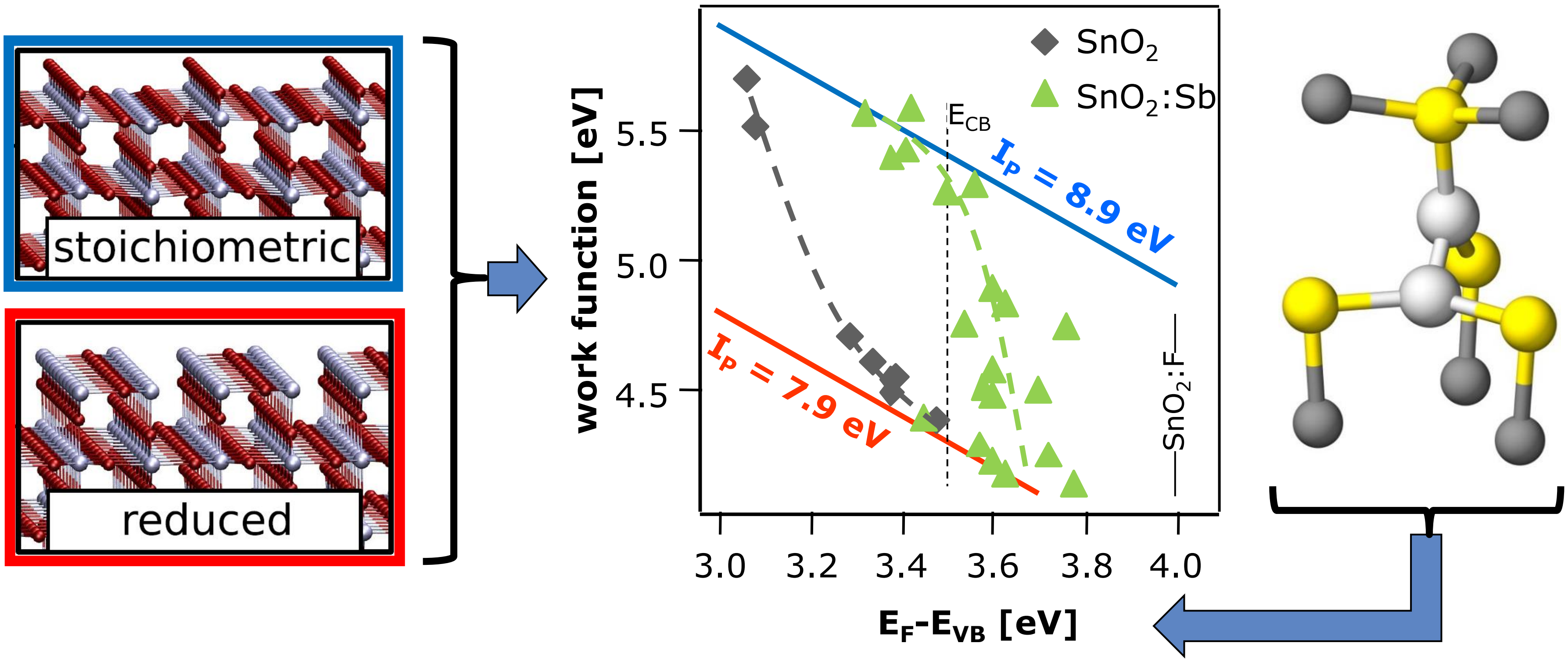
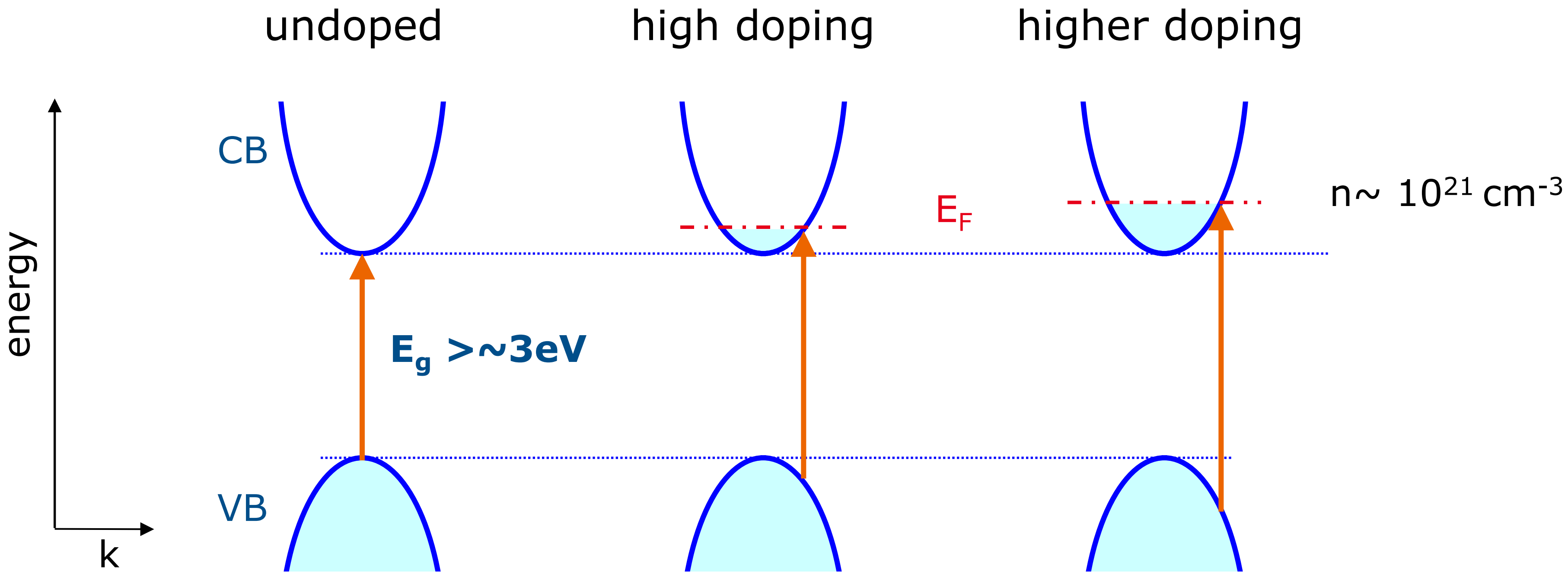
Do TCOs contribute to electrical fatigue of organic LEDs

Andreas Klein *Surface Science* (D3)

Karsten Albe *Materials Modelling* (C2)



What is a TCO



- **Optical transparent material by large band gap**
- **Highly conducting material by degenerate doping**

→ **Doped ZnO, SnO_2, In_2O_3**

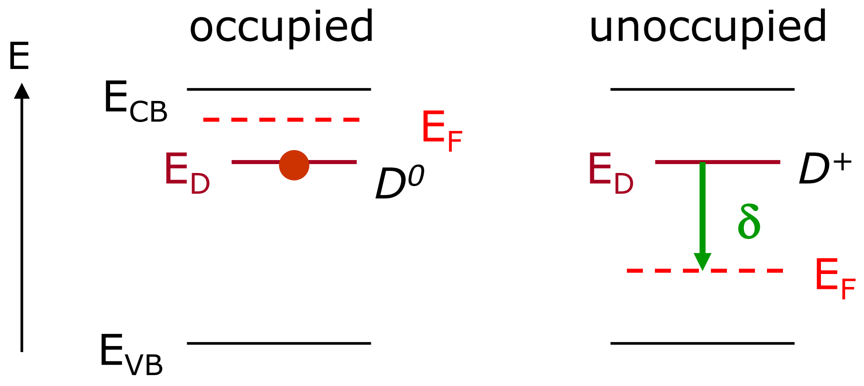
In_2O_3:Sn (ITO)

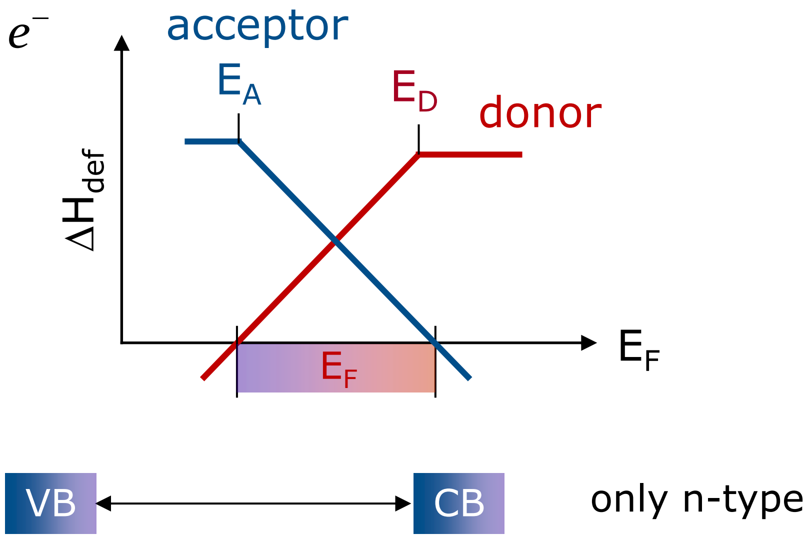
- Highest conductivity and transparency of TCO materials
- Good structurability by chemical etching
- Surface properties modified by oxidation treatments (increase of work function)
- Bixbyite crystal structure with 80 atom unit cell and plenty interstitial positions
- Typically 10 mole% SnO_2 doping
- Sn dopants mainly compensated by interstitial oxygen

Self-compensation

- **The formation of defects requires a certain amount of energy ΔH_{def}**
- **The charge state of the defect depends on the Fermi level position**

Example: Donor type defect (V_O) $D \rightarrow D^+ + e^-$

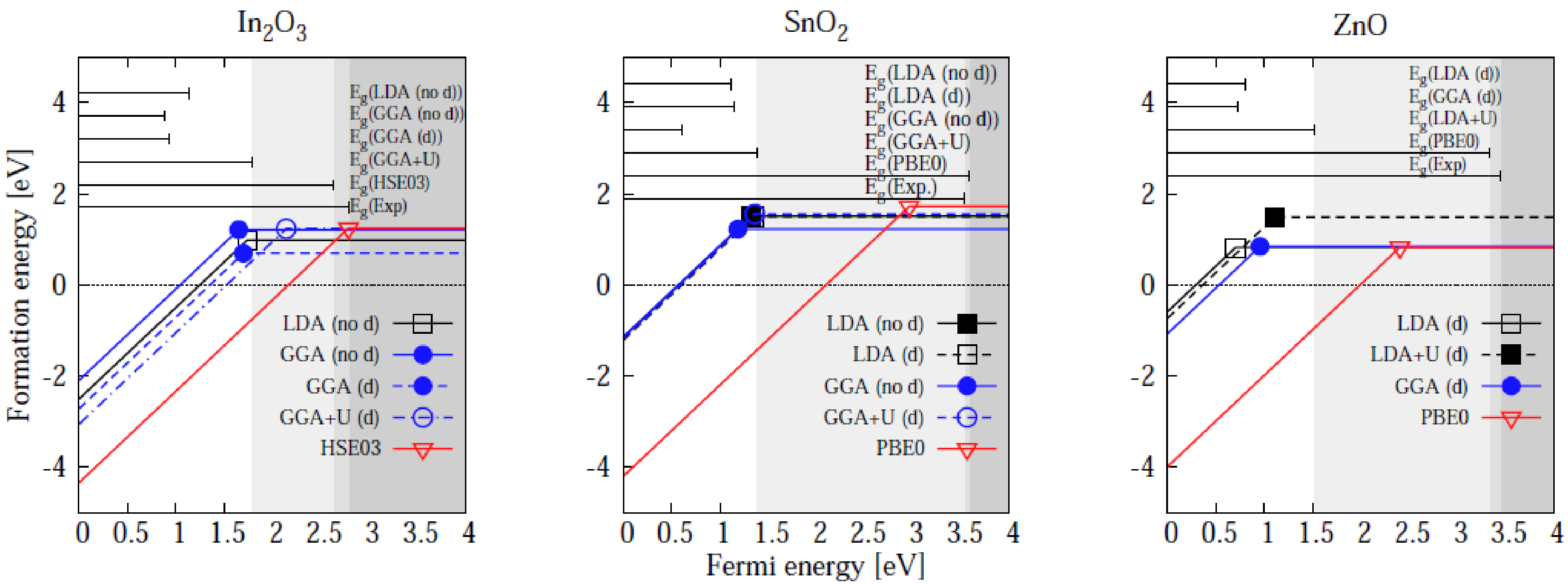




Compensating defects (O_i in ITO) are formed spontaneously only when the Fermi energy is deep in the conduction band

J Am Ceram Soc 96 (2013) 331

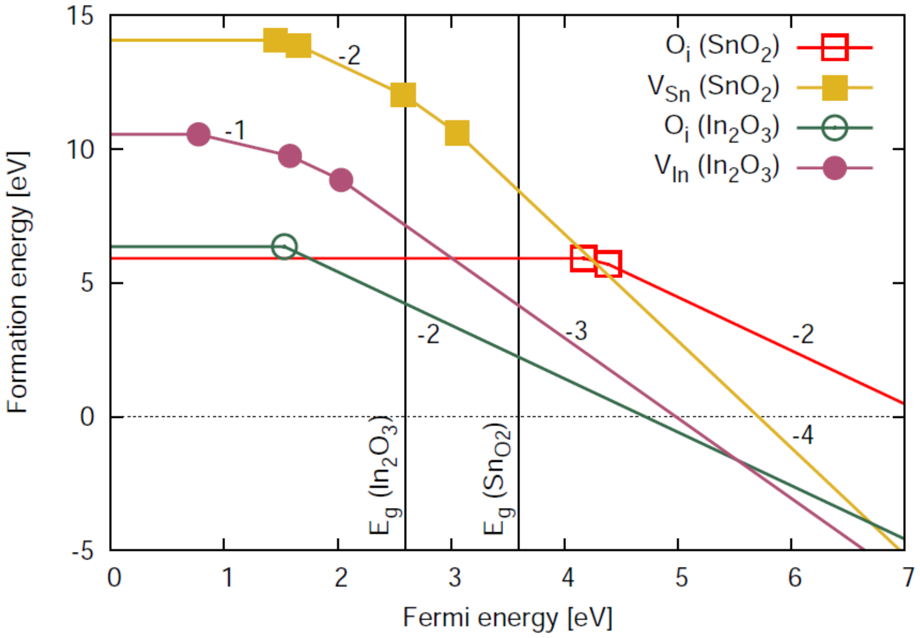
Oxygen vacancies

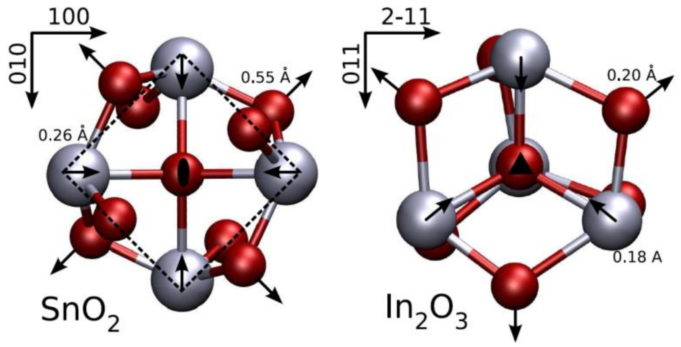


- Indium oxide and tin oxide are truly intrinsically n-type semiconductors
- The behavior is more complex for ZnO

Phys Rev Lett 103 (2009) 245501

Compensating acceptors

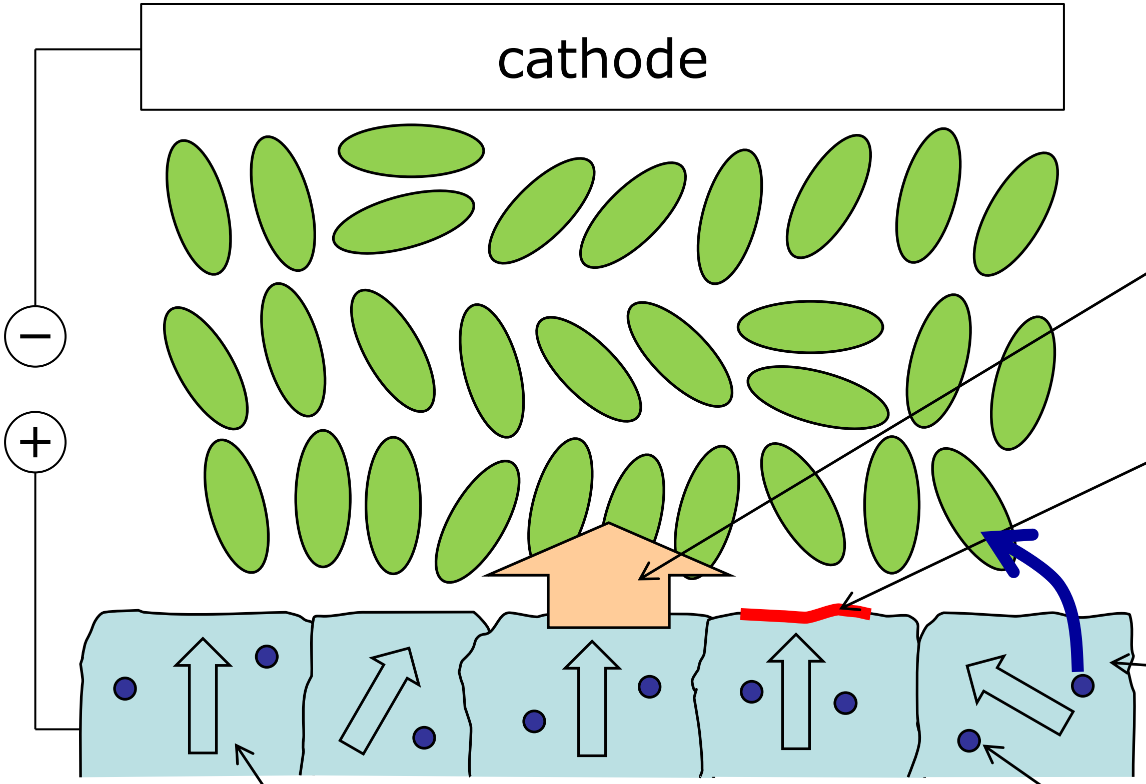




- Charged oxygen interstitials are very unfavorable in SnO_2
- Oxygen transport only via oxygen vacancies in SnO_2
- Stability of acceptor defects increases with increasing Fermi energy

J Appl Phys 108 (2010) 053511

The TCO electrode in OLEDs



Hole injection determined by workfunction

Workfunction determined by surface orientation and termination

Oxygen exchange determined by surface properties

grain orientation determined by surface energy & deposition

Defect concentration (e.g. O_i) and mobility determined by material properties and doping

Possible contributions to fatigue

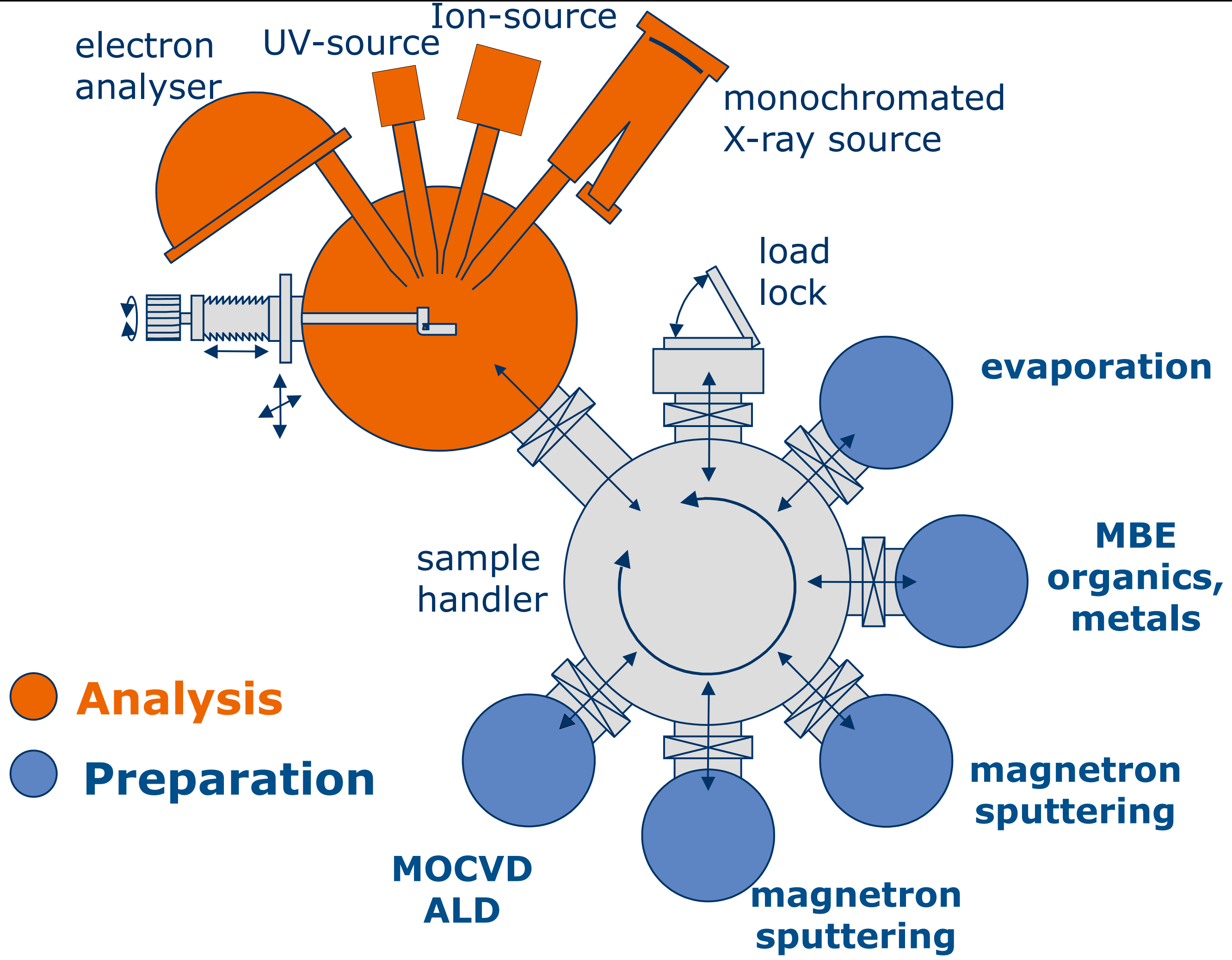
- **Change of injection barrier during operation**
  - Change of work function
    → surface termination
    → Fermi level position (oxygen concentration)
  - Interfacial reaction

- **Release of oxygen**
  - Chemical decomposition of organic
  - Change of TCO conductivity
  - Oxygen exchange → surface vs. diffusion limitation

Performed work

- **Experimental**
  - **Systematic determination of TCO work functions**
  - **Interfaces between ITO and organic semiconductors**
  - **Conductivity relaxation experiments (oxygen exchange)**
  - **Building test OLEDs and study fatigue behaviour (→ D4)**
- **Theoretical**
  - **Thermodynamics of point defects in ZnO, In_2O_3 and SnO_2**
  - **Anion and cation diffusion in ZnO and In_2O_3**
  - **Thermodynamics of surface structures of In_2O_3 and SnO_2**
  - **Defect at (101) twin boundary in SnO_2**
  - **Adsorption behaviour of organic compounds**

DAISY-MAT (XPS/UPS + preparation)



electron analyser

UV-source

Ion-source

monochromated X-ray source

load lock

sample handler

evaporation

MBE organics, metals

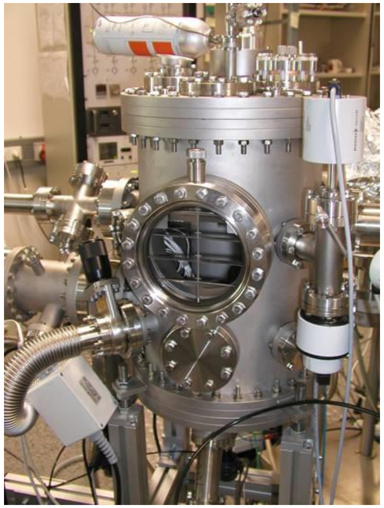
magnetron sputtering

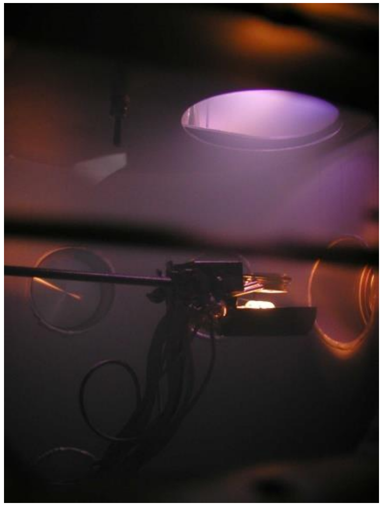
magnetron sputtering

MOCVD ALD

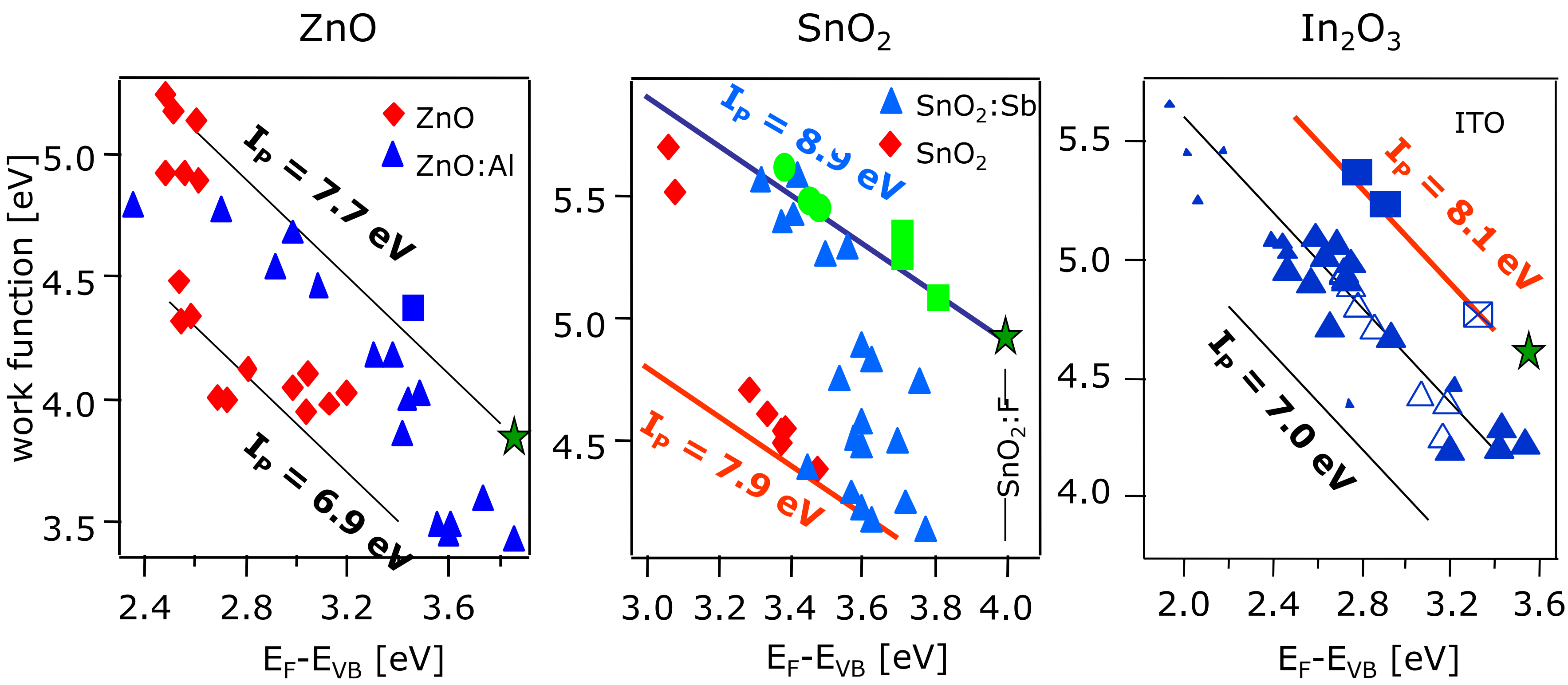
● **Analysis**

● **Preparation**





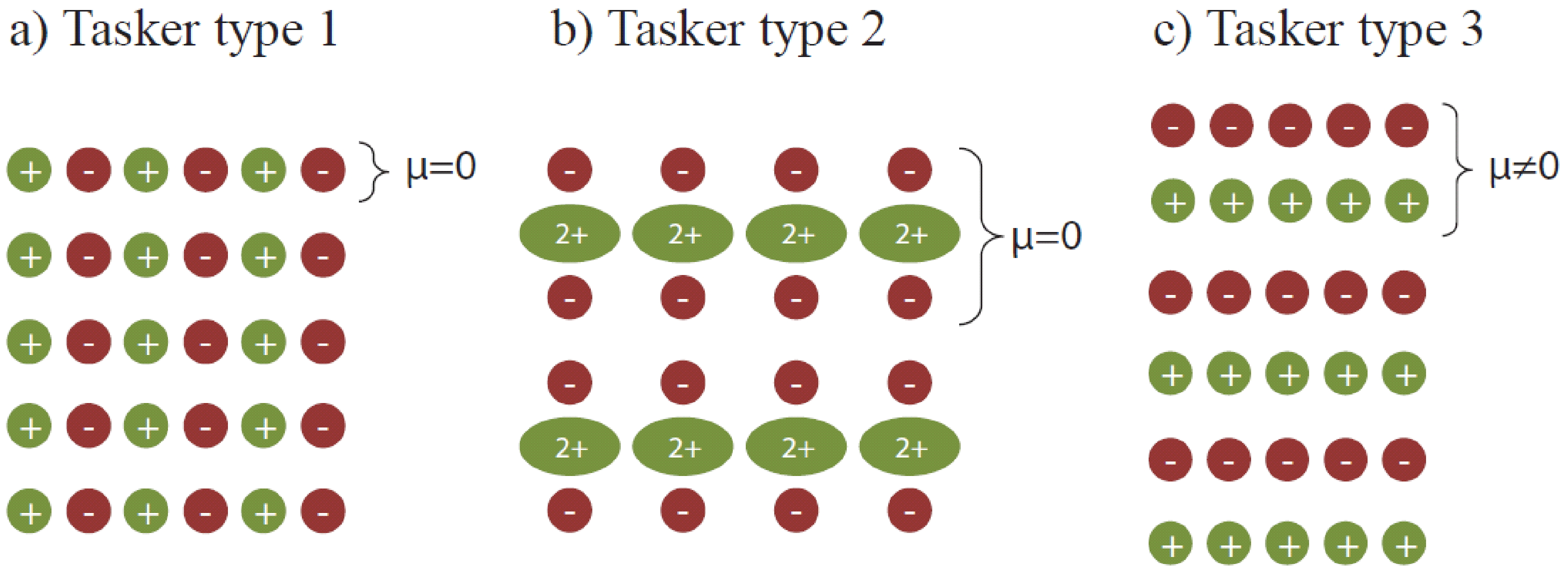
TCO work functions



Large variation of work function due to changes in Fermi level position, surface orientation and termination

Thin Solid Films 518 (2009) 1197

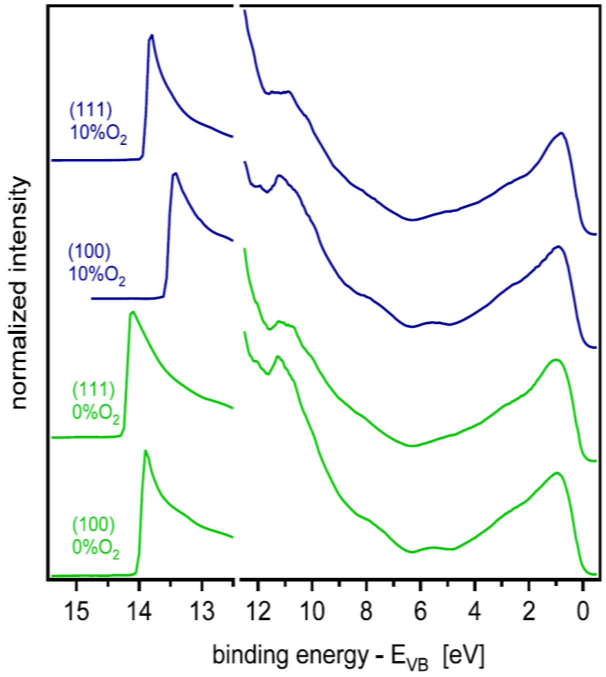
Types of surfaces



In_2O_3 (110)	In_2O_3 (111)	In_2O_3(100)
non-polar	polar - stable	polar - unstable
stoichiometric	stoichiometric	non-stoichiometric
stable composition	stable composition	variable composition

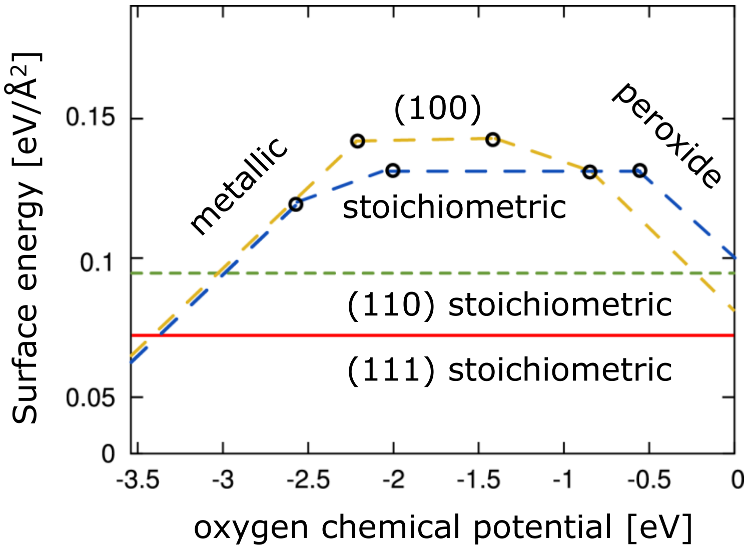
In_2O_3 surfaces

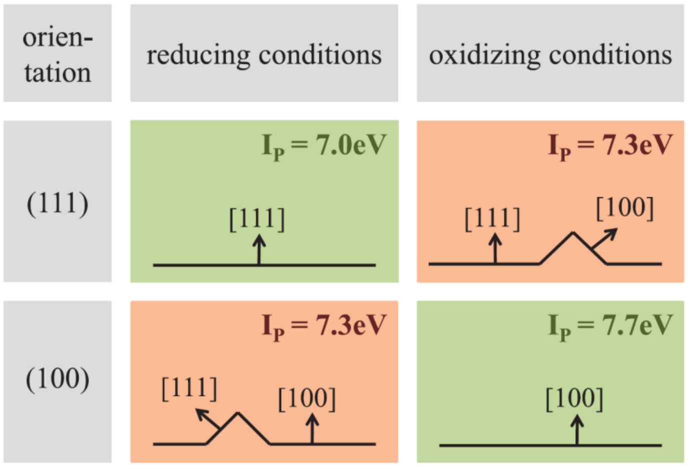
UPS of epitaxial In_2O_3 films



Calculated ionization potentials

100-perox	100-met	100-st	111
7.7 eV	6.8 eV	8.6 eV	**7.1 eV**

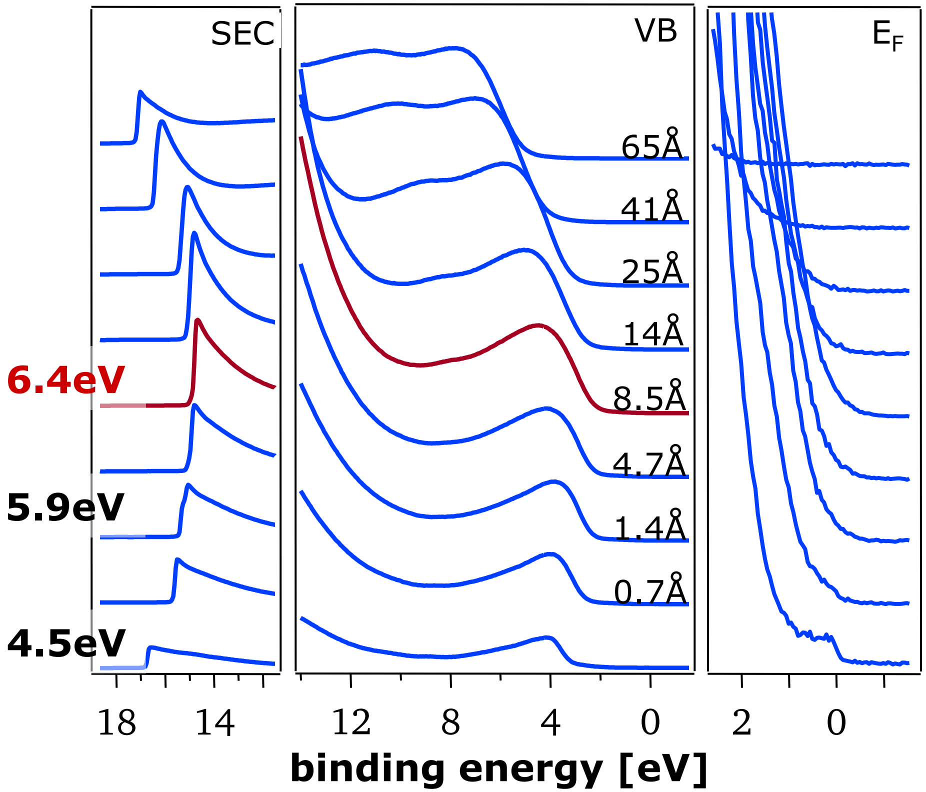


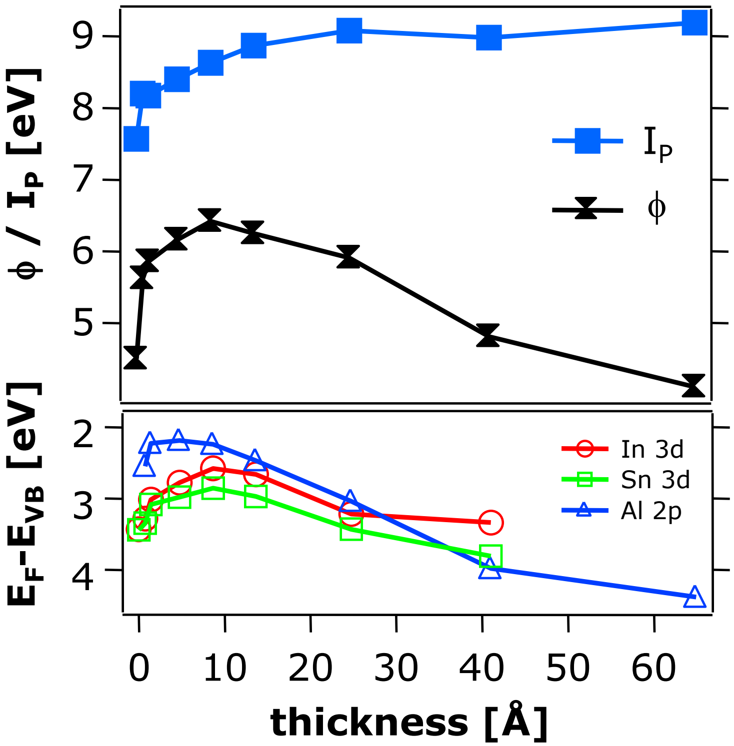


orien-tation	reducing conditions	oxidizing conditions
(111)	$I_P = 7.0$eV [111]	$I_P = 7.3$eV [111] [100]
(100)	$I_P = 7.3$eV [111] [100]	$I_P = 7.7$eV [100]

J Phys CM 23 (2011) 334203

ITO/Al_2O_3 interface





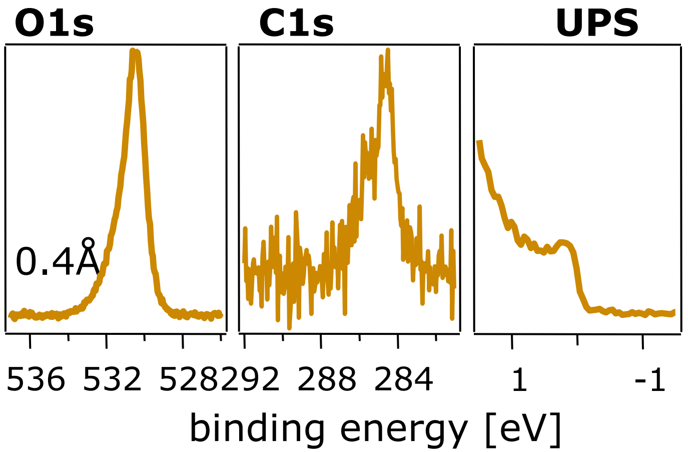
strong increase in work function

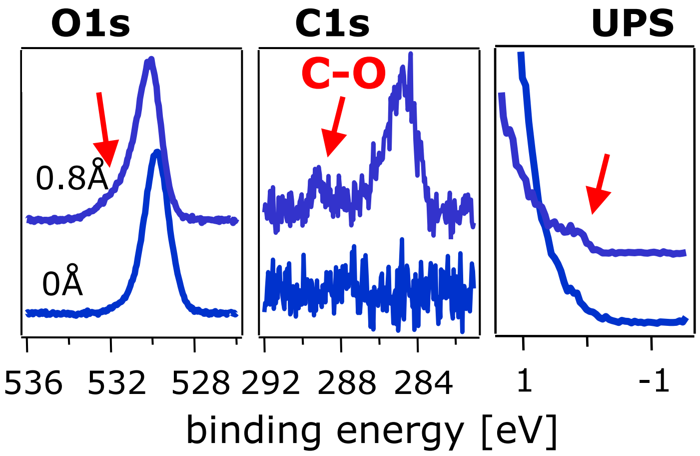
initial dipole formation

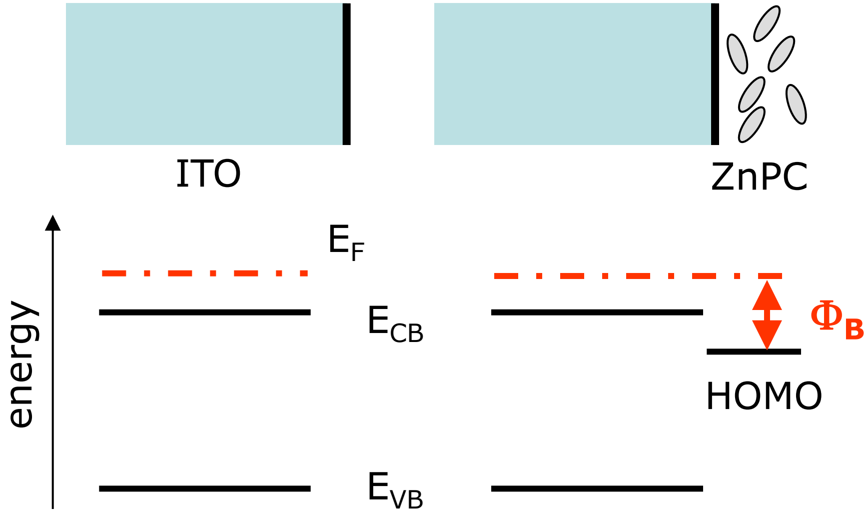
Change to anion-terminated surface ?

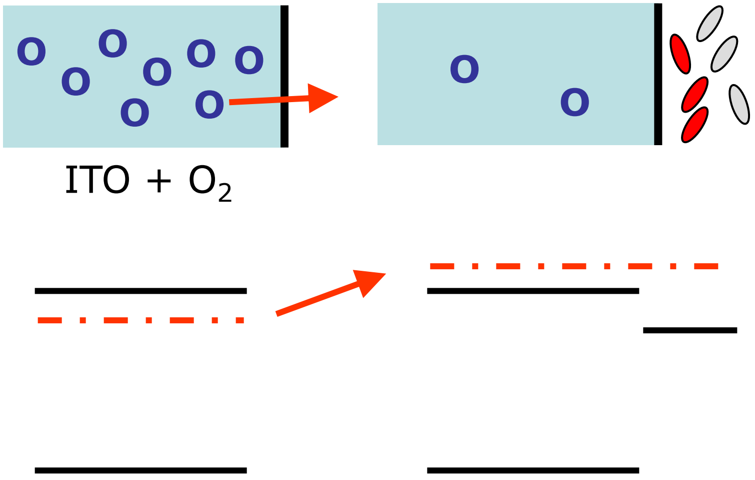
Phys Chem Chem Phys 11 (2009) 3049

ITO/organic interface



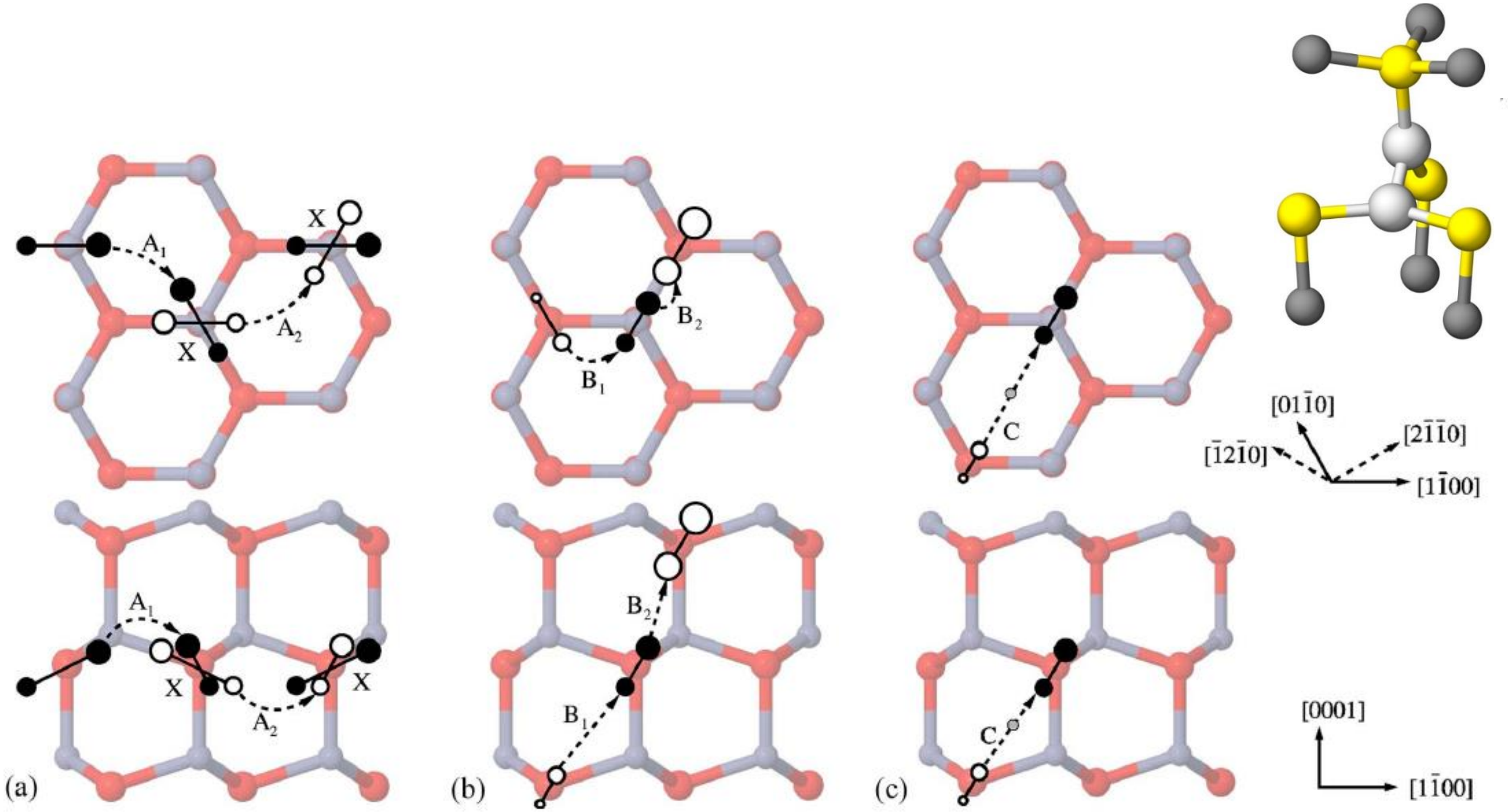






J Phys Chem B 110 (2006) 4793

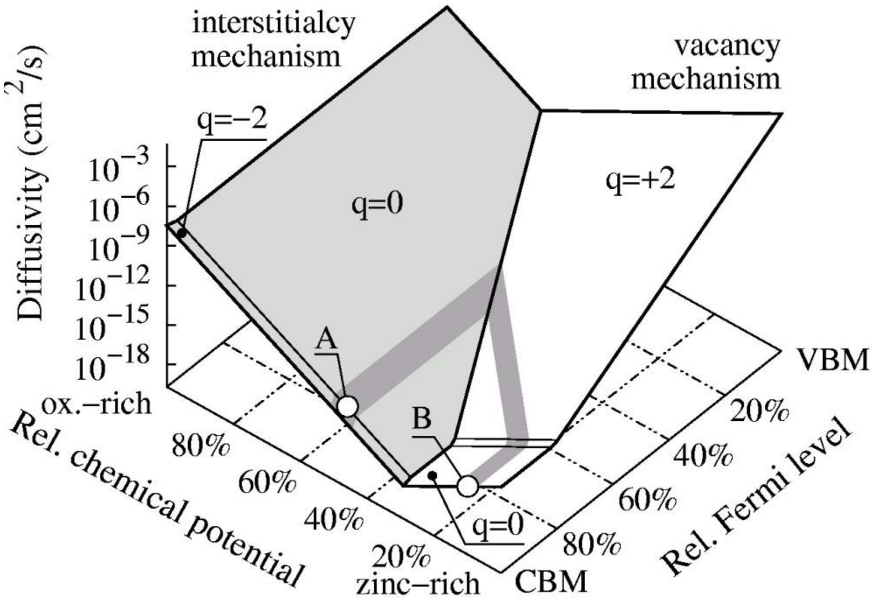
O-interstitialcy diffusion in ZnO

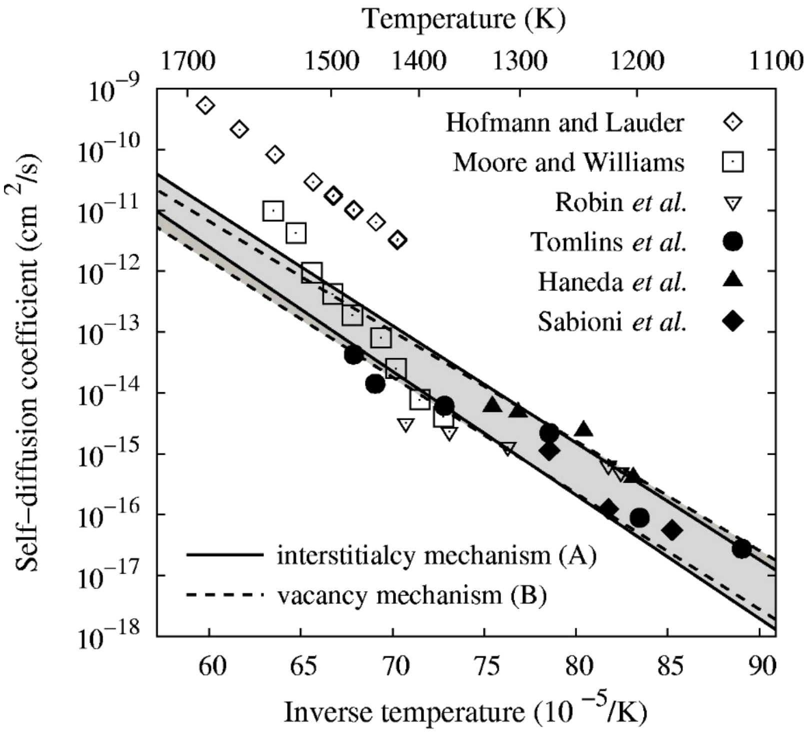


Phys Rev B 73 (2005) 115207

Oxygen diffusion in ZnO

Interstitialcy mechanism, neutral and positive charge states

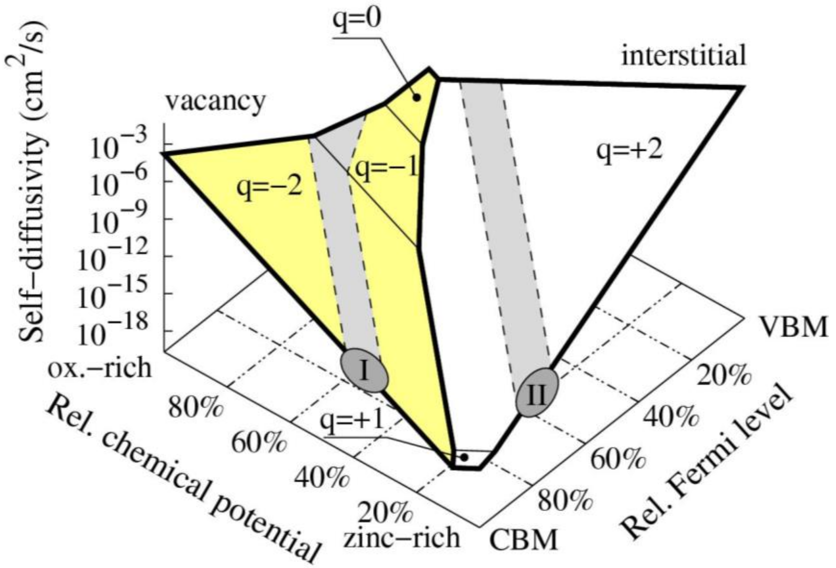


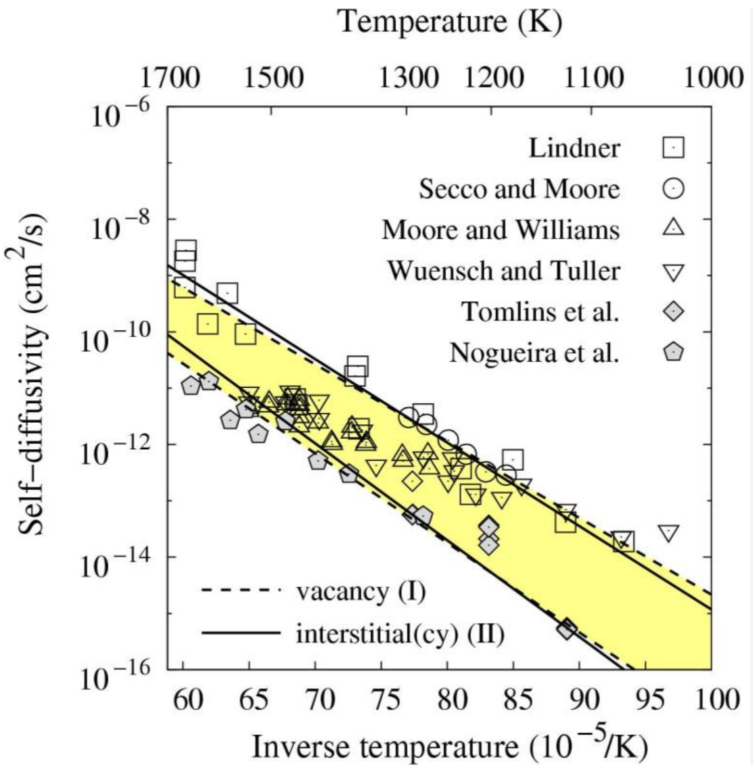


Dependence of diffusivity on Fermi level and chemical potential

Phys Rev B 73 (2005) 115207

Zn diffusion in ZnO

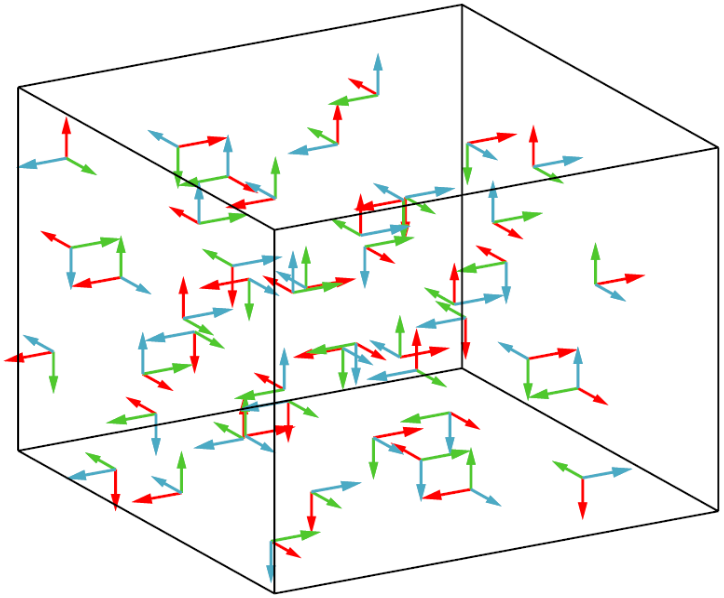




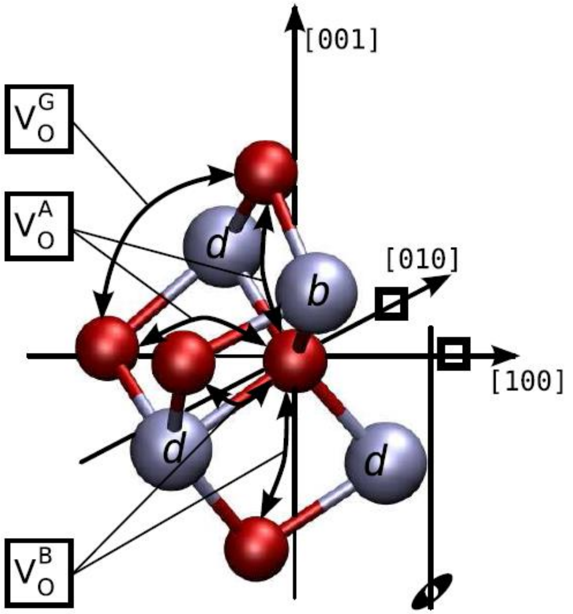
- **Hierarchy of mobilities:**
  - zinc interstitials
  - oxygen interstitials
  - zinc vacancies
  - oxygen vacancies

Appl Phys Lett 88 (2006) 201918

Diffusion in In_2O_3



Combined DFT+KMC Ansatz



$V_O^{\bullet\bullet}$

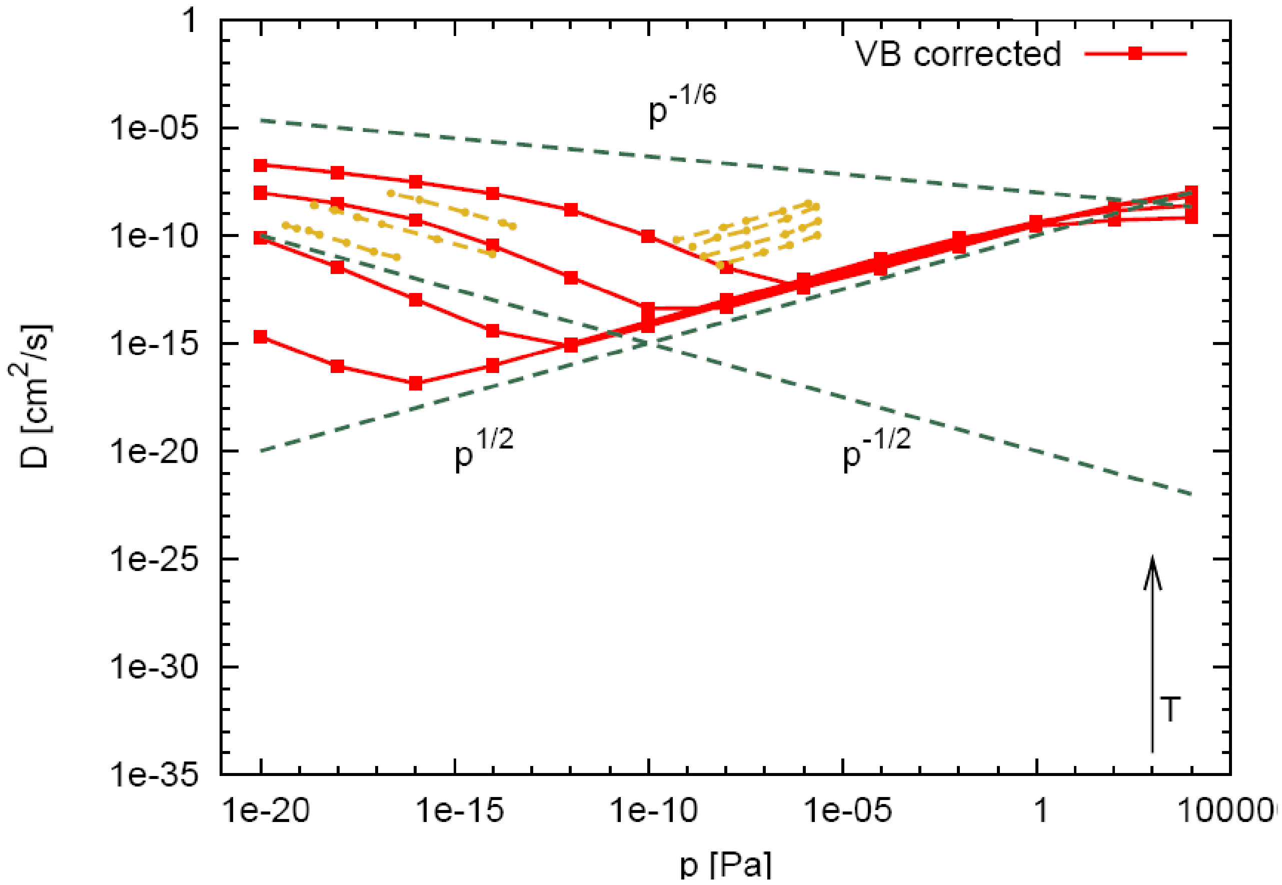
$E_B(A) = 0.99$ eV

$E_B(B) = 1.28$ eV

$E_B(G) = 3.82$ eV

Phys Rev B 81 (2010) 195205

Diffusion in In_2O_3



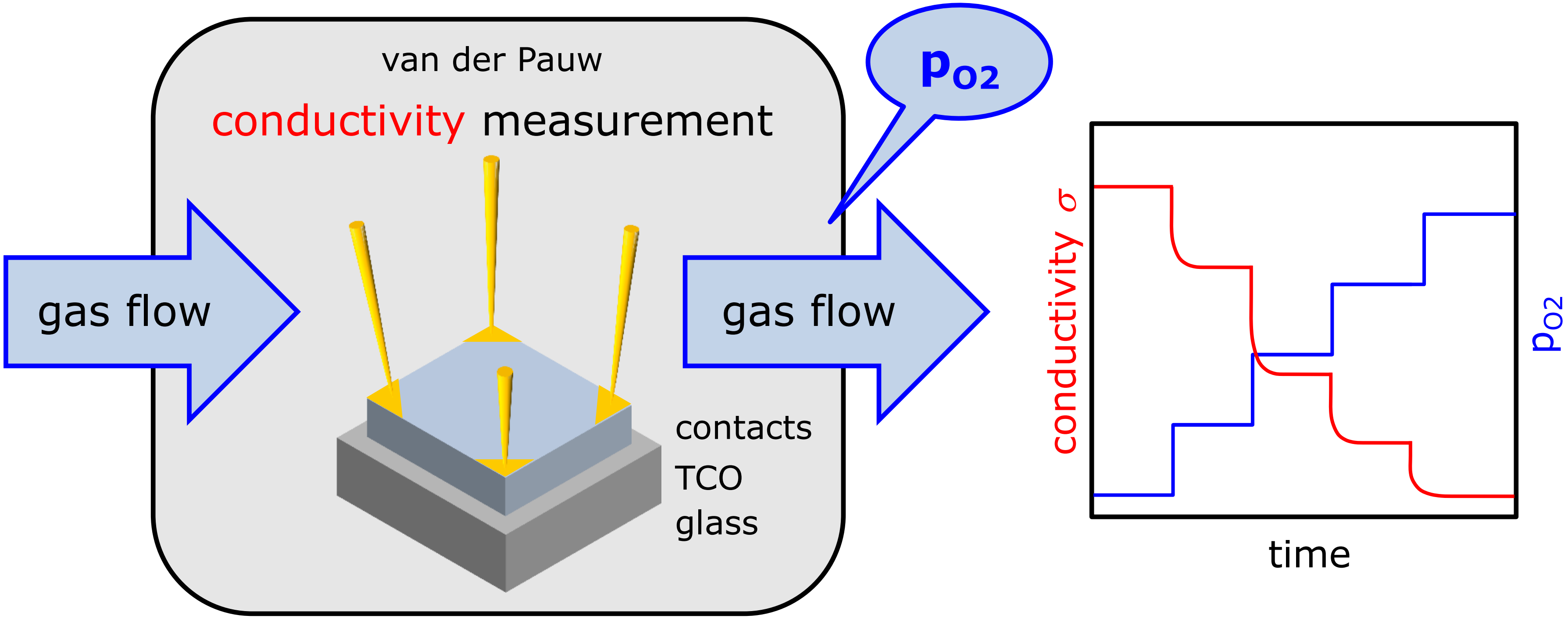
$E_M(V_O) = 1.01$ eV

$E_M(O_i) = 1.40$ eV

G. P. Wirtz and H. P. Takiar, J. Am. Ceram. Soc. 64, 748 (1981).

Phys Rev B 81 (2010) 195205

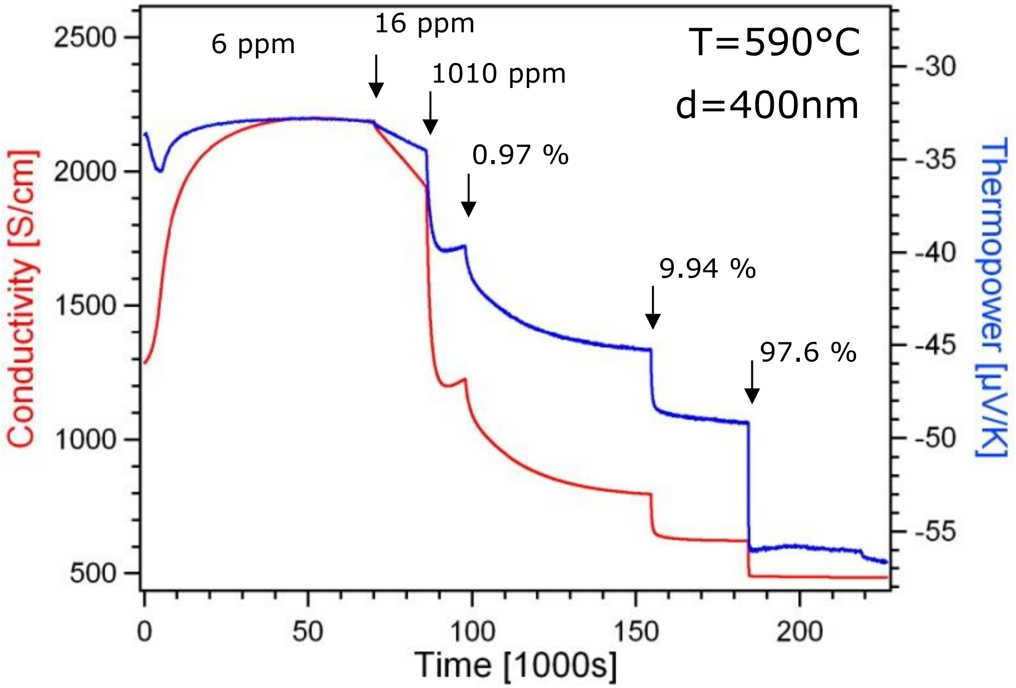
Conductivity relaxation

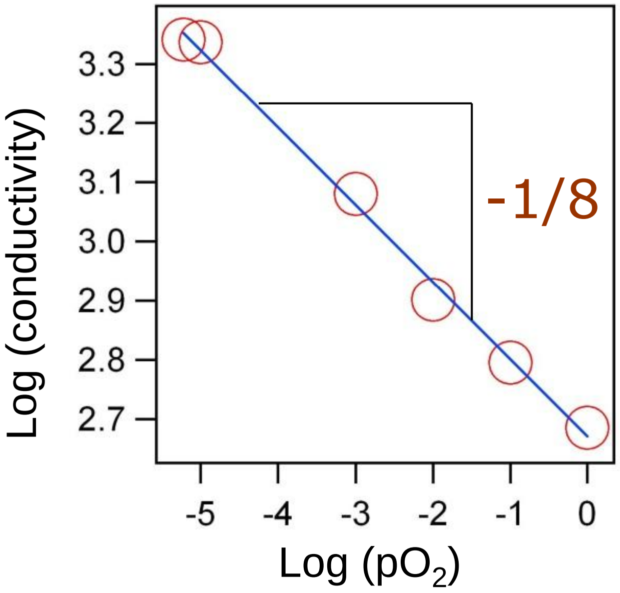


Surface oxygen exchange reaction

$$O_{2,g} \longrightarrow O_{2,ad} \xrightarrow{+e} O^{-}_{2,ad} \xrightarrow{+e} O^{2-}_{2,ad} \longrightarrow 2O^{-}_{ad} \xrightarrow{+2e+2V_O} 2O^{2-}_{s} \longrightarrow 2O^{2-}$$

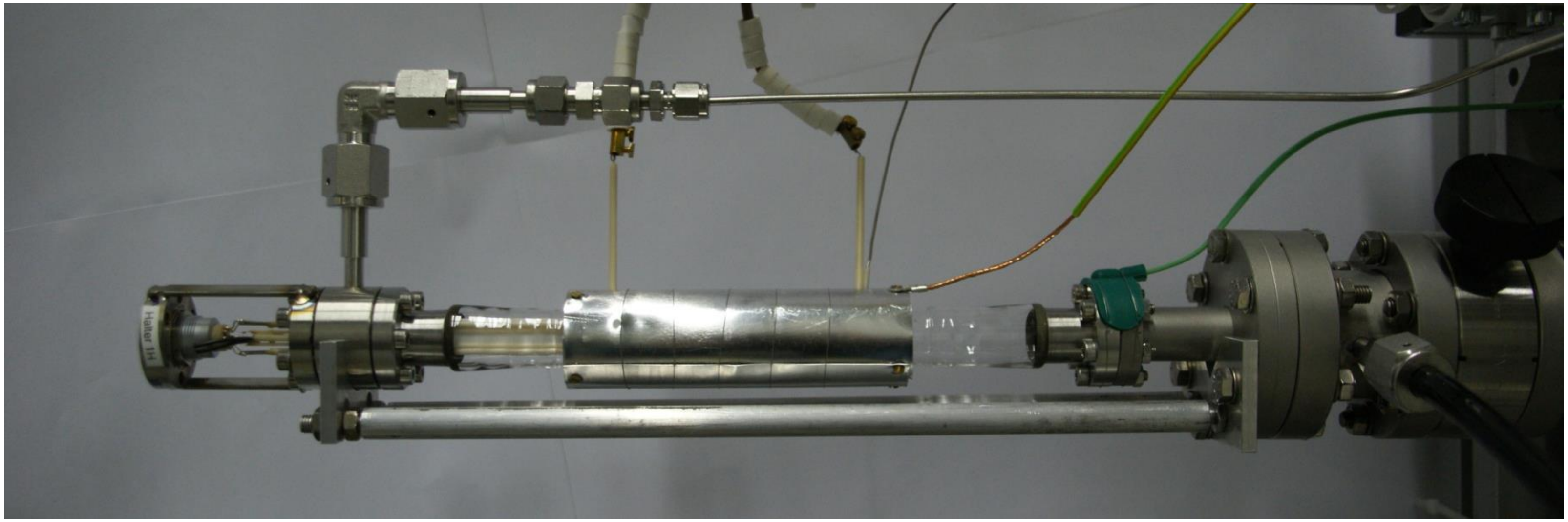
Conductivity relaxation of ITO (1 bar)

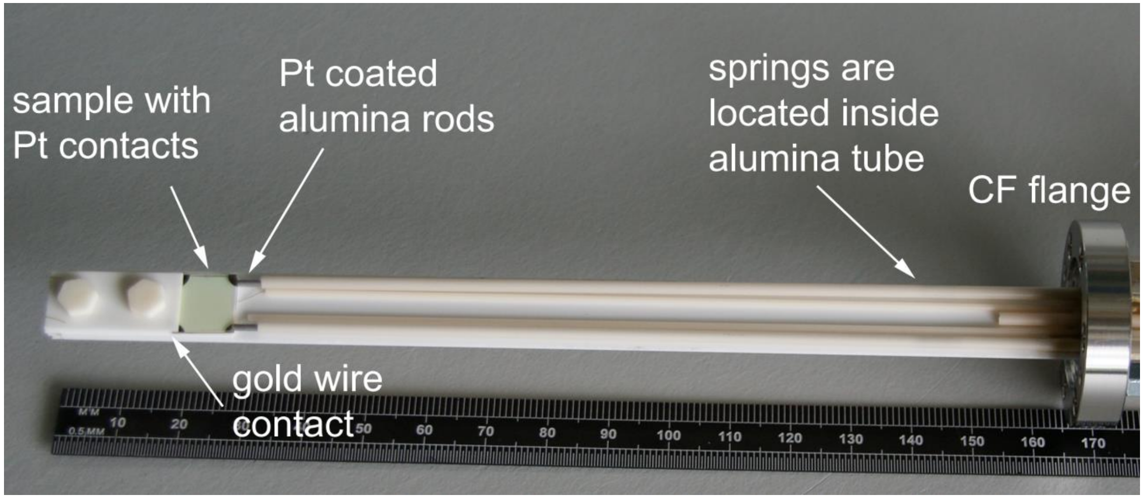




- **Conductivity depends on oxygen pressure**
- **Slope related to dominant defect species**

Hall effect and conductivity relaxation





sample with Pt contacts

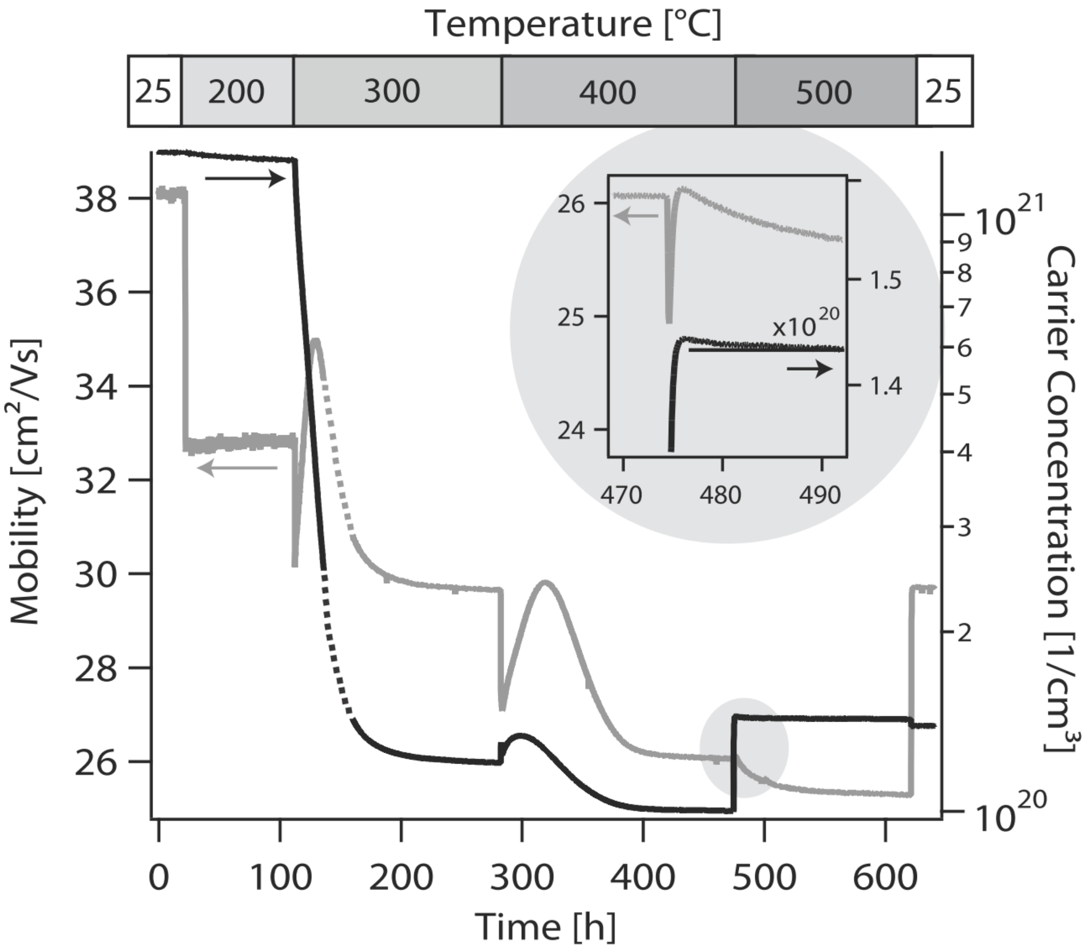
Pt coated alumina rods

springs are located inside alumina tube

CF flange

gold wire contact

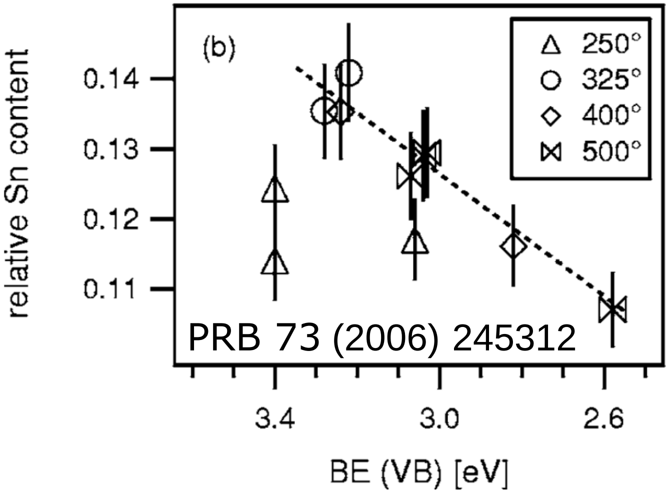
Hall effect measurement of ITO



- Changes much slower than expected from oxygen diffusion
- Changes not monotonic

→ **Cation diffusion is also involved**

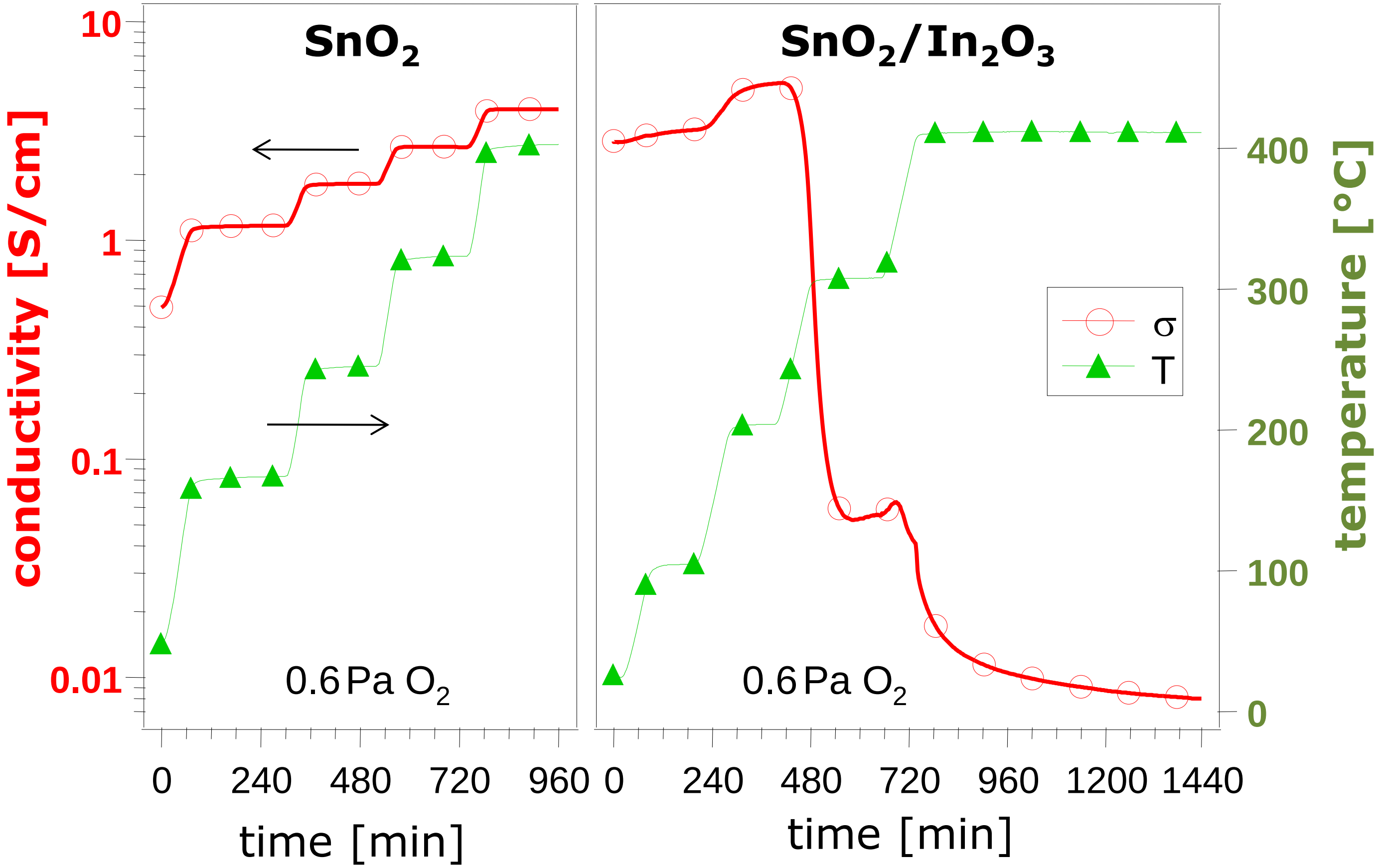
- Agrees with pO_2 dependent Sn segregation from XPS



PRB 73 (2006) 245312

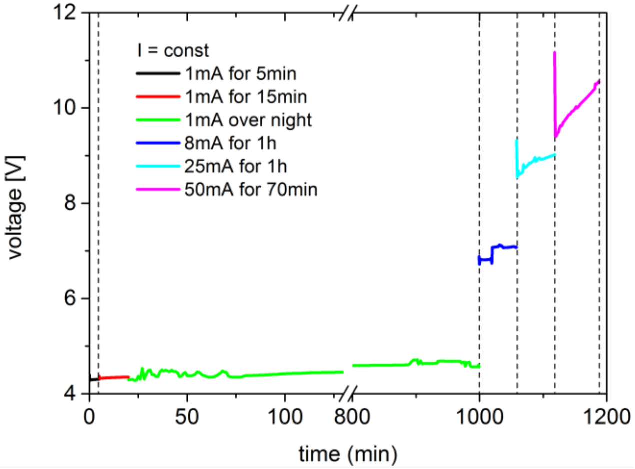
Solid State Ionics 262 (2014) 636

Enhancement of exchange by In_2O_3



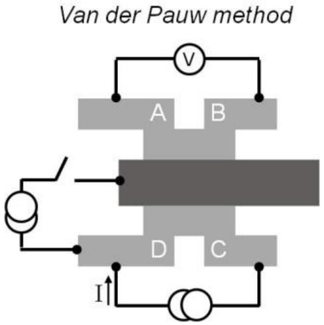
Exchange at SnO_2 possible with 1nm In_2O_3 on surface

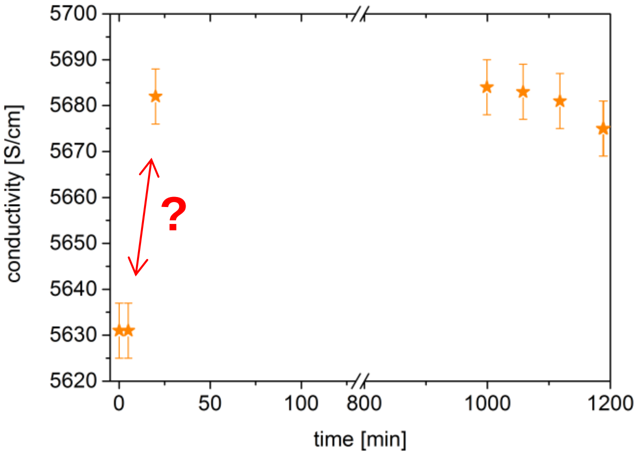
ITO conductivity during OLED operation



1st step: new contacting method in order to assure reproducibility

2nd step: remeasure, also with ITOs with different oxygen content:





ITO	Conductivity [S/cm]	concentration [1/cm³]	Mobility µ [cm²/Vs]
Commercial ITO	**7400**	**1E+21**	**40**
Commercial ITO after lithography	**5800**	**1E+21**	**35**
most reduced ITO 100% Ar	**7700**	**1E+21**	**41**
ITO 1% O_2	**1900**	**3E+20**	**36**
ITO 10% O_2	**70**	**3E+19**	**17**

Summary

- Carrier concentration in TCOs determined by doping and intrinsic defects (self-compensation)
- Work function determined by doping, surface orientation and surface termination

  → Inhomogeneous work function (charge injection)

- Oxygen exchange at ITO limited by bulk diffusion and not by surface exchange coefficient in contrast to SnO_2

  → Oxygen exchange in principle also at $T < 200°C$

→ No dominant influence of ITO electrode on OLED fatigue identified

Contributors

- **Ph.D. students**
  - **Paul Erhart, Péter Ágoston, Arno Fey, Yvonne Gassenbauer, André Wachau, Mareike Frischbier (Hohmann)**

- **Bachelor, Master, Diploma students**
  - **Péter Ágoston, Arno Fey, Thorsten Bayer, Kai Kühne, André Wachau, Mareike Hohmann, Karsten Rachut, Hans Wardenga, Robert Schafranek, Mirko Weidner, Timo Noll, Jonas Deuermeier**

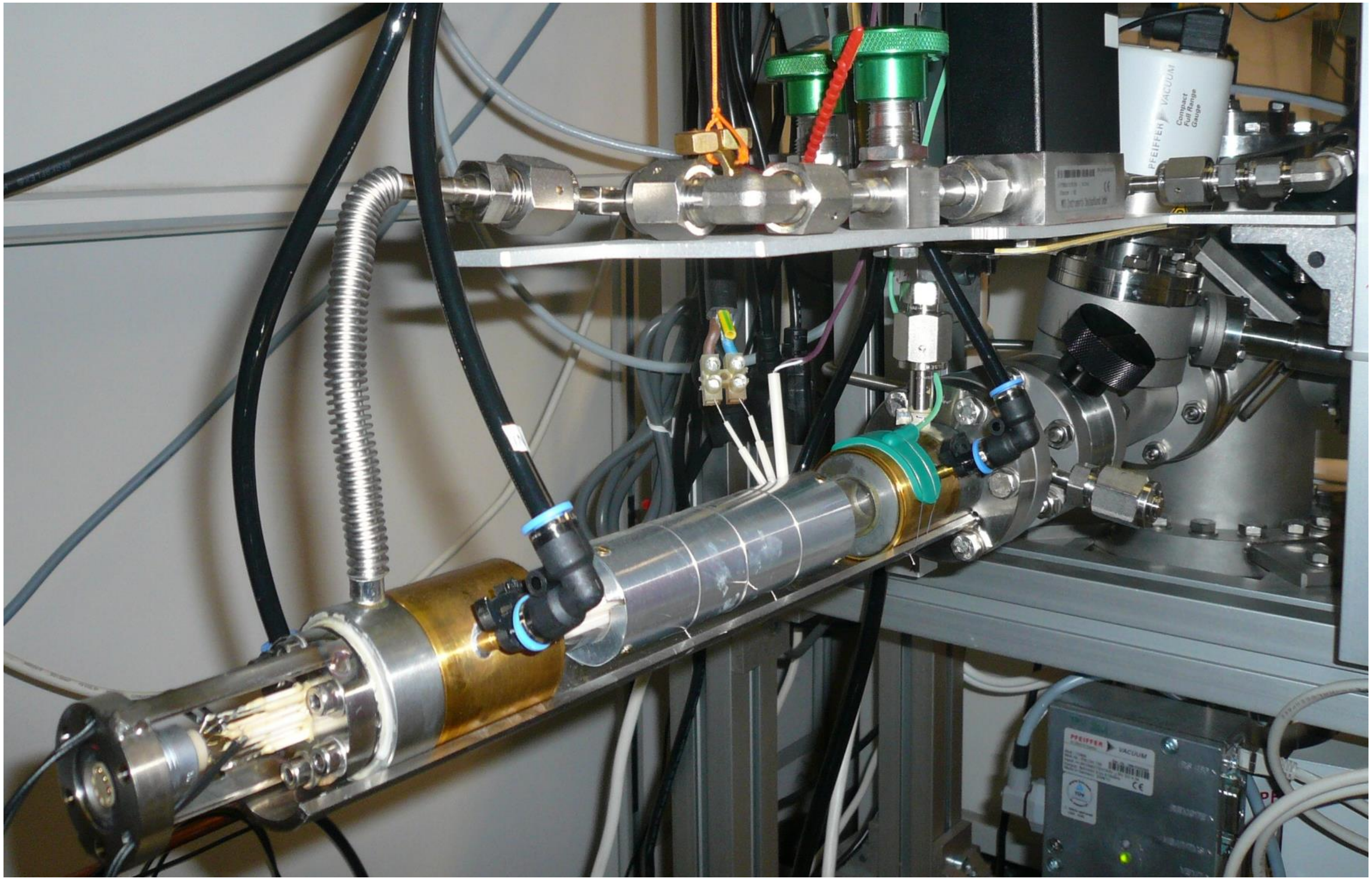
- **International cooperations**
  - **T.O. Mason (Northwestern University), R.G. Egdell (Oxford), Y. Shigesato (Yokohama), R. Nieminen, K. Nordlund (Helsinki)**

Publication Highlights

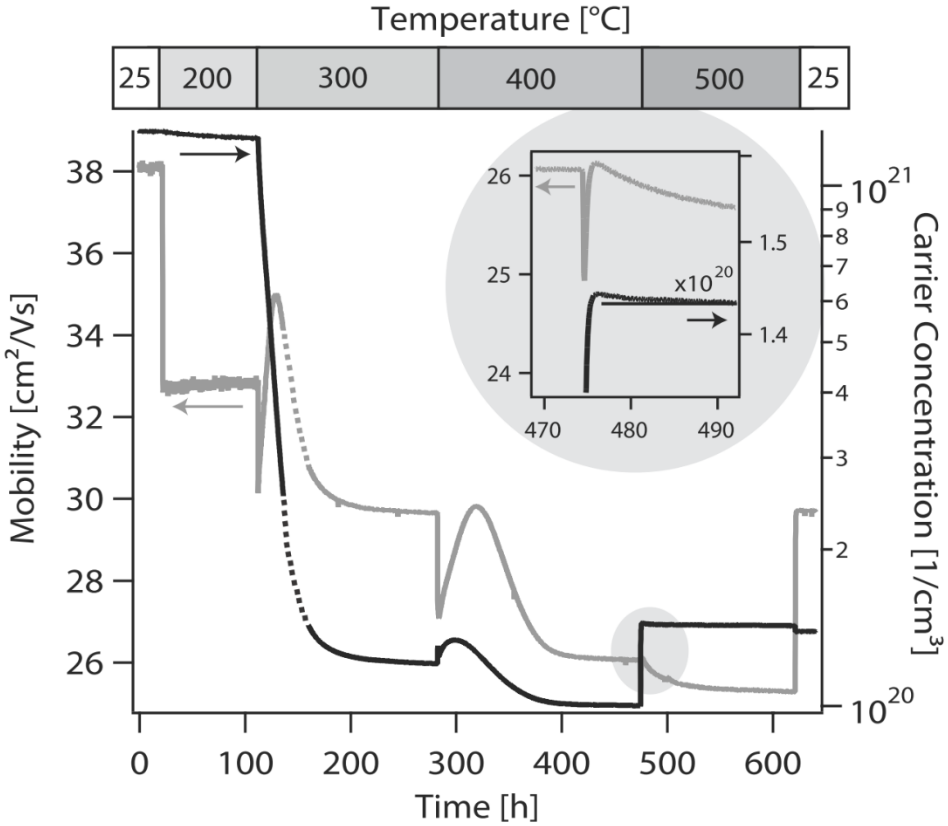
7 joint publications with 432 citations

34 publication of project D3 with 1253 citations

Relaxation setup

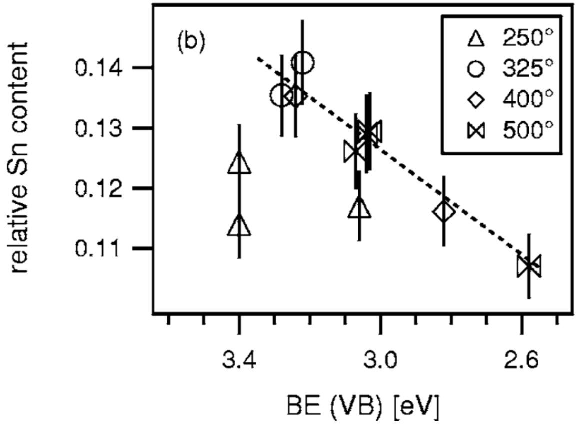


Discussing the carrier concentration



Effects affecting carrier concentration *n*:

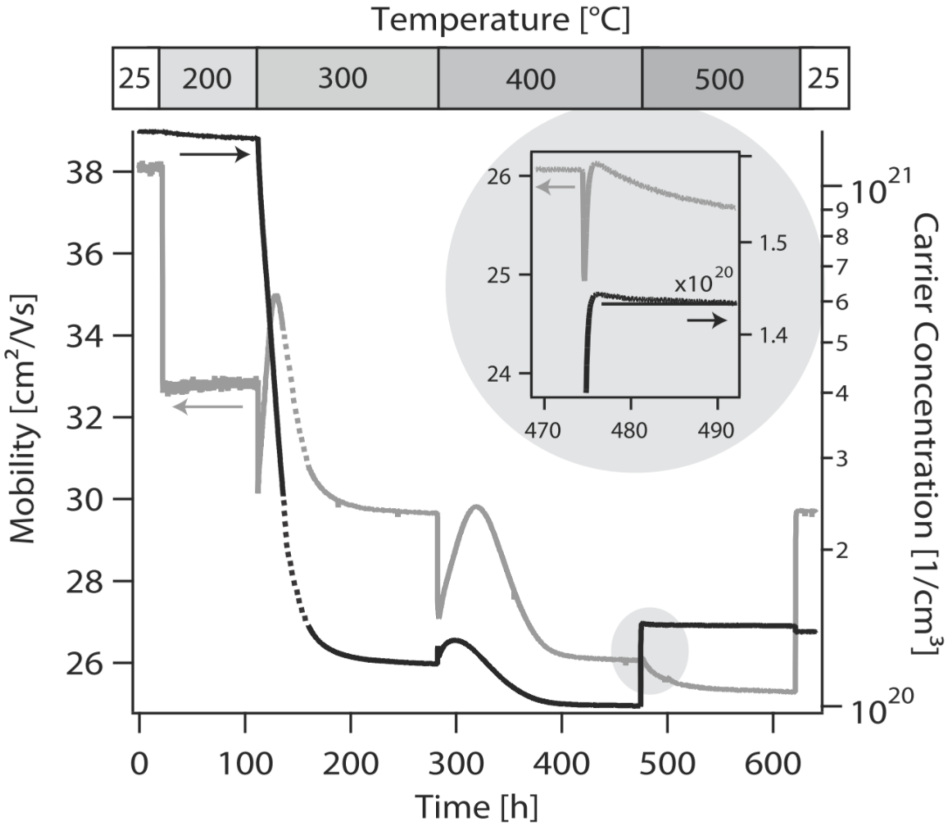
1. oxygen incorporation $n \downarrow$
2. Sn segregation $n \downarrow$
3. T↑ $\mu_O = \mu_0 + RT \ln \frac{p_O}{p_0}$ μO ↓ $n \uparrow$



Gassenbauer, Y., et al. (2006). Physical Review B 73: 245312.

30.09.2013 | Mareike Hohmann | SFB Meeting Bad Orb | 32

Discussing the carrier concentration



Effects affecting carrier concentration *n*:

1. oxygen incorporation n ↓
2. Sn segregation n ↓
3. T ↑ μ_O ↓ n ↑

$$\mu_O = \mu_0 + RT \ln \frac{p_O}{p_0}$$

$$O_i'' + 2Sn_{In}^{\bullet}$$

$$\Updownarrow$$

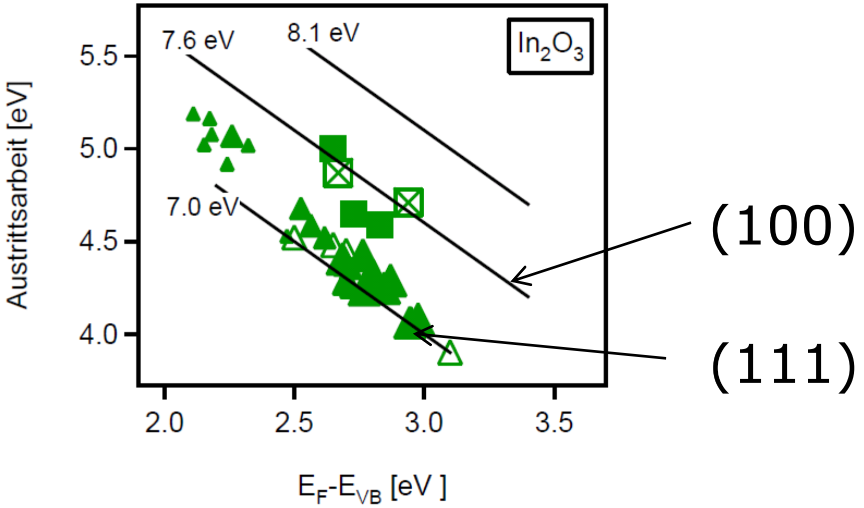
$$\frac{1}{2}O_2 + 2Sn_{In}^{\bullet} + 2e'$$

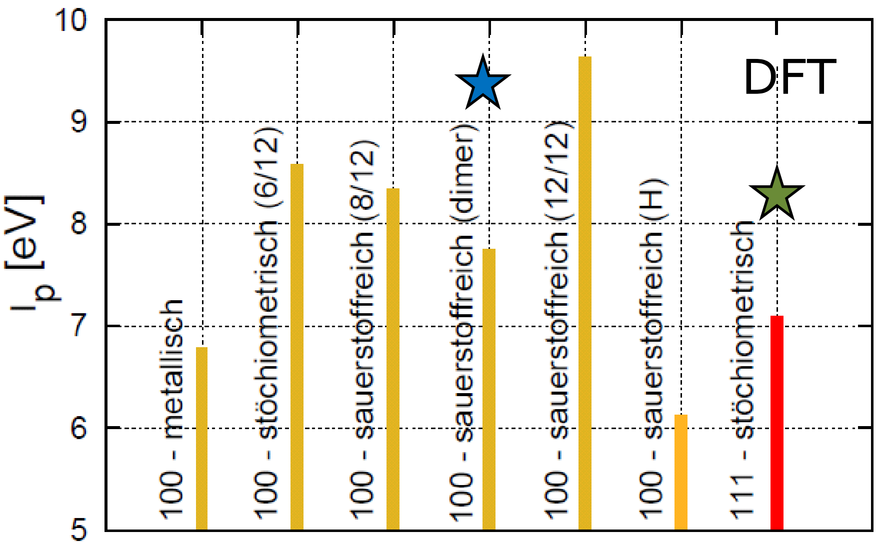
$$\Updownarrow$$

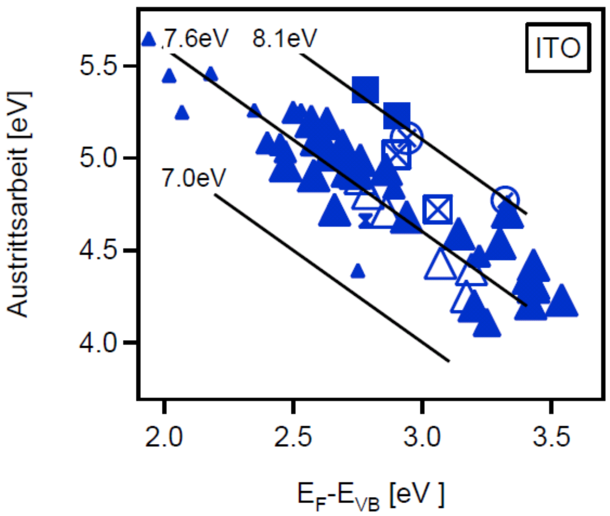
$$\frac{1}{2}O_2 + 2Sn_{seg}$$

First ideas on complex interplay of several effects

In_2O_3 – work function



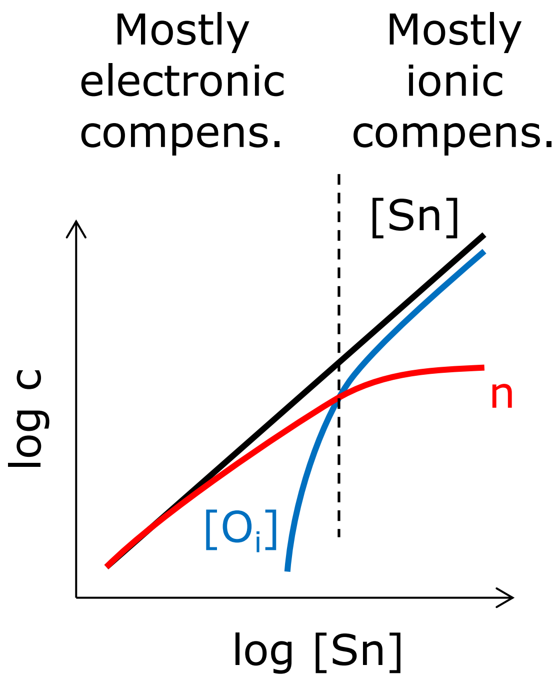


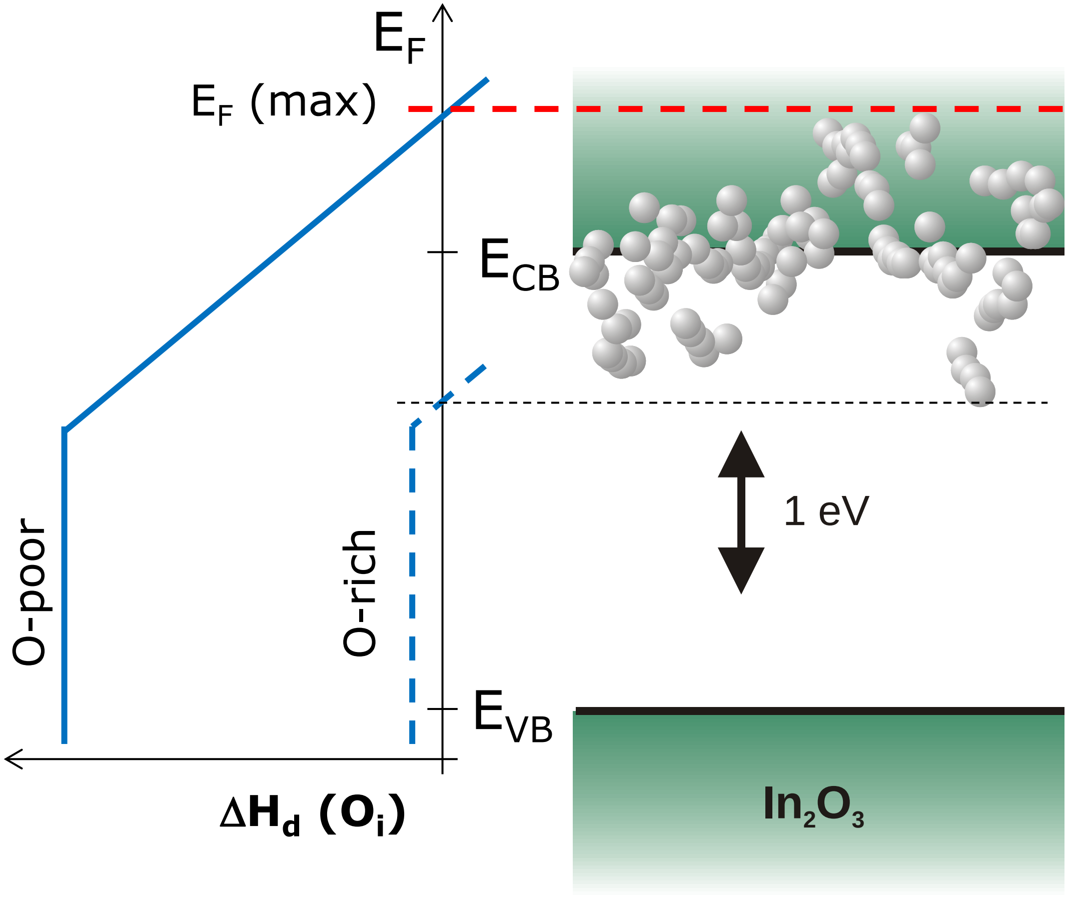


- **Almost no change of surface termination with oxygen**
- **Work function depends on surface orientation**
- **Differences between In_2O_3 and ITO explained by texture of films**
- **Surface oxidation (e.g. via ozone) only possible for (100) orientation**

J. Phys. CM **23** (2011) 334203

Doping limit of ITO (In_2O_3:Sn)

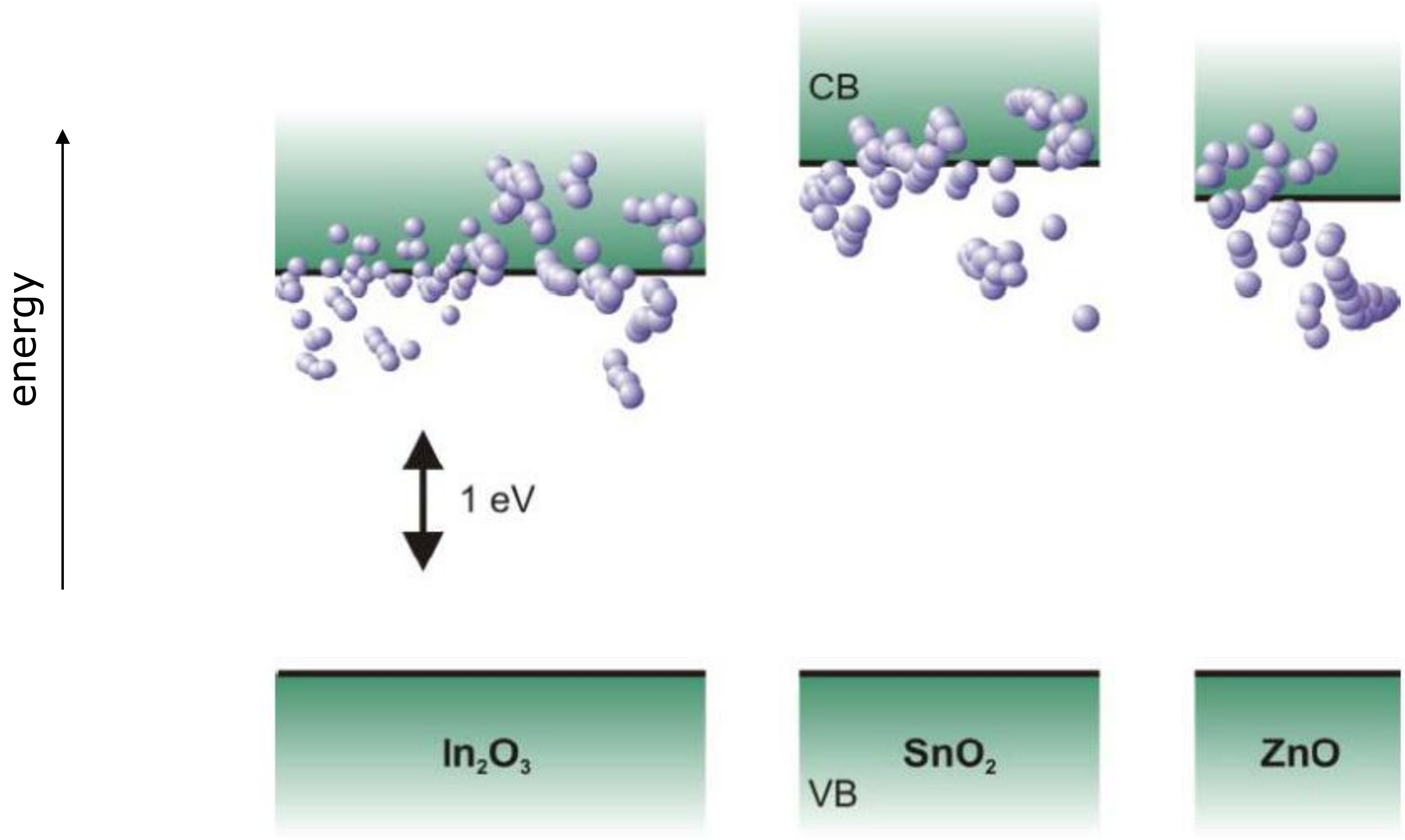




Self-compensation provides a natural explanation for the transition from electronic to ionic compensation of Sn_{In}

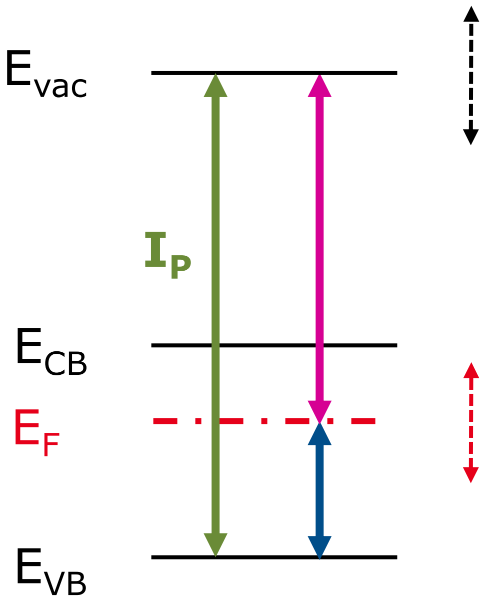
J Am Ceram Soc 96 (2013) 331

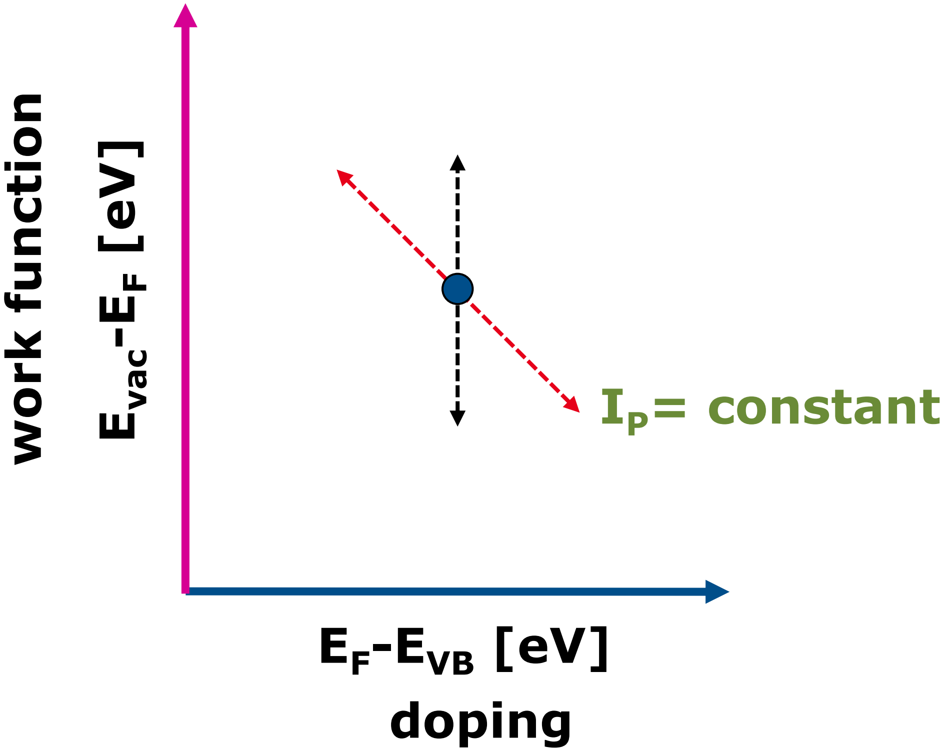
Fermi level of TCO films



J. Am. Ceram. Soc. **96** (2013) 331

Work function and ionisation potential



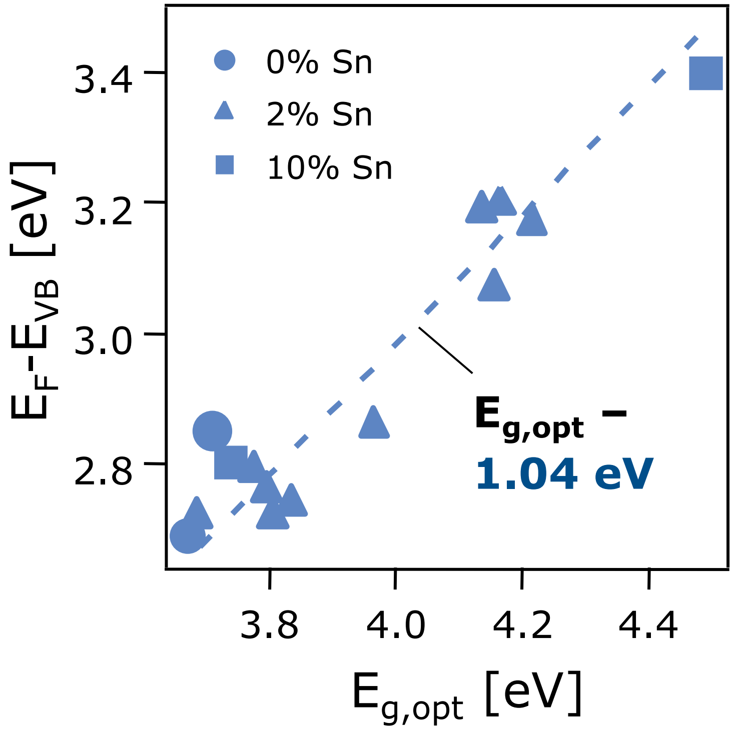


Work function affected by Fermi level and ionisation potential

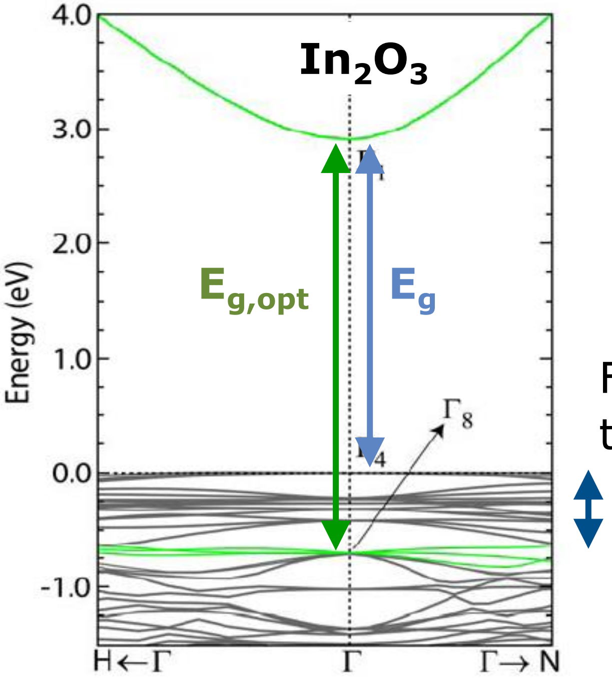
Band gap of In_2O_3 and ITO

ITO = In_2O_3:Sn

XPS vs. Optik



Theorie

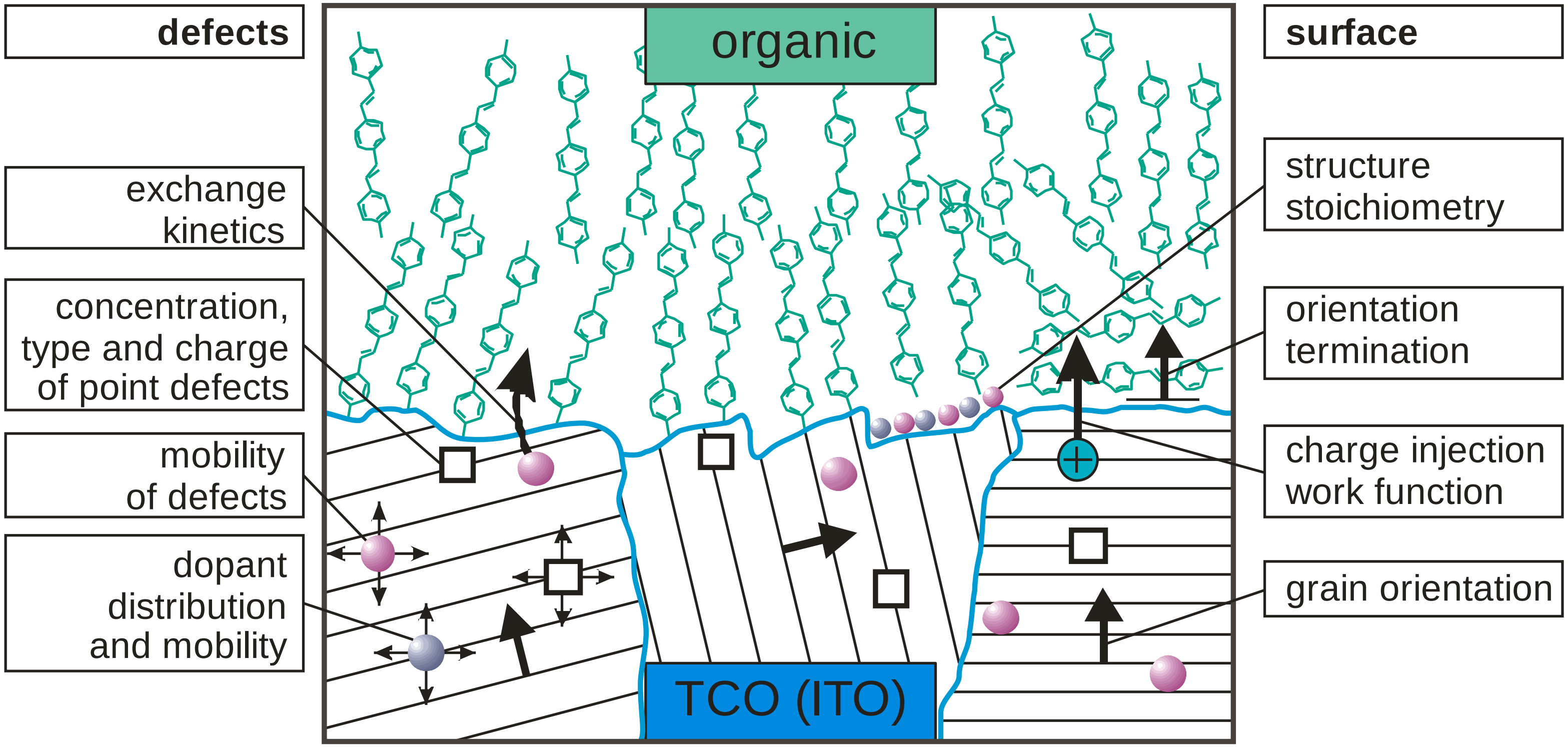


Forbidden transitions

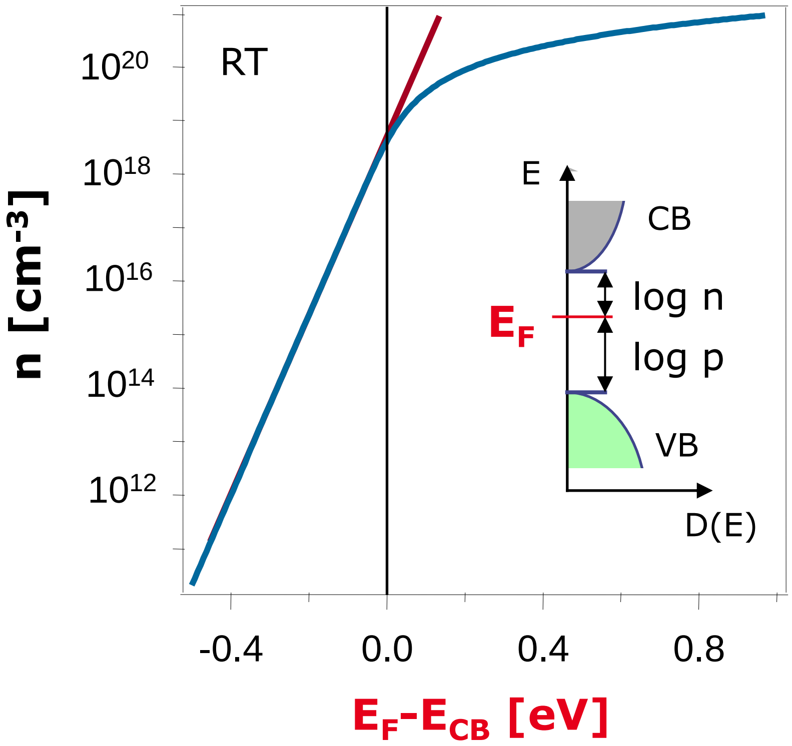
0.8 eV

- ➢ **ΔE_F (XPS) ~ ΔE_F (optic)**
- ➢ **Fundamental gap E_g ~ 2.8 eV**

PRL 100 (2008) 167402


defects
exchange kinetics
concentration, type and charge of point defects
mobility of defects
dopant distribution and mobility
organic
TCO (ITO)
surface
structure stoichiometry
orientation termination
charge injection work function
grain orientation

Conductivity and carrier concentration



Conductivity $\sigma = en\mu_e + ep\mu_h$

Electron concentration

$$n = \int_{E_{CB}}^{\infty} D(E) f(E) dE$$

Non-degenerate semiconductors

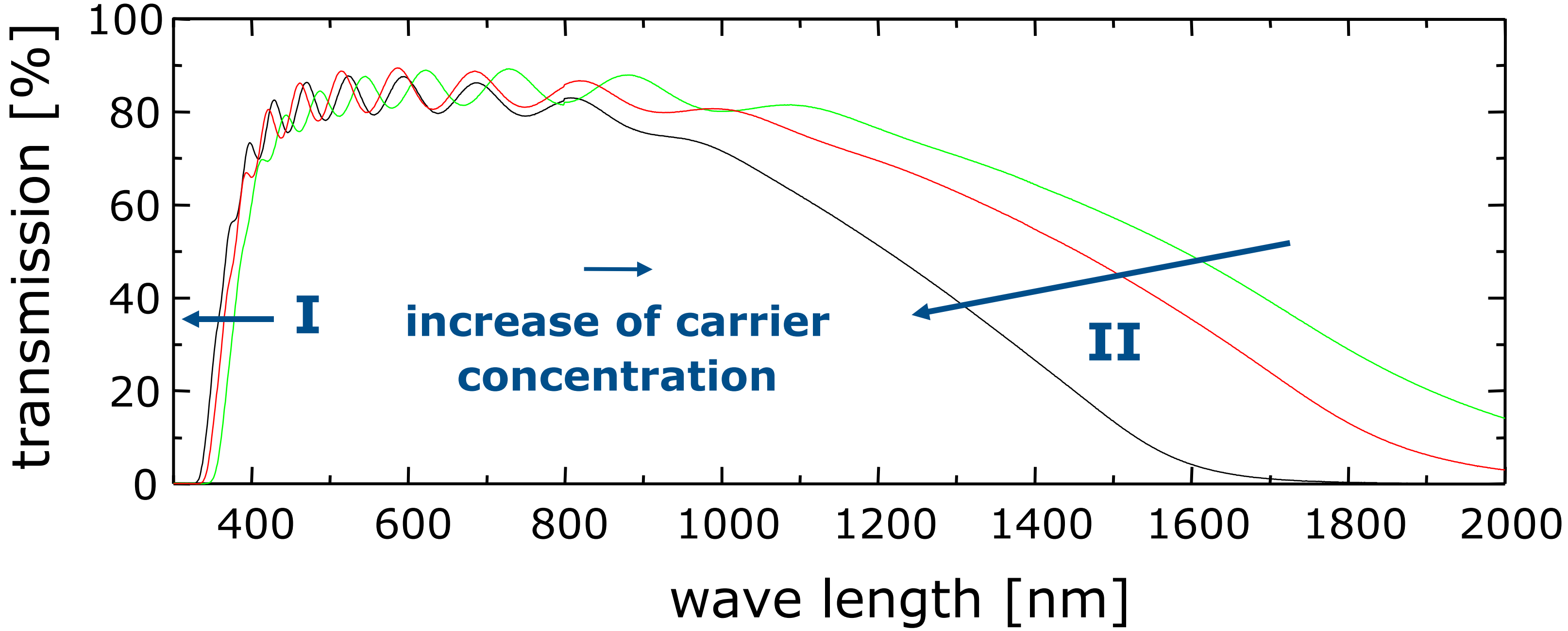
→ $E_{CB}-E_F > 3\ k_BT$

$$n = N_C \exp\left(-\frac{E_{CB}-E_F}{kT}\right)$$

Electrical conductivity determined by carrier concentration

Carrier concentration determined by Fermi level position

Optical properties



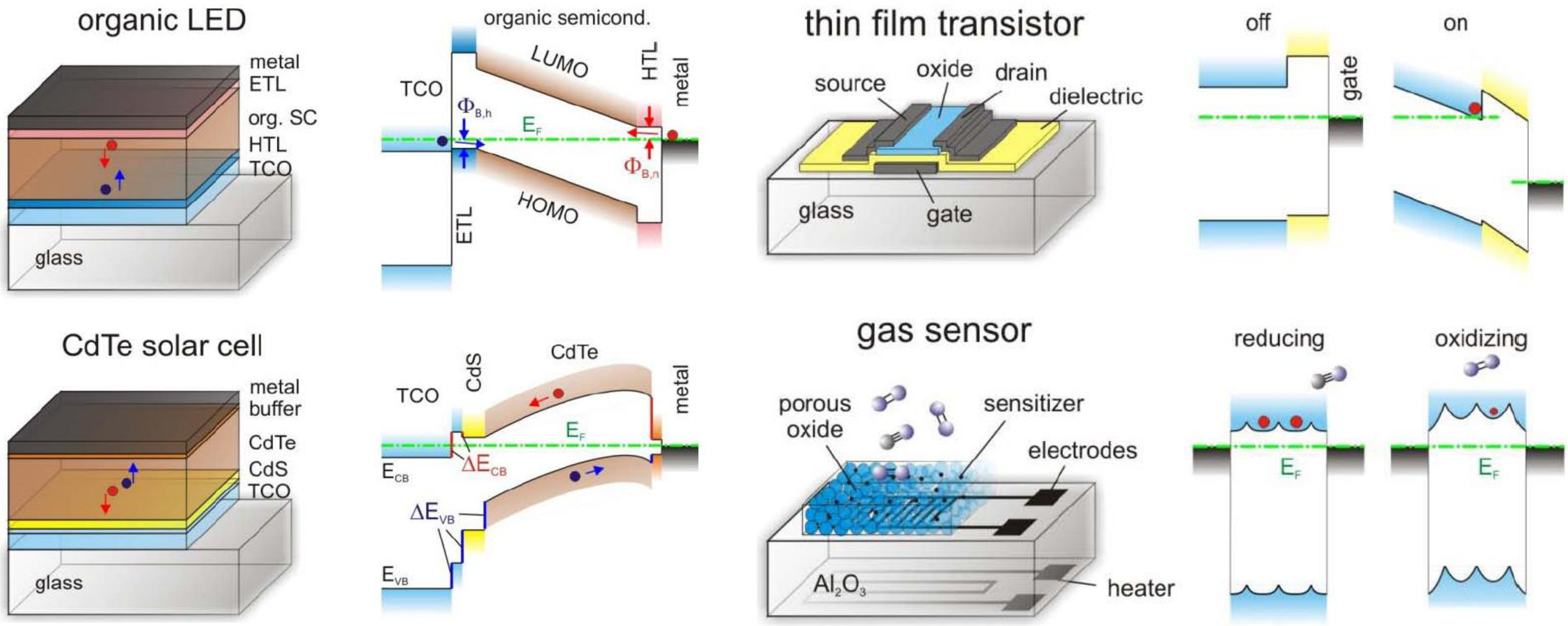
I: Burstein-Moss shift

II: Free-carrier induced infrared absorption

Plasmon energy (Drude theory): $\omega^2 \approx \frac{n \cdot e^2}{\varepsilon_0 \cdot m^*} \sim 0.5eV$

data: K. Orgassa, IPE Stuttgart

TCO applications



Energy band alignment at interfaces important for function

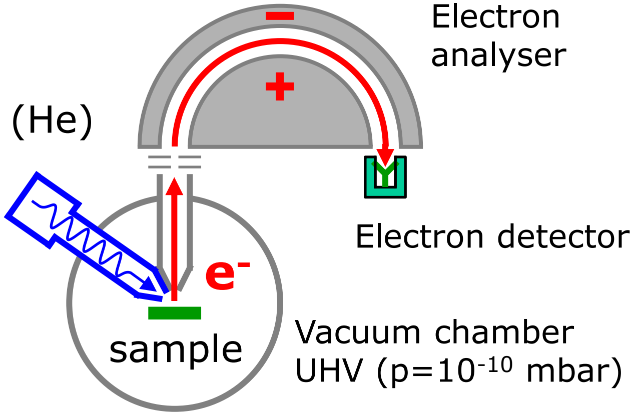
Topics

- Transparent conducting oxides
  - Basic electrical and optical properties
  - Applications and importance of surfaces and interfaces
- **Experimental Approach**
- Surface Properties
  - Work function and ionization potential
  - Oxygen exchange
- Interface properties
  - Energy band alignment
  - Redox processes at interface

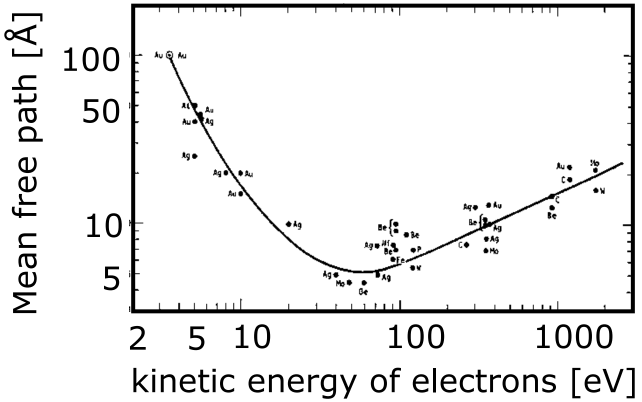
Photoemission (XPS, UPS) – Basics

schematics

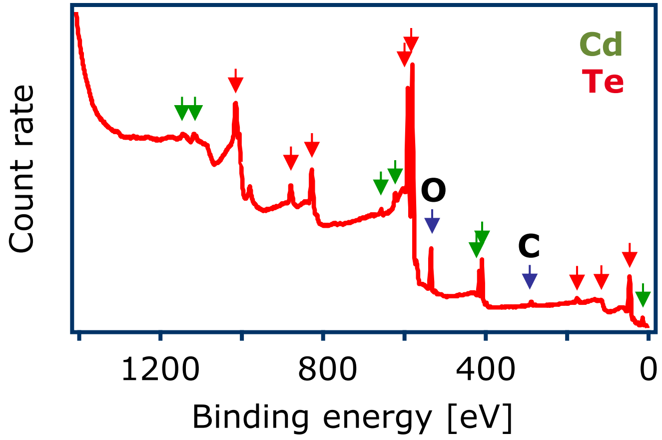
Light source:
- X-ray (Mg, Al)
- Gas discharge (He)
- Synchrotron



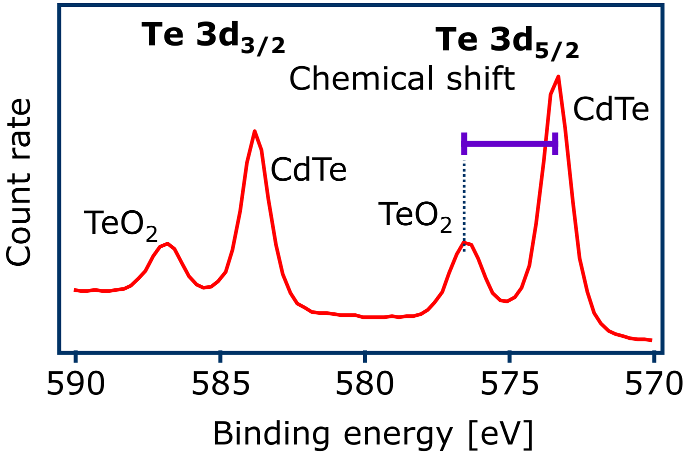
Surface sensitivity



Elemental analysis

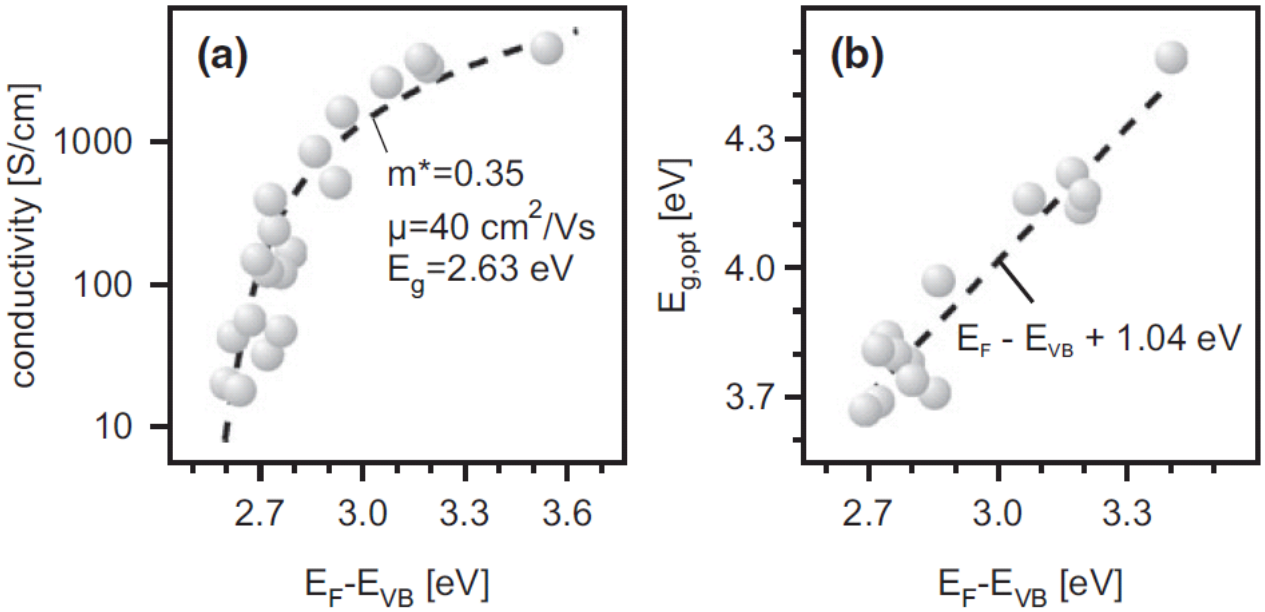


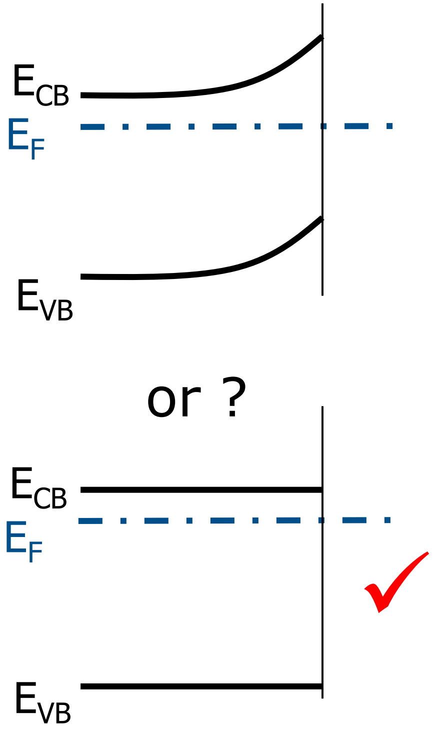
Chemical analysis



Surface vs. Bulk Fermi level

In_2O_3(:Sn)

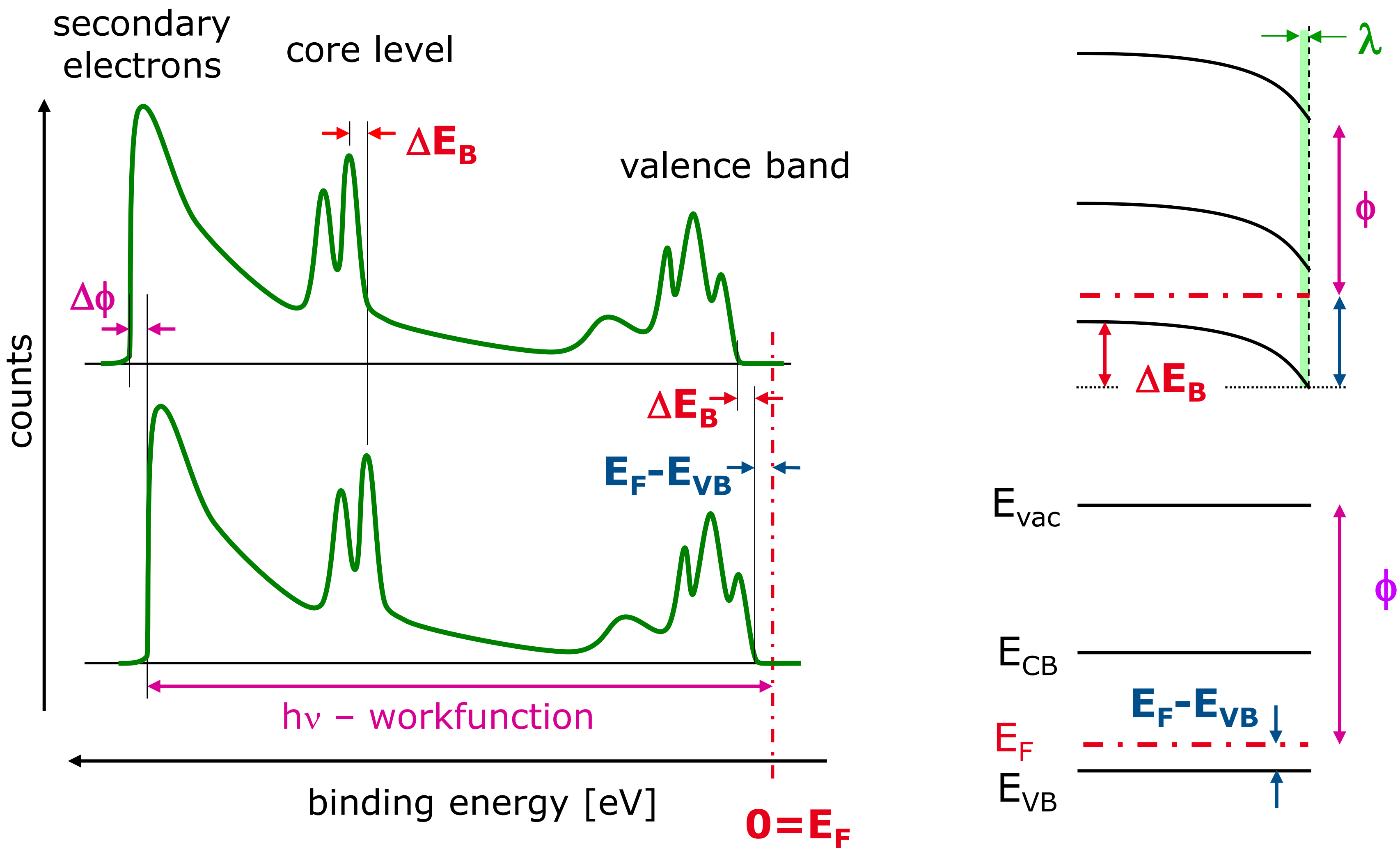




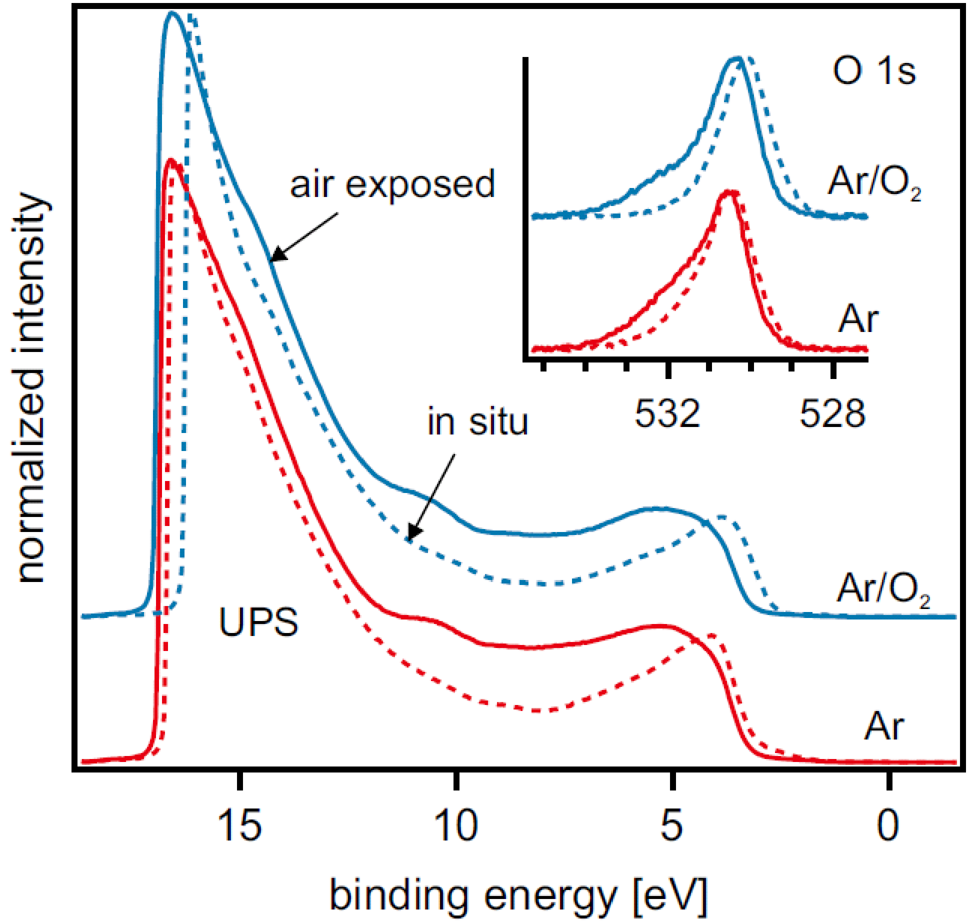
Fermi level in bulk corresponds with Fermi level at surface

J. Am. Ceram. Soc. **96** (2013) 331

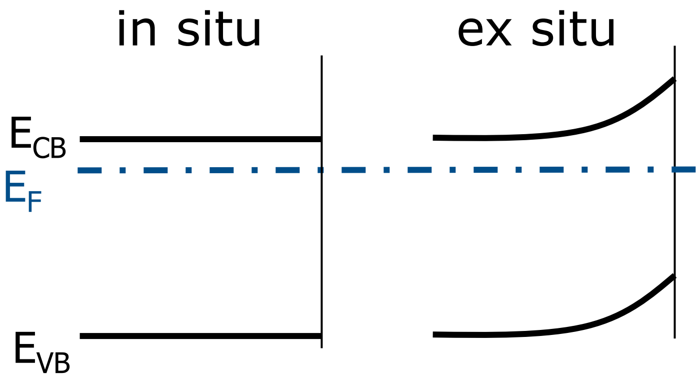
Photoemission – Semiconductors



In-situ vs. ex-situ



Spectral shape and binding energies (Fermi level position in band gap) are affected by contact with air

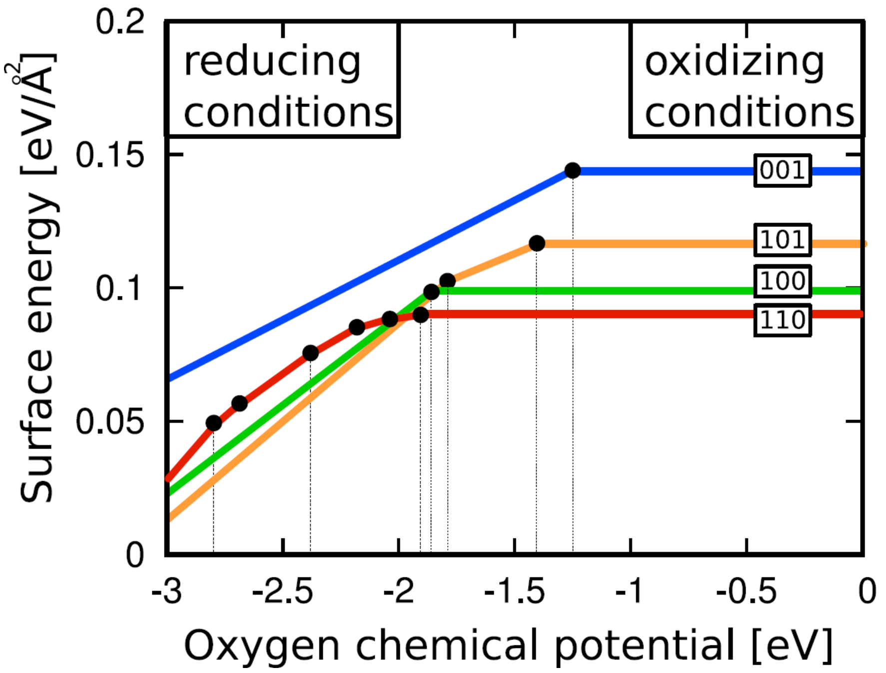


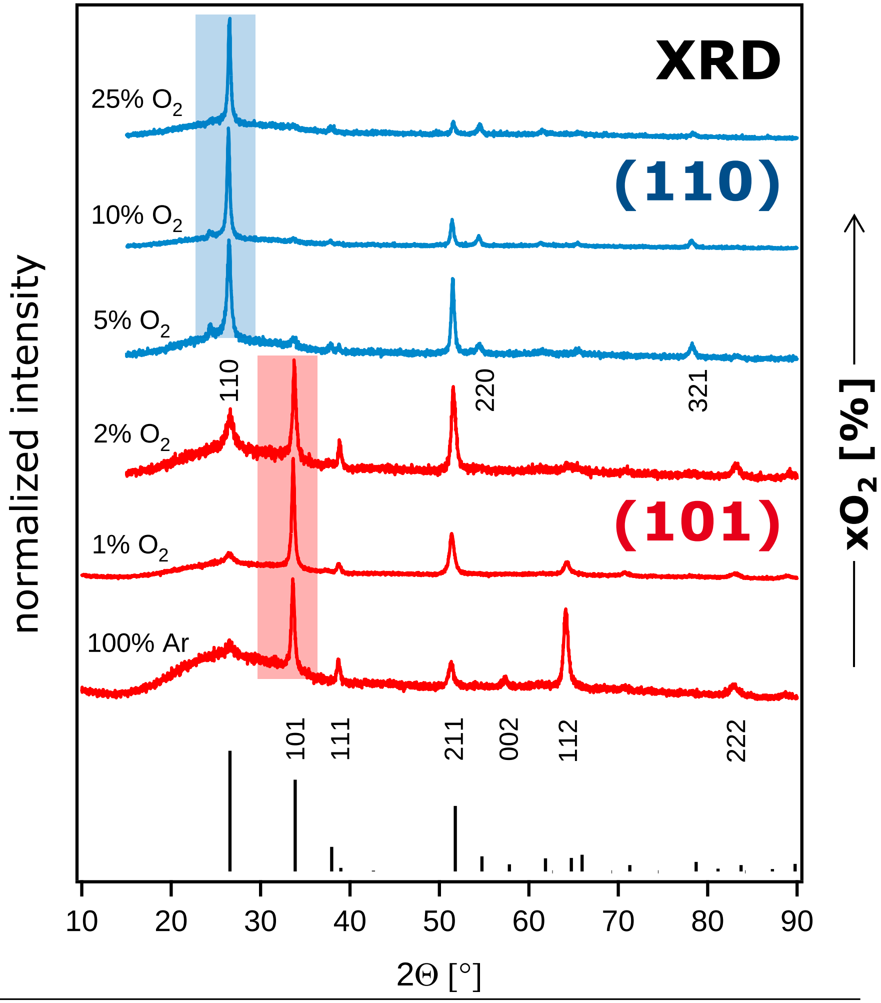
J. Am. Ceram. Soc. **96** (2013) 331

Topics

- Transparent conducting oxides
  - Basic electrical and optical properties
  - Applications and importance of surfaces and interfaces
- Experimental Approach
- **Surface Properties**
  - **Work function and ionization potential**
  - **Oxygen exchange**
- Interface properties
  - Energy band alignment
  - Redox processes at interface

Preferred orientation

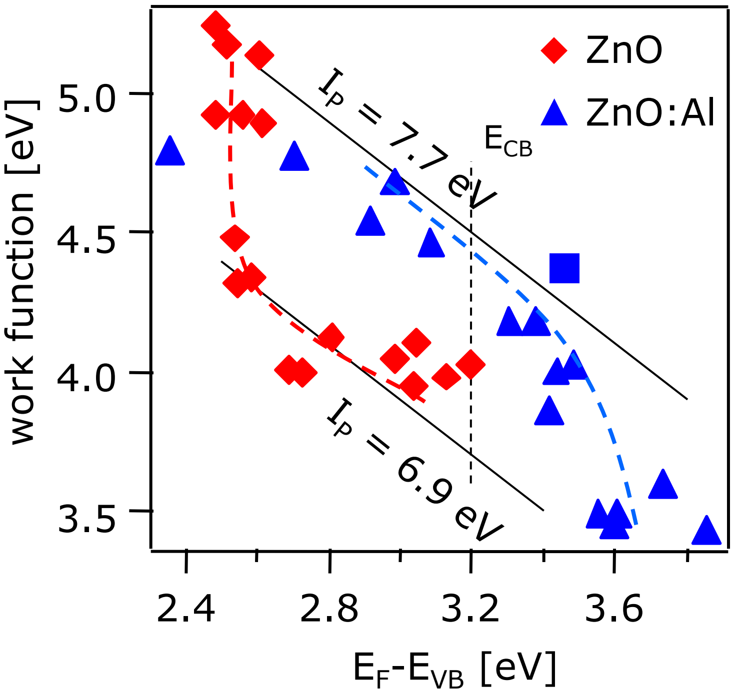




- **Change of stable surface orientation with oxygen pressure**

J. Phys. D **43** (2010) 055301

ZnO – work function



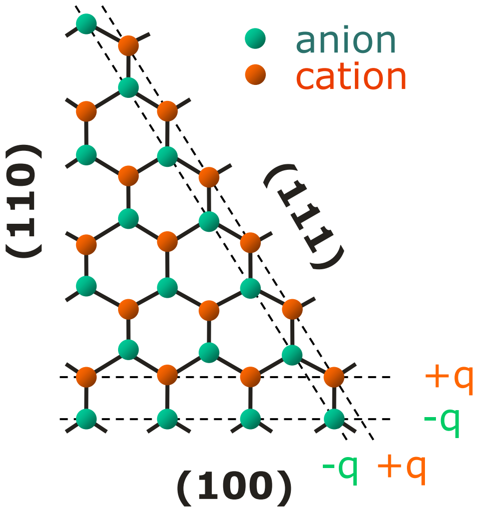
Single crystal ZnO (wurtzite)

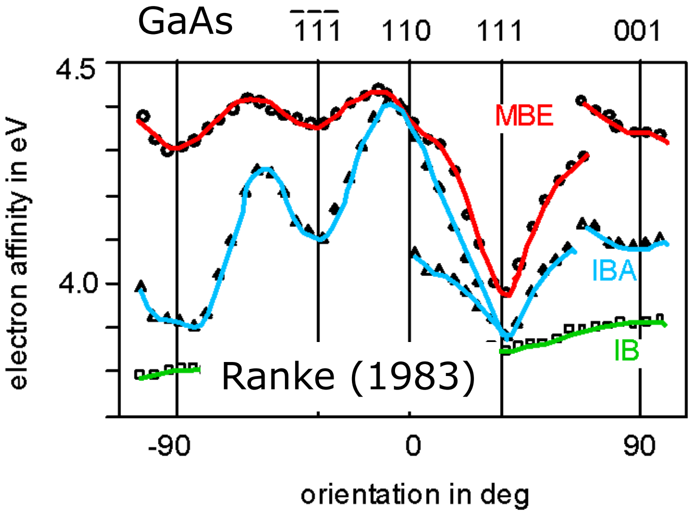
I_P = 7.0eV (0001)

I_P = 7.8eV (000-1)

I_P = 7.8eV (10-10)

Swank (1967)
Jacobi (1984)



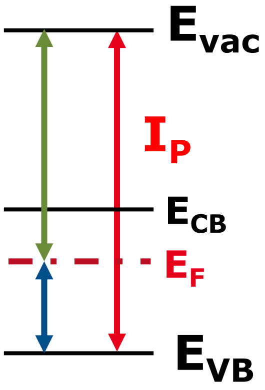


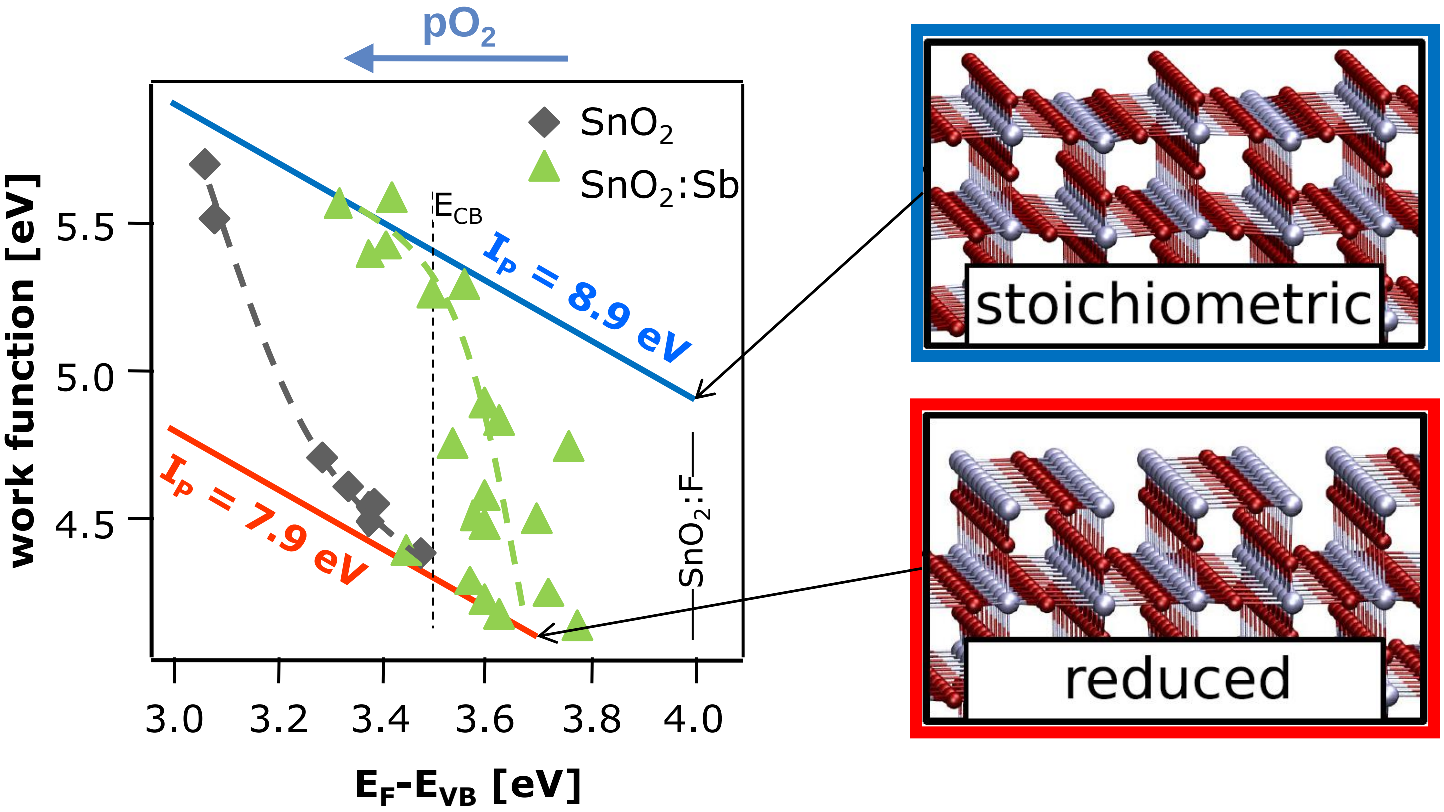
Ranke (1983)

Change of ionisation potential due to different surface orientation

TSF **518** (2009) 1197 Materials **3** (2010) 4892

SnO_2 – work function



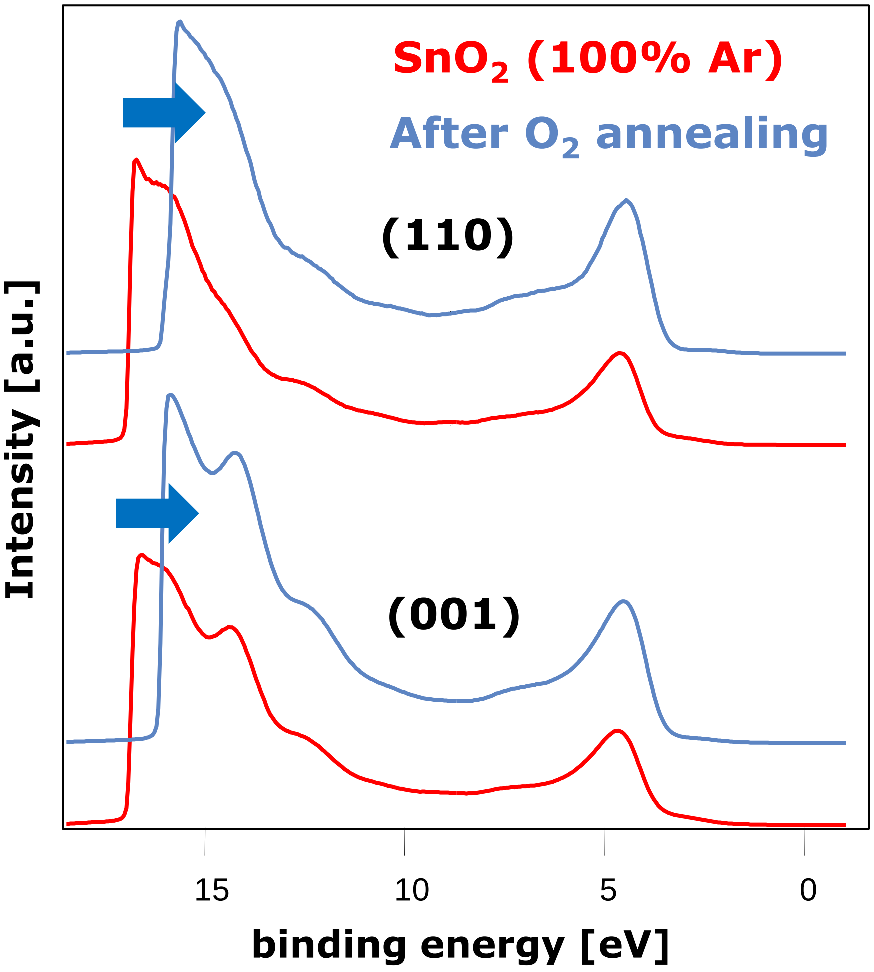


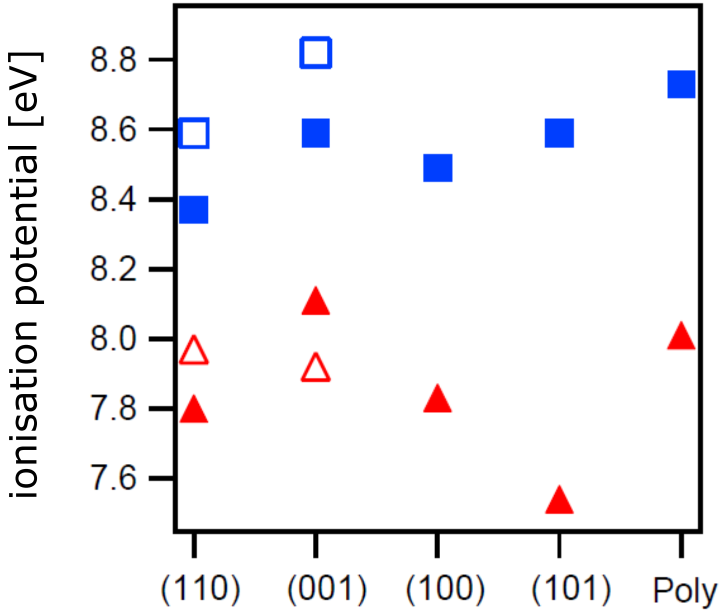
Change of ionization potential with surface termination

Change of surface termination with oxidation/reduction

TSF **518** (2009) 1197 Materials **3** (2010) 4892

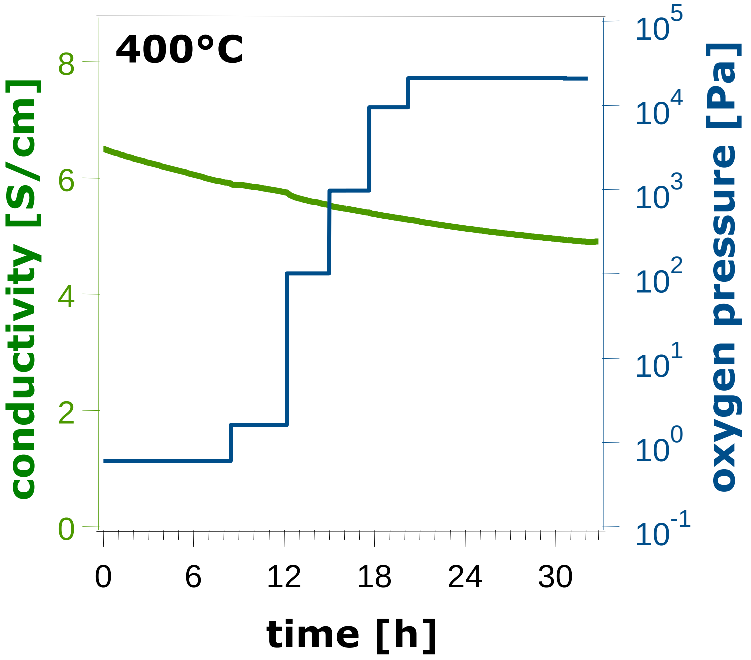
Post deposition treatment

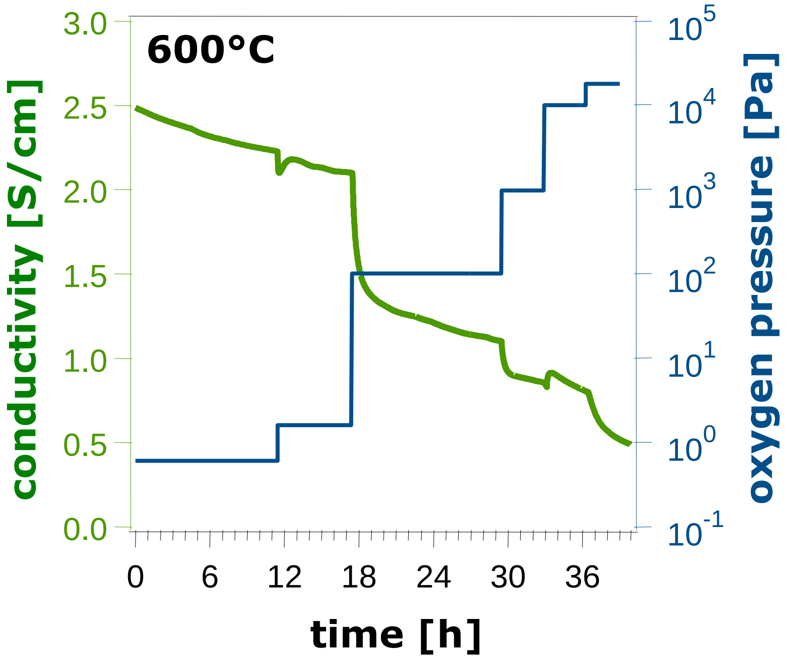




Large change of work function and ionization potential independent on orientation

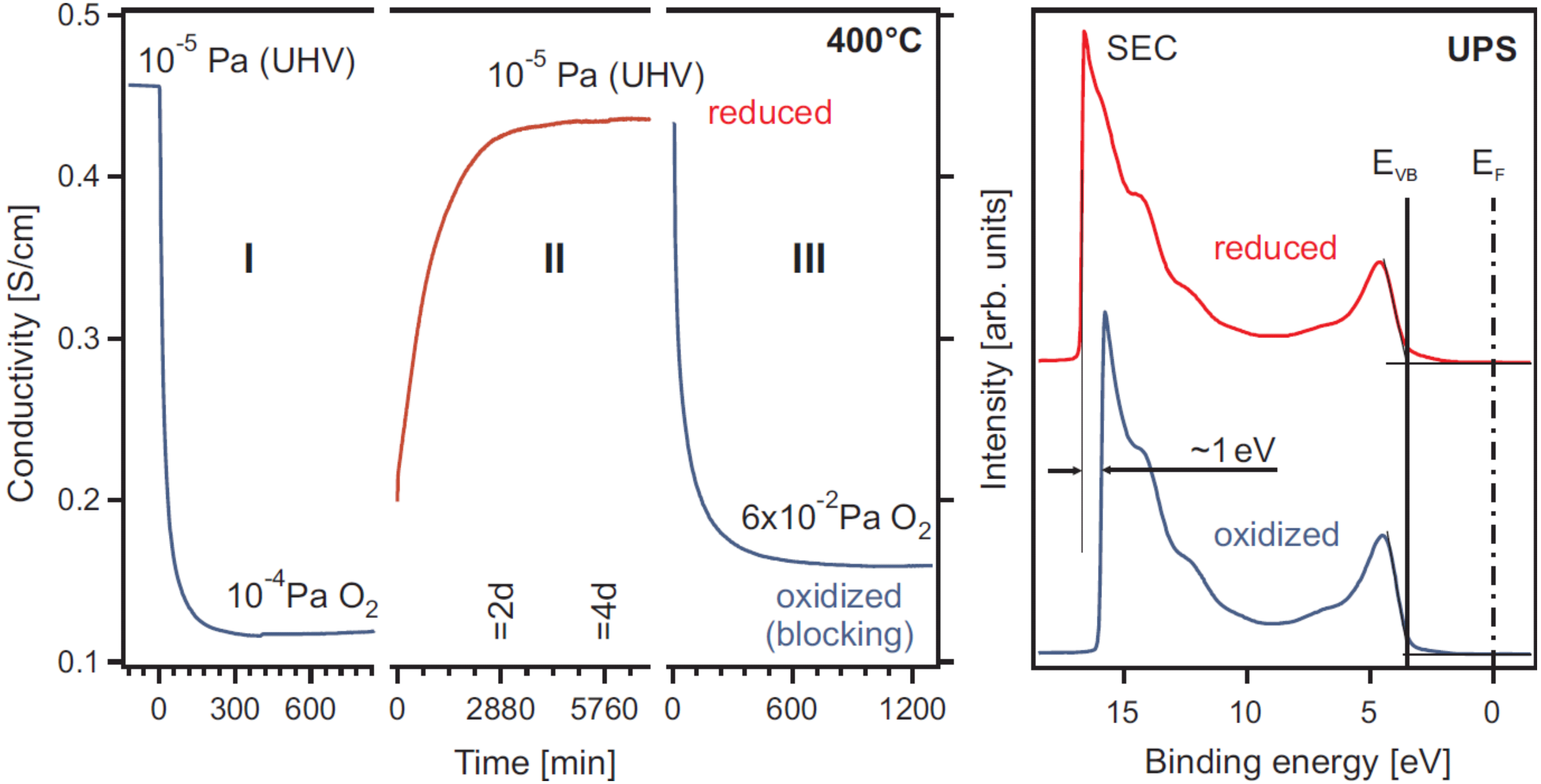
Conductivity relaxation of SnO_2 (1 bar)





- ➢ **Almost no change of σ with pO_2 at 400°C**
- ➢ **Equilibrium carrier concentration not achieved**

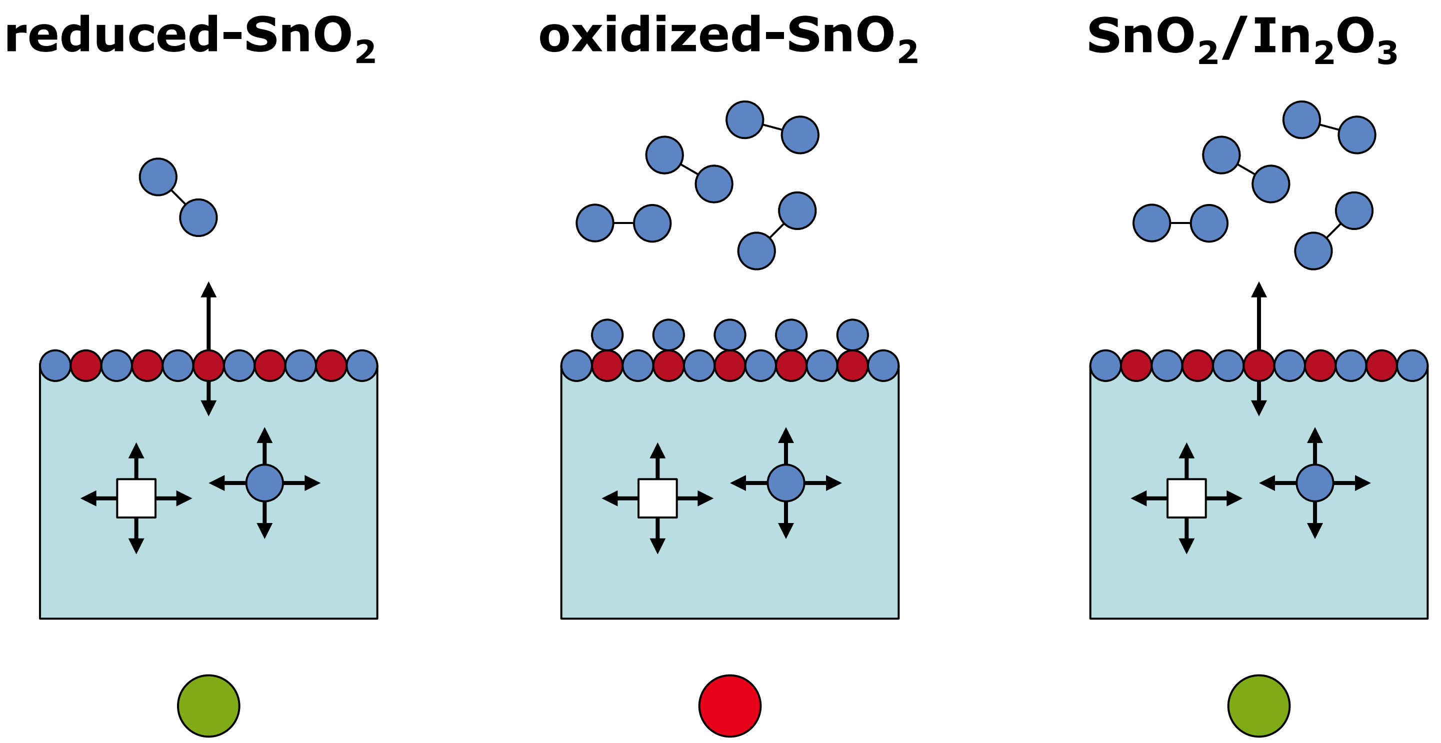
Relaxation at low pressure



- **Relaxation observed when starting from reduced surface**
- **Saturated conductivity does not correlate with pO_2**

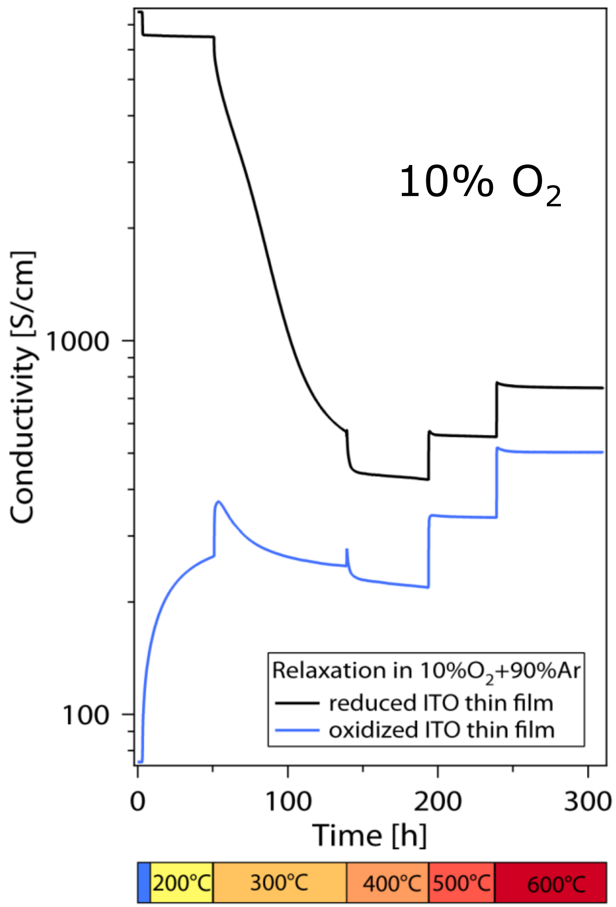
PCCP **13** (2011) 3223

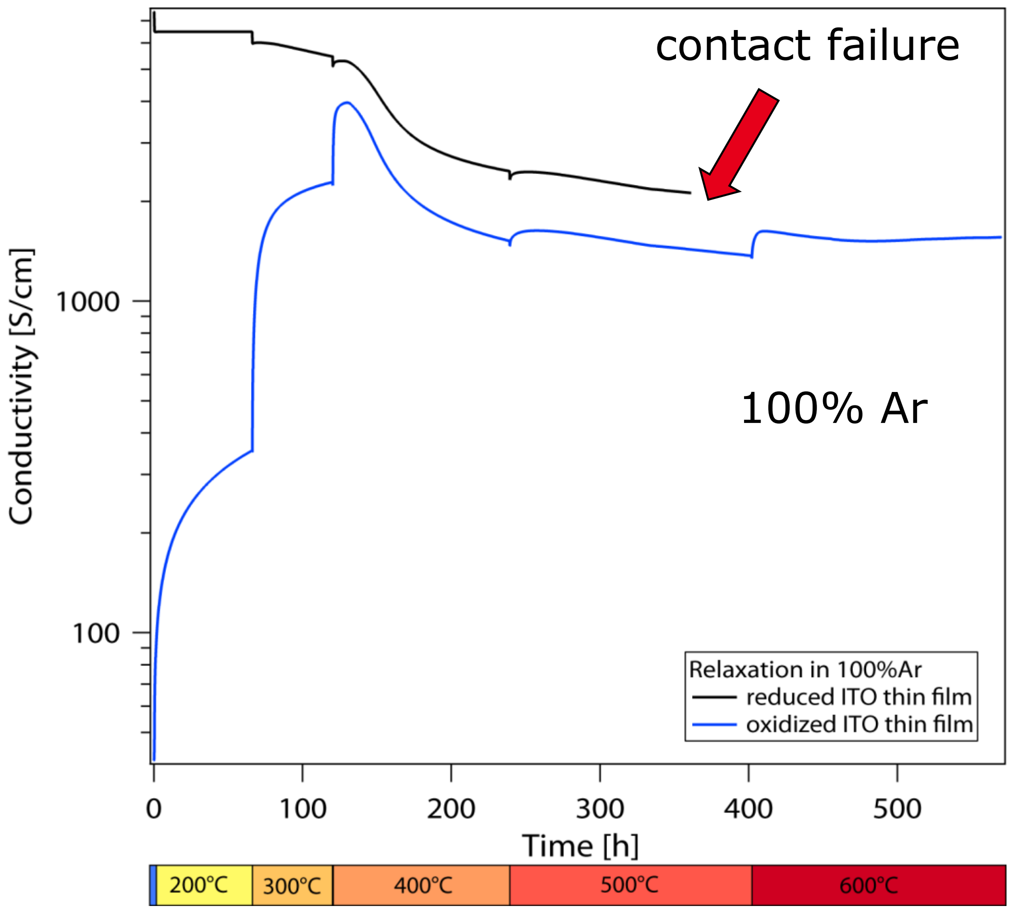
Oxygen exchange of SnO_2



- **Surface properties are crucial for oxygen exchange**

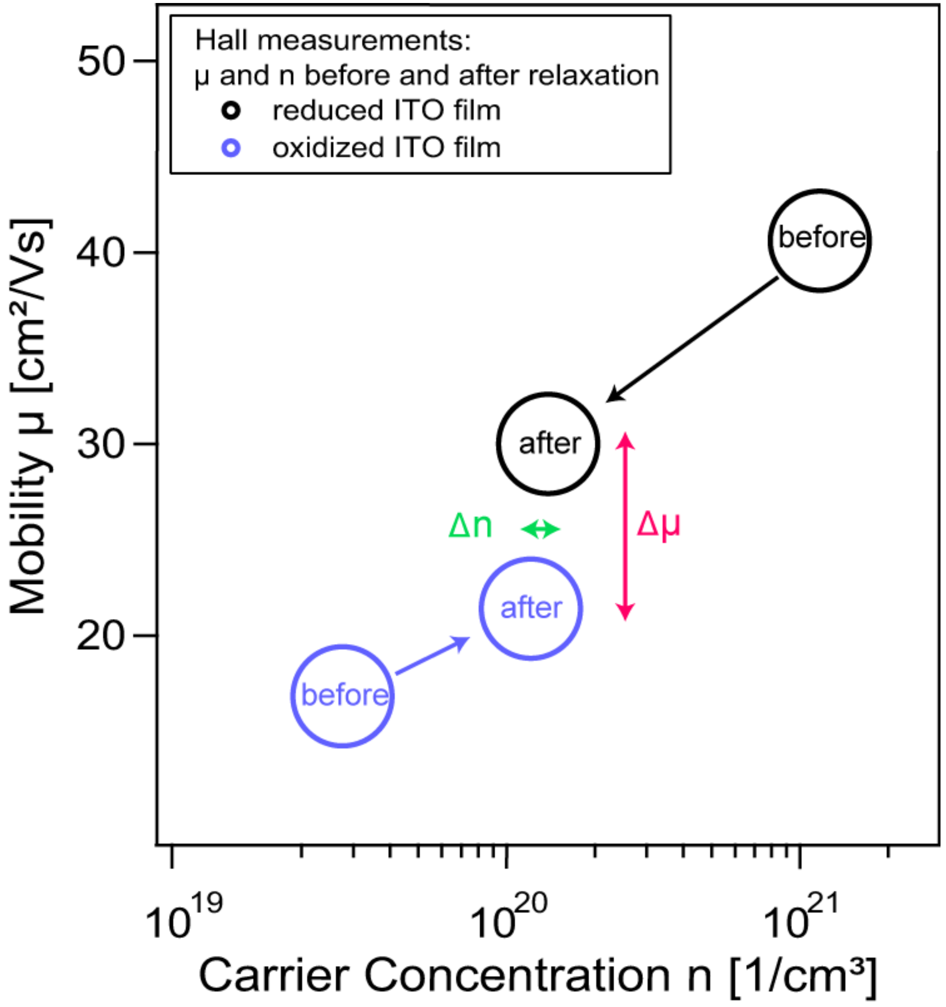
Relaxation measurements





- ➢ **Kinetics of oxygen exchange not accessible**

Mobility and carrier concentration

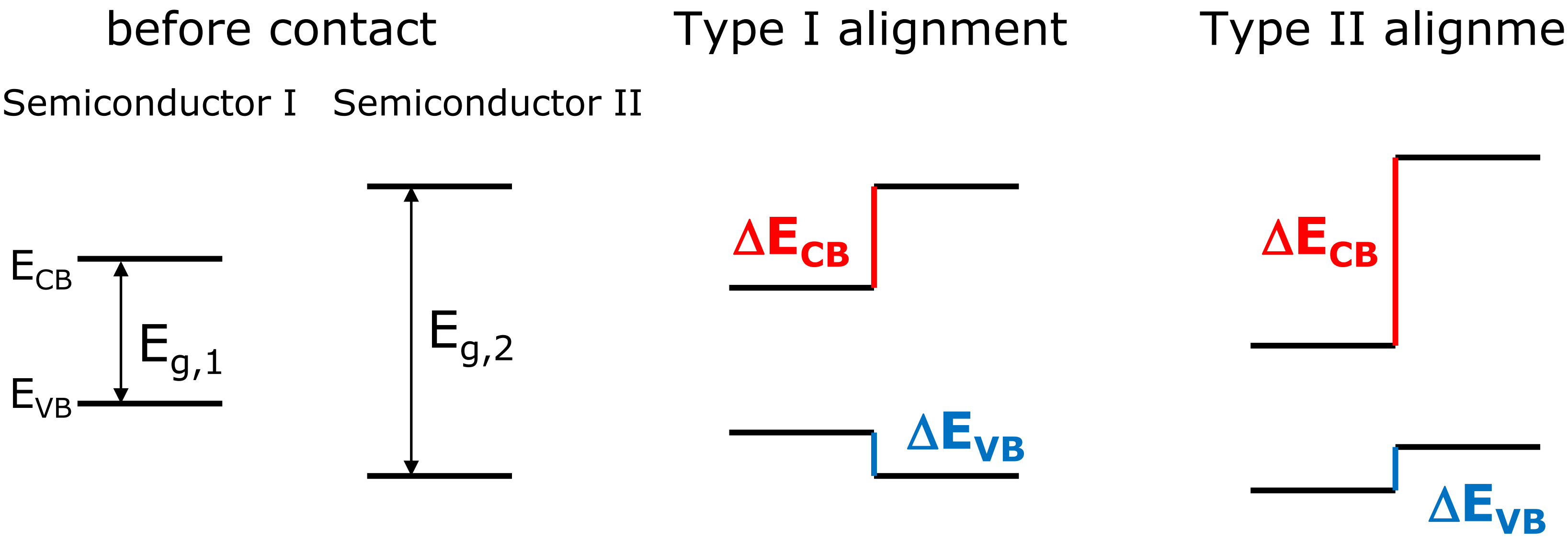


- **Carrier concentration (defect concentration) in equilibrium**
- **Carrier mobility different for differently prepared samples**
- **Possible influence of microstructure (texture, grain size, segregation)**
- **Necessary to understand the evolution and the control of microstructure**

Topics

- Transparent conducting oxides
  - Basic electrical and optical properties
  - Applications and importance of surfaces and interfaces
- Experimental Approach
- Surface Properties
  - Work function and ionization potential
  - Oxygen exchange
- **Interface properties**
  - **Energy band alignment**
  - **Redox processes at interface**

Band alignment



before contact

Semiconductor I Semiconductor II

E_{CB}

$E_{g,1}$

E_{VB}

$E_{g,2}$

Type I alignment

ΔE_{CB}

ΔE_{VB}

Type II alignment

ΔE_{CB}

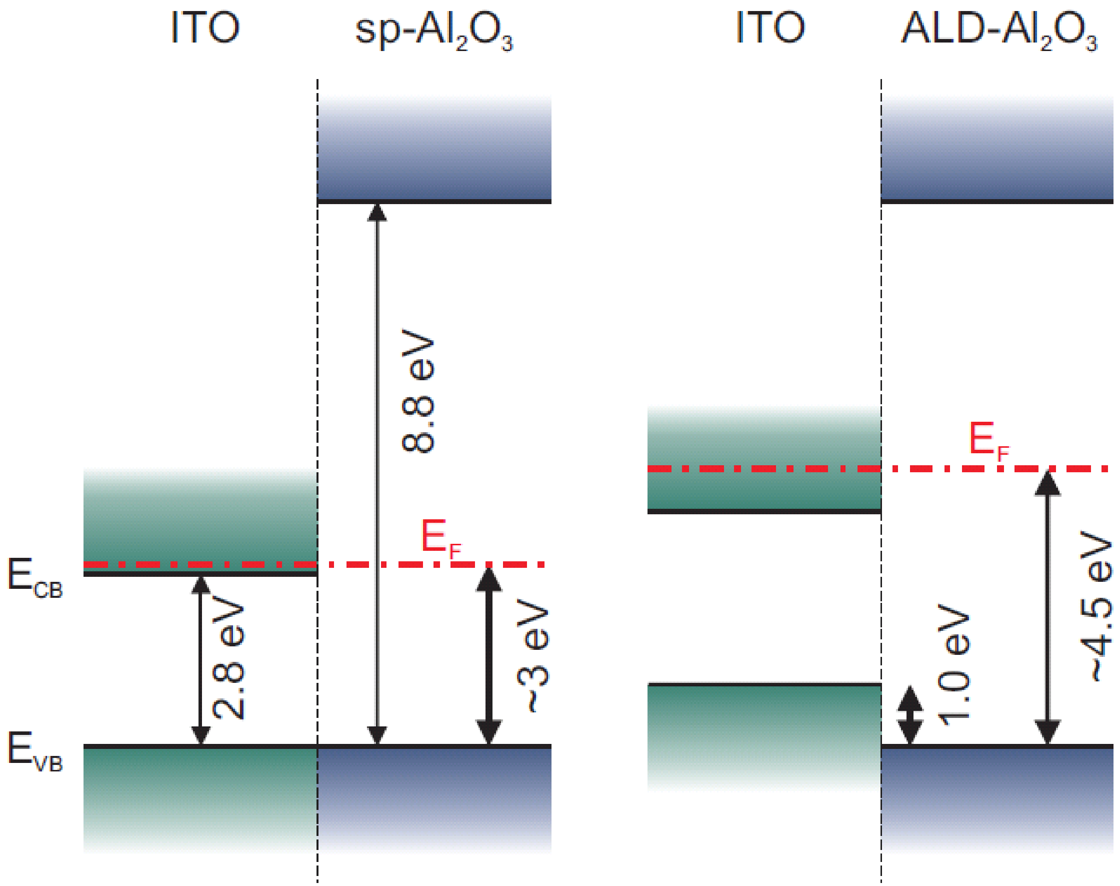
ΔE_{VB}

ΔE_{CB}: conduction band discontinuity (offset)

ΔE_{VB}: valence band discontinuity (offset)

- **Energy band alignment described by band discontinuities**
- **Each material combination has characteristic alignment**

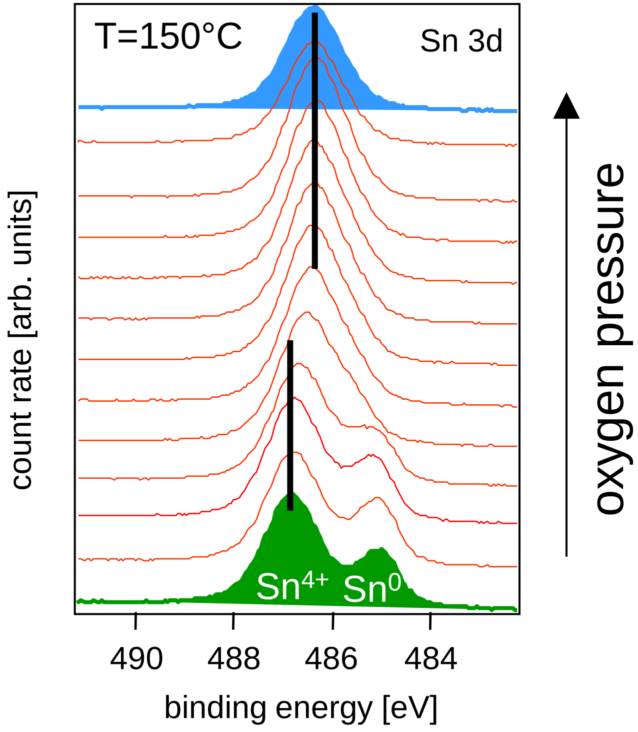
Interface ITO/Al_2O_3

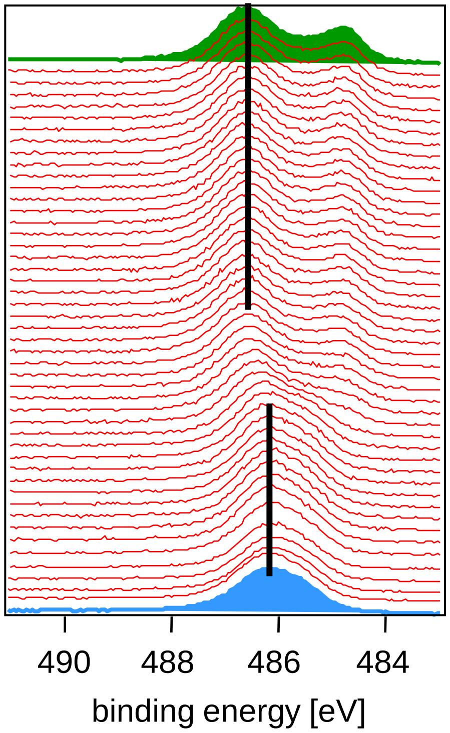


- ➢ **Pinning in ALD-Al_2O_3 leads to modified band alignment**

PCCP **11** (2009) 3049, Chem. Mater. **24** (2012) 4503

SnO_2/Pt – interface chemistry


oxidation @ 150°C

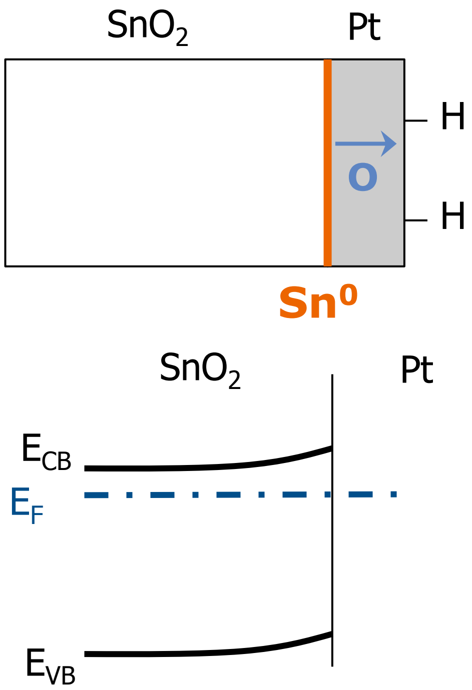

reduction @ 150°C

- **150°C: Sn^0 <-> Sn^{4+} with intermediate Sn^{2+} state**
- **100°C: Sn^0 <-> Sn^{2+}**
- **Oxidation/reduction not observable for**
  - **- large Pt islands**
  - **- bare SnO_2 surface**

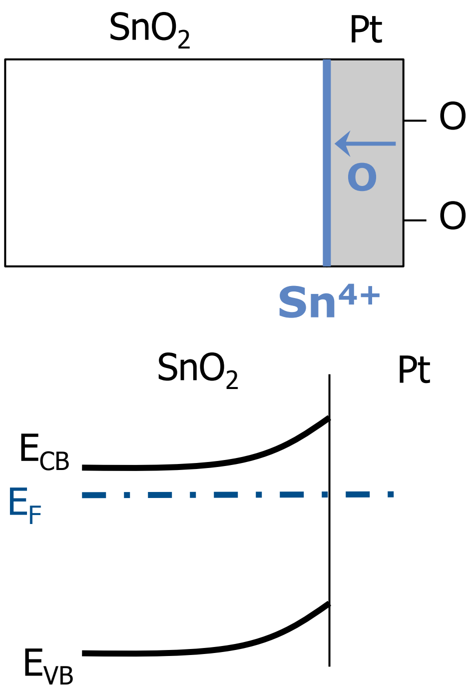
Reversible oxidation/reduction of Sn

Chemistry at buried interface

Reducing environment



Oxidizing environment



- ➢ **Oxygen is reversibly transported to/from the interface**
  - ➢ **Barrier changes with oxidation/reduction**

Summary

- **Transparent Conducting Oxides are important technological materials**
- **Surface and Interface properties can be systematically adressed using photoelectron spectroscopy with in-situ sample preparation**
- **Work function and oxygen exchange determined by doping, surface orientation and surface termination**
- **Energy band alignment governed by orbital contribution to the valence band density of states**
- **Defects limit dopability and can modify the energy band alignment**

Acknowledgement

- Frank Säuberlich, Yvonne Gassenbauer, Christoph Körber, André Wachau, Jürgen Gassmann, Mareike Hohmann, Thorsten Bayer, Jonas Deuermeier, Mirko Weidner, Anne Fuchs, Sebastian Siol
- Paul Erhart, Péter Ágoston, Karsten Albe (TUD – Modelling)
- Steven P. Harvey, Diana E. Proffit, E. Mitch Hopper, Thomas O. Mason (Northwestern University)
- German Science Foundation (SFB 595) MWN program)
- BMBF (ZnO network project)
- State of Hessen (LOEWE center AdRIA)

- Work summarized in: J. Am. Ceram. Soc. **96**, 331-345 (2013)
  Transparent Conducting Oxides: Electronic Structure – Property Relationship from Photoelectron Spectroscopy with in-situ Sample Preparation