SFB 595

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Conductivity and Hall effect relaxation of undoped and doped In_2O_3 thin films

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Project D3

Motivation

- Transparent Conductive Oxides (**TCO**) are used as electrode materials in solar cells, OLEDs and as sensor material
- **Oxygen exchange** at surface/interface is important for **electrical properties** – conductivity $\boldsymbol{\sigma}$, carrier concentration $\boldsymbol{n}$ and mobility $\boldsymbol{\mu}$ are crucial for device functionality

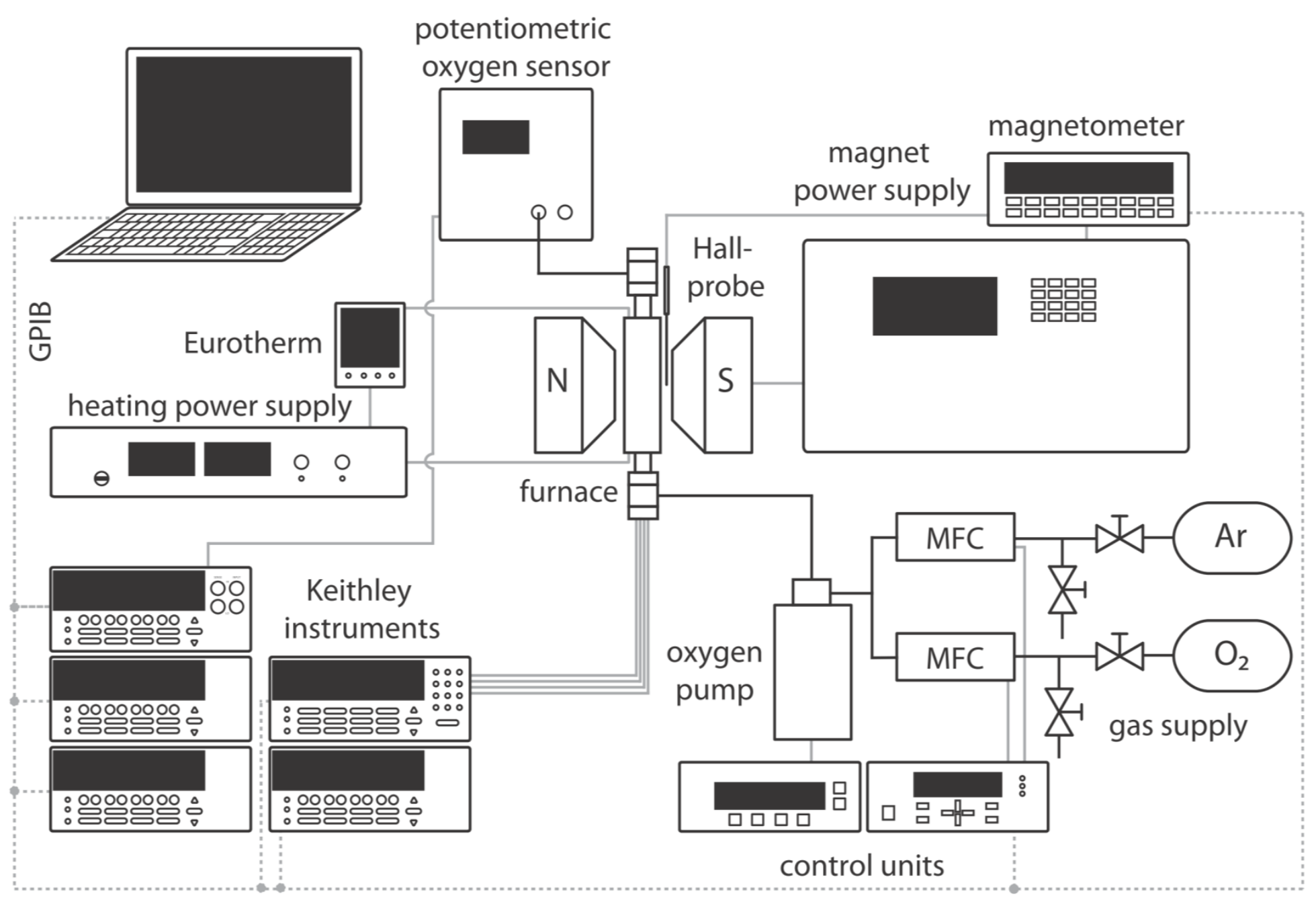
$$\sigma = e\, n\, \mu$$

Discrimination of effects on n and effects on μ is needed!

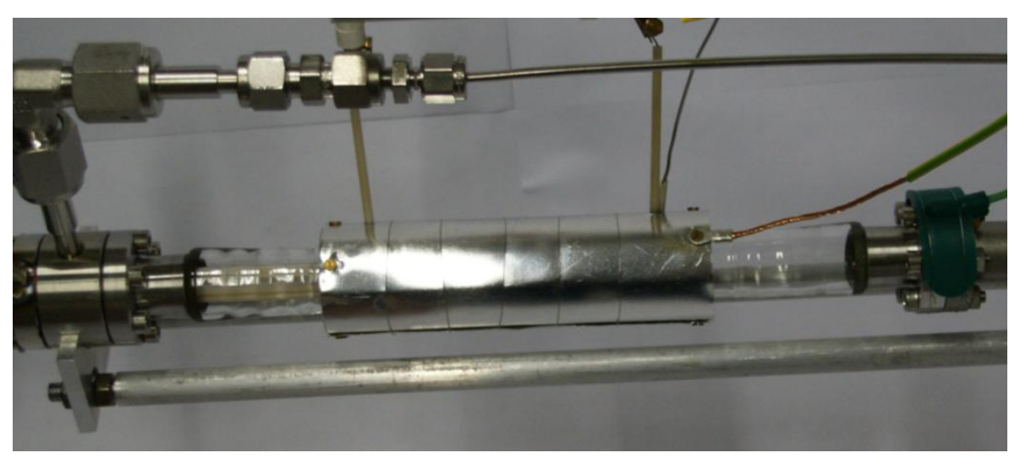
➡ **Hall effect measurements**

Material

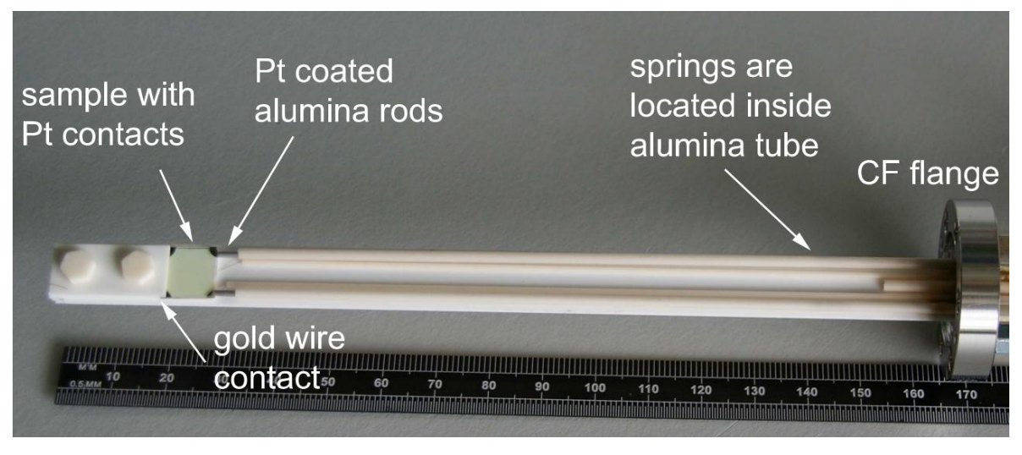
- Sn doped In_2O_3 (ITO) is the most common TCO: high conductivity (up to 10^4 S/cm)
- Doping of In_2O_3 by Sn is accomplished by substitutional Sn atoms on In lattice sites Sn_{In} : one electron per Sn atom
- $Sn^{\bullet}$ donors can be compensated by O''_i forming neutral defect complexes $(2Sn_{In}O_i)^{\times}$
- HERE: rf magnetron sputtered thin films are used (thickness ~ 400nm)



Furnace



Sample holder



Measurement Setup:

Simultaneous Conductivity and Hall measurements of thin films depending on

- **Temperature** (up to 600 °C)
- **Gas atmosphere**, variable oxygen/argon ratio, oxygen content controlled by oxygen pump, monitored with oxygen sensor

Requirements for furnace and sample holder:

- Non magnetic materials
- All furnace materials stable in oxidizing and reducing conditions
- Slim design for space reasons between poles of electromagnet

Publications last funding period

1) Körber, C., et al. (2011). "Self-Limited Oxygen Exchange Kinetics at SnO_2 Surfaces." Physical Chemistry Chemical Physics **13: 3223-3226.**

2) Deuermeier, J., et al. (2011). "Reactive magnetron sputtering of Cu_2O: Dependence on oxygen pressure and interface formation with indium tin oxide." Journal of Applied Physics **109(11).**

3) Hohmann, M. V., et al. (2011). "Orientation dependent ionization potential of In_2O_3: a natural source for inhomogeneous barrier formation at electrode interfaces in organic electronics." Journal of Physics-Condensed Matter **23(33).**

4) Zakutayev, A., et al. (2011). "Interdiffusion at the BaCuSeF/ZnTe interface." Thin Solid Films **519(21): 7369-7373.**

5) Klein, A. (2012). "Energy band alignment at interfaces of semiconducting oxides: A review of experimental determination using photoelectron spectroscopy and comparison with theoretical predictions by the electron affinity rule, charge neutrality levels, and the common anion rule." Thin Solid Films **520(10): 3721-3728.**

6) Proffit, D. E., et al. (2012). "Surface studies of crystalline and amorphous Zn–In–Sn–O transparent conducting oxides." Thin Solid Films **520(17): 5633-5639.**

7) Bayer, T. J. M., et al. (2012). "Atomic Layer Deposition of Al_2O_3 onto Sn-Doped In_2O_3: Absence of Self-Limited Adsorption during Initial Growth by Oxygen Diffusion from the Substrate and Band Offset Modification by Fermi Level Pinning in Al2O3." Chemistry of Materials **24(23): 4503-4510.**

8) Hopper, E. M., et al. (2013). "Surface electronic properties of polycrystalline bulk and thin film In2O3$(ZnO)_k$ compounds." Applied Surface Science **264(0): 811-815.**

9) Rein, M. H., et al. (2013). "An in situ x-ray photoelectron spectroscopy study of the initial stages of rf magnetron sputter deposition of indium tin oxide on p-type Si substrate." Applied Physics Letters **102(2).**

10) Klein, A. (2013). "Transparent Conducting Oxides: Electronic Structure–Property Relationship from Photoelectron Spectroscopy with in situ Sample Preparation." Journal of the American Ceramic Society **96(2): 331-345.**

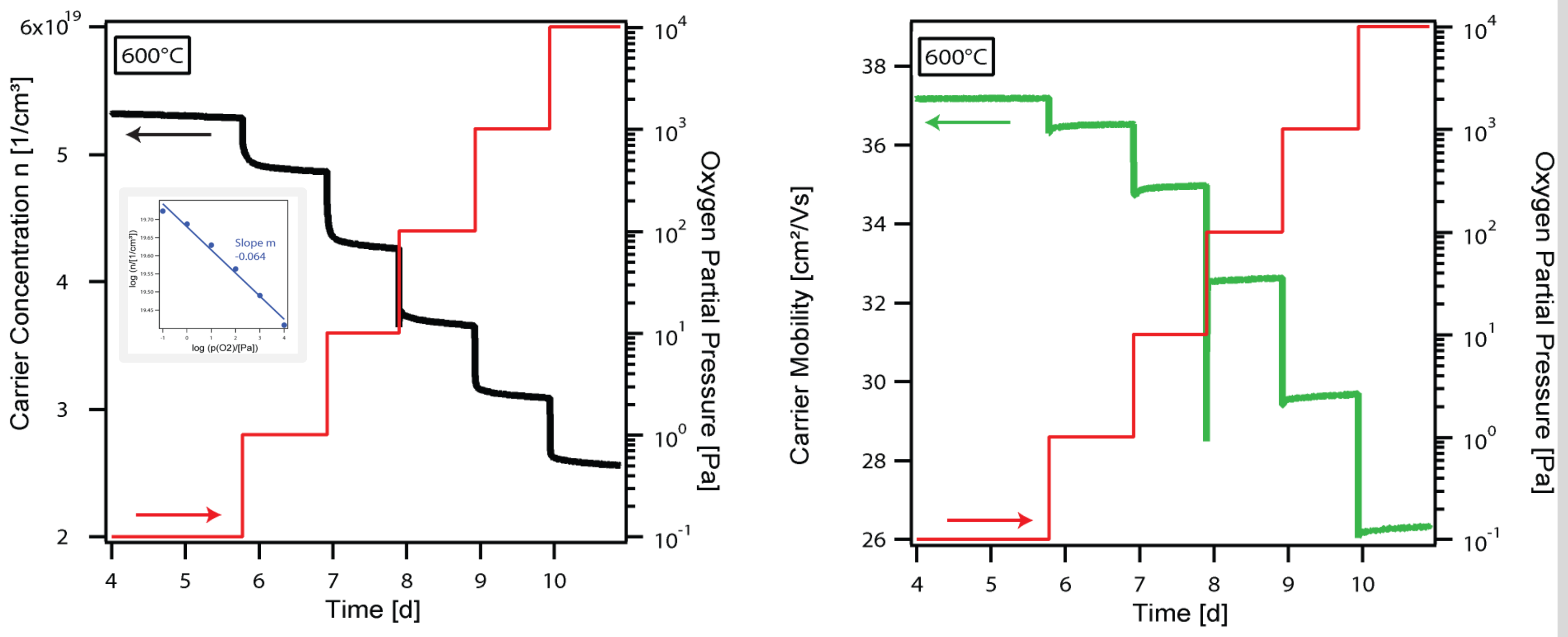
11) Pfeifer, V., et al. (2013). "Energy Band Alignment between Anatase and Rutile TiO_2." The Journal of Physical Chemistry Letters **4(23): 4182-4187.**

12) Rachut, K., et al. (2014). "Growth and surface properties of epitaxial SnO_2." Physica Status Solidi (a): n/a-n/a.

13) Hohmann, M. V., et al. (2014). "In situ Hall effect and conductivity measurements of ITO thin films." Solid State Ionics **262(0): 636-639.**

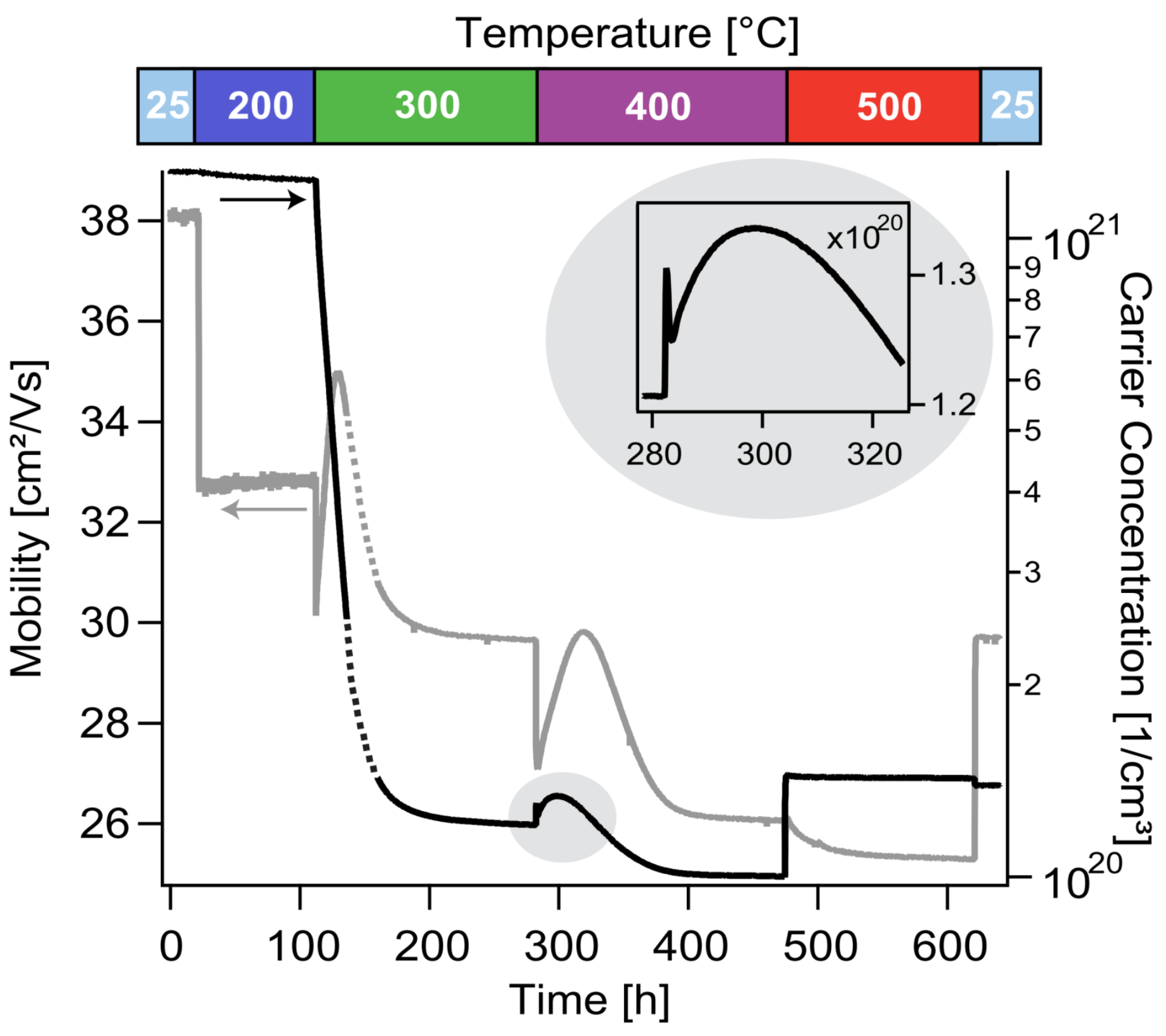
Results: Relaxation Measurements

$p(O_2)$ dependent relaxation measurement of In_2O_3



- Carrier concentration changes reversibly with oxygen partial pressure
- Carrier mobility also depends on oxygen partial pressure due to changes in carrier concentration and changes in GB barrier
- Fast changes followed by long-term drift
- Slope of Brouwer plot does not correspond to expected $pO_2^{-1/6}$ dependence

T dependent relaxation measurement of ITO



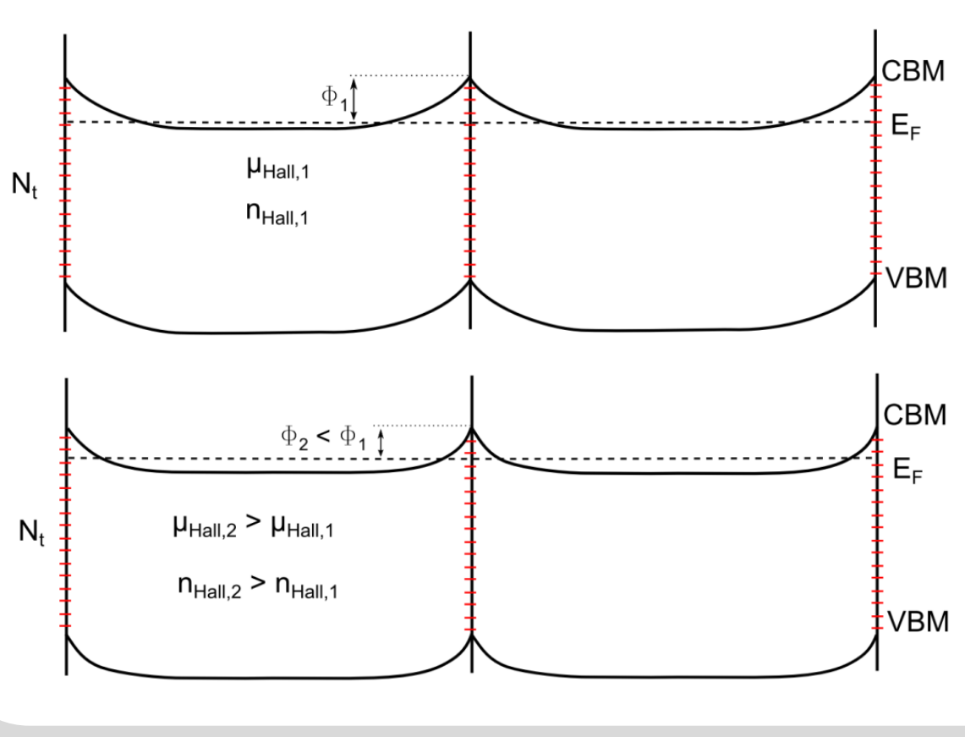
- Changes in conductivity caused by changes in carrier concentration *and* mobility
- Non-monotonic change of carrier mobility
- Changes in mobility related to dopant segregation
- Significant changes for T > 200 °C

Grain boundary scattering

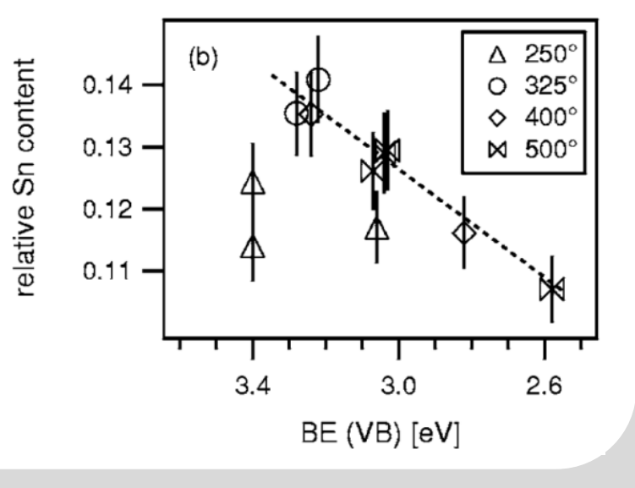
$$\mu_{GB} = \mu_0 \cdot \exp\left(-\frac{\Phi}{k_B T}\right)$$

Φ : *grain boundary barrier*
μ_0 : *bulk mobility*

„Setos Modell“



- Effective carrier concentration and mobility affected by GB barriers (trap density) and grain size
- GB barrier influenced by segregation
- Sn segregation was measured with XPS on ITO surfaces:
  function of temperature
  and Fermi level position
  (= carrier concentration)



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

5 Key Publications (2003-2014)

1) Gassenbauer, Y., et al. (2006). "Surface states, surface potentials and segregation at surfaces of tin-doped In_2O_3." Physical Review B **73: 245312.**

2) Erhart, P., et al. (2006). "First-principles study of intrinsic point defects in ZnO: Role of band structure, volume relaxation, and finite-size effects." Physical Review B **73(20).**

3) Walsh, A., et al. (2008). "Nature of the band gap of In_2O_3 revealed by first-principles calculations and X-ray spectroscopy." Physical Review Letters **100(16).**

4) Klein, A., et al. (2009). "Surface Potentials of Magnetron Sputtered Transparent Conducting Oxides." Thin Solid Films **518: 1197–1203.**

5) Klein, A. (2013). "Transparent Conducting Oxides: Electronic Structure–Property Relationship from Photoelectron Spectroscopy with in situ Sample Preparation." Journal of the American Ceramic Society **96(2): 331-345.**