Fermi energy limits in Cu-oxides

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Alternative Title:

About the difficulties to achieve high photovoltages and conversion efficiencies with CuO and other Cu-oxides

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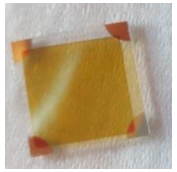
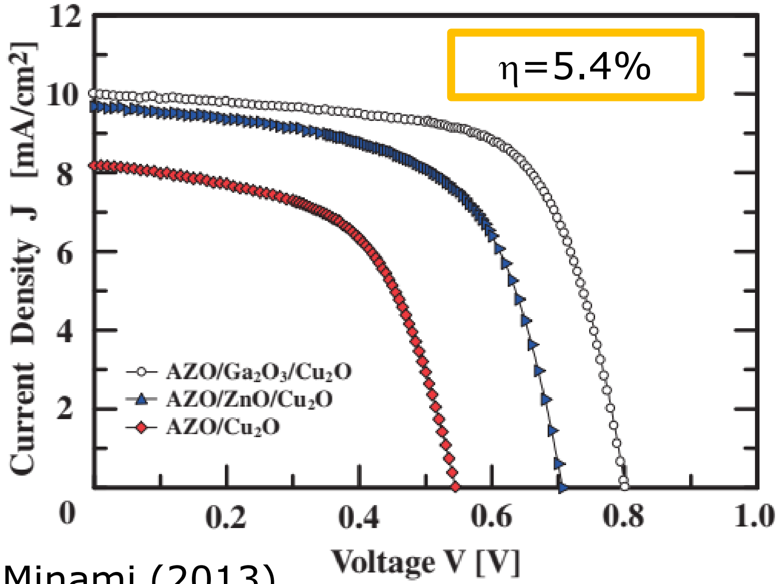
Cu-oxides for solar cells

Cu_2O

direct band gap: 2.3 eV





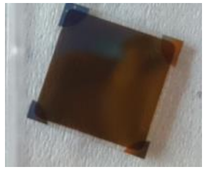
Minami (2013)

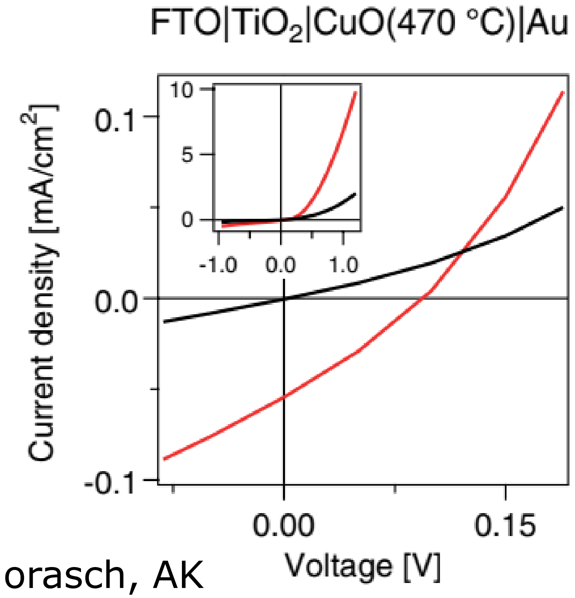
Photovoltage lower than for good solar cells systems

CuO

direct gap: 1.5-1.7 eV

indirect gap: 1.2 eV





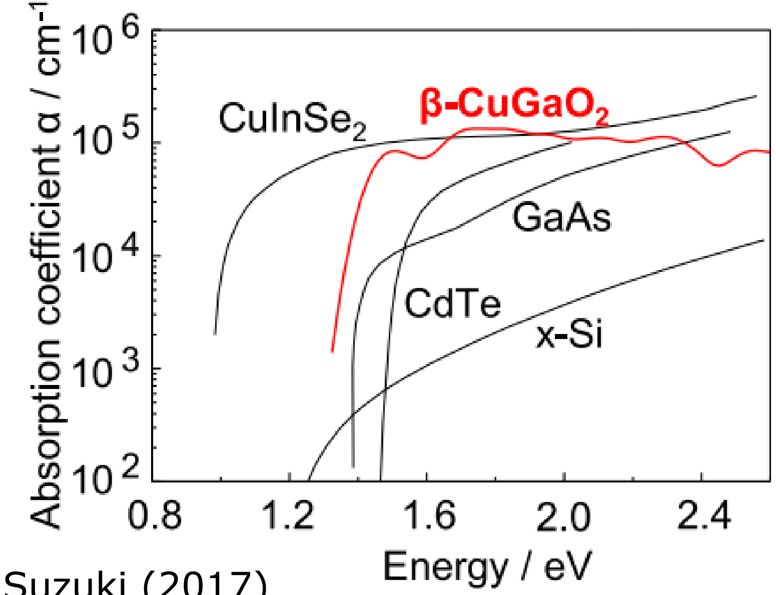
Morasch, AK (2016)

Low photocurrent and low photovoltage

β-$CuGaO_2$

direct gap: 1.5 eV

absorption: >10^5 /cm



Suzuki (2017)

No PV properties published yet

The Fermi energy in ionic semiconductors

The Fermi energy in a material is determined by **charge neutrality**

- Charge neutrality in covalent semiconductors: $\mathrm{n} + N_A^- = \mathrm{p} + N_D^+$
- Charge neutrality in ionic semiconductors includes additional defects:

$$[\mathrm{h}] + k[\mathrm{D}^{k+}] + l[\mathbf{D}_{\mathbf{intr}}^{l+}] + [\mathbf{Cat}_{\mathbf{cat}}^{+}] + [\mathbf{An}_{\mathbf{An}}^{+}] = [\mathrm{e}] + m[\mathrm{A}^{m-}] + n[\boldsymbol{A}_{\boldsymbol{intr}}^{\boldsymbol{n-}}] + [\mathbf{Cat}_{\mathbf{cat}}^{-}]$$

Positive charges

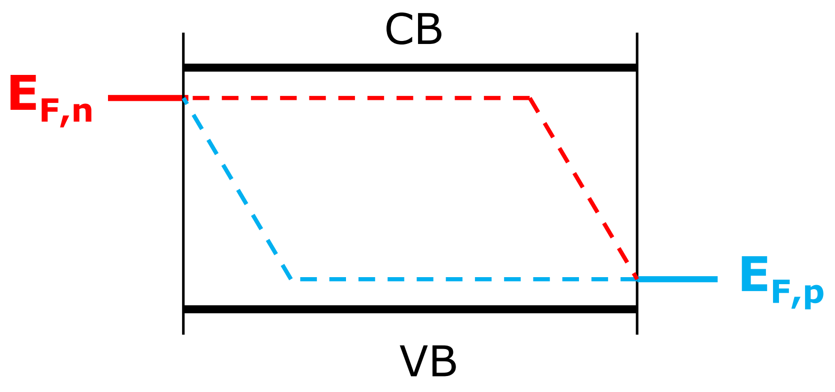
- Free holes
- Extrinsic donors
- **Intrinsic donors**
  (anion vacancies, cation interstitials)
- **Trapped holes**

Negative charges

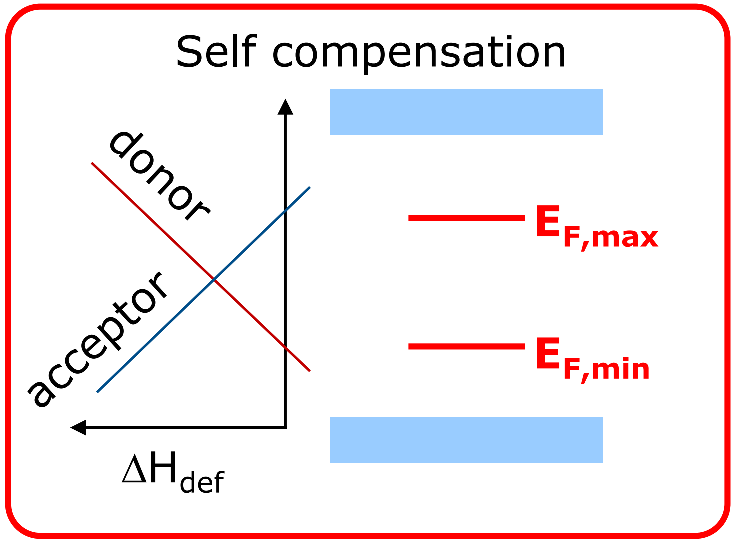
- Free electrons
- Extrinsic acceptors
- **Intrinsic acceptors**
  (cation vacancies, anion interstitials)
- **Trapped electrons**

Limitation of the Fermi energy in ionic semiconductors

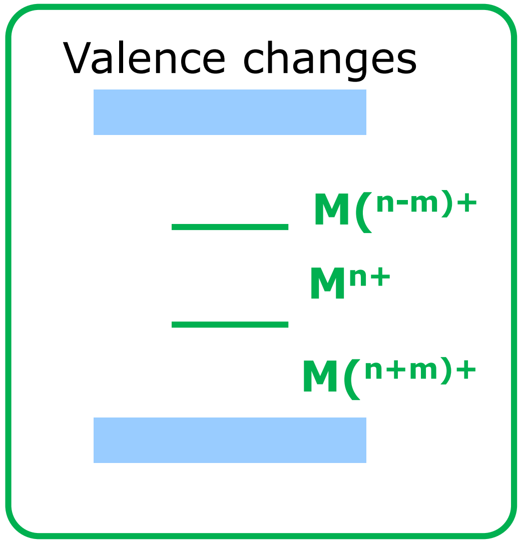
The photovoltage of a solar cell is determined by the splitting of the quasi Fermi levels under illumination



Intrinsic defects



Charge trapping



- The formation of compensating defects requires exchange of species, which can happen during synthesis at elevated T, but is typically suppressed at room temperature (operating conditions)
- On the contrary, charge trapping can occur at any temperature when charges are introduced into the valence or conduction by absorption or injection
- **Charge trapping can limit the variation (splitting) of the Fermi energy**

Experimental setup

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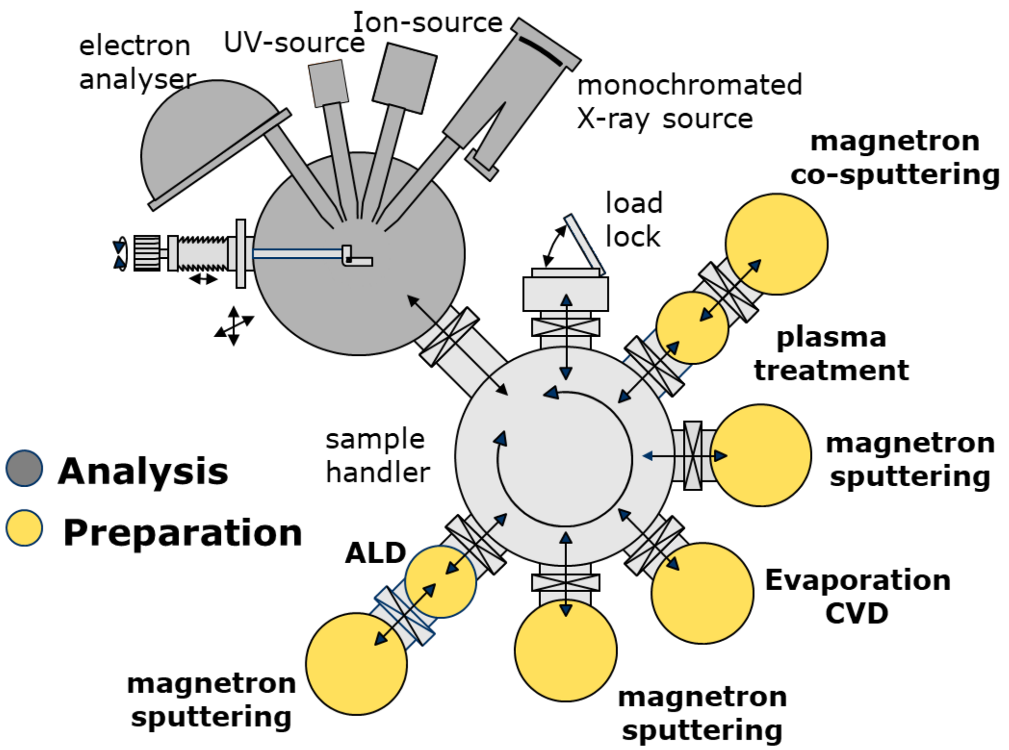
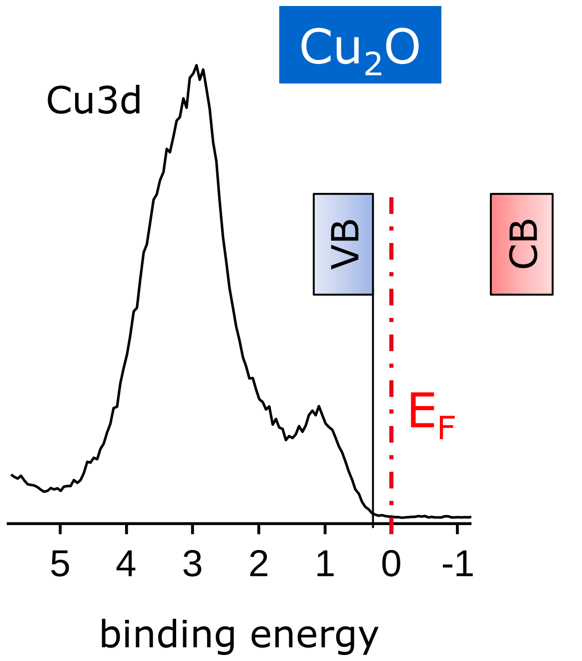
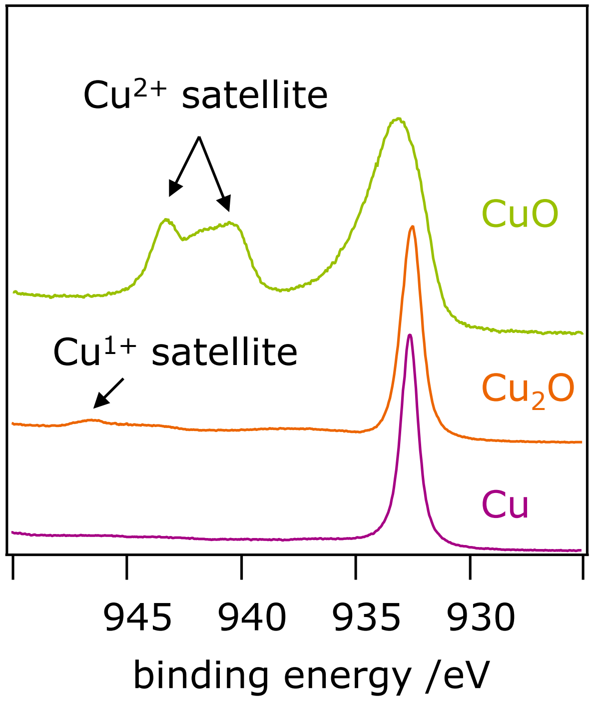
Cluster tool DAISY-MAT



➢ **in-situ deposition and processing**

X-ray Photoelectron spectroscopy

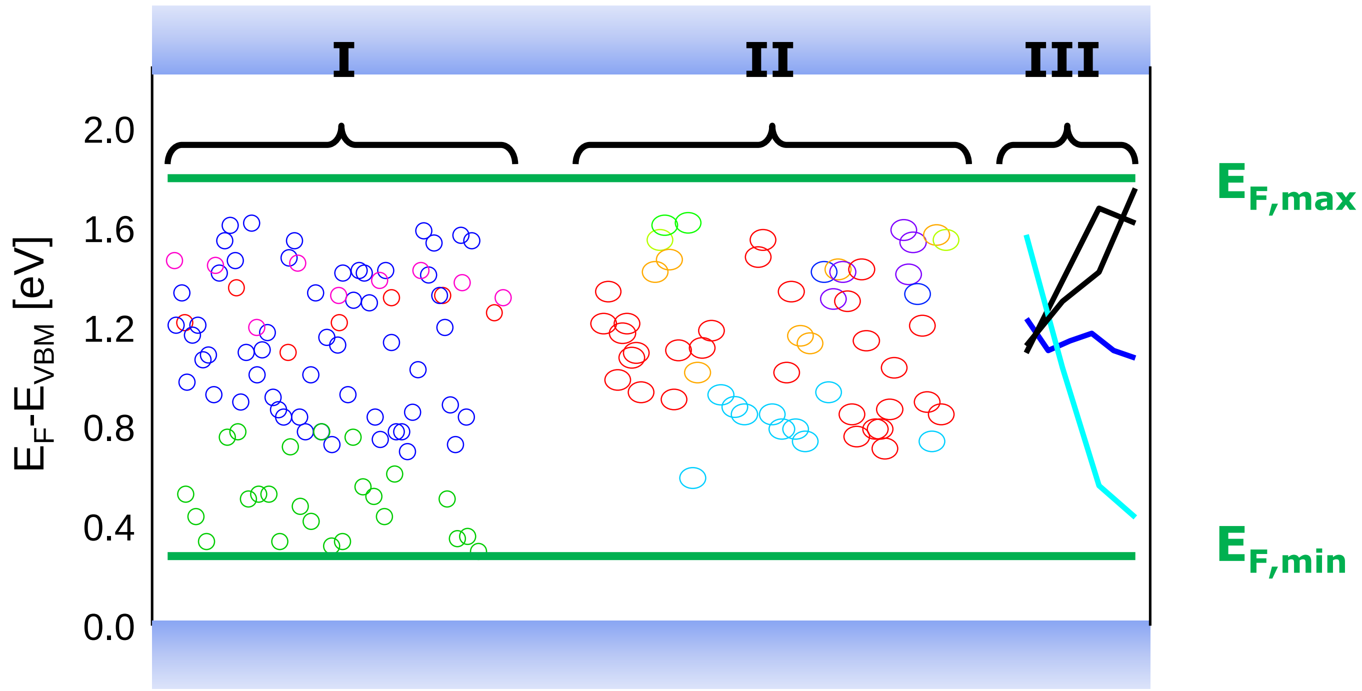




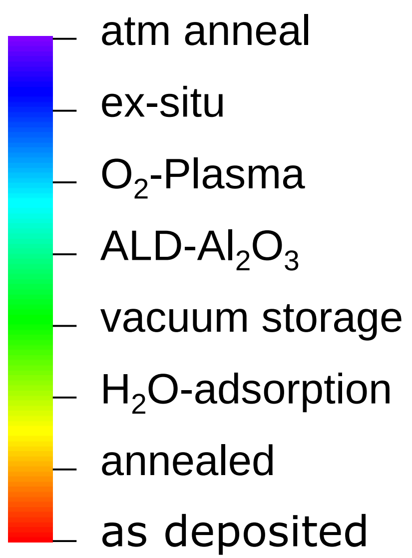
➢ **direct determination of Fermi energy**

➢ **direct determination of Cu oxidation state**

How to find the limits of E_F (e.g. Fe_2O_3)



II. Post-deposition treatments

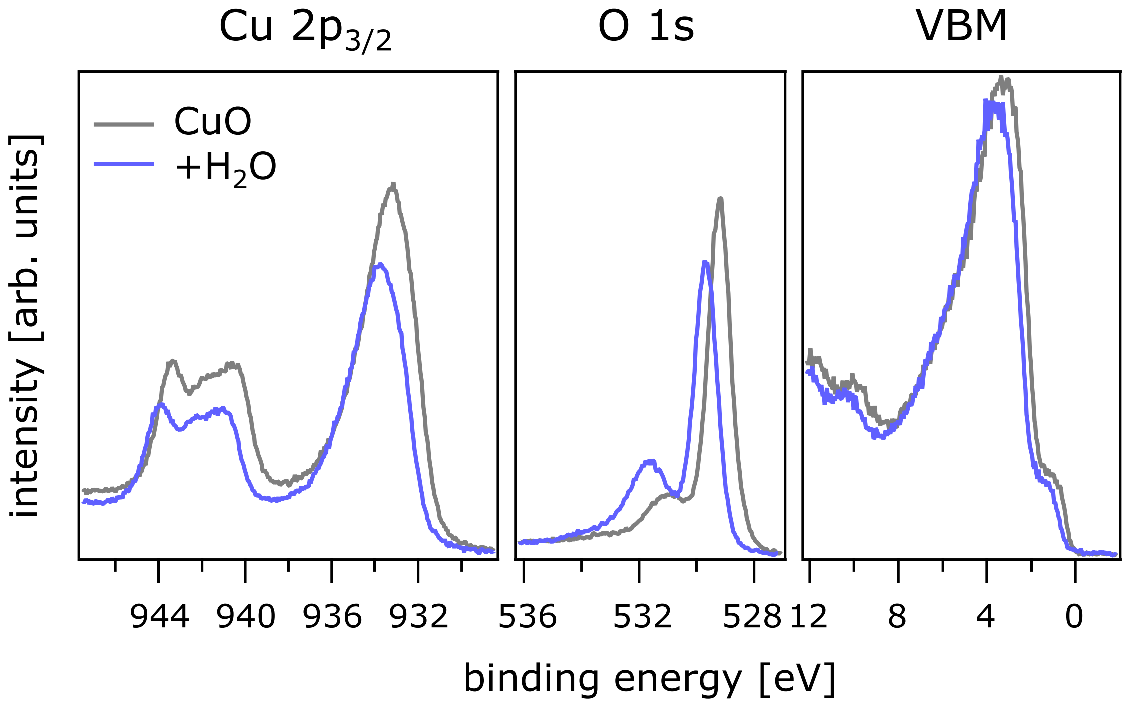


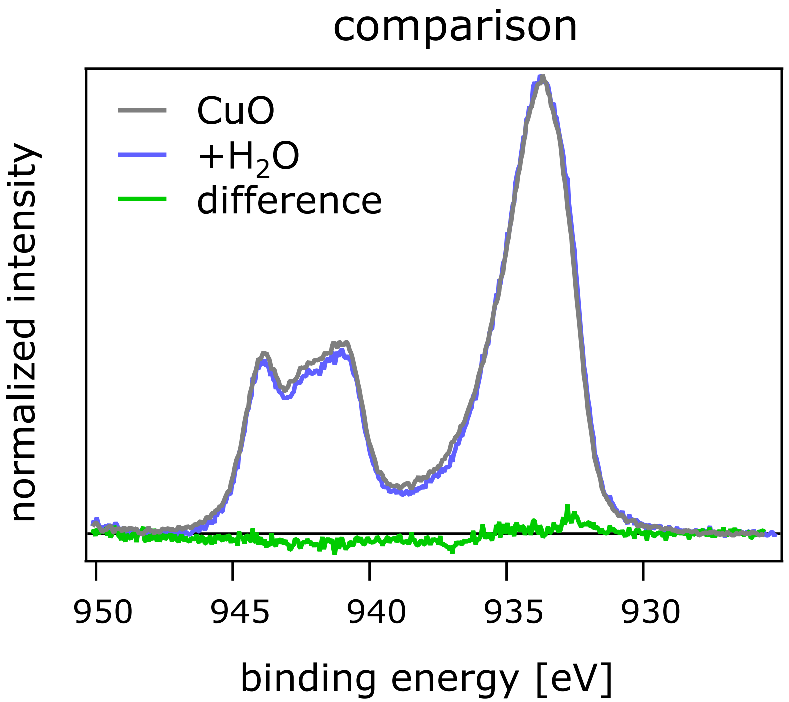
I. Doping: Mg, Si, Zr

III. Interfaces: RuO_2, NiO, ITO

Similar limits of Fermi energy for doped and treated Fe_2O_3 and at interfaces

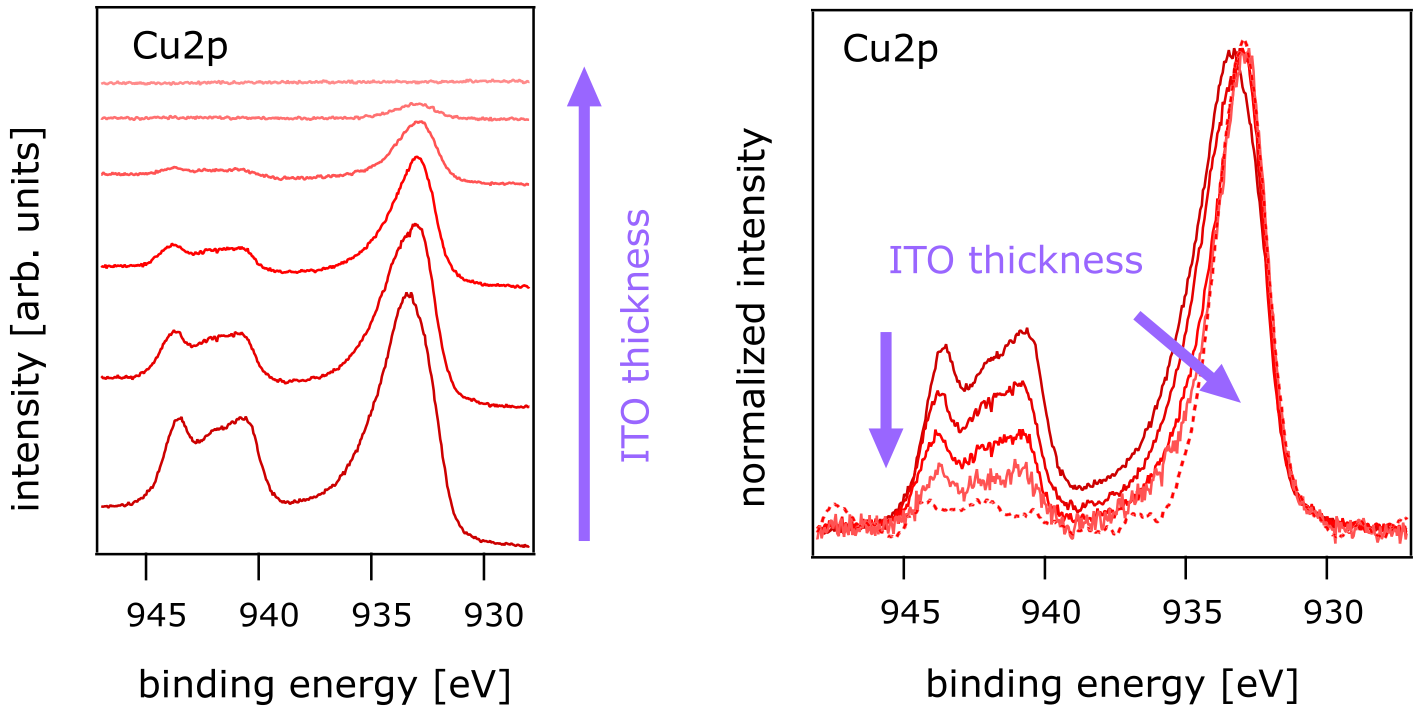
Water exposure to CuO





- Water adsorption leads to an upward shift of the Fermi energy
  → also observed for SnO_2, ZnO, NiO, Fe_2O_3, $BiVO_4$, $CuFeO_2$, $BiFeO_3$, …
- The intensity of the Cu^{2+} satellite intensity of slightly reduced → partial reduction of Cu

CuO/ITO interface formation



- upward shift of the Fermi energy
- narrowing of the Cu 2p emission
- reduction of Cu^{2+} satellite intensity

$Cu^{2+} \rightarrow Cu^{1+}$

- **Upper limit of Fermi energy by electrochemical reduction of Cu**
- **Corresponds to electron trapping at Cu^{2+} sites**

Summary

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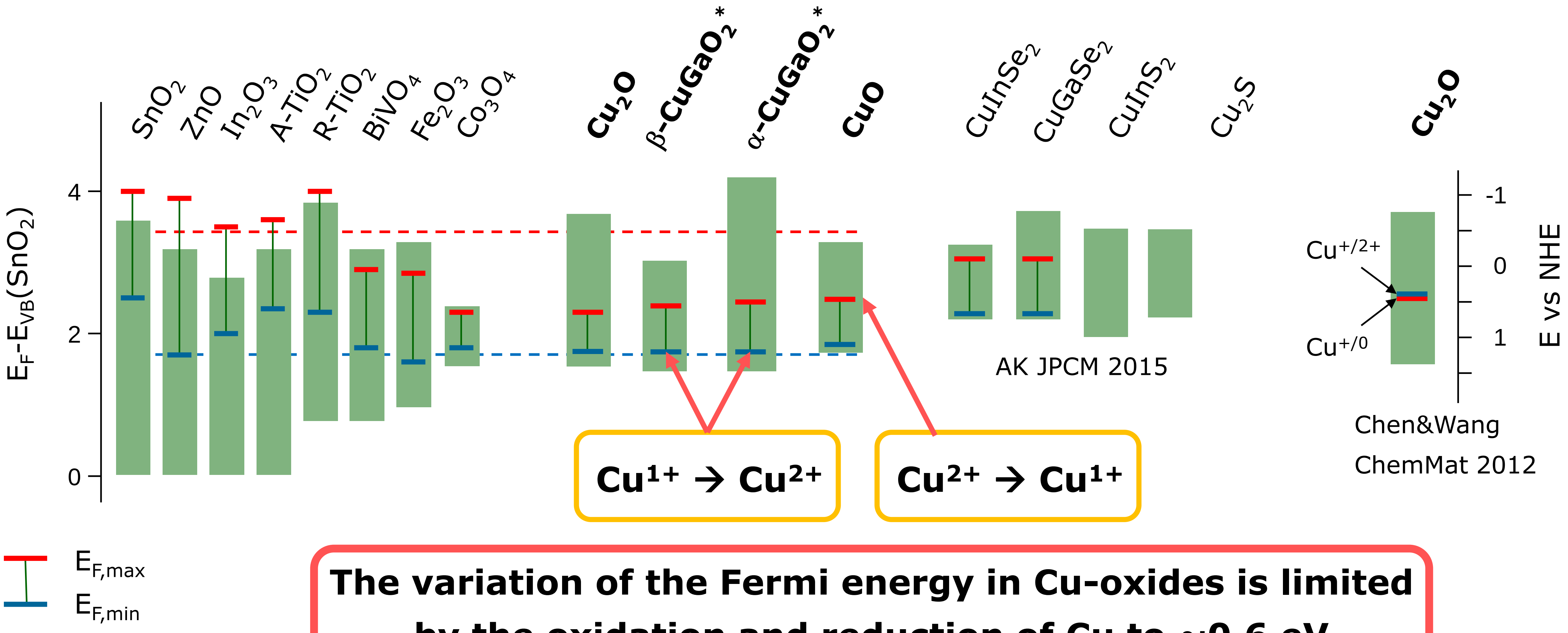

The variation of the Fermi energy in Cu-oxides is limited by the oxidation and reduction of Cu to ~0.6 eV

* Suzuki et al (submitted)