Surfaces and Interfaces of Transparent Conducting Oxides

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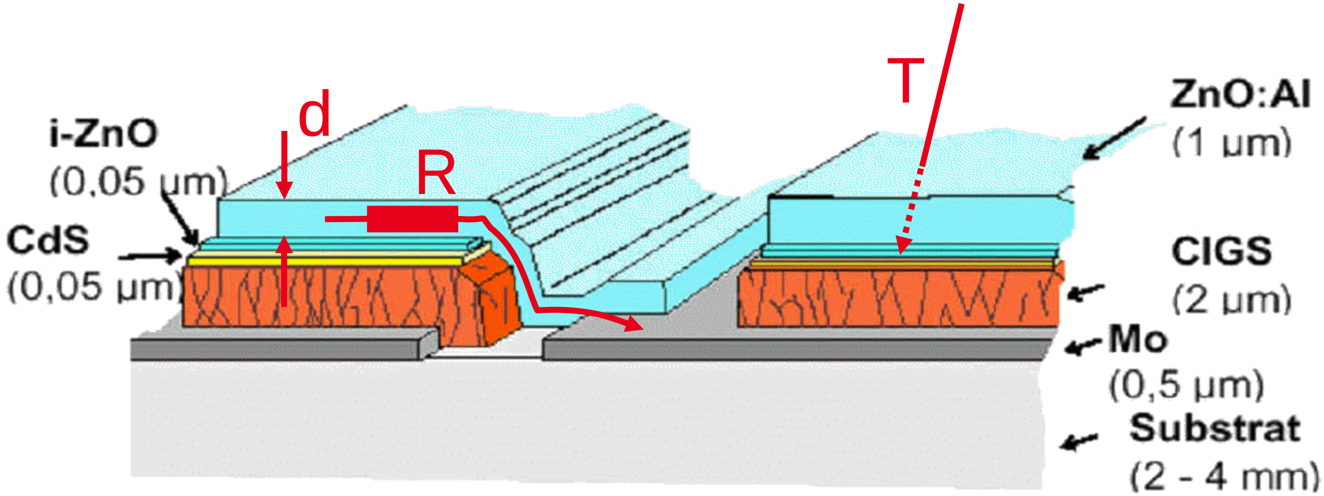
Transparent conducting oxides

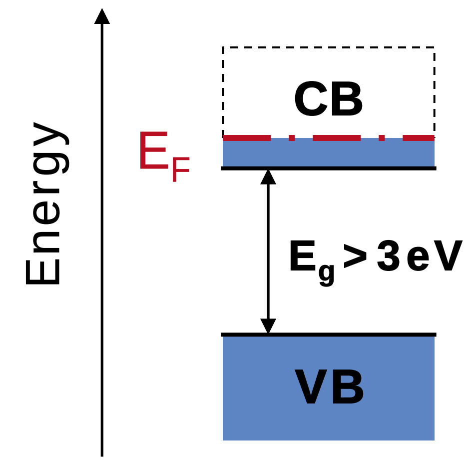


- high electrical conductivity (>10³ /Ωcm)
- high optical transparency (>80%)
- high infrared reflectivity

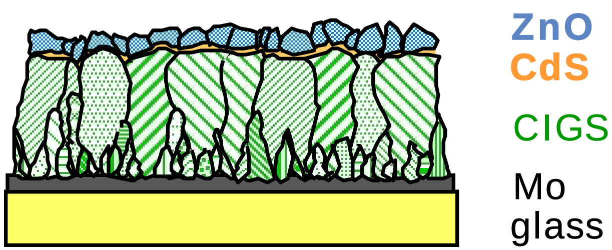
Realization:

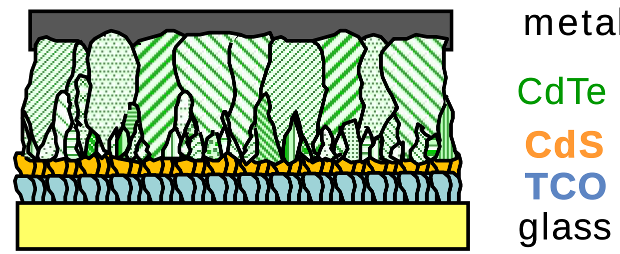
Degenerately doped oxides (d¹⁰-systems)

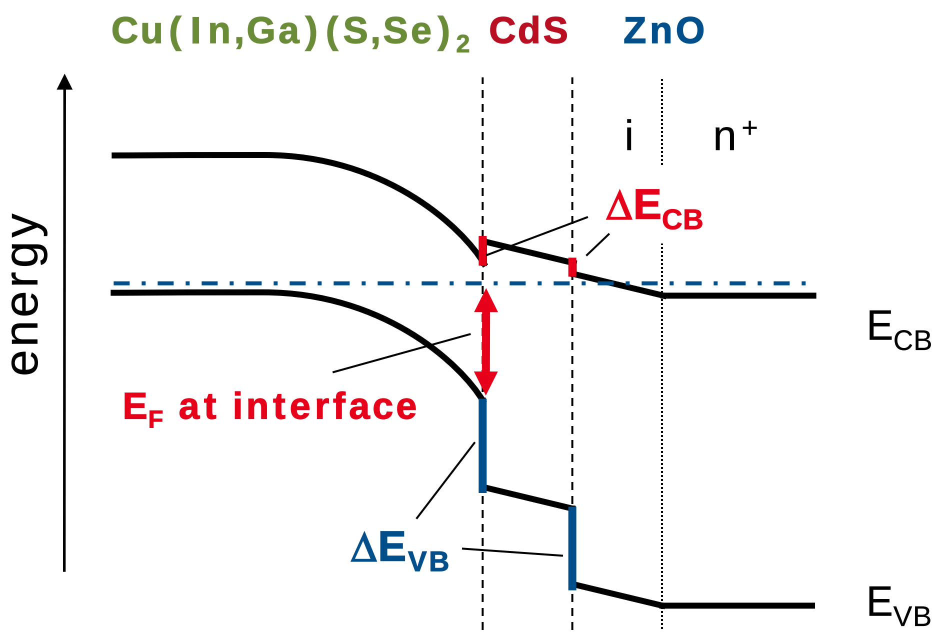
(ZnO, In_2O_3, SnO_2, CdO and mixed oxides)

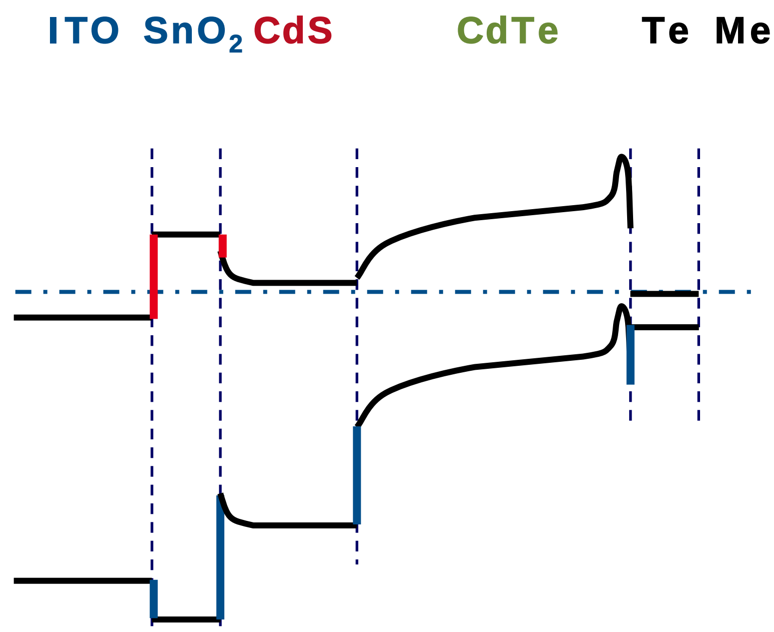


Thin film solar cells

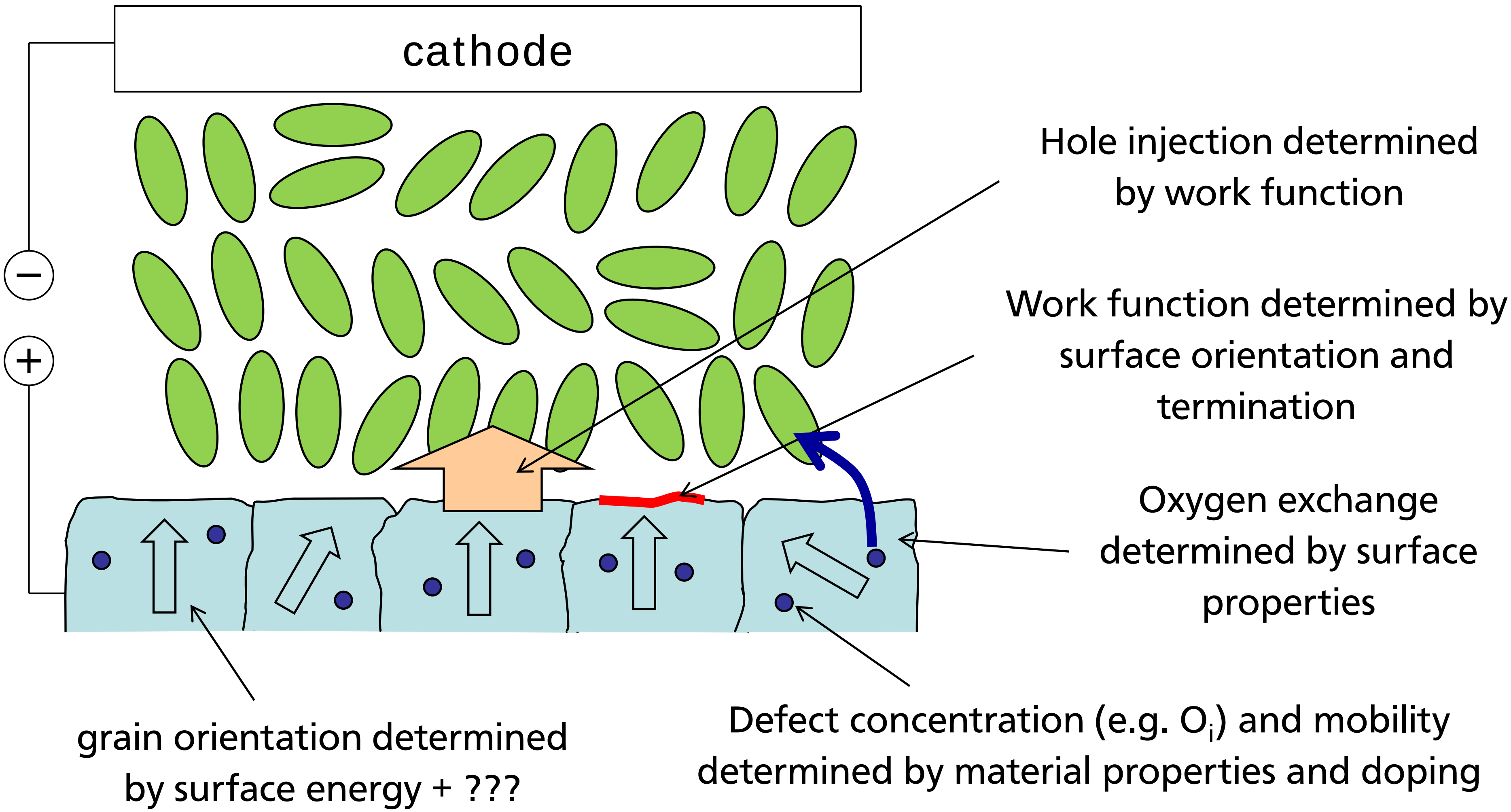




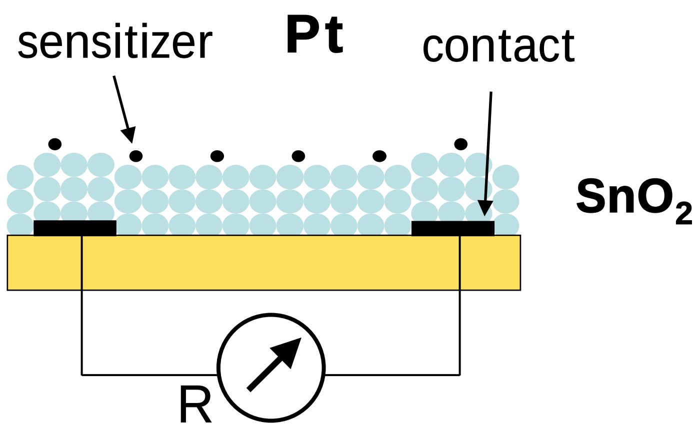


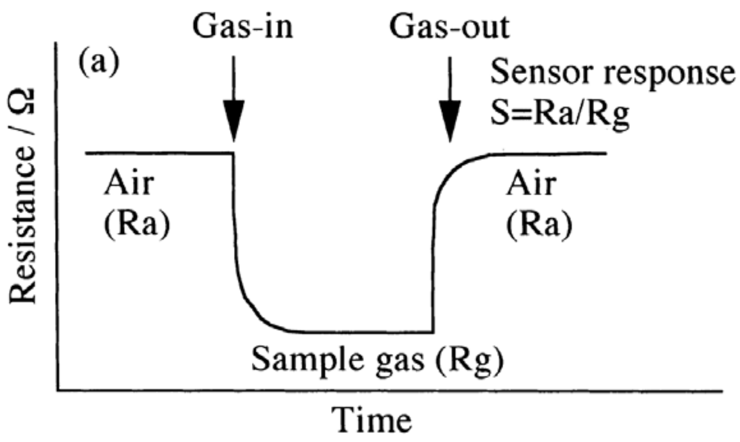


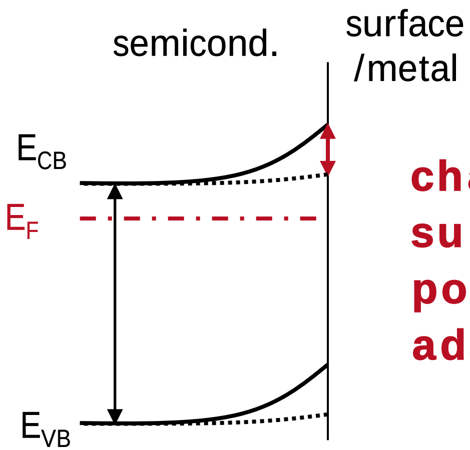
The TCO electrode in OLEDs



Chemical gas sensors







change of surface potential by adsorption

- **Sensor response explained by surface potential changes (ionosorption model)**
- **Changes of SnO_2 bulk doping, (e.g. changes in $[V_O]$) neglected**

Issues of TCO surfaces and interfaces

- **Surface properties**
  - **Workfunction of TCOs**
  - **Oxygen Exchange at TCO surfaces**
- **Interfaces Properties**
  - **Reactivity of interfaces**
  - **Energy level alignment (barrier heights)**

TCO oxide surfaces and interfaces are considerably more complex than those of conventional semiconductors

defect properties

Defects in semiconductors

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- Vacancies (V_{cation} (acceptor), V_{anion} (donor))
- Interstitials (Cat_i (donor), An_i (acceptor))
- Antisite defects (e.g. Ga_{As} and As_{Ga} in GaAs)

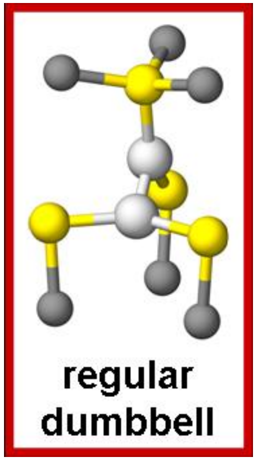
} not stoichiometric, charged

- Schottky defect pair (V_{cat} + V_{an}), (Cat_i + An_i)
- Frenkel defect pair (V_{cat} + Cat_i), (V_{an} + An_i)

} stoichiometric, uncharged

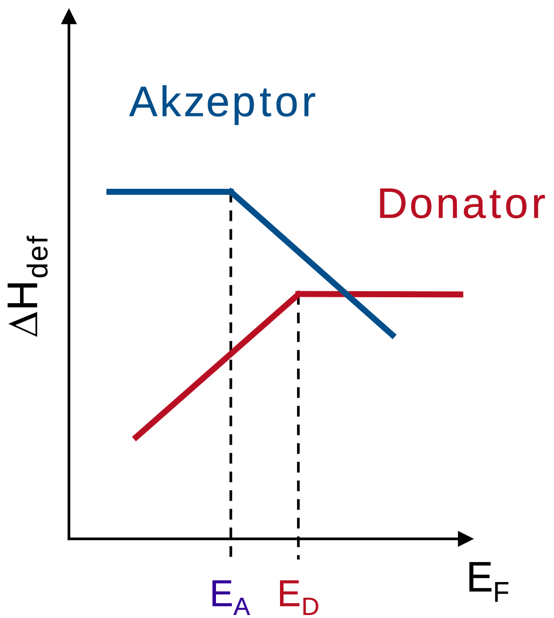
- F-centers (vacancy + e, h)
- Polarons
- Electrons and holes
- Impurities (substitutional, interstitial)

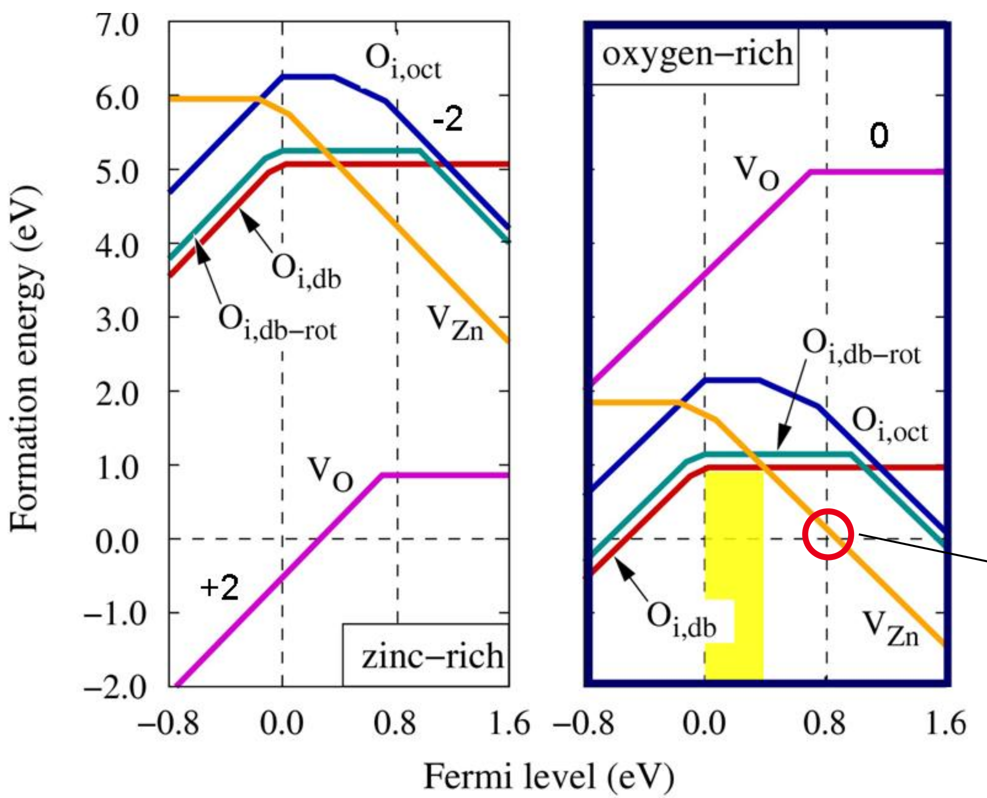
defect concentration $$N_d \approx N \cdot \exp\left(-\frac{\Delta h_d}{k_B T}\right)$$

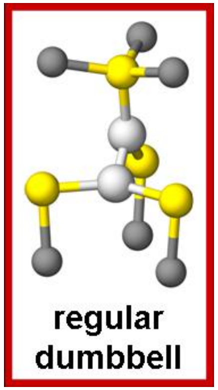


oxygen interstitial in ZnO

ZnO – Defects

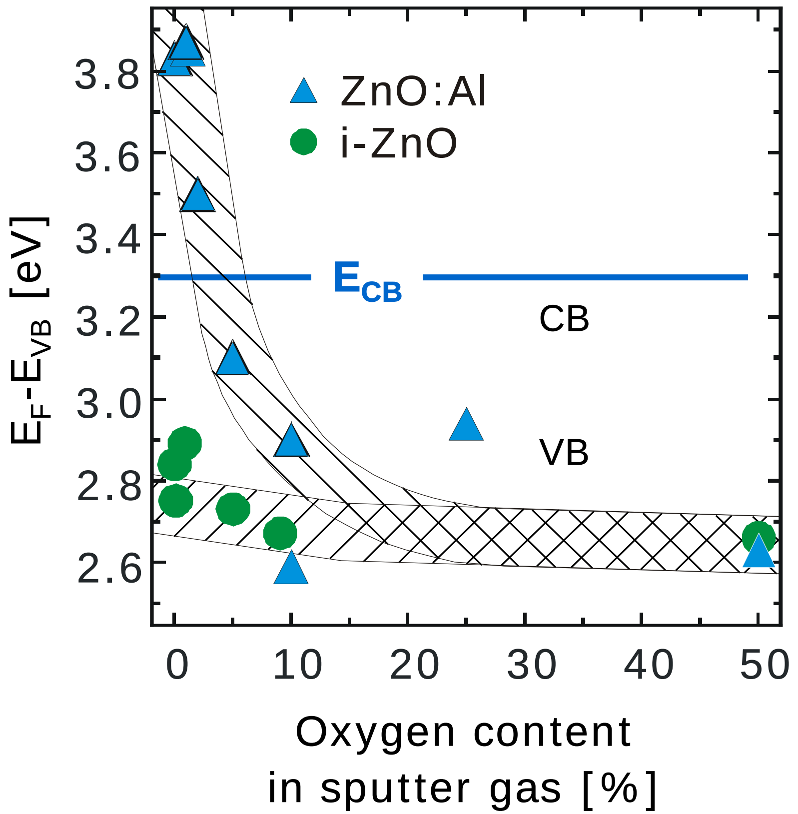


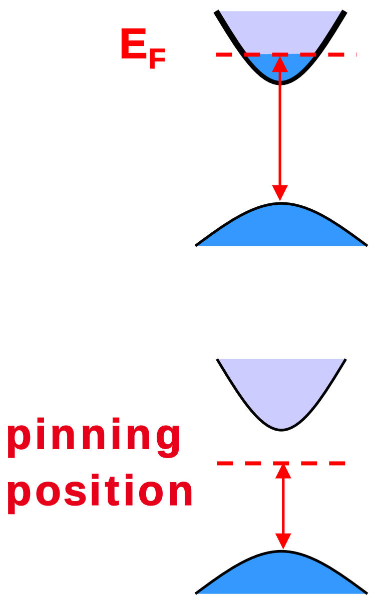




- **compensation of donors by Zinc-vacancies (V_{Zn}) under oxygen rich conditions**

ZnO – Fermi level





low O_2 content

➢ Highly doped film

high O_2 content

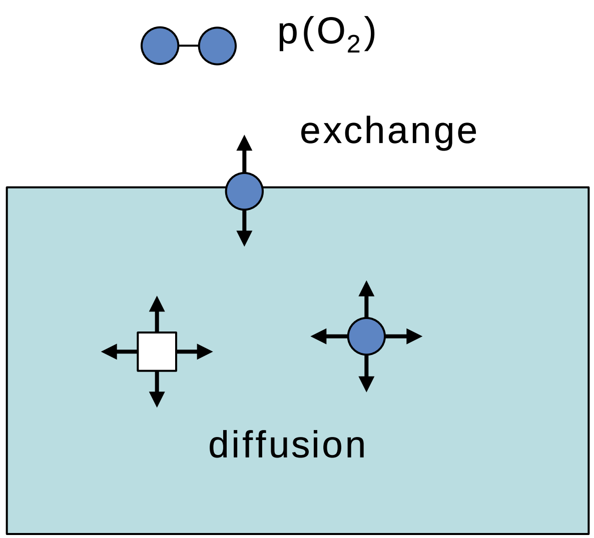
➢ Low doped film

➢ **Change of doping with pO_2**

➢ **Pinning by Zn-vacancies**

Intrinsic defects of TCOs

material	defects
ZnO	V_{Zn}, Zn_i, V_O
ZnO:Al	**Al_{Zn}, V_{Zn}**
In_2O_3	V_O
In_2O_3:Sn	**Sn_{In}, O_i**
SnO_2	V_O
SnO_2:Sb	**Sb_{Sn}, ??**



- **Conductivity determined by doping and intrinsic defects (Stoichiometry)**
- **Changes of conductivity by changes of stoichiometry require oxygen exchange and diffusion**

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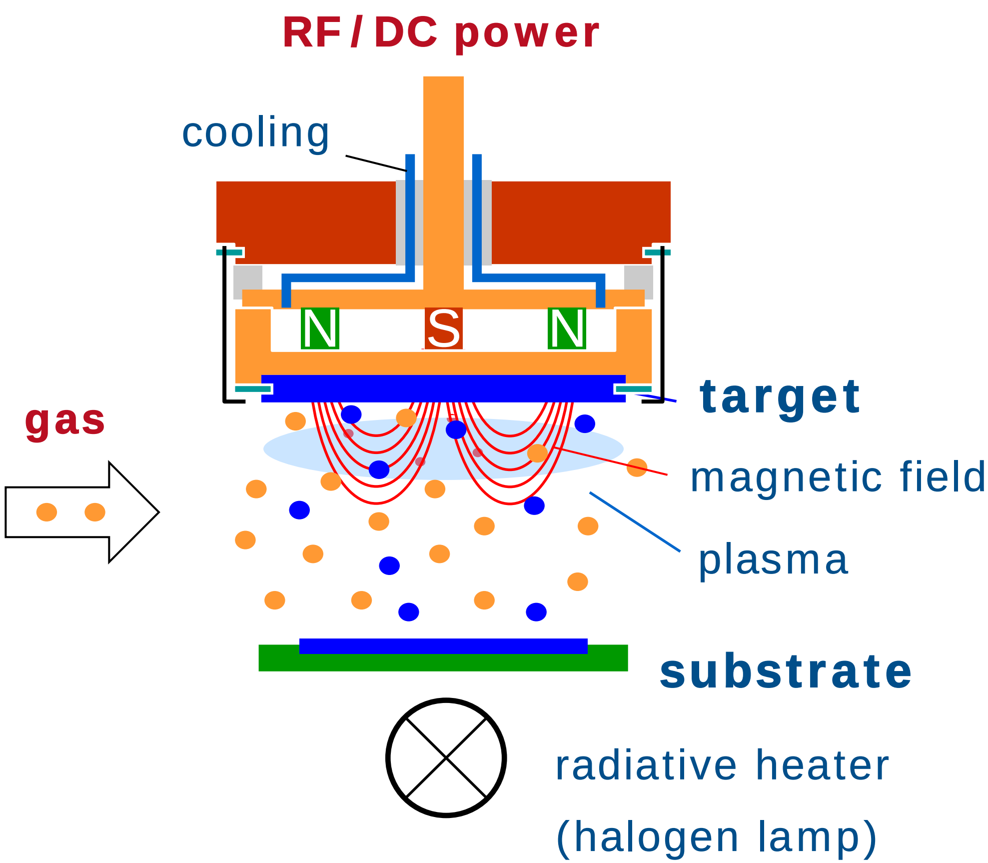
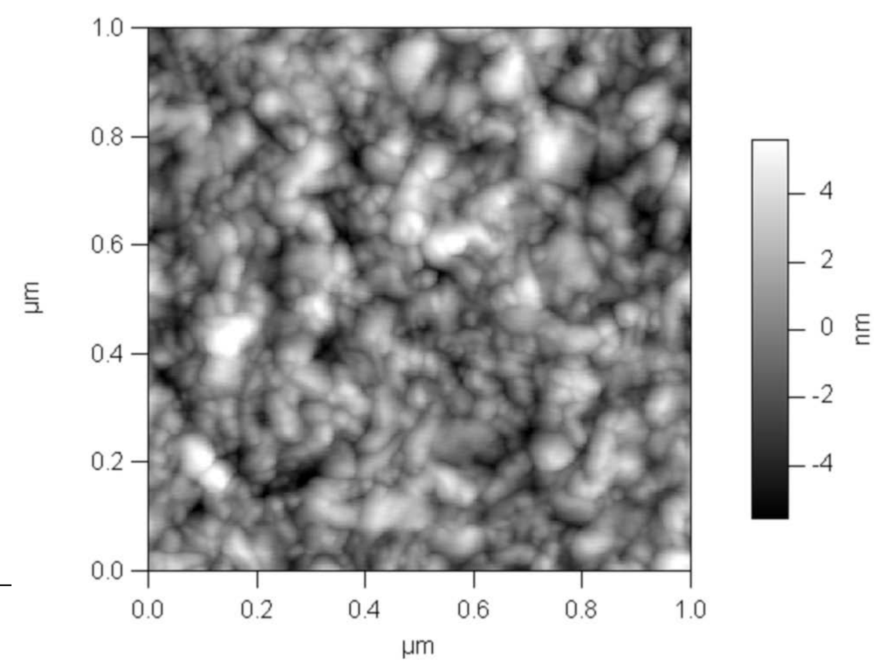
Assessment of surface and interface properties

Thin film deposition

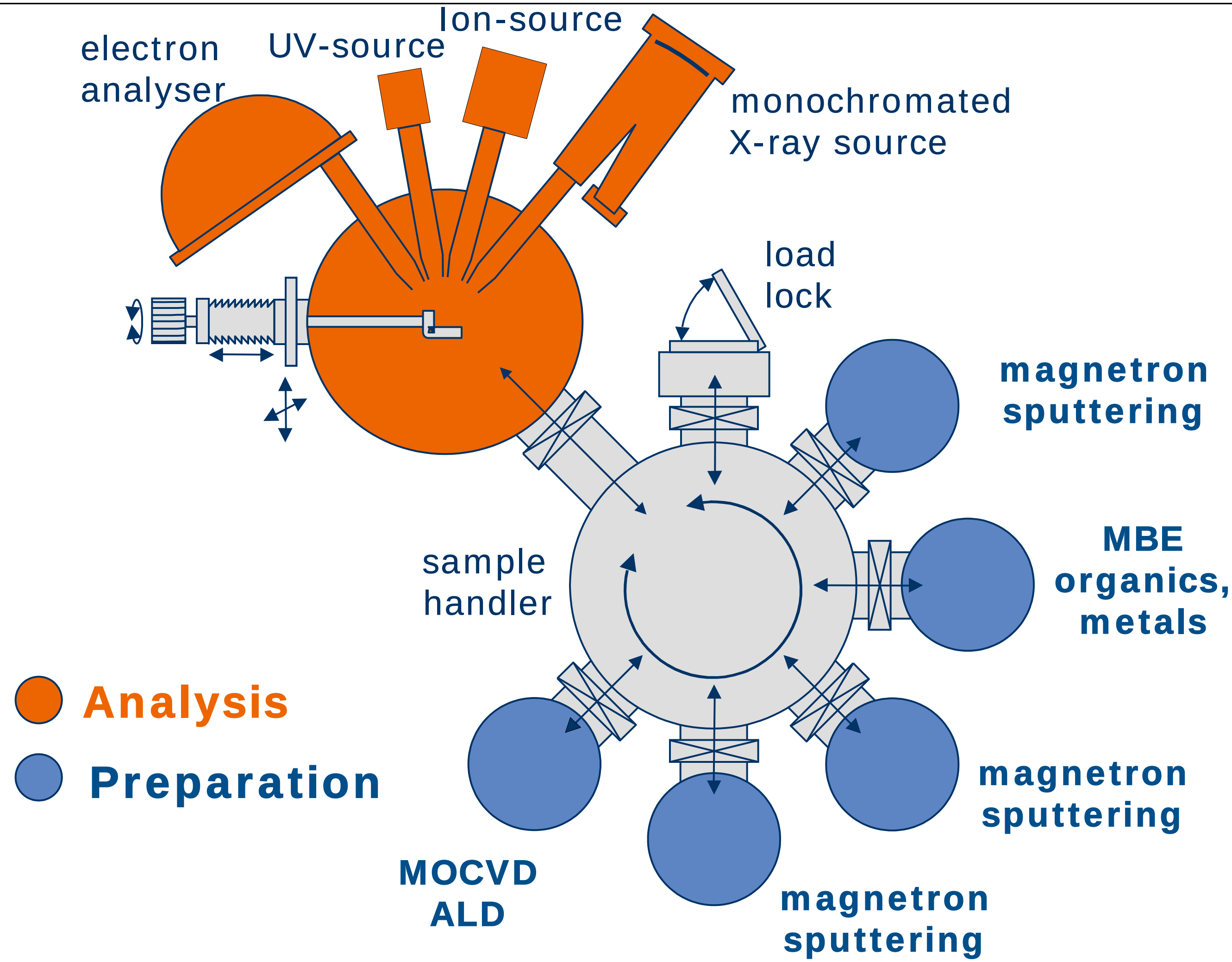
magnetron sputtering

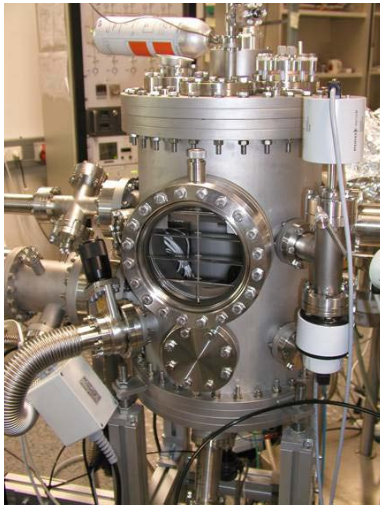


- ✓ Wide range of materials
- ✓ low substrate temperatures
- ✓ epitaxial growth possible
- ✓ wide range of parameter variation
- ✓ high deposition rates
- ✓ large area deposition

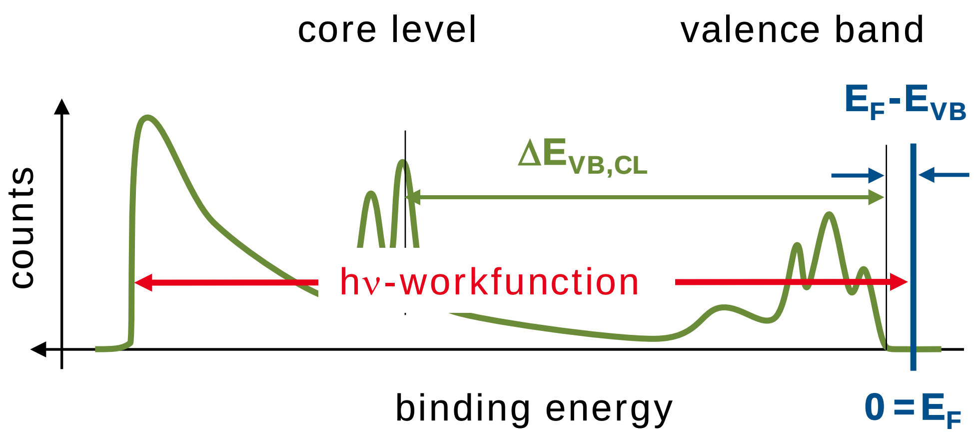


Integrated System – DAISY-MAT

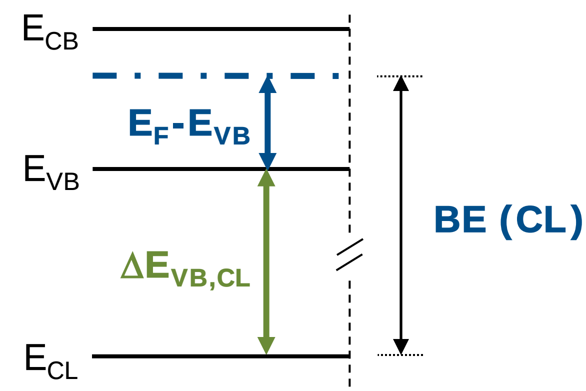




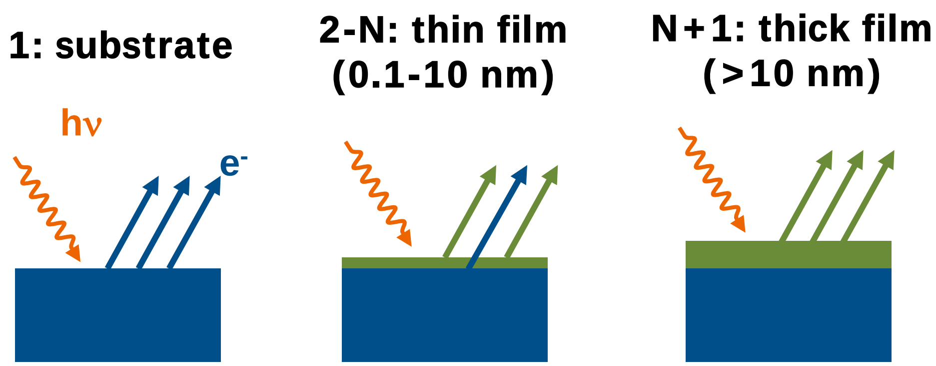
Photoemission – Barrier Heights



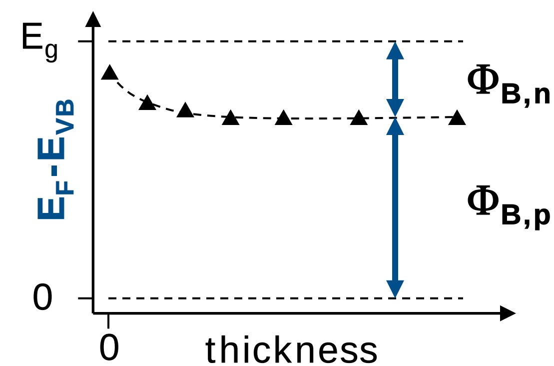
energy diagram



Interface experiment



Schottky barrier



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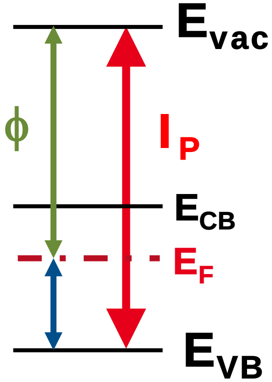
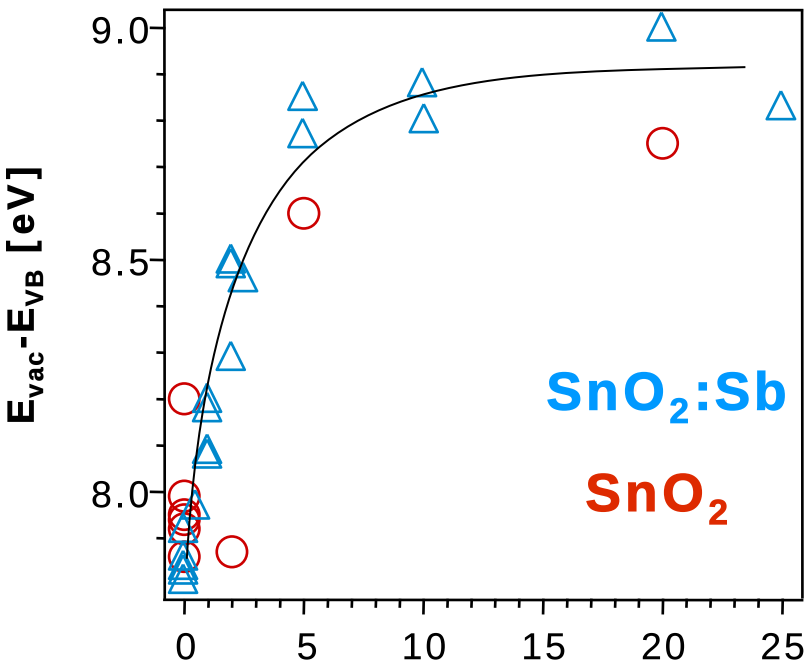
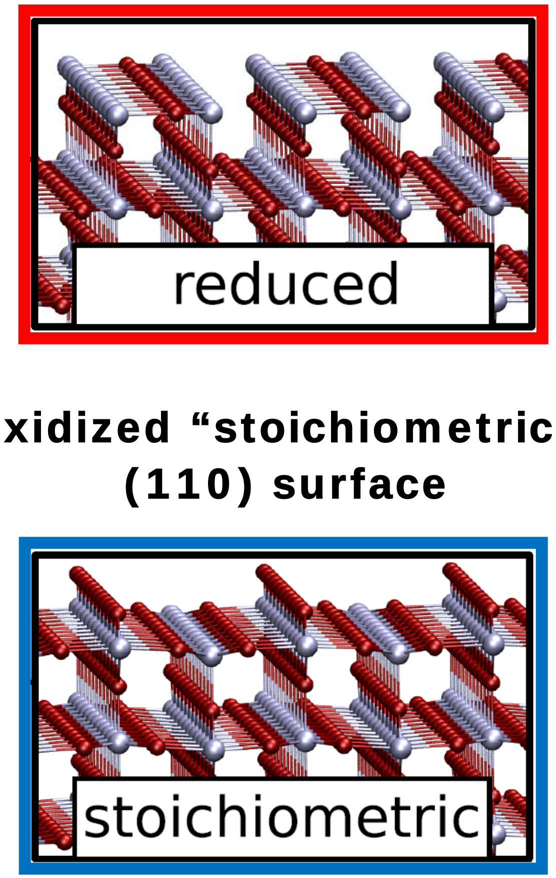
work functions of TCOs

SnO_2 – ionization potential



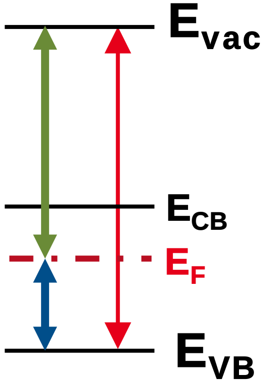


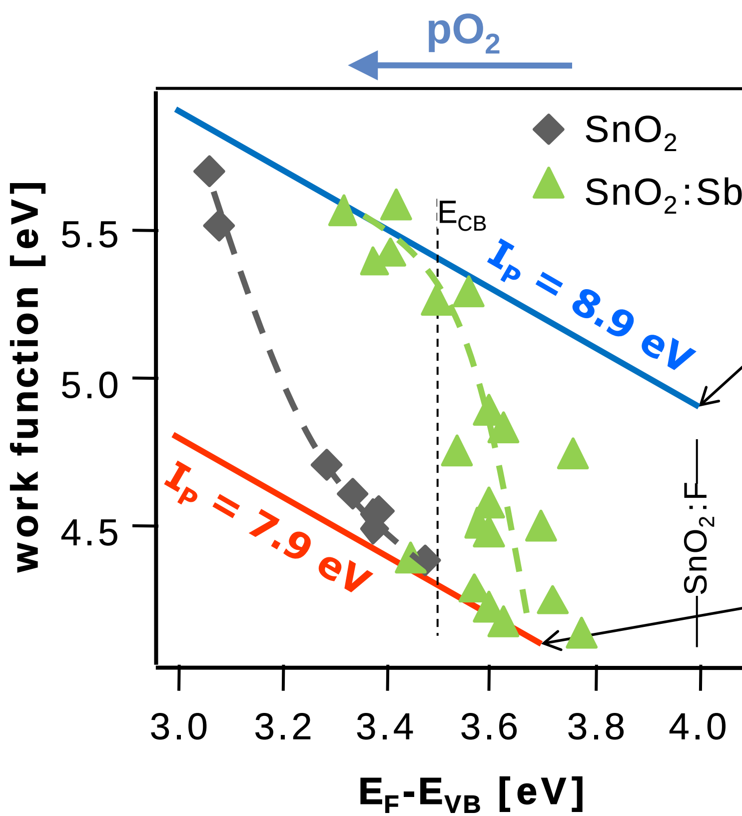
reduced (110) surface

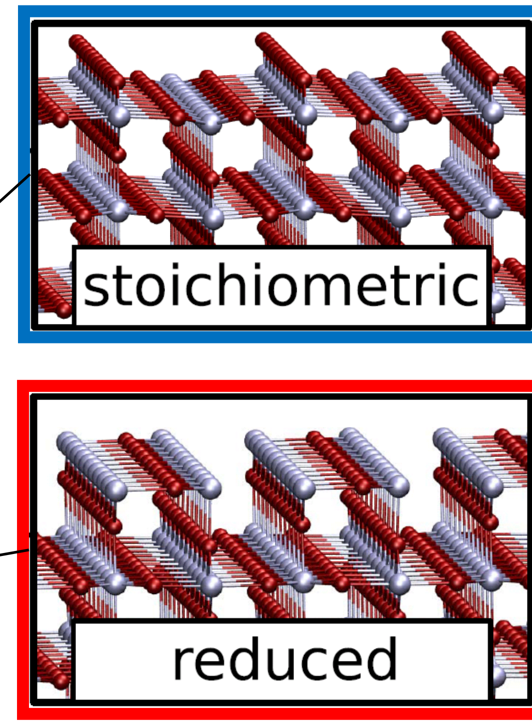


oxidized "stoichiometric" (110) surface

SnO_2 – work function



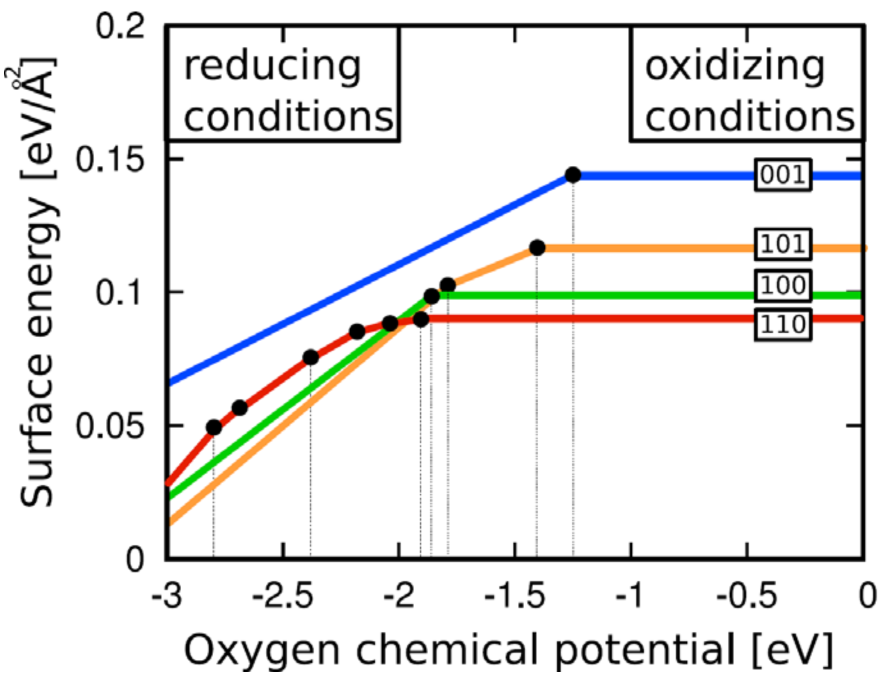


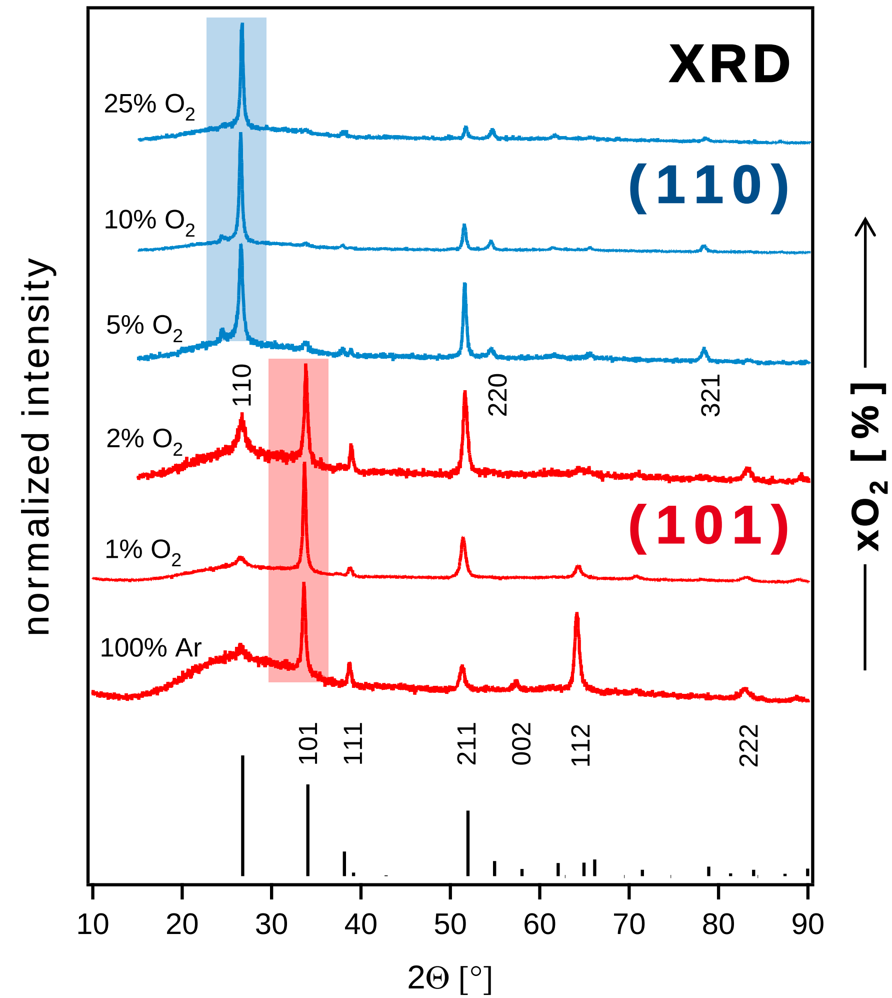


➢ **Identification of surface termination by ionization potential**

Thin Solid Films 518, 1197 (2009)

SnO_2 – preferred orientation

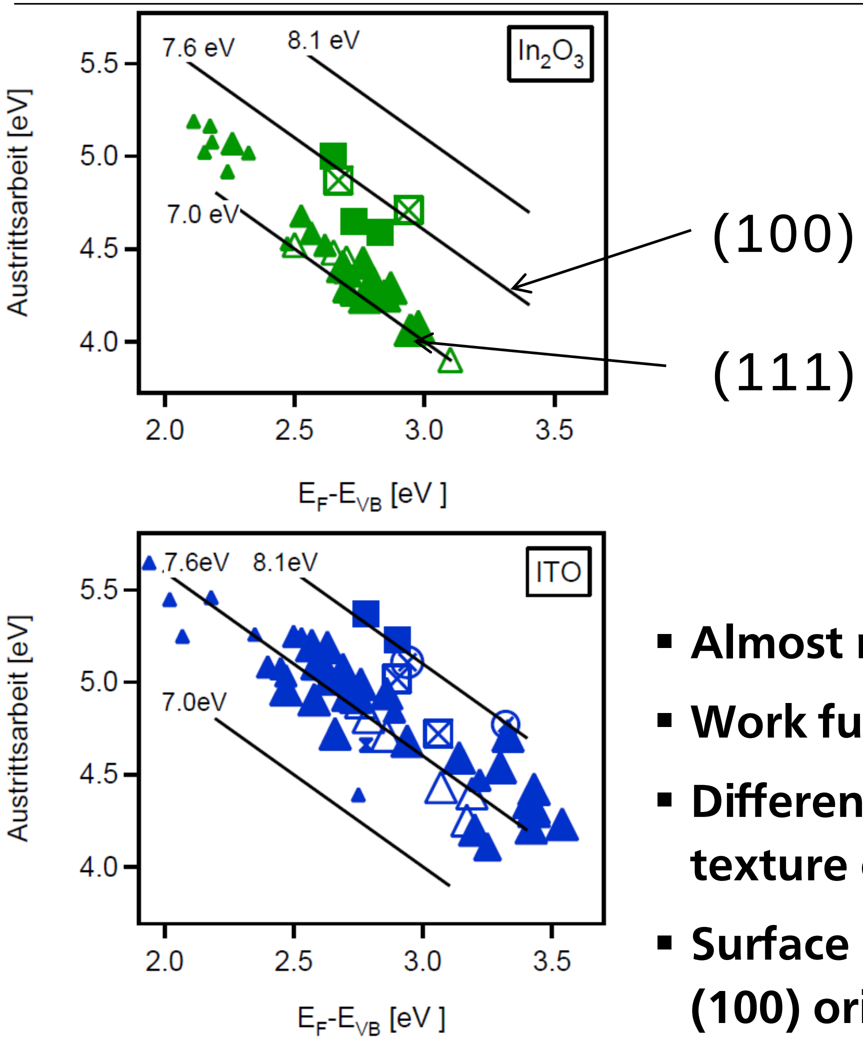


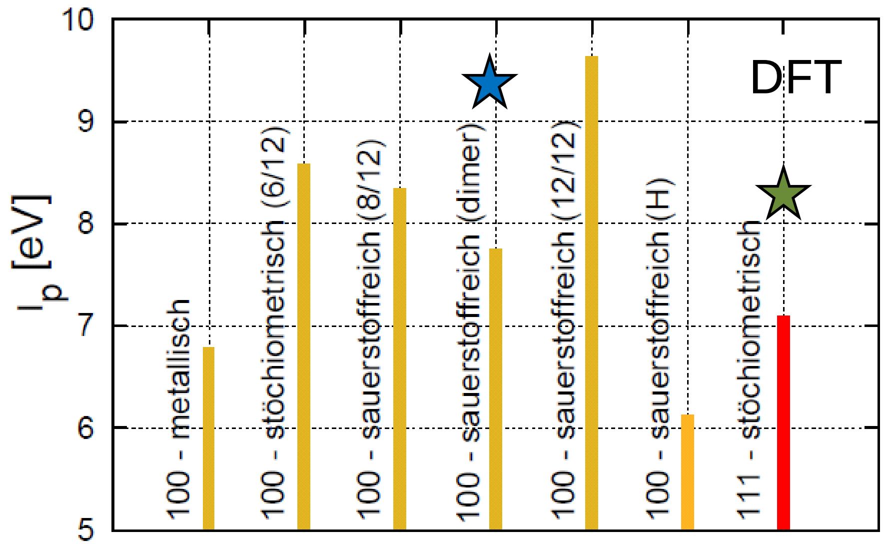


- **Change of stable surface orientation with oxygen pressure**

J. Phys. D 43, 055301 (2010)

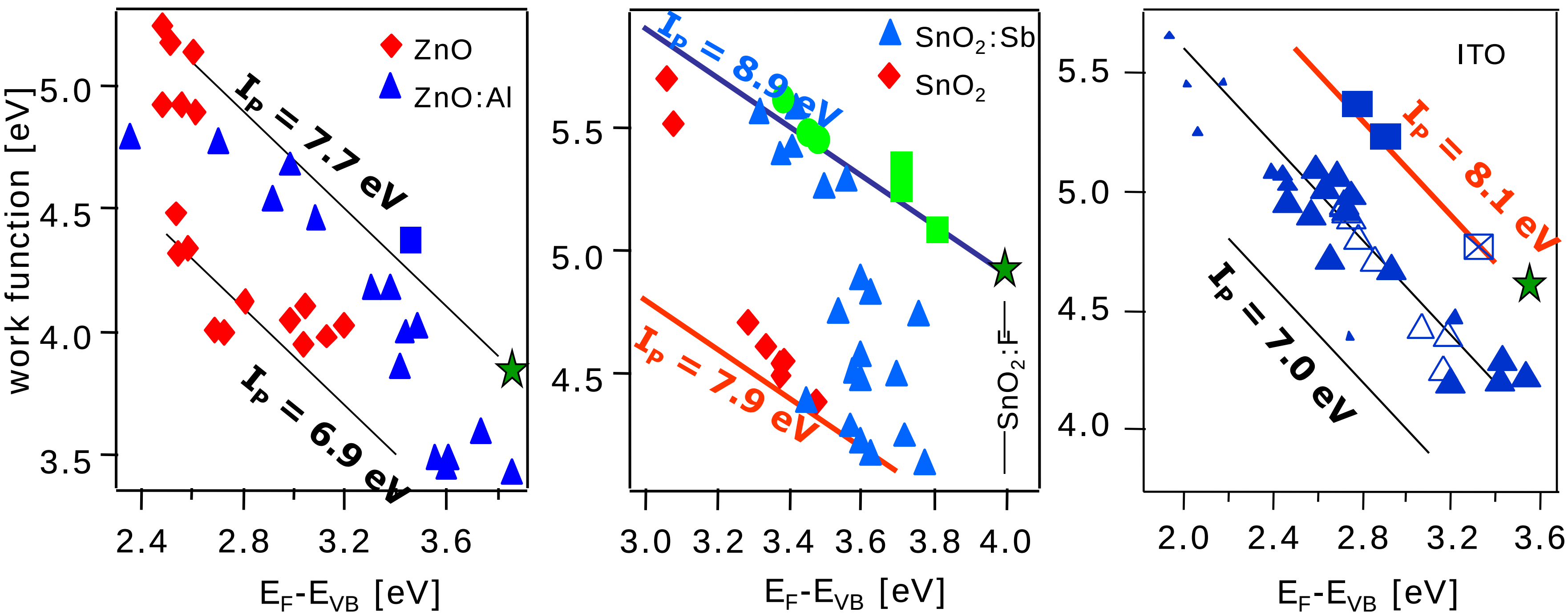
Work function of In_2O_3 and ITO





- **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**

TCO work functions



➢ **Large variation of work function**

but ΔE_{VB} does not depend on work function

Thin Solid Films **518**, 1197 (2009)

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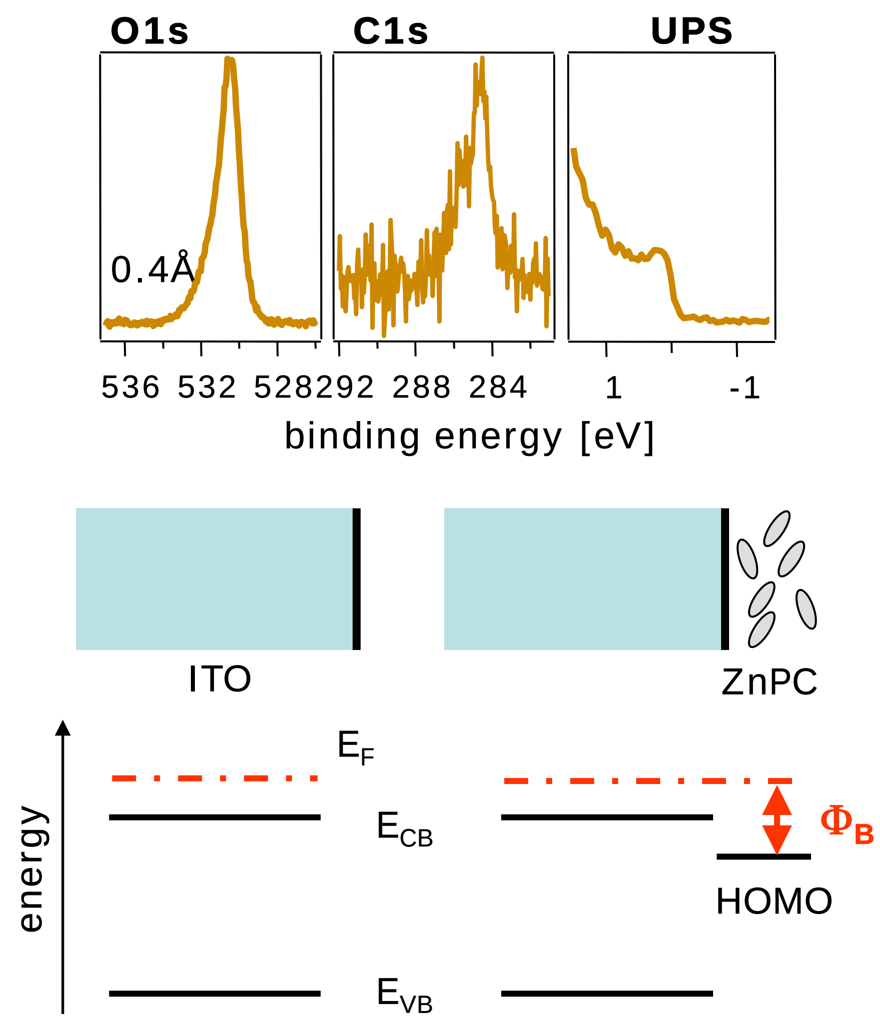
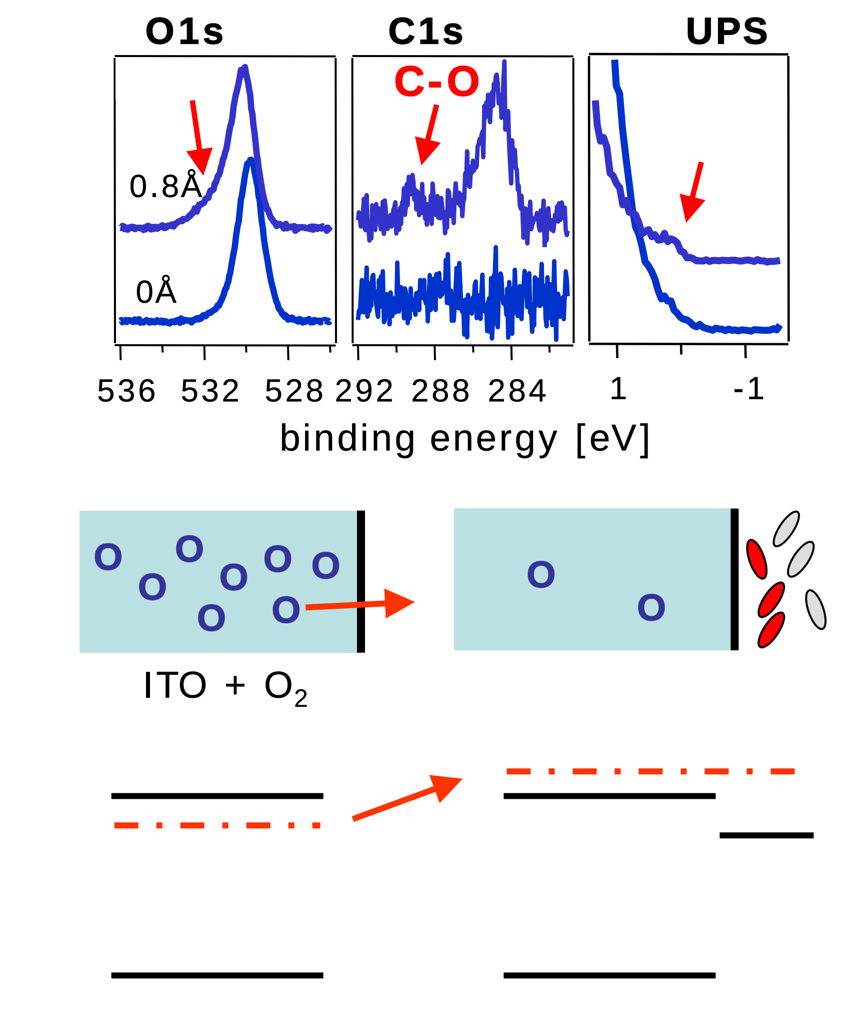
Oxygen Exchange

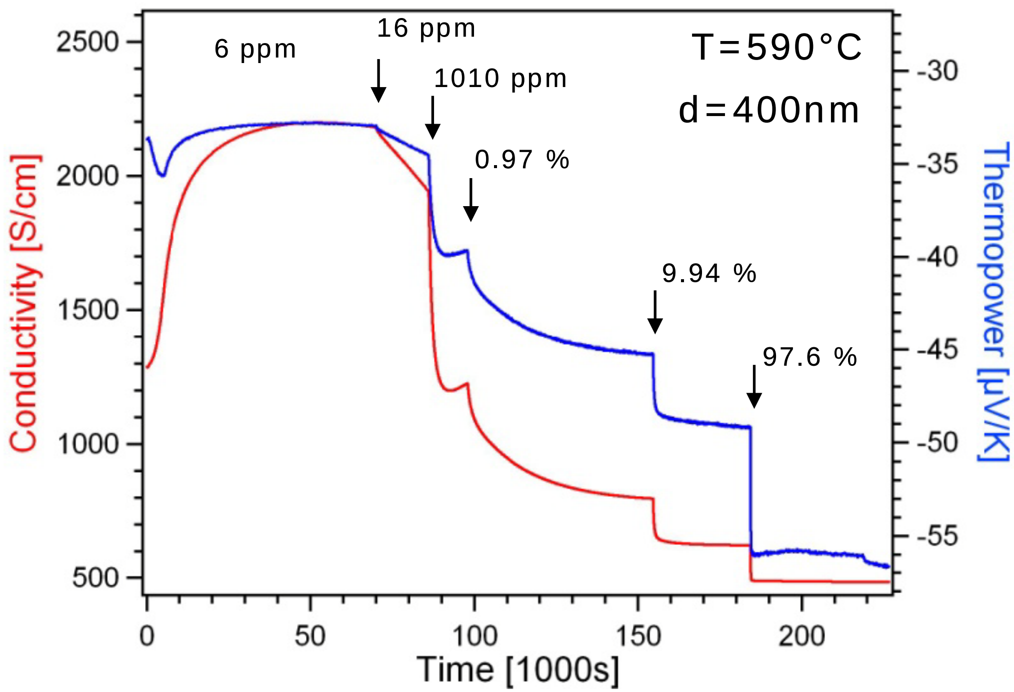
ITO / organic interface

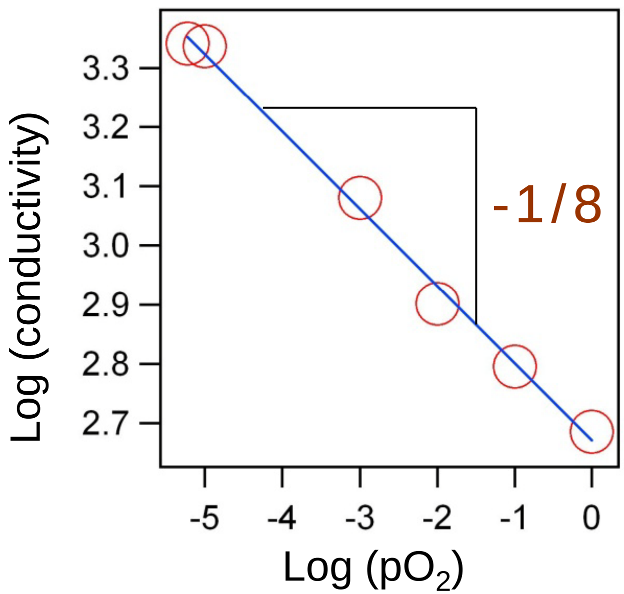




J. Phys. Chem. B 110, 4793 (2006)

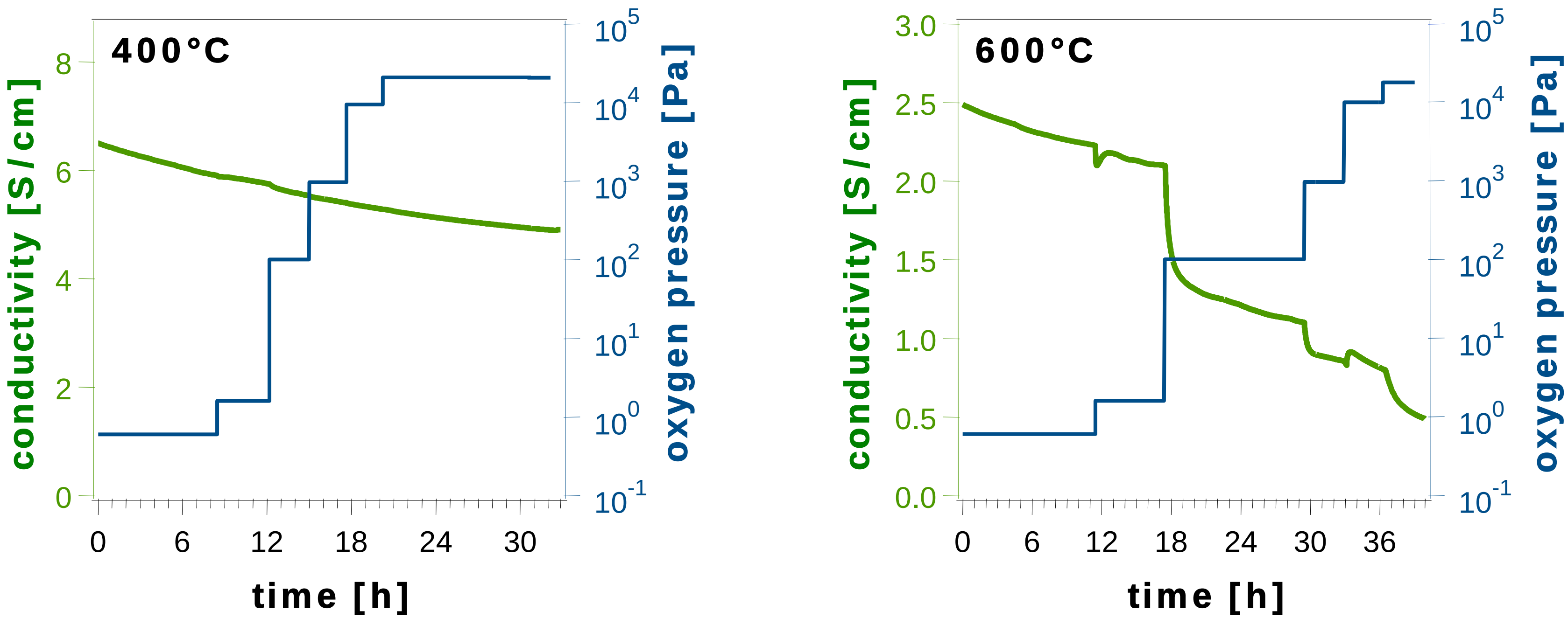
Conductivity relaxation of ITO (1 bar)





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

Conductivity relaxation of SnO_2 (1 bar)

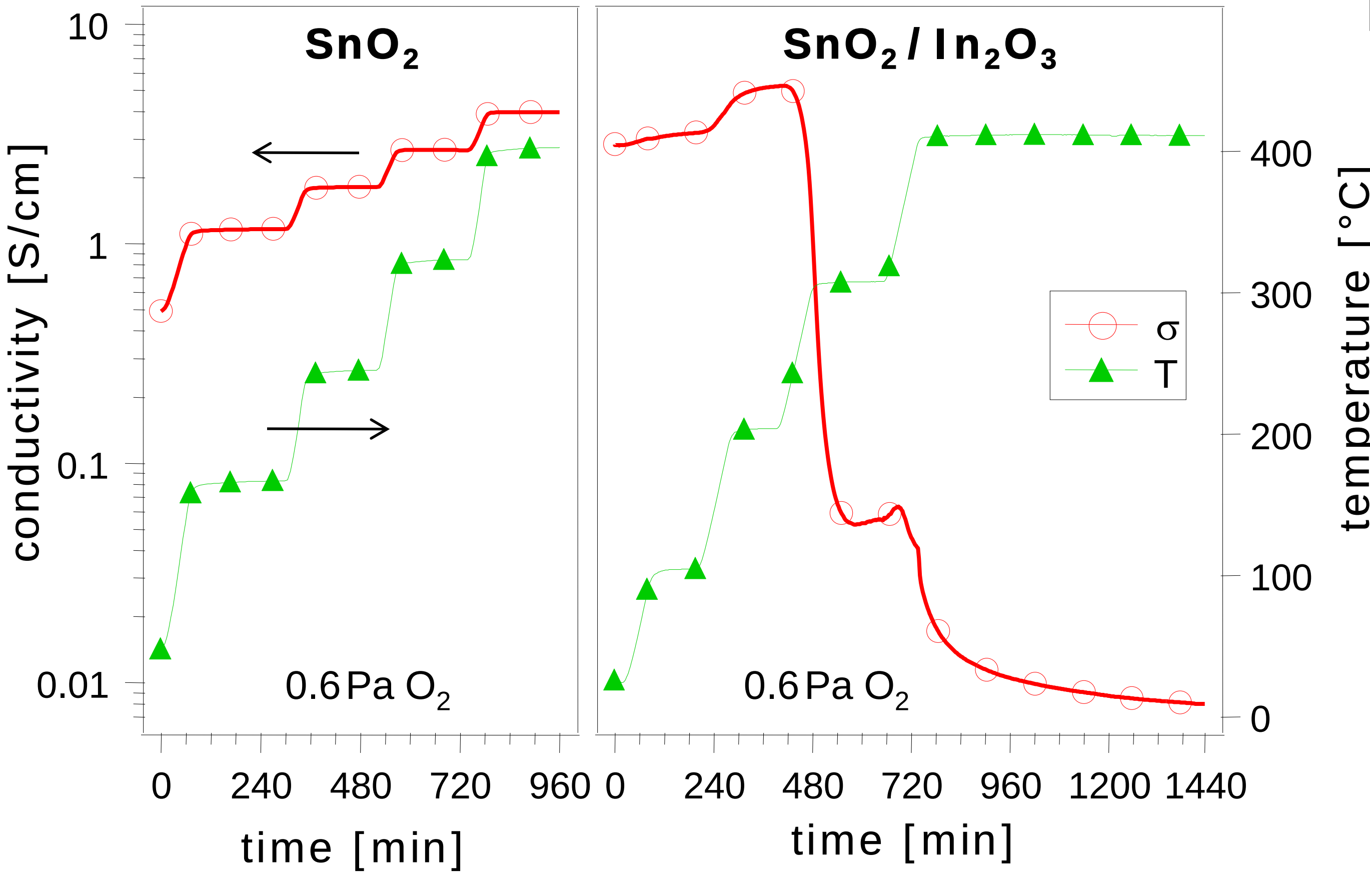


➢ **Almost no change of σ with pO_2 at 400°C**

➢ **Equilibrium carrier concentration not achieved**

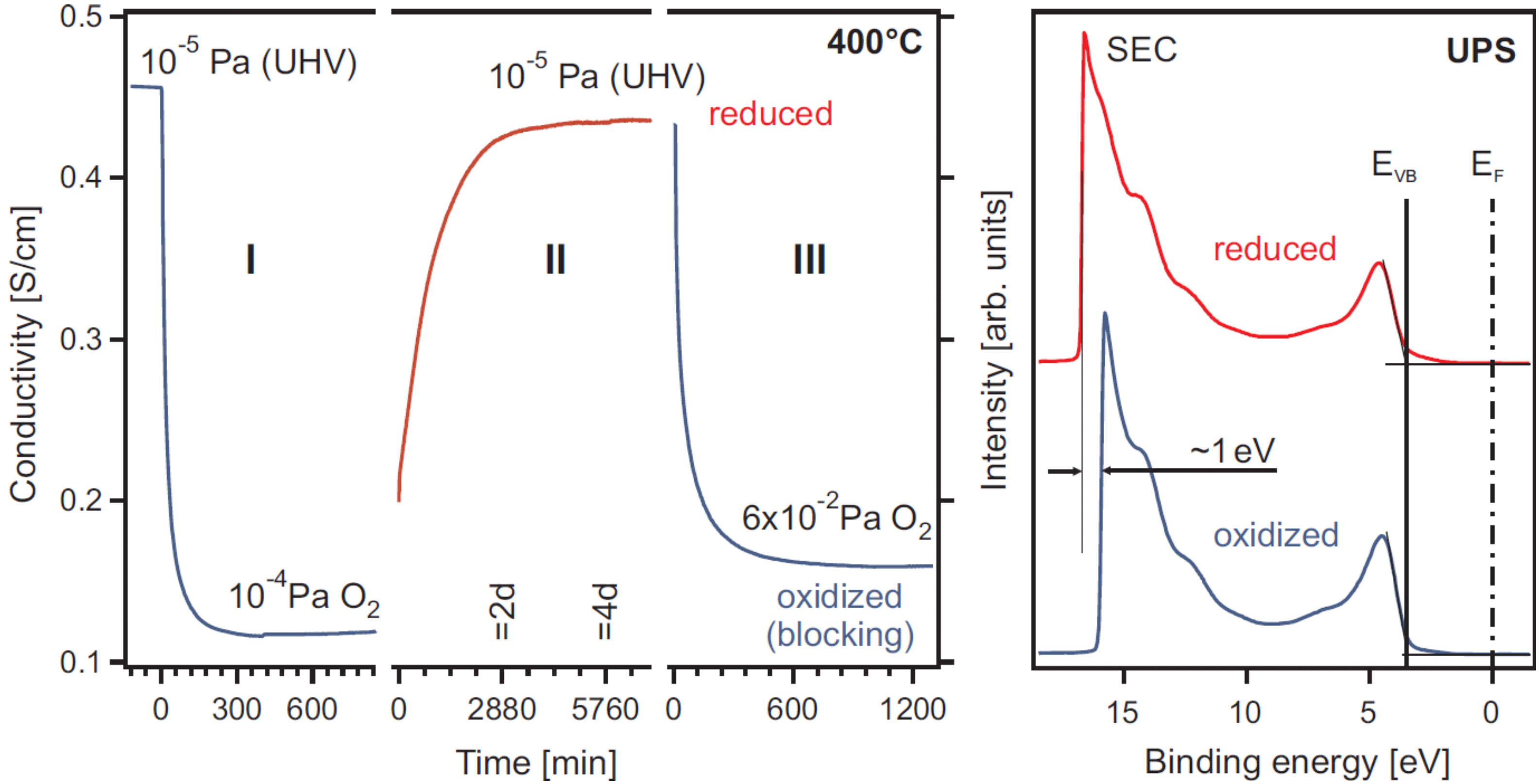
Surface modification

P = 1 bar



➢ **Exchange at SnO_2 possible with 1nm In_2O_3 on surface**

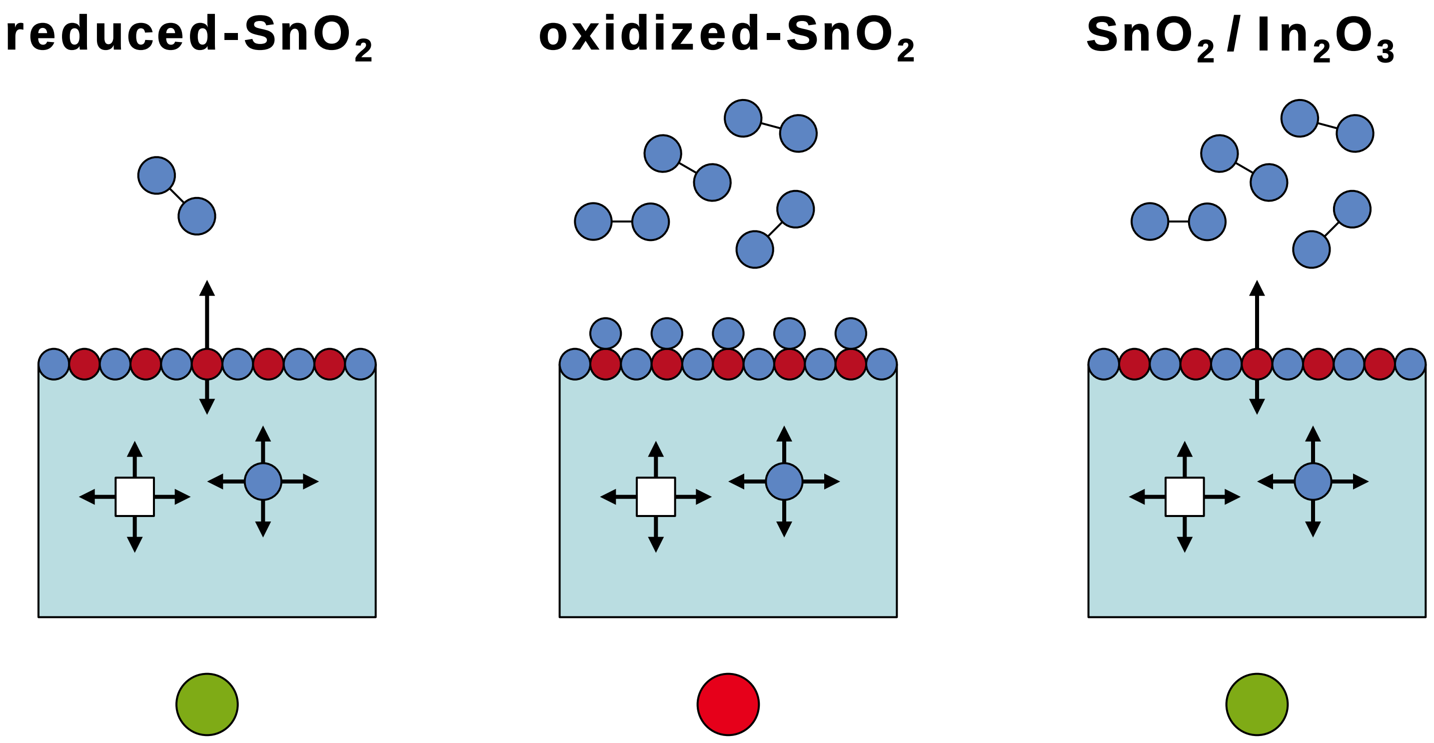
Relaxation at low pressure



➢ **Relaxation observed when starting from reduced surface**

➢ **Oxidation of surface faster than oxidation of bulk**

Oxygen exchange of SnO_2



➢ **Surface termination is important for oxygen exchange**

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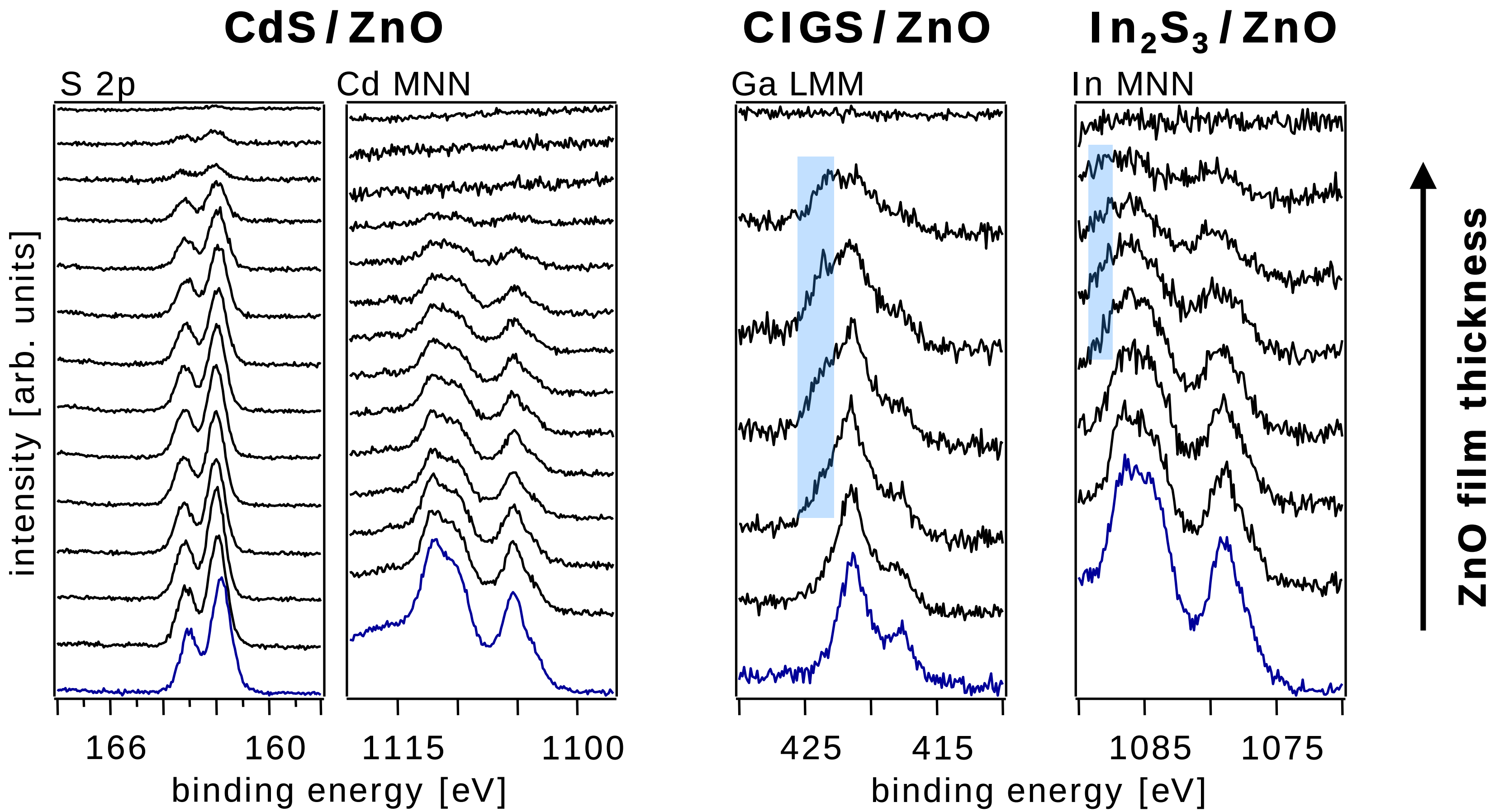
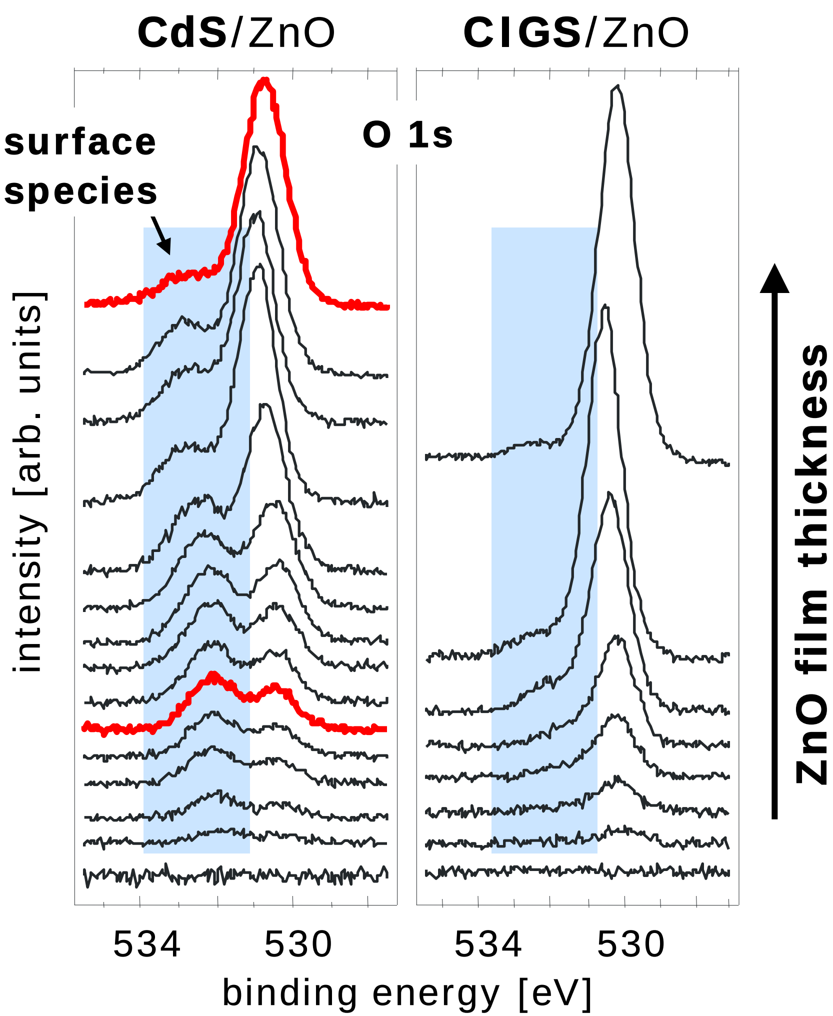
Interface Formation

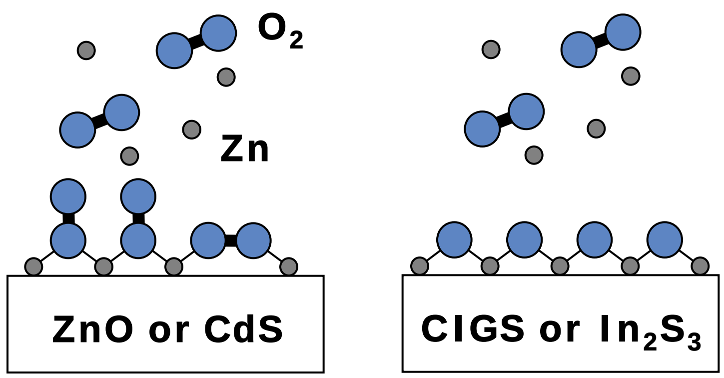
CdS / ZnO – substrate oxidation



no oxidation of substrate **oxidation of substrate**

CdS / ZnO – initial growth





dissociation of O_2 not possible

non-reactive

dissociation of O_2 possible

reactive

➢ **catalytic activity of surface responsible for substrate oxidation**

CdS / ZnO – interface properties

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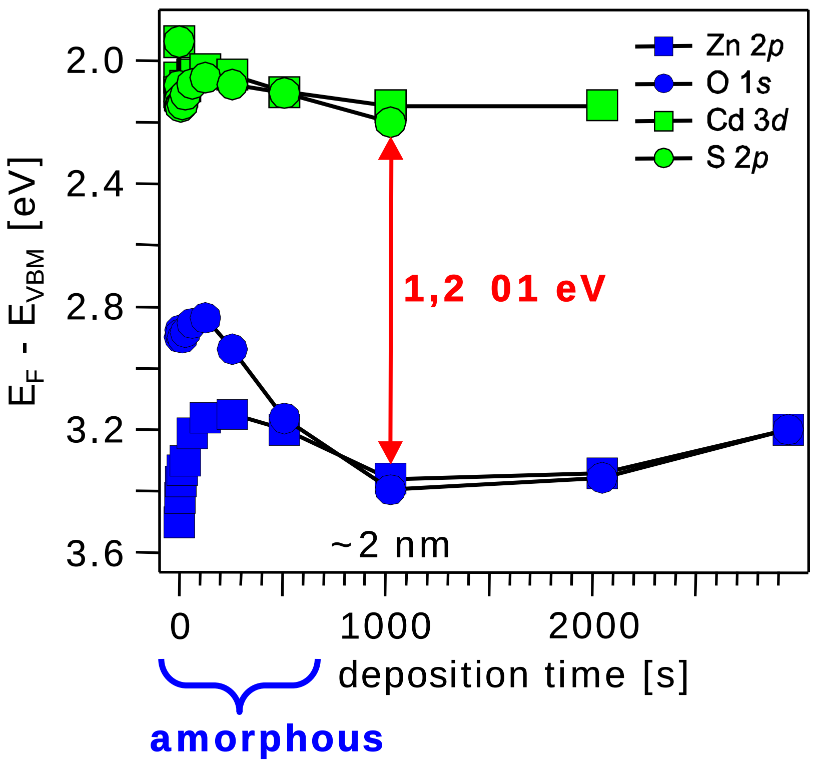
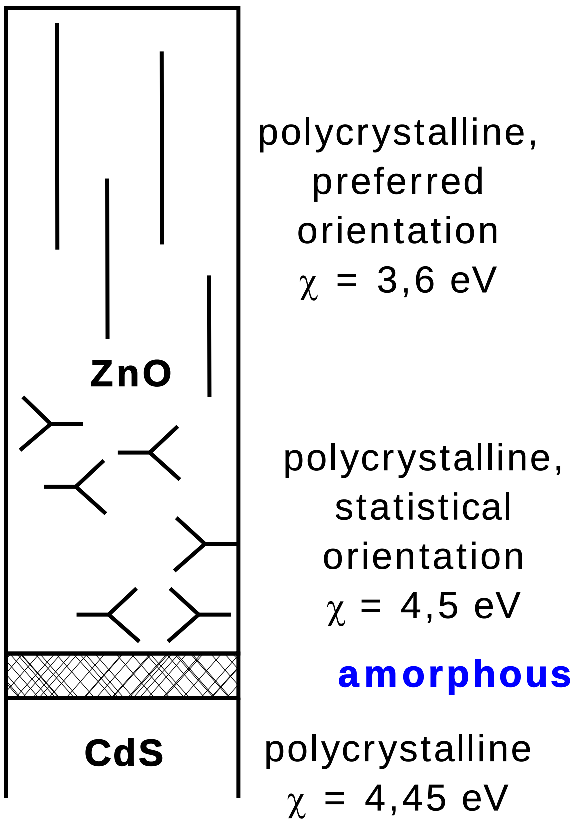
band alignment

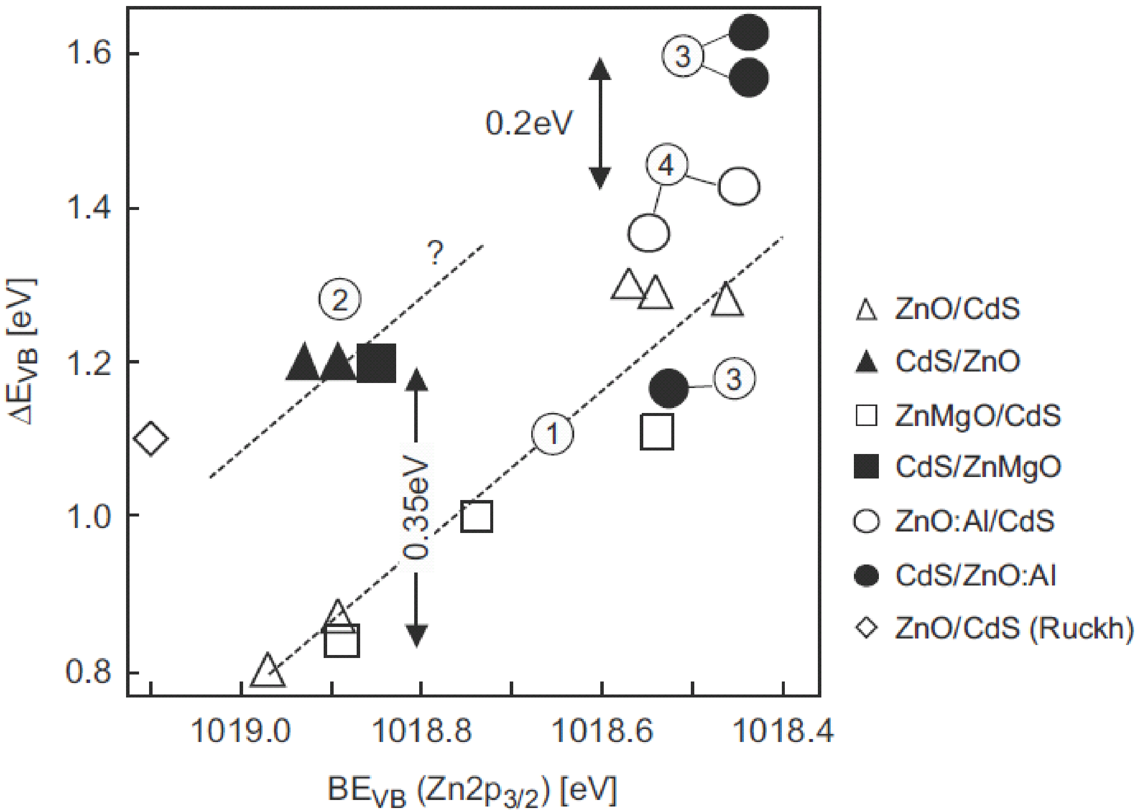


microstructure



Venkata Rao et al., Appl. Phys. Lett. **87** (2005), 032101.

CdS / ZnO band alignment



Large variation of band alignment

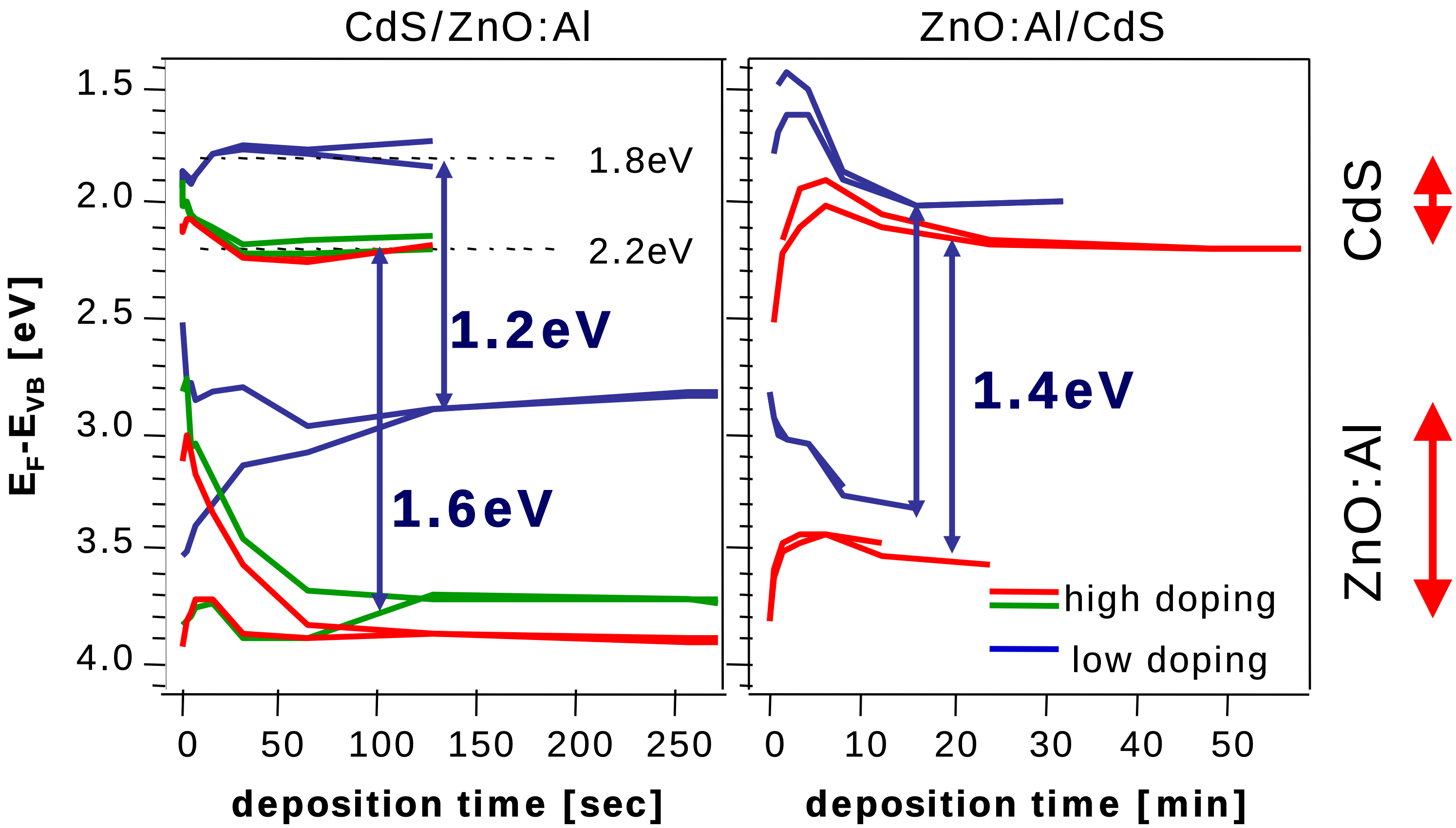
ΔE_{VB} depends on

- Deposition sequence
- ZnO dep. temperature
- **ZnO doping**

details explained in:

Ellmer, Klein, Rech *Transparent Conductive Zinc Oxide (Springer, 2008), chap 4*

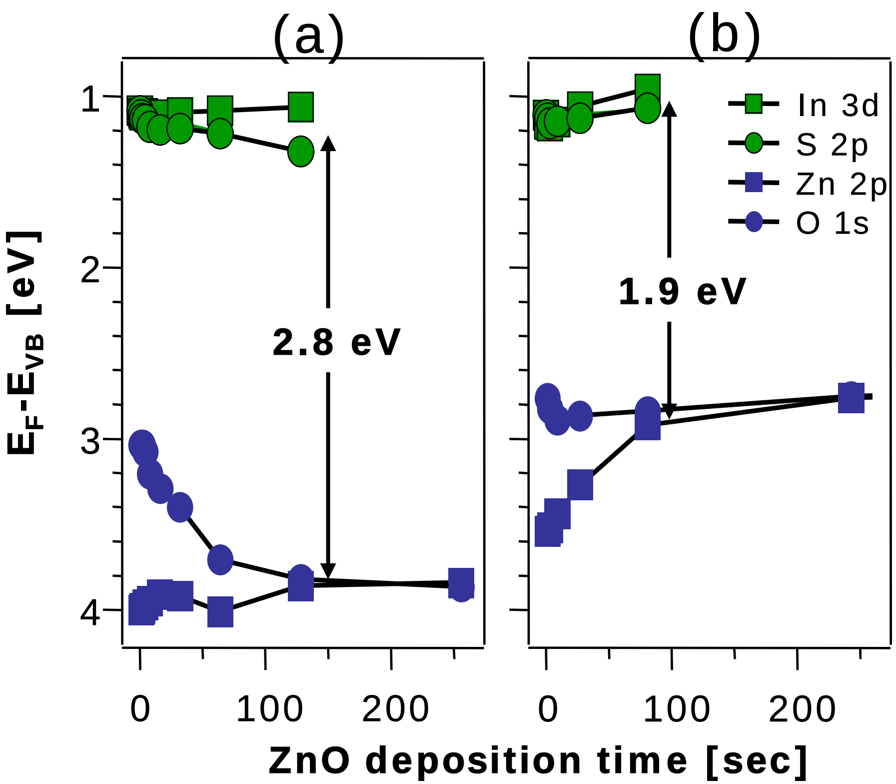
CdS / ZnO Fermi level pinning

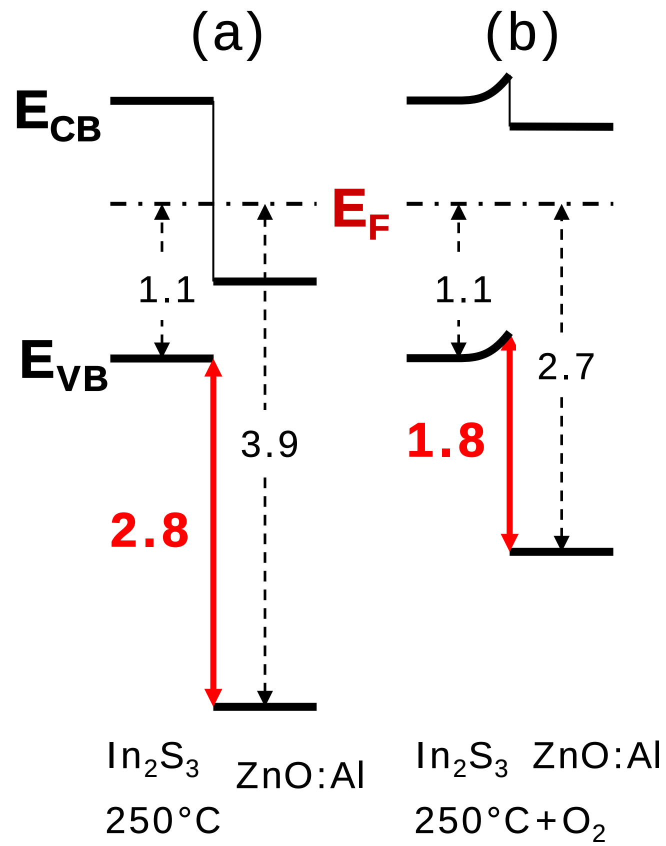


Fermi level in CdS substrate restricted to 2.0 ± 0.2 eV

Ellmer, Klein, Rech *Transparent Conductive Zinc Oxide* (Springer, 2008), chap 4

In_2S_3 / ZnO Fermi level pinning





- **No band bending in In_2S_3 and ZnO**
- **Band alignment defined by doping levels**

Klein et al., J. Mater. Sci. **42** (2007), 1890.

TCO / CdS – band alignment

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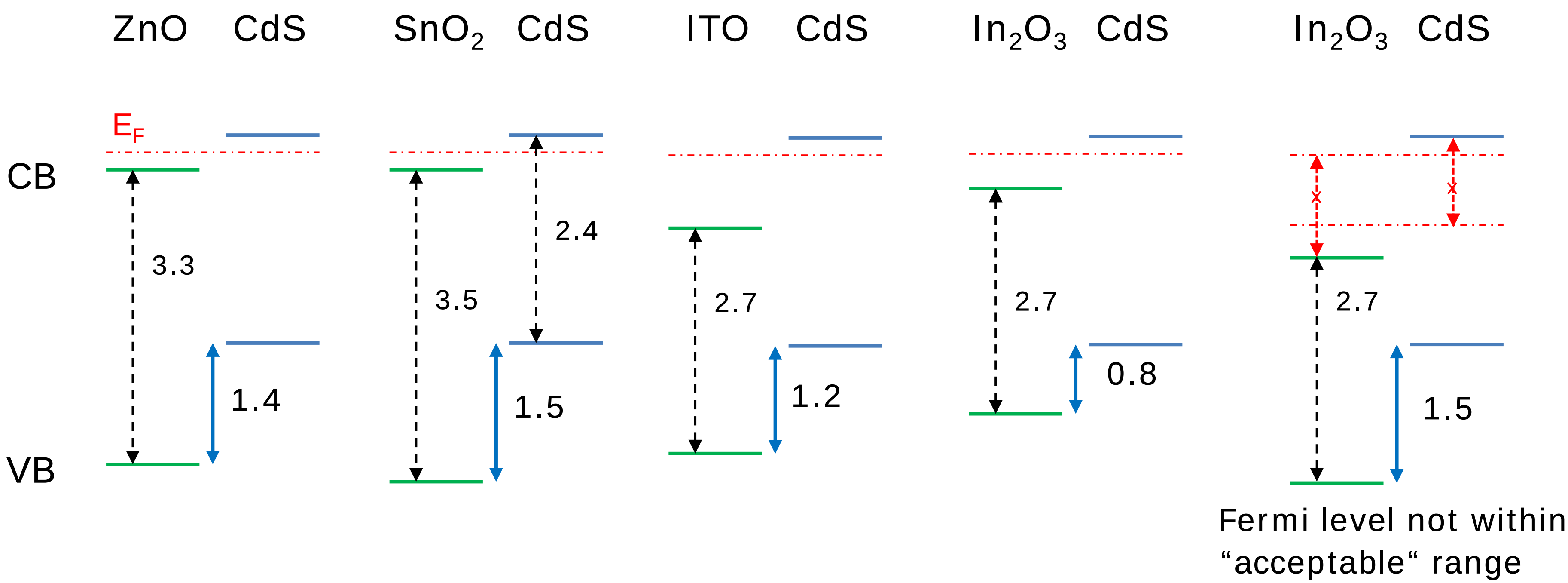
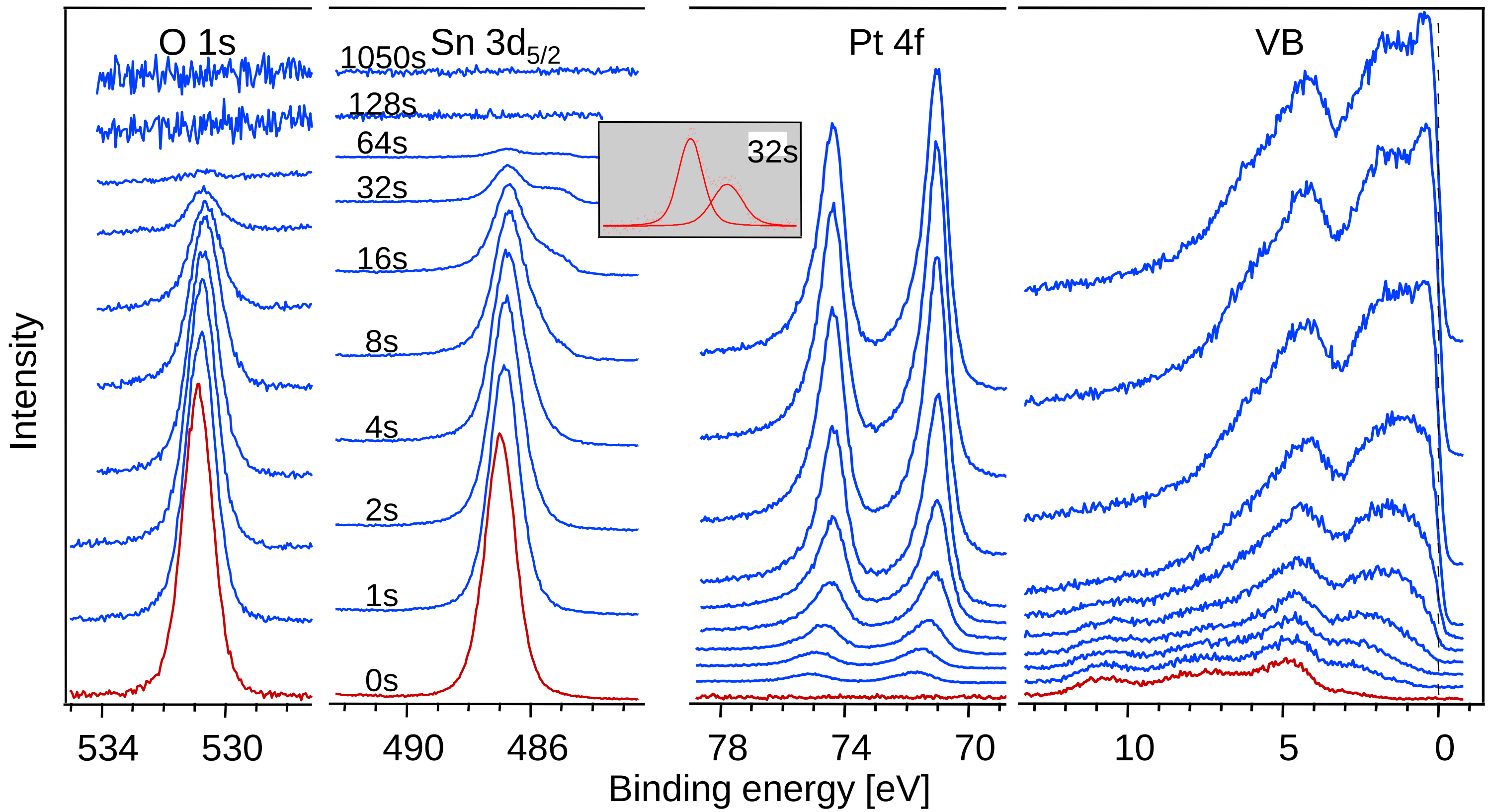


➢ **Valence band maxima of TCOs at comparable energy**
but: Band alignment influenced by TCO gap and doping due to Fermi level pinning in CdS

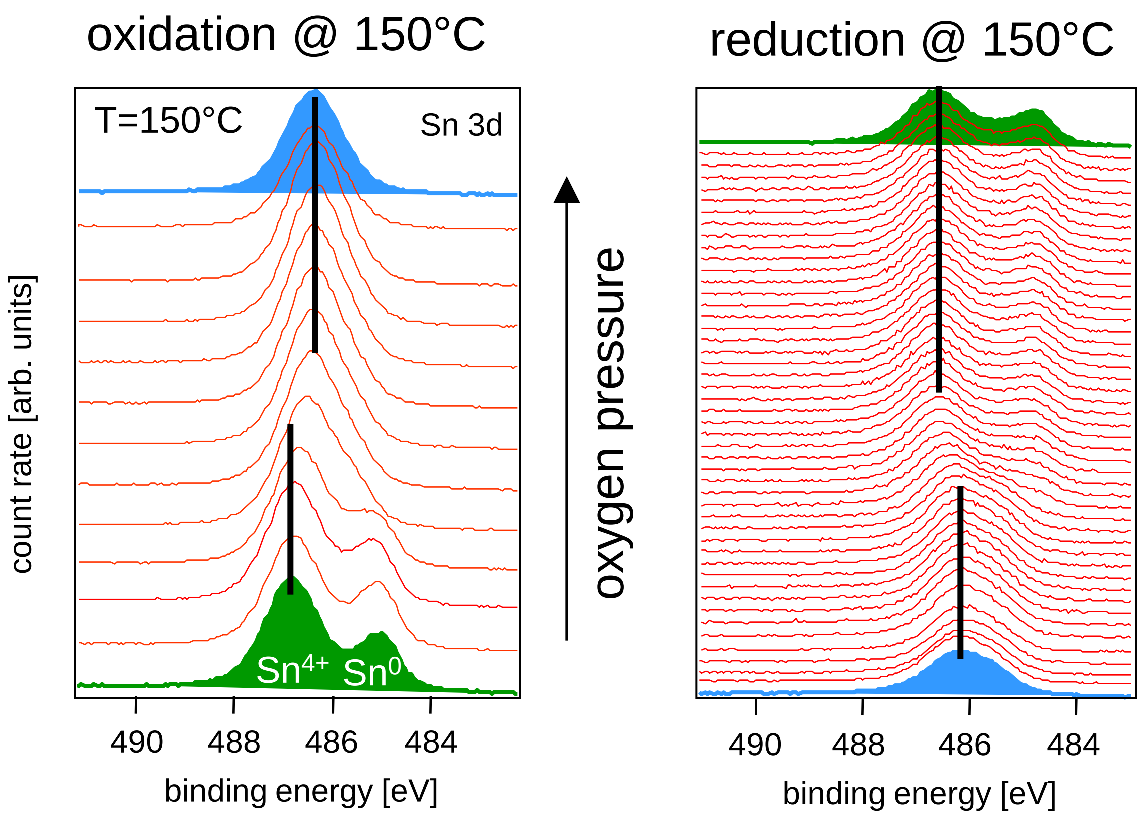
SnO_2 / Pt – interface formation



Reduction of SnO_2 during deposition

Surf. Sci. **602** (2008), 3246.

SnO_2 / Pt – interface chemistry



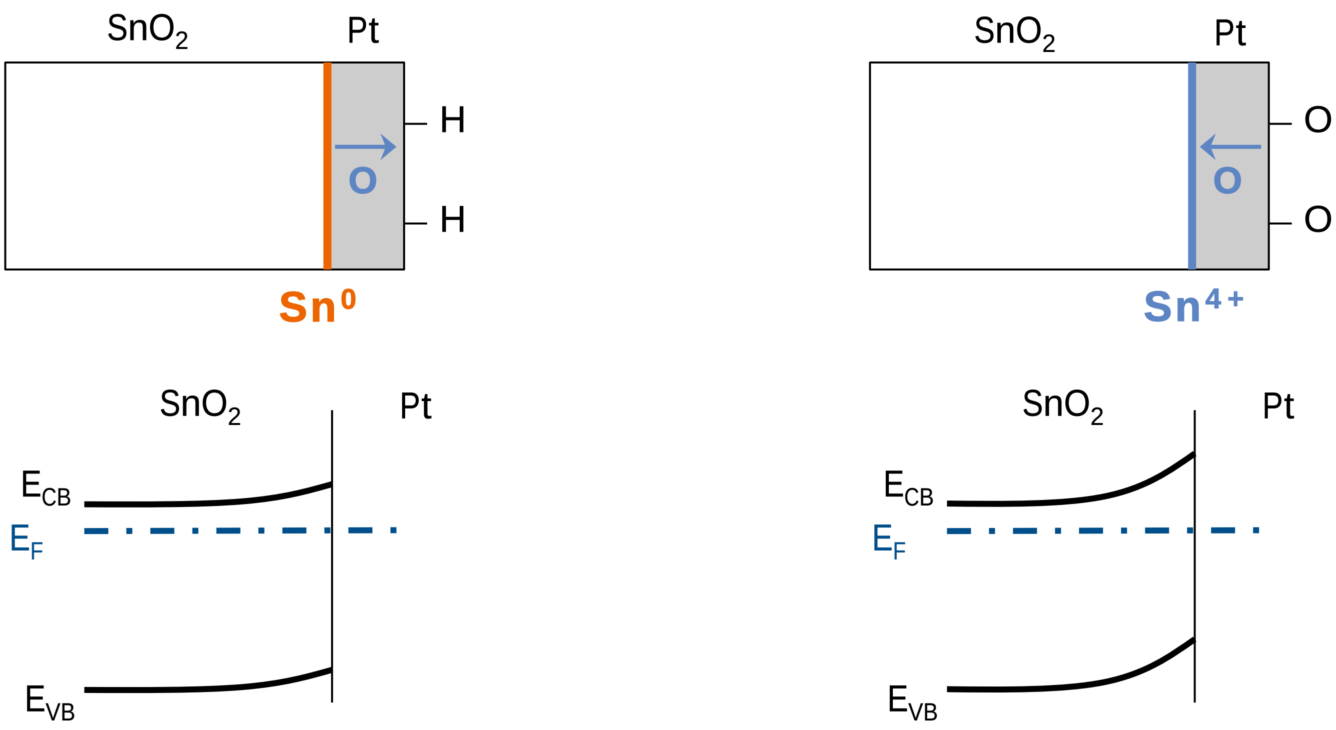
- **150°C: Sn^0 <-> Sn^{4+} with intermediate Sn^{2+} state**
- **100°C: Sn^0 <-> Sn^{2+}**
- **Oxidation / reduction not observable for**
  - **large Pt islands**
  - **bare SnO_2 surface**

Reversible oxidation / reduction of Sn

Chemistry at buried interface

Reducing environment

Oxidizing environment



Oxygen is reversibly transported to / from the interface

Summary

- Work functions depend on doping, surface orientation (ZnO, In_2O_3, SnO_2?) and surface termination (In_2O_3, SnO_2)
- Oxygen exchange generally possible for In_2O_3 but can be suppressed at stoichiometric SnO_2 surfaces
- Reactivity of interfaces determined by catalytic activity of surface for dissociation of oxygen
- Energy band alignment characterized by similar valence band energies but may be affected by Fermi level pinning
- Schottky barrier heights can depend on oxygen pressure

Thanks

TECHNISCHE UNIVERSITÄT DARMSTADT

- Frank Säuberlich, Yvonne Gassenbauer, Christoph Körber, André Wachau, Mareike Hohmann, Karsten Rachut (Surface Science)
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- S.P Harvey, T.O. Mason (Northwestern University)

- BMBF (ZnO), DFG (SFB 595), DFG-NSF (Materials World Network)