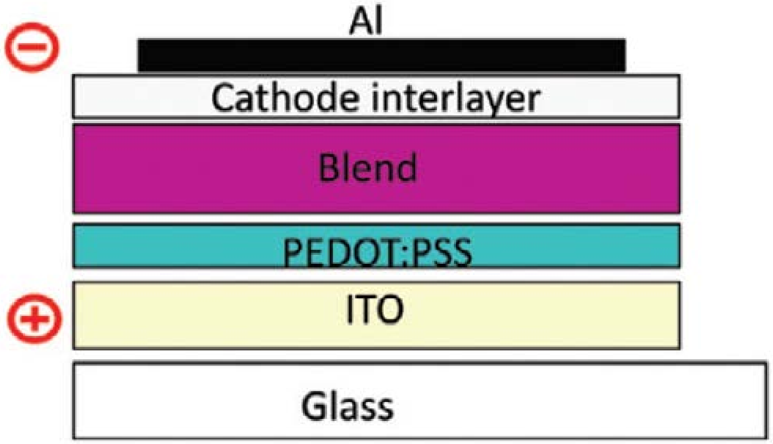
Organic Photovoltaic (OPV)



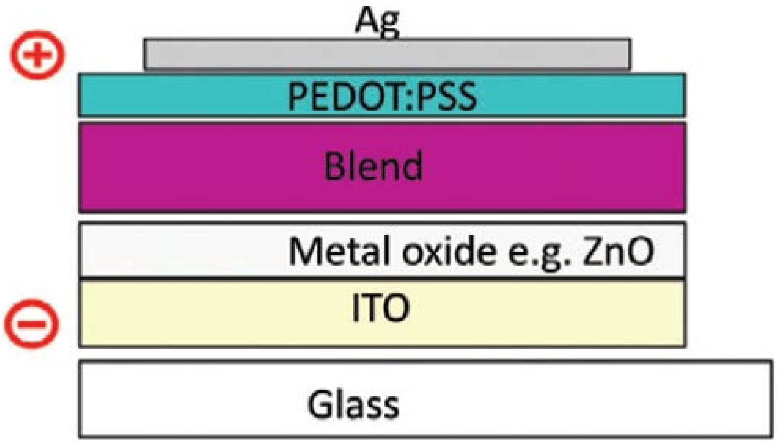
- TCOs play an integral role as electrically transparent contacts in solar cells
- Device performance depends on Ohmic contacts with electrodes
- Contact type depends on band alignment between layers

TCOs in Traditional/Inverted Cells

Traditional Polarity



Inverted Polarity



Want high work function: > 5eV

Want low work function: < 4eV

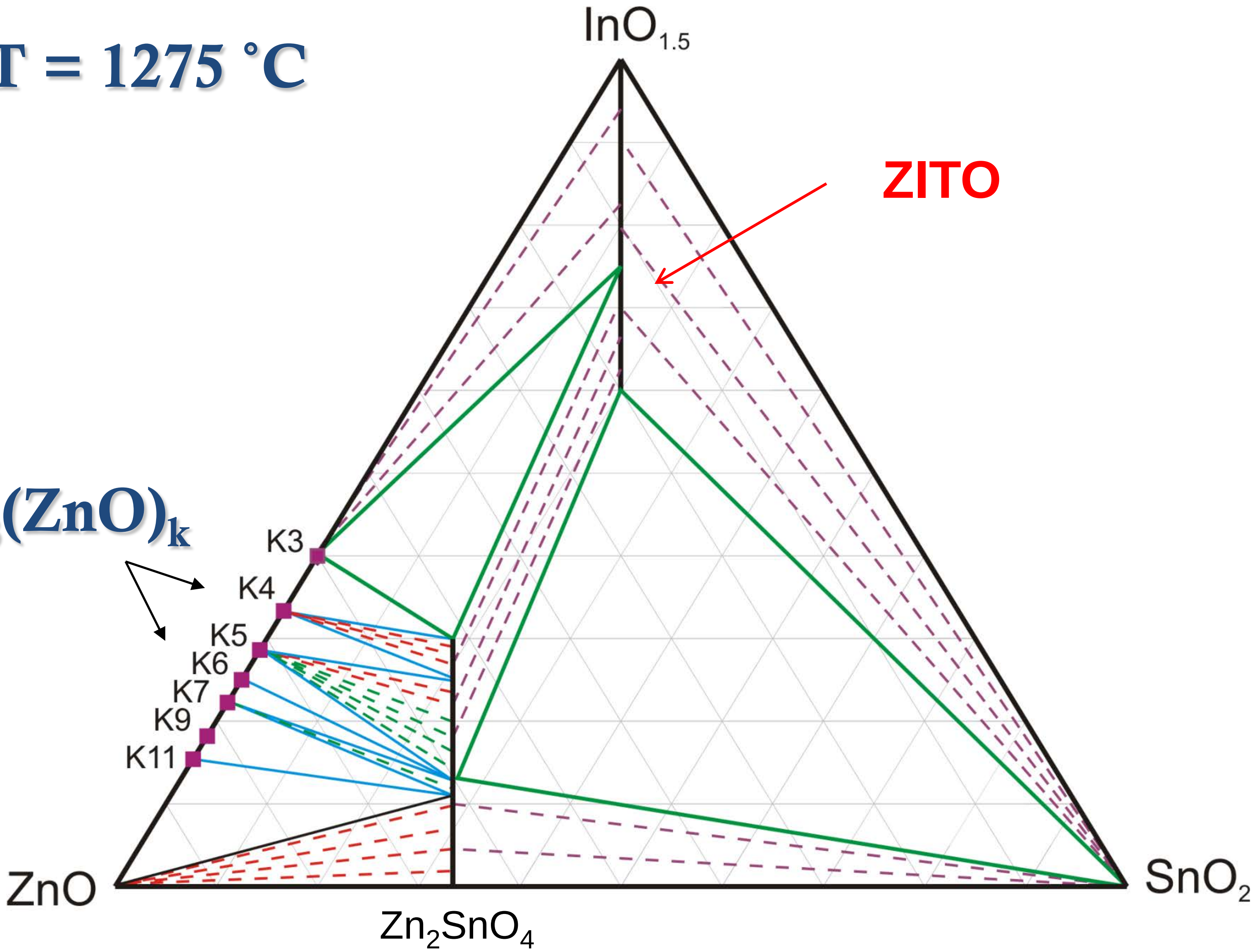
Both: Want high Fermi level (high conductivity)

J. Nelson, Materials Today, 14 (2011) 462

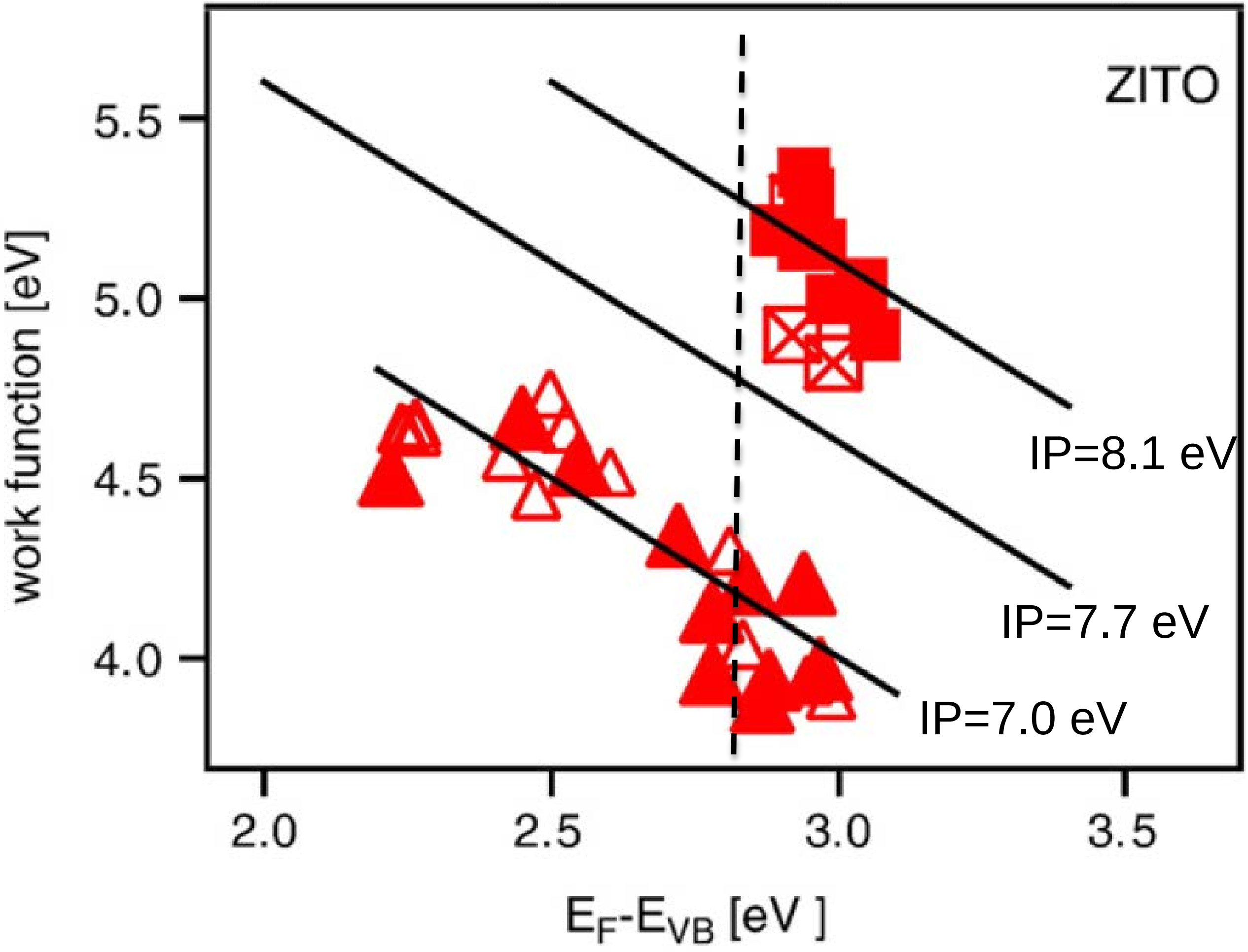
The Zn-In-Sn-O System

T = 1275 °C

$In_2O_3(ZnO)_k$

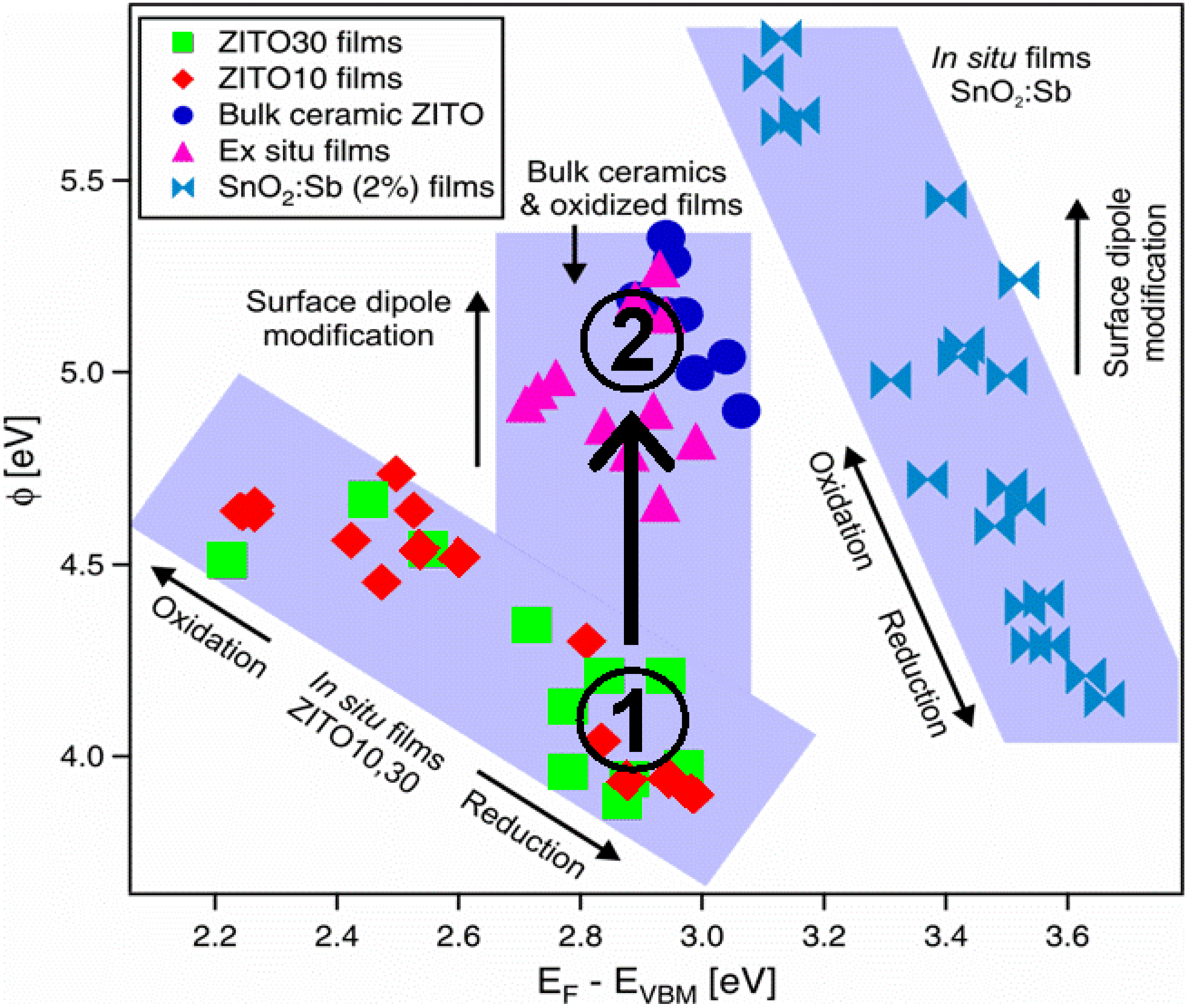


ZITO (Zn,Sn co-substituted ITO) Surfaces



A. Klein et al., Thin Solid Films, 518 (2009) 1197

Two-Step Processing



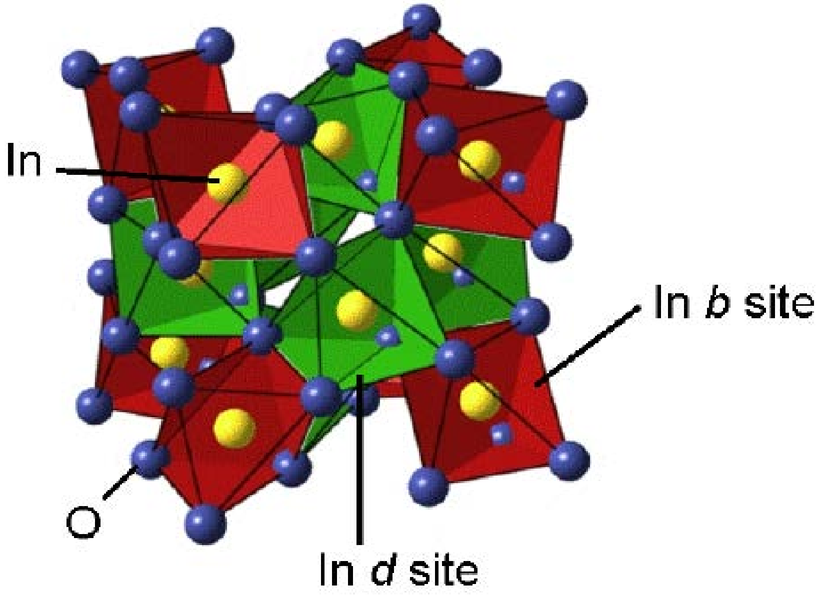
C-ZITO Bulk Structure: Bixbyite

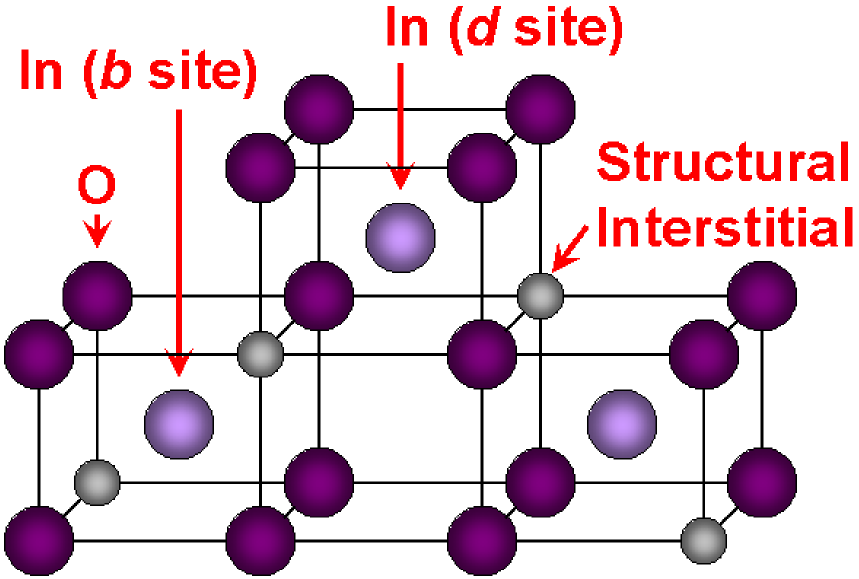
In_2O_3

bixbyite = fluorite with ¼ of the anions missing

Two different cation positions

Structural oxygen interstitial positions



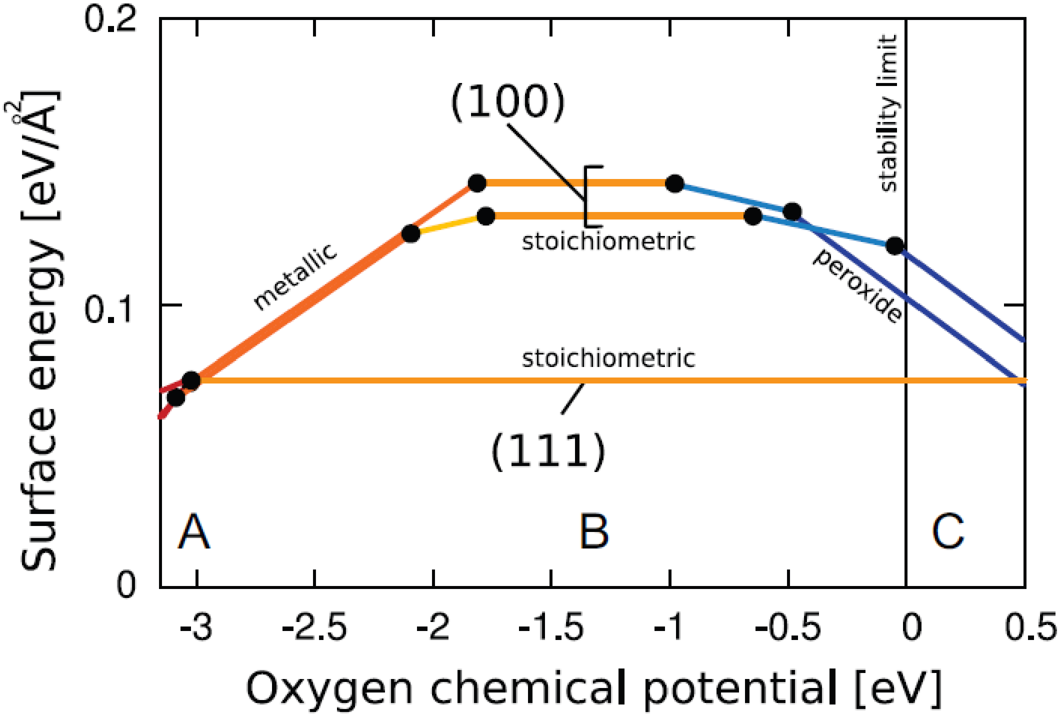


Blue = oxygen
Yellow = indium

G. Frank and H. Kostlin. Appl. Phys. A ***27****, (1982) 197*

Gonzalez and Mason, et al. J.A.P. ***96****(7) (2004) 3912*

In_2O_3 Surfaces

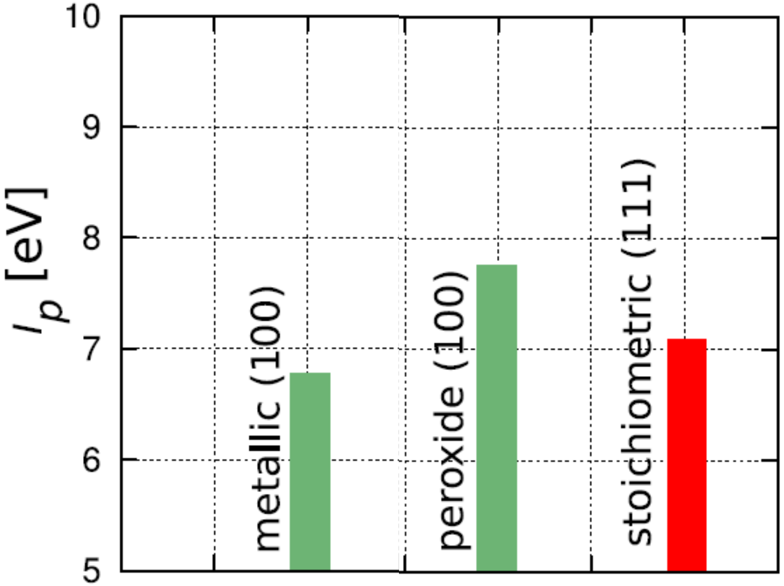


- High μ_O can produce a high In_2O_3 work function on a peroxidized (100) surface)

- Polycrystalline materials will exhibit inhomogeneous surface work functions: "hot spots," "cold spots"

M.V. Hohmann et al., J. Phys.: Condens. Matter 23 (2011) 334203

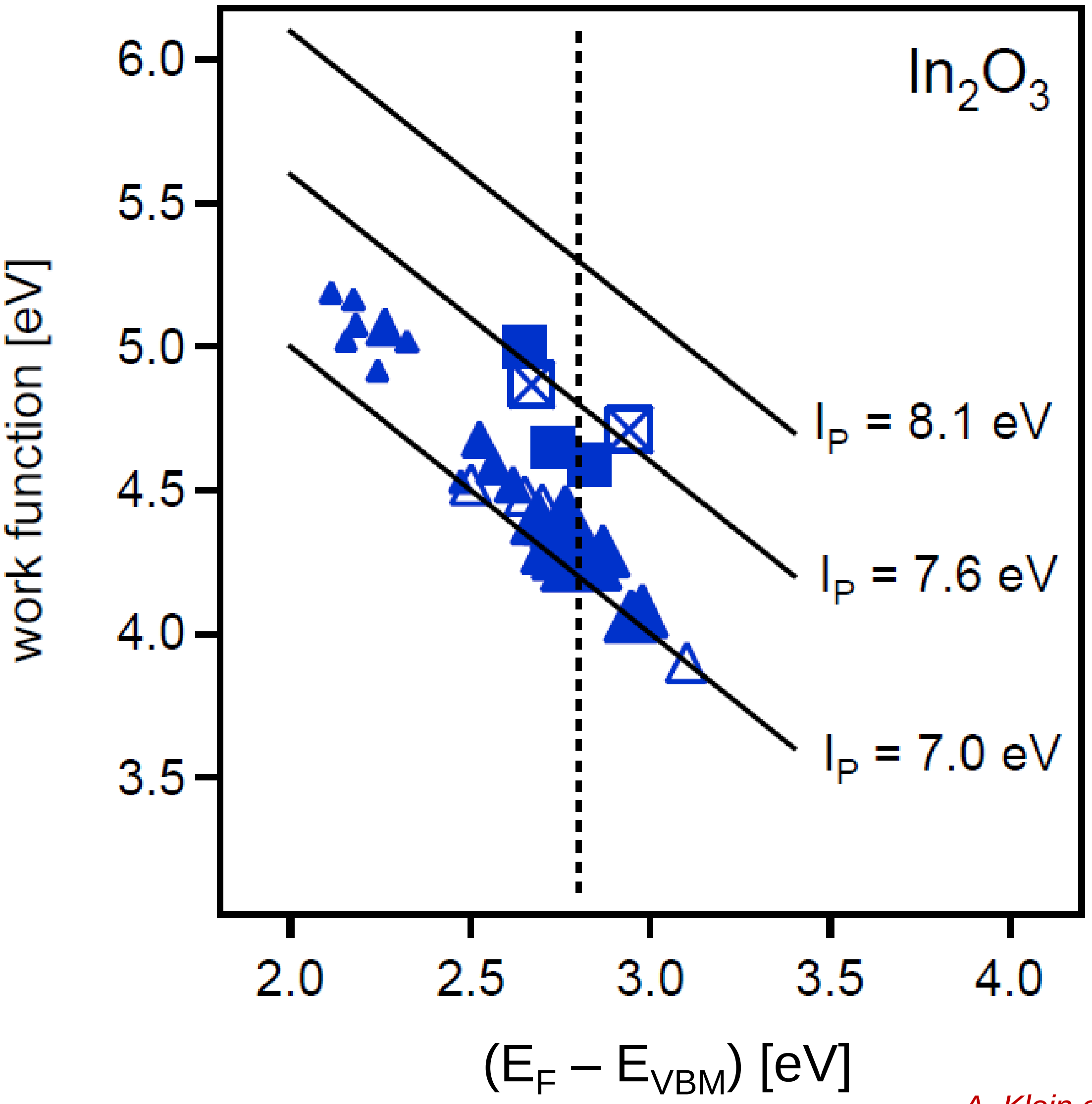
Predicted Ionization Potentials



- Ionization potentials –
  - – Vary little on (111) and (110) surfaces
  - – Vary greatly on (100) surface
    - Metallic termination = low ionization potential
    - Oxide termination = high ionization potential

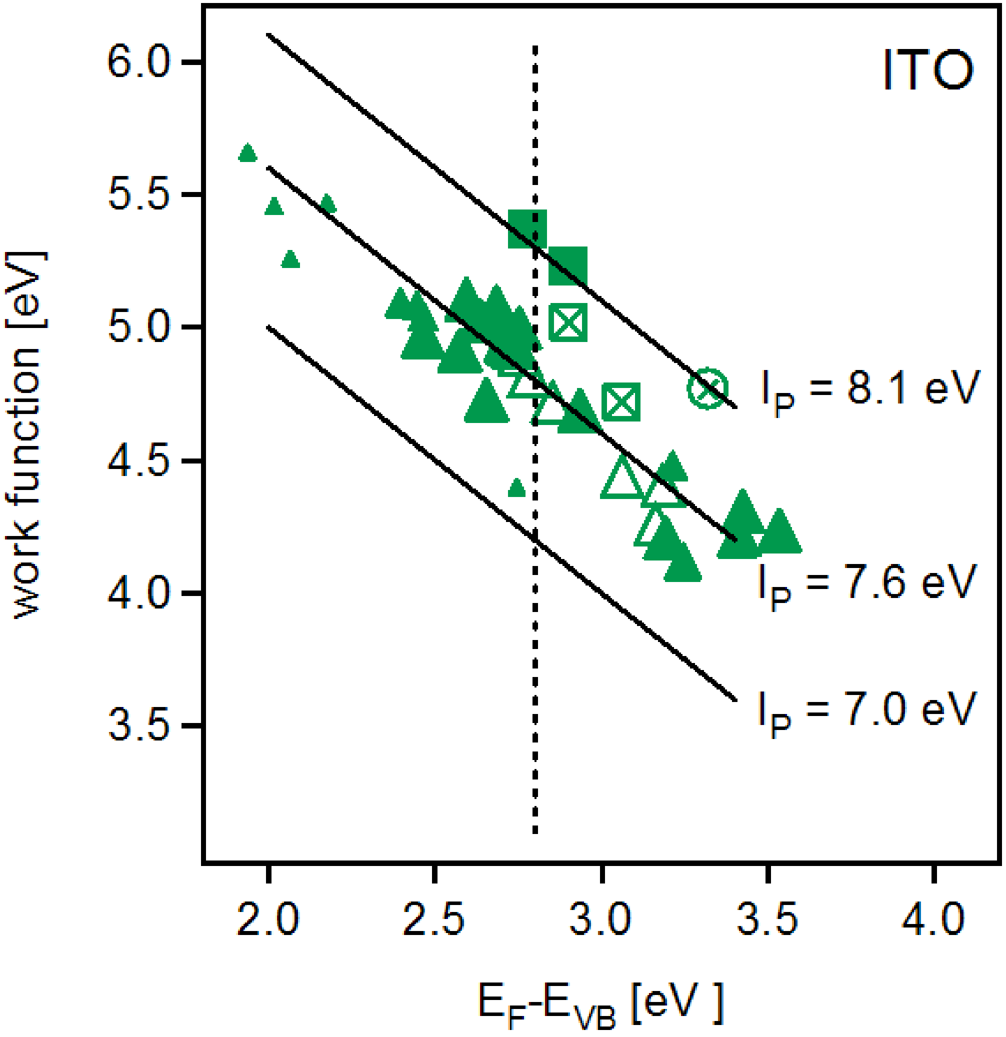
M.V. Hohmann et al., J. Phys.: Condens. Matter 23 (2011) 334203

In_2O_3 Surfaces



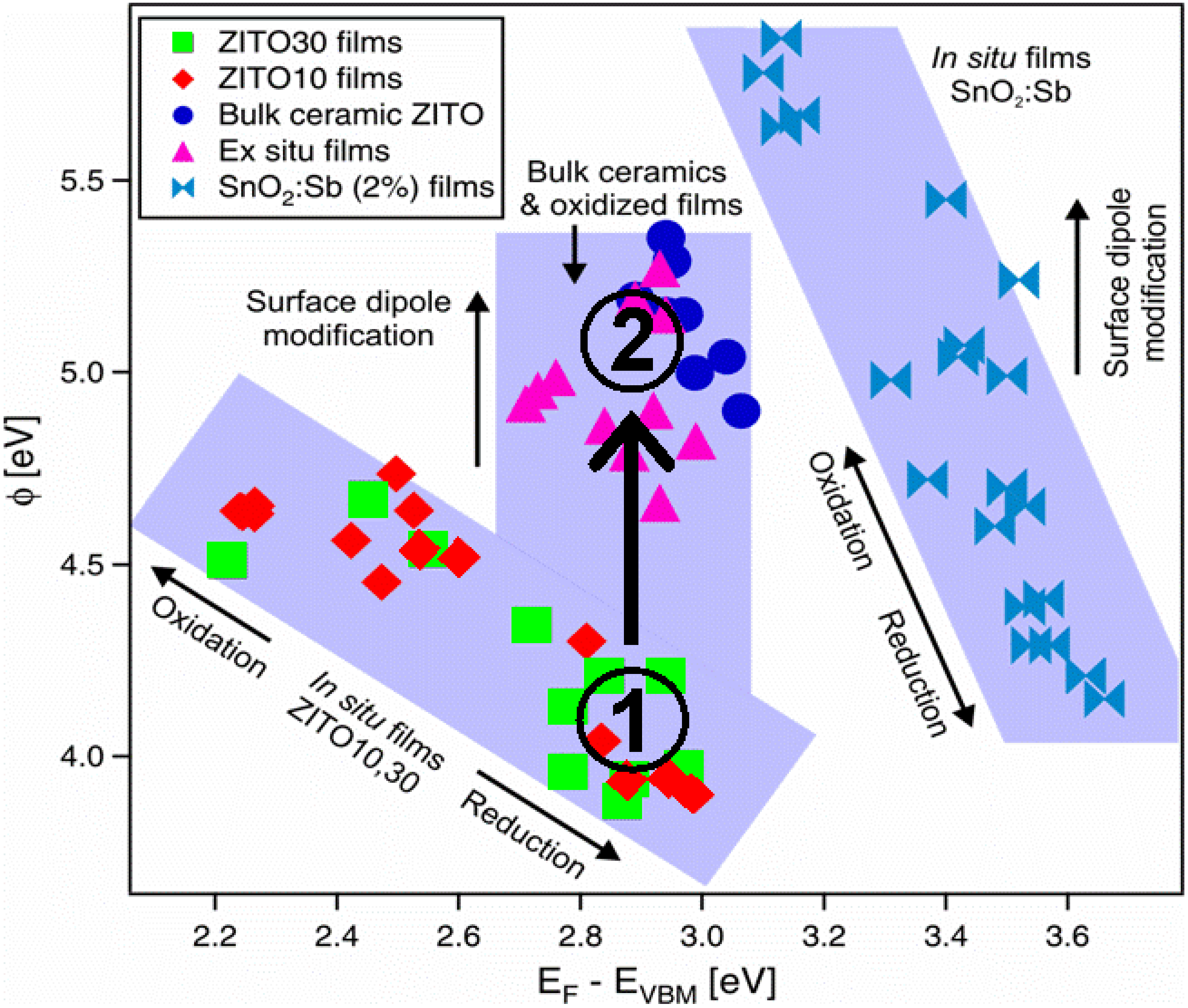
A. Klein et al., Materials, 3 (2010) 4892

ITO Surfaces



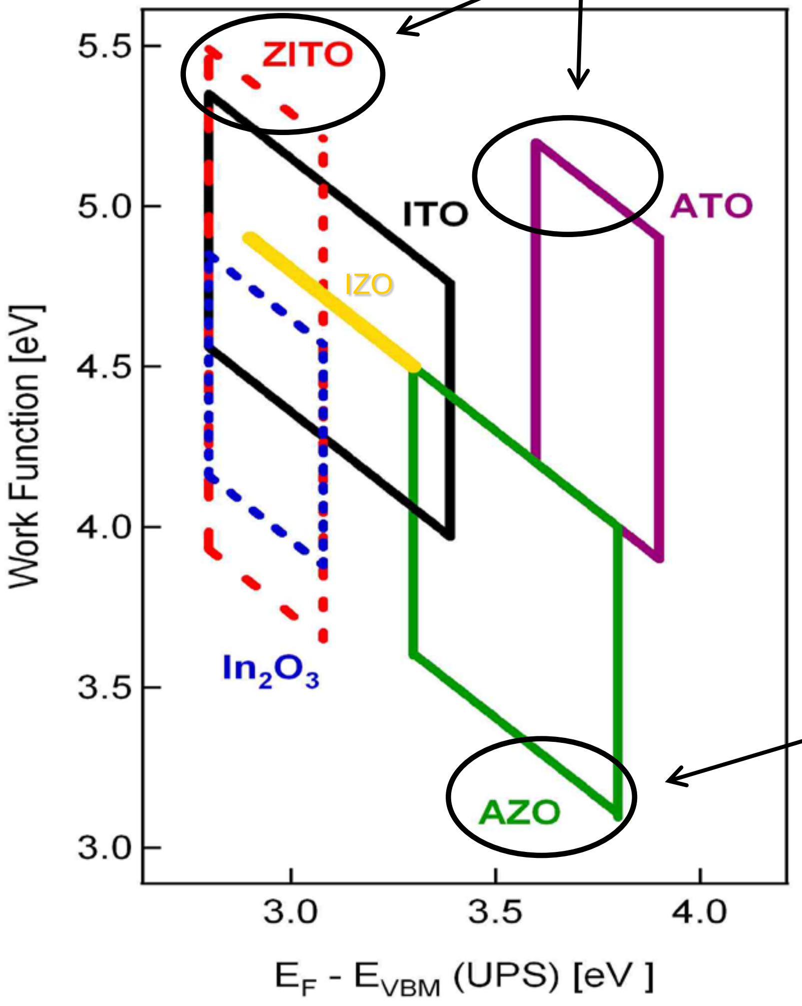
A. Klein et al., Materials, 3 (2010) 4892

Two-Step Processing



Parallelogram Plots

- Left side:
  Fundamental
  Band-gap
- Right side:
  maximum
  Burstein-Moss shift
- Top and bottom:
  achievable ionization
  potential ranges



traditional OPVs

Inverted OPVs

ITO: Tin-doped In_2O_3

ZITO: Zn,Sn-doped In_2O_3

ATO: Sb-doped SnO_2

AZO: Al-doped ZnO

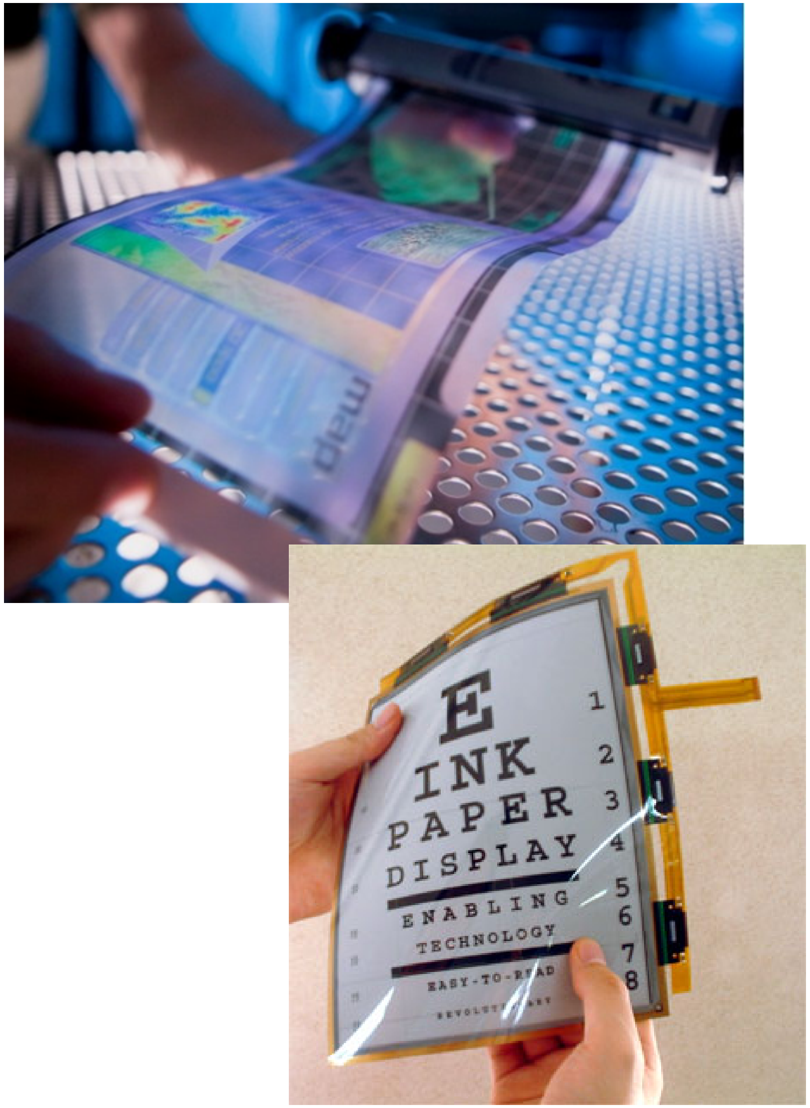
IZO: $In_2O_3(ZnO)_k$

A. Klein et al., Materials, 3 (2010) 4892

Amorphous TCOs

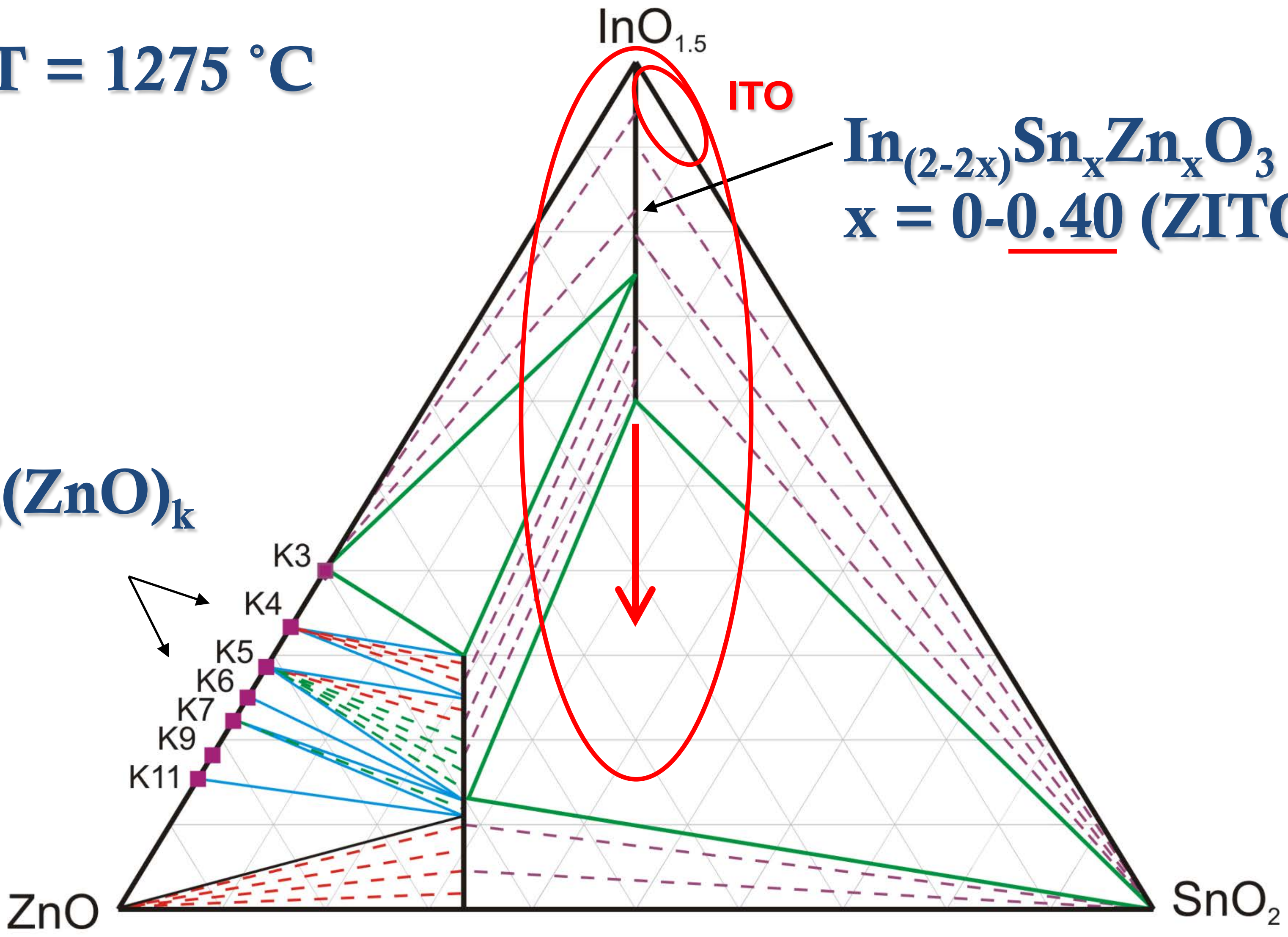
Advantages of Amorphous TCOs

- Easier, cheaper processing
  - Low temperature
  - Flexible substrates
  - Better etching characteristics
- Smoother surfaces
- Wide composition range
  - Minimization of toxic/expensive elements
- No hot/cold spots



Amorphous ZITO TCOs

T = 1275 °C



$In_{(2-2x)}Sn_xZn_xO_3$
x = 0-0.40 (ZITO)

$In_2O_3(ZnO)_k$

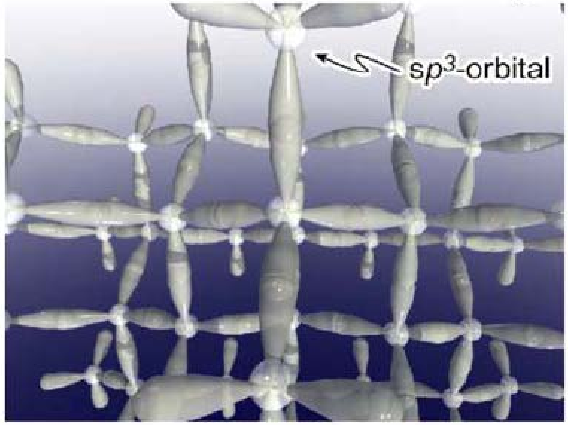
Harvey et al., J. Am. Ceram. Soc. ***91*** *11 (2008)*

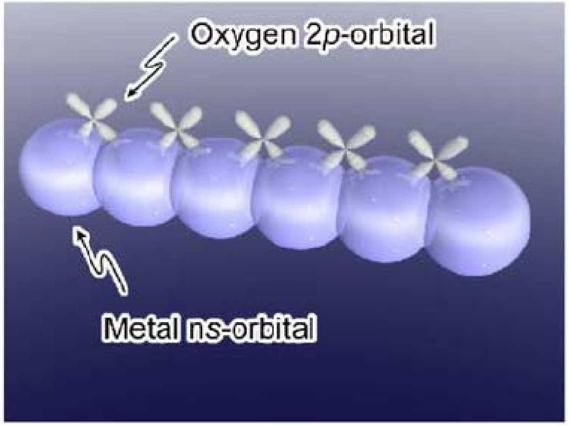
Why a-TCOs Have Good Properties

Conventional Semiconductor
(silicon)

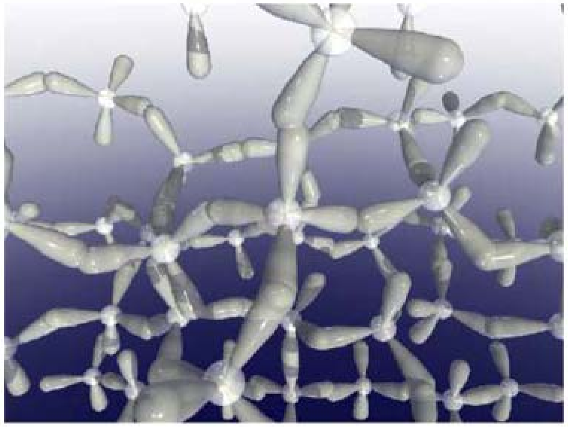
Traditional TCO
(indium oxide)

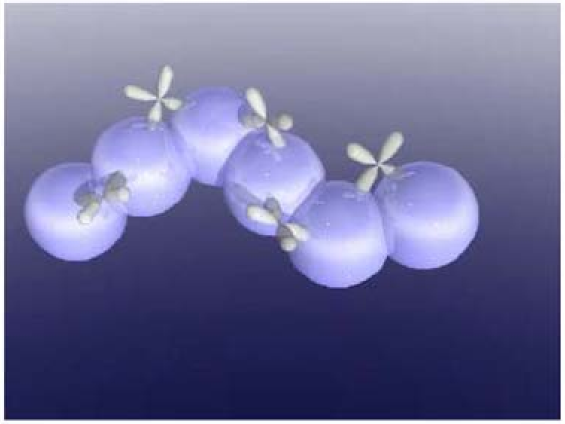
Crystalline





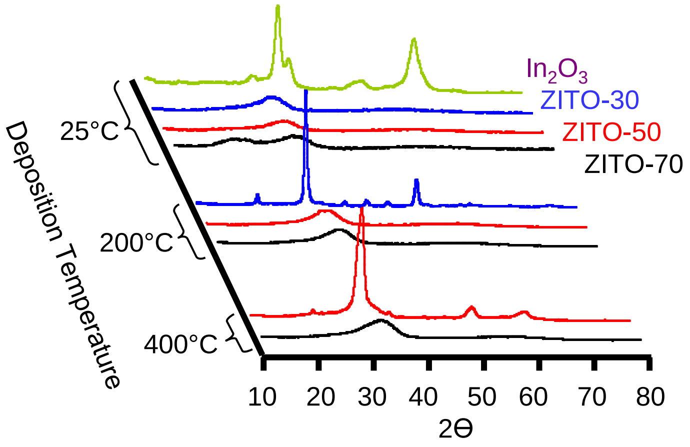
Amorphous





Hosono, H., J. Noncryst. Sol. ***352****, 851-858 (2006)*

Pulsed Laser Deposited a-ZITO Films

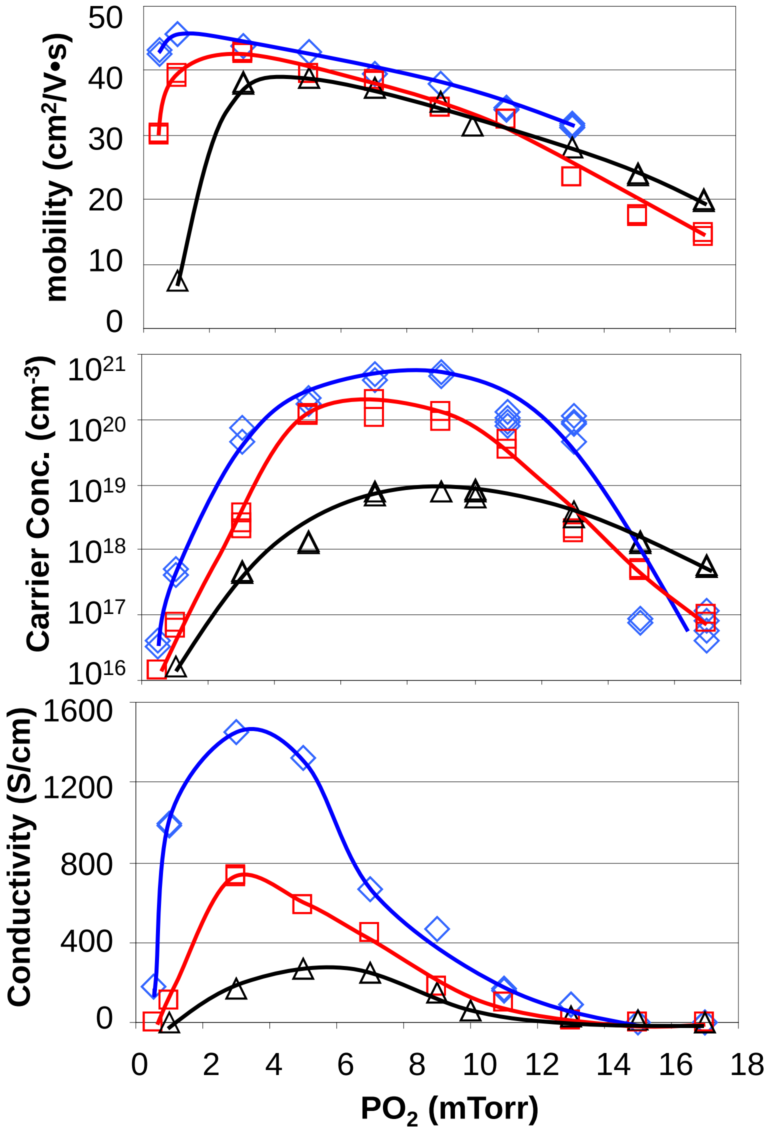


$In2O3$: No cosubstitution

ZITO-30: 30 at.% cosubstituted

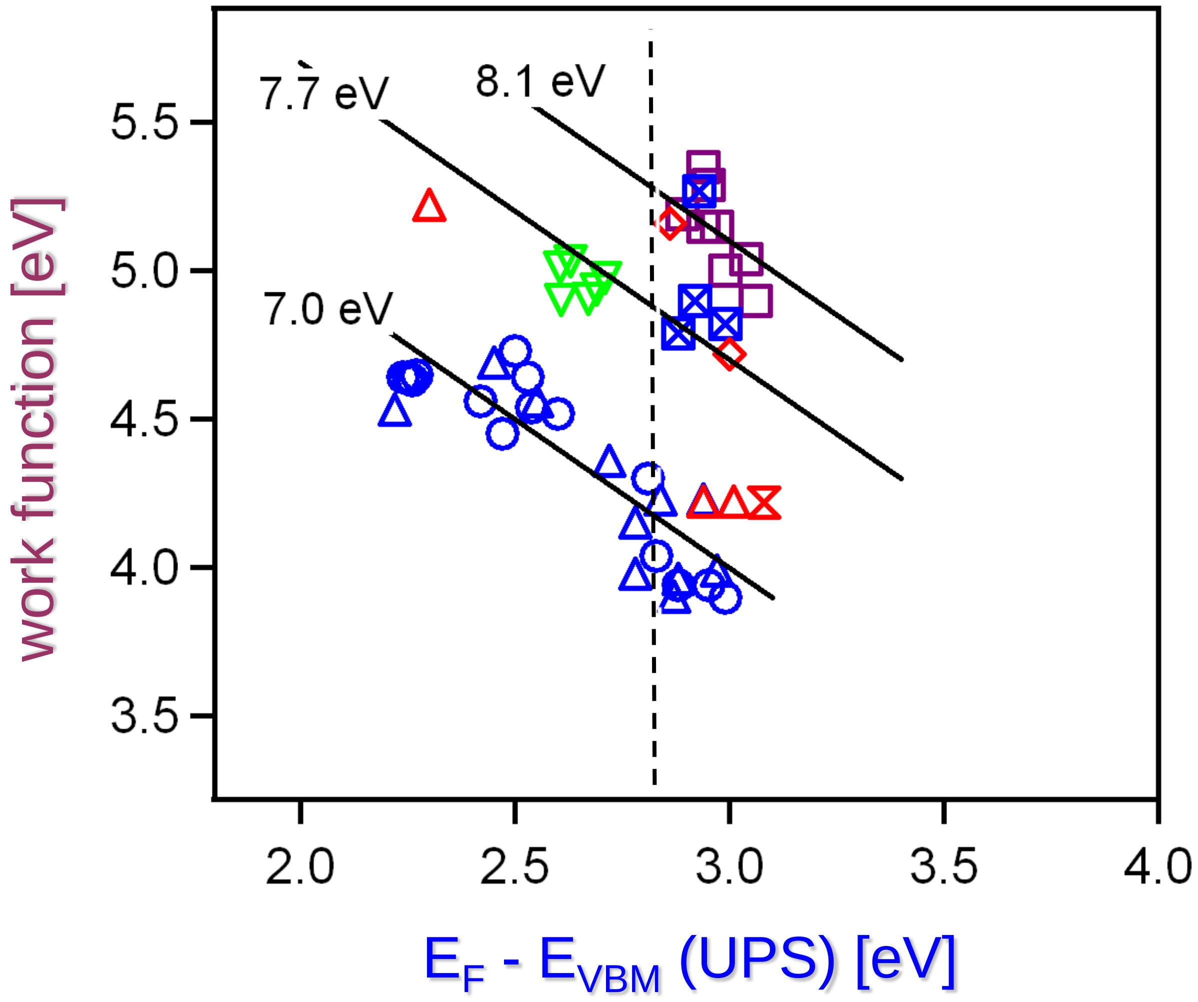
ZITO-50: 50 at.% cosubstituted

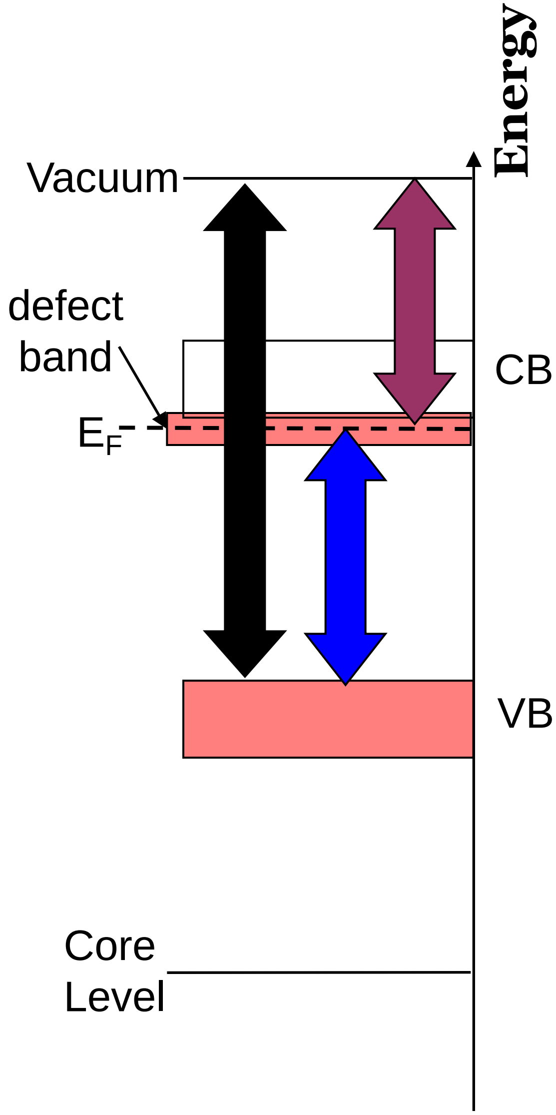
ZITO-70: 70 at.% cosubstituted



How a-ZITO Compares

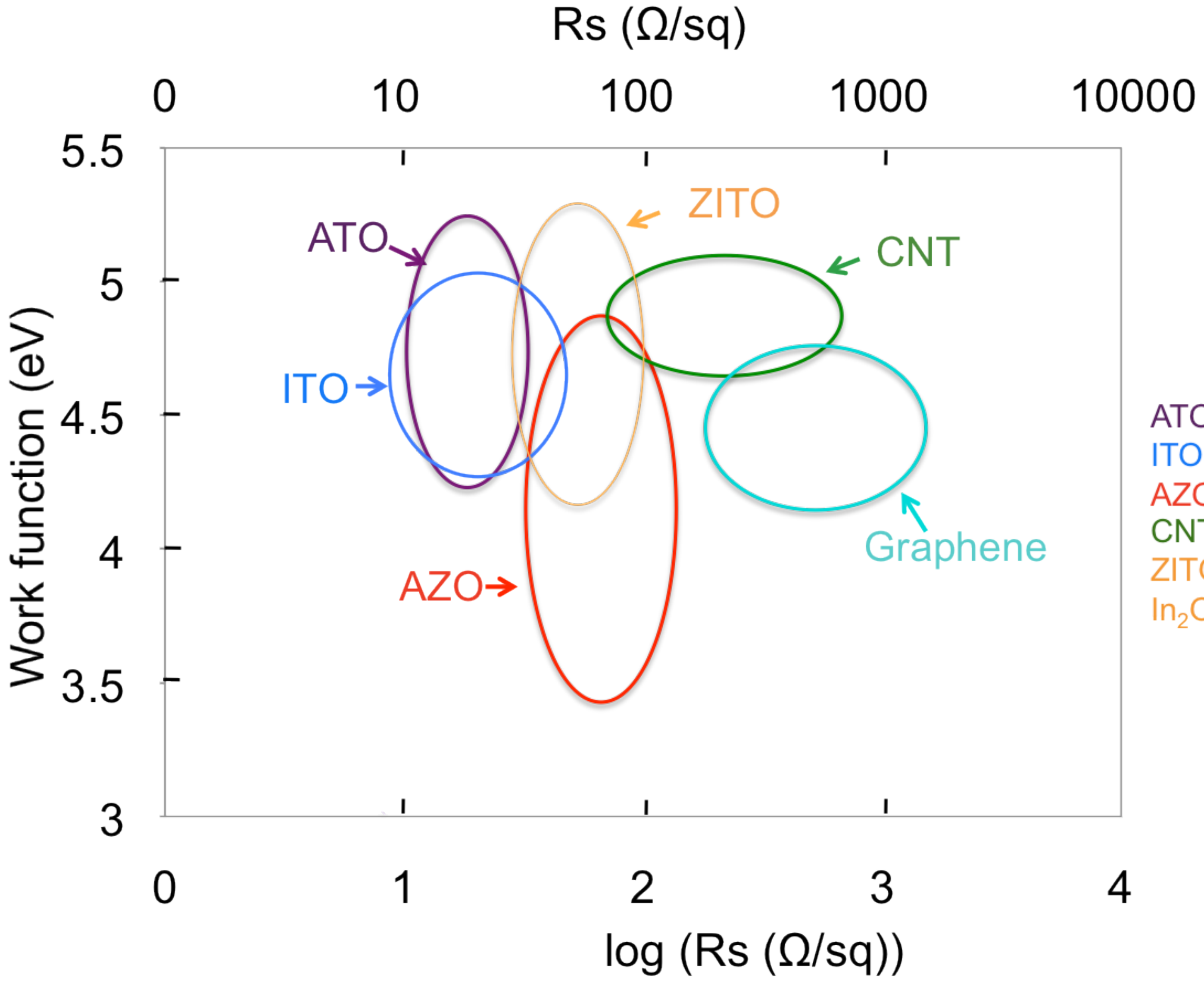
Red symbols: a-ZITO





D. E. Proffit et al., Thin Solid Films (submitted)

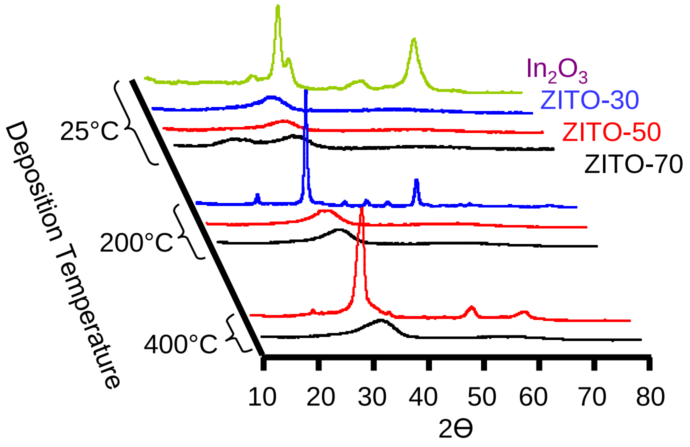
Ashby Plot of TCO Properties



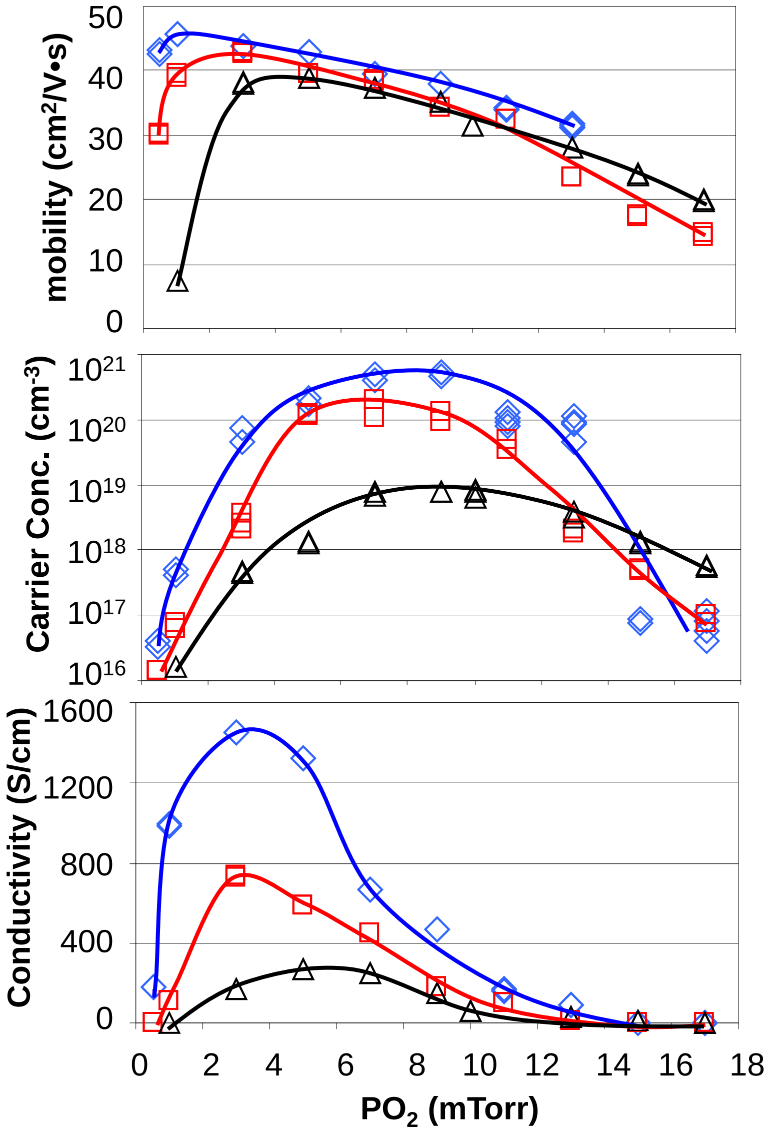
ATO: Sb-doped SnO_2
ITO: Sn-doped In_2O_3
AZO: Al-doped ZnO
CNT: Carbon nanotube
ZITO: Zn,Sn codoped In_2O_3

What the Future Holds

Pulsed Laser Deposited a-ZITO Films

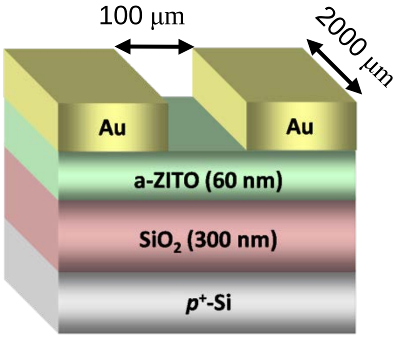


In2O3: No cosubstitution
ZITO-30: 30 at.% cosubstituted
ZITO-50: 50 at.% cosubstituted
ZITO-70: 70 at.% cosubstituted



Application of ZITO TCO & TOS for FETs

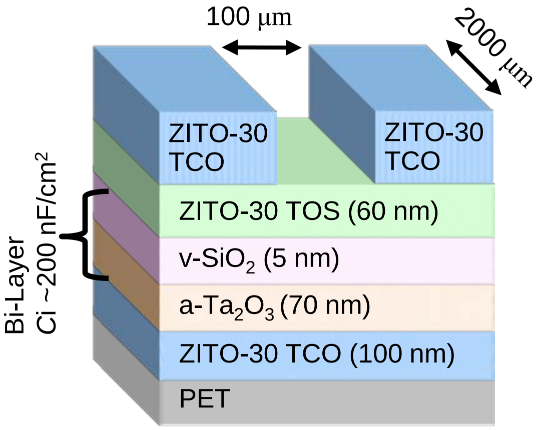
TOS ZITO-30 used for Field Effect Transistor (FET) Channel Layer



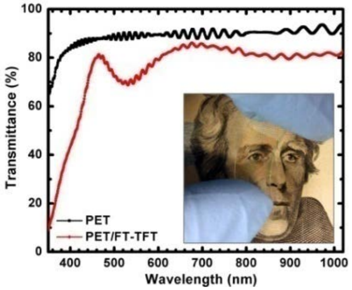
C_i for 300 nm SiO_2: ~10 nF/cm^2
V_G and V_{DS}: ~100 V
μ_{FE}: ~10 cm^2/V·s
I_{on}:I_{off}: ~10^6
VT: ~18 V
SS: ~5.2 V/decade
Air and light stable

TCO ZITO-30 used for Gate, Source & Drain
TOS ZITO-30 used for Channel Layer

On plastic substrate to form all amorphous, flexible, transparent FET



V_G and V_{DS} ~4.0 V
μ_{FE} ~20 cm^2/V·s
I_{on}:I_{off} ~10^5
V_T ~ 1.2 V
SS ~0.26 V/decade
Good Mechanic Flexibility
Transparency ~75%



ZITO Films Grown at Room Temperature by PLD

Conclusions

- TCO work functions can be modified “intrinsically” through:
  - Fermi level shifts (via donor doping—defect chemistry plays a vital role!)
  - Surface dipole modifications by:
    - Changing surface orientations (e.g., Al-doped ZnO)
    - Altering surface terminations (e.g., Sb-doped SnO_2)
    - By changing surface stoichiometry (e.g., peroxidation, Sn-doped In_2O_3 or ITO, Zn,Sn-cosubstituted In_2O_3 or ZITO)

Conclusions (cont’d)

- Work function vs. Fermi level “parallelogram plots” allow comparison of candidate TCOs for OPV applications
  - AZO (Al-doped ZnO) or alternatives (Ga-doped ZnO) are best for low work function applications, e.g., in inverted OPV designs
  - ZITO (Zn-In-Sn-O) or ATO (Sb-doped SnO_2) and alternatives (FTO, F-doped SnO_2) are best for high work function applications, e.g., in traditional OPV designs
- Amorphous TCOs exhibit work functions and Fermi levels comparable to their crystalline counterparts (e.g., ZITO)
- An emerging “frontier” for TCOs is as Amorphous Oxide Semiconductors (AOSs)