Interface of Ferroelectrics

Shunyi Li, Feng Chen, Andreas Klein

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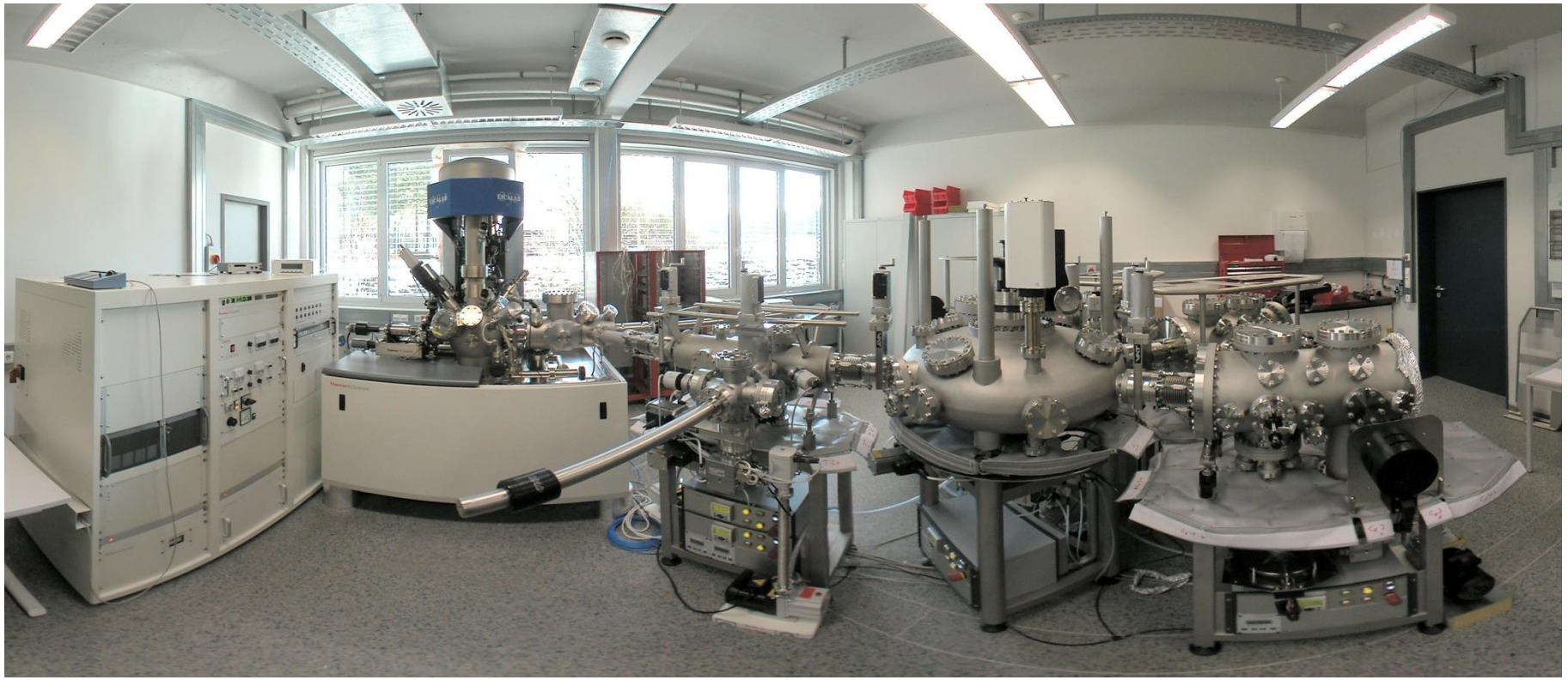
Surface Science



Task of project B7

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Elucidate the effect of polarization and charge for electrical fatigue in ferroelectrics

Part I: Switching dynamics → Poster S. Zhukov, H. von Seggern

Part II: The role of electrode interfaces to electrical fatigue

- **Barrier heights and band alignment**
- **Influence of ferroelectric polarization**
- **Electrochemical destabilization**

DAISY-MAT (XPS/UPS + preparation)

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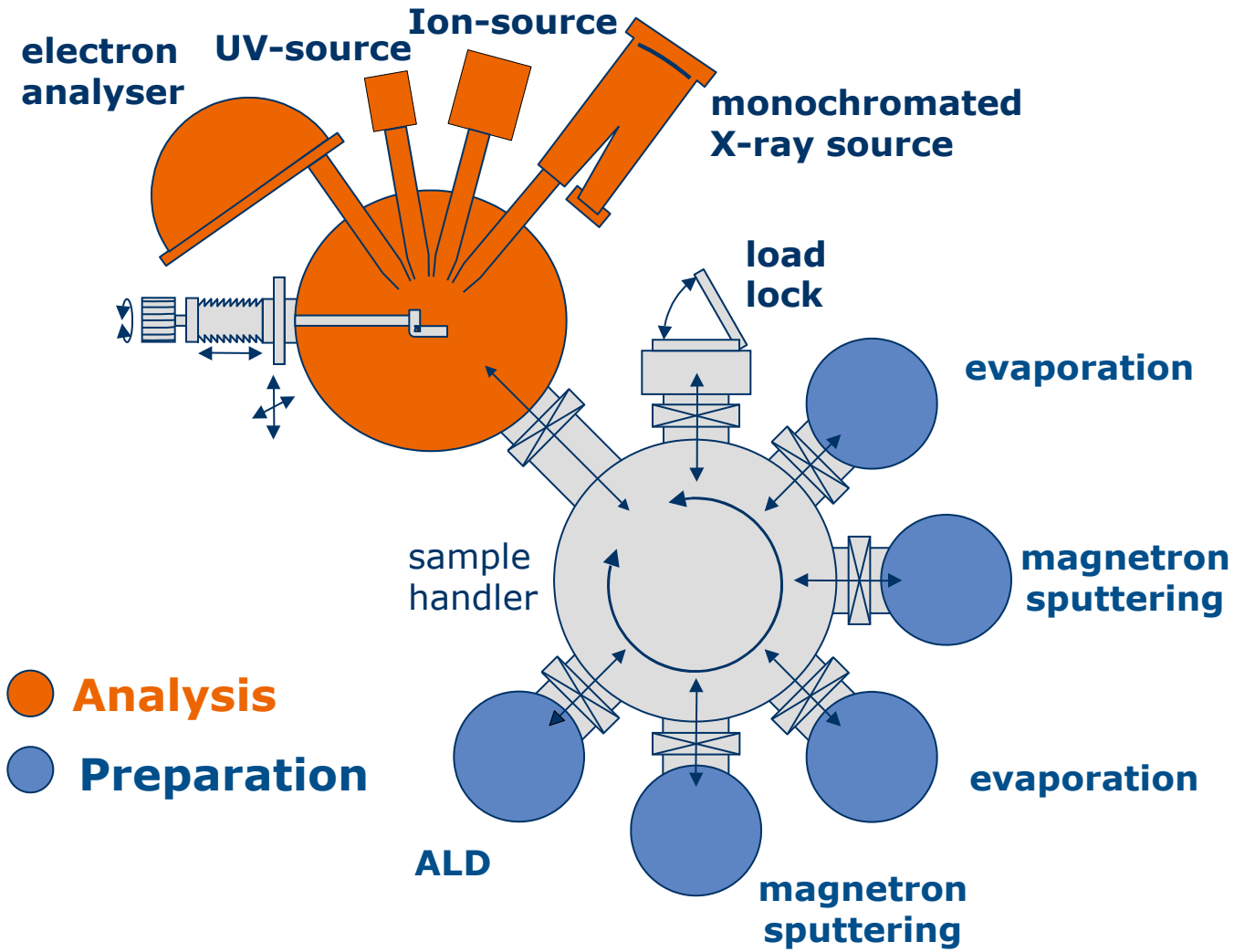
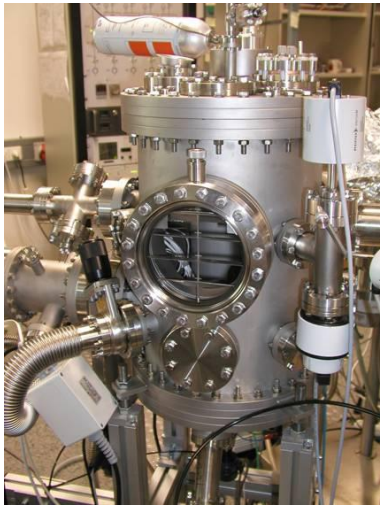
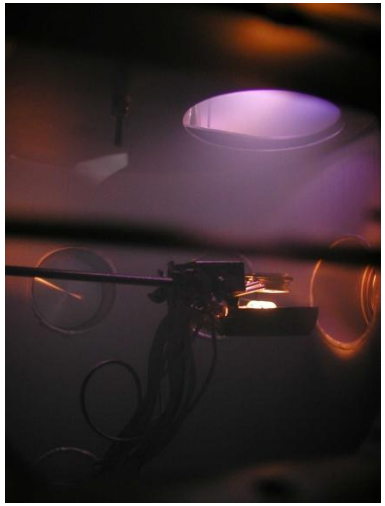
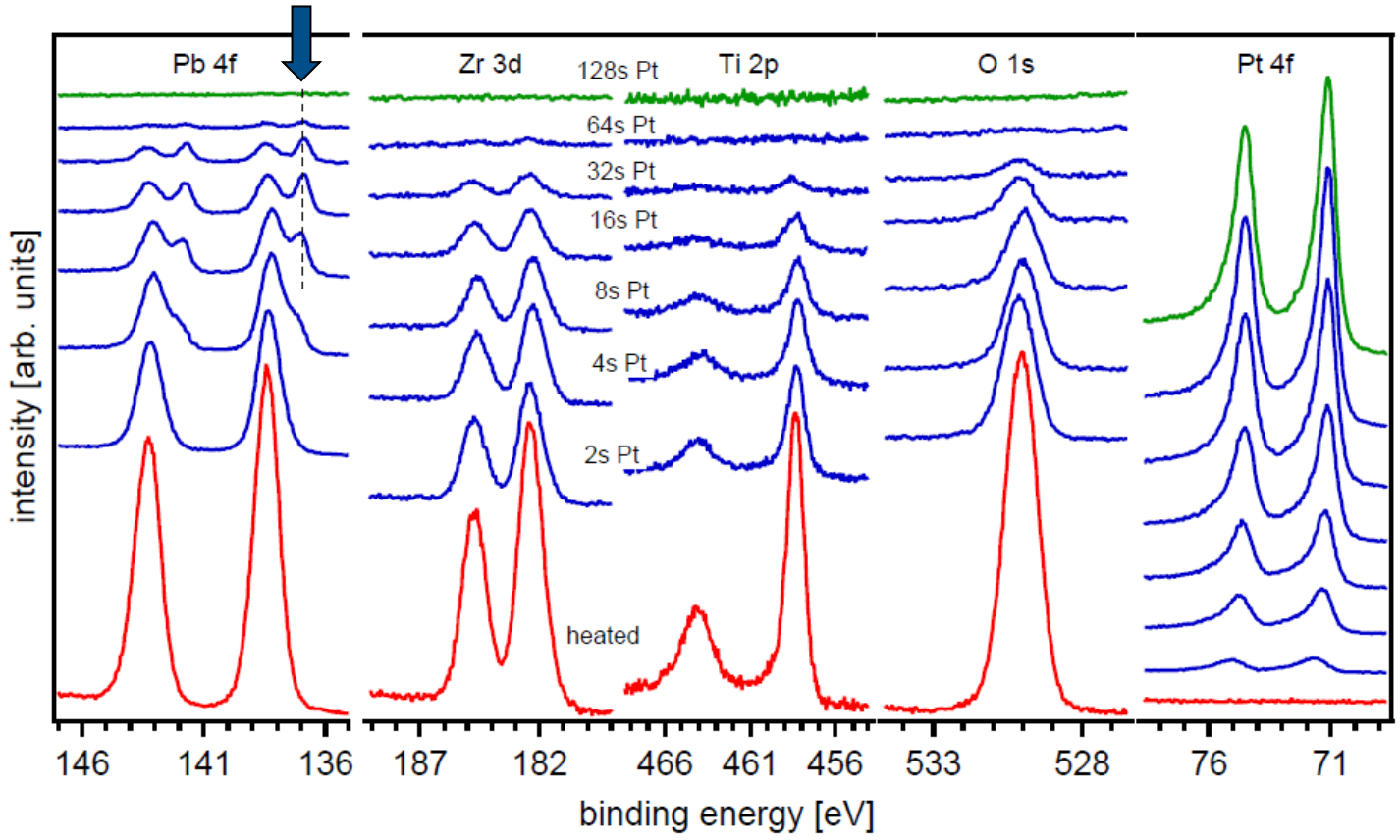






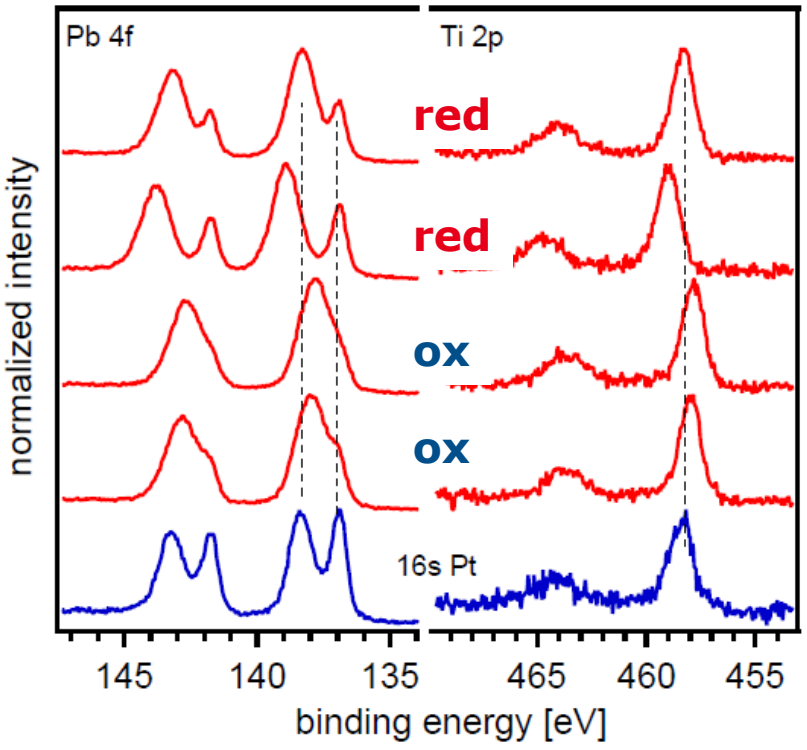
PZT/Pt interface formation

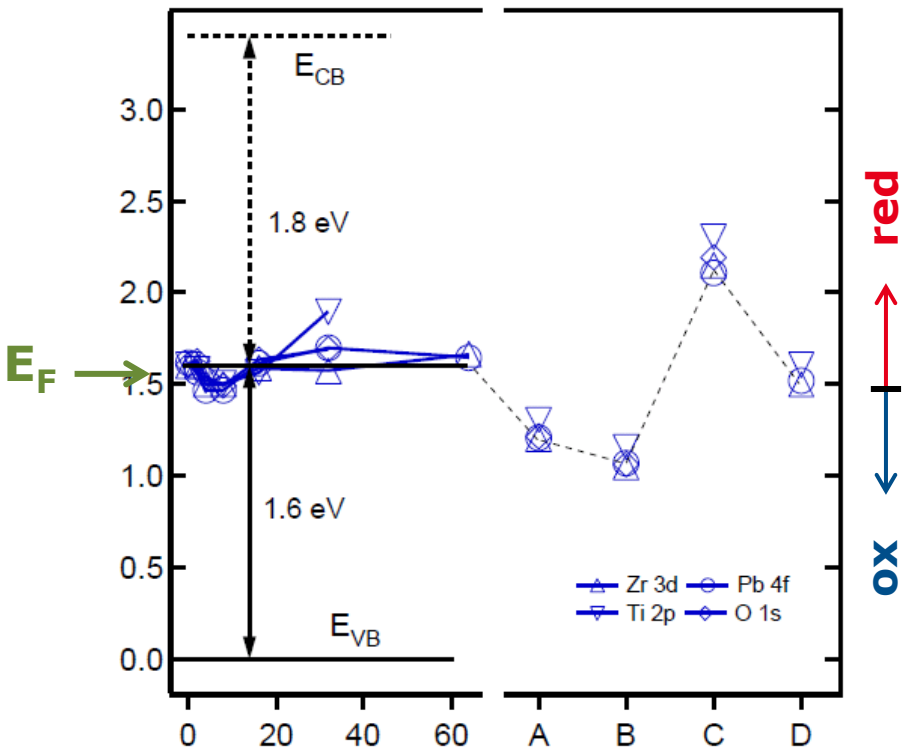


→ **Chemical decomposition of PZT during Pt deposition**

J. Phys. D **42** (2009) 215302

PZT/Pt interface treatment





→ **Reversible oxidation/reduction of PZT**

J. Phys. D **42** (2009) 215302

BFO/Pt interface treatment

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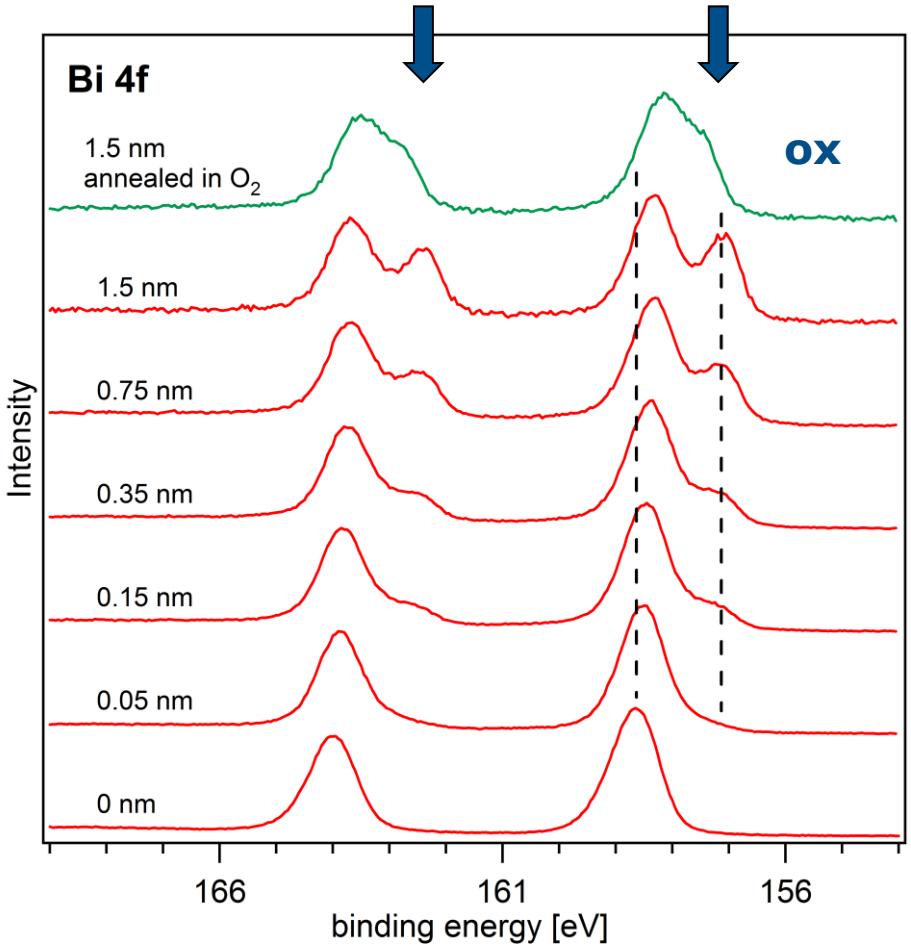
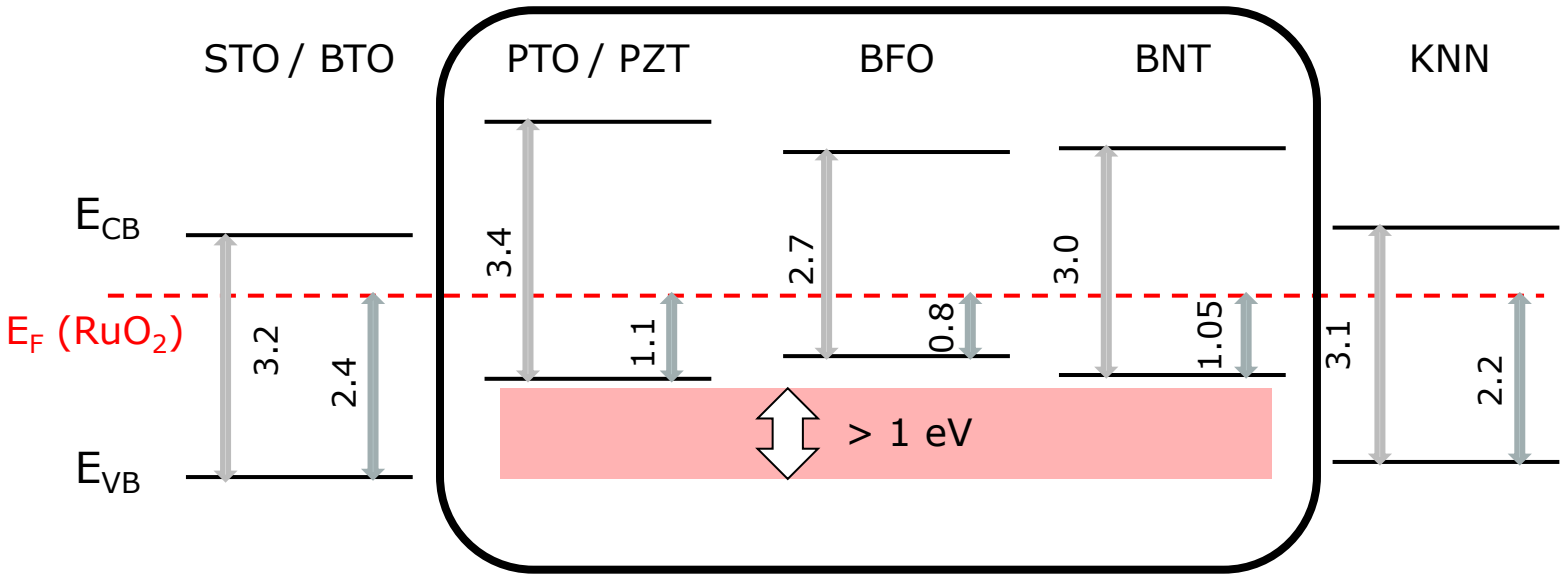


Energy band alignment of ferroelectrics



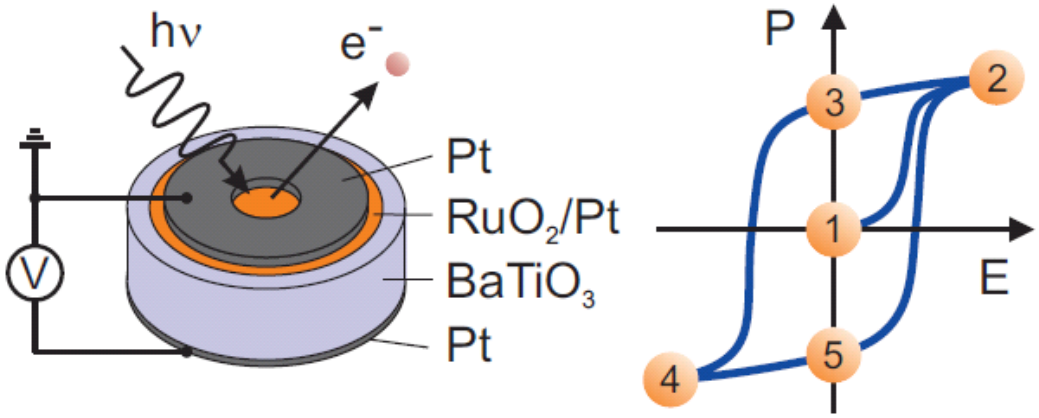
Strong defect formation with metal electrode

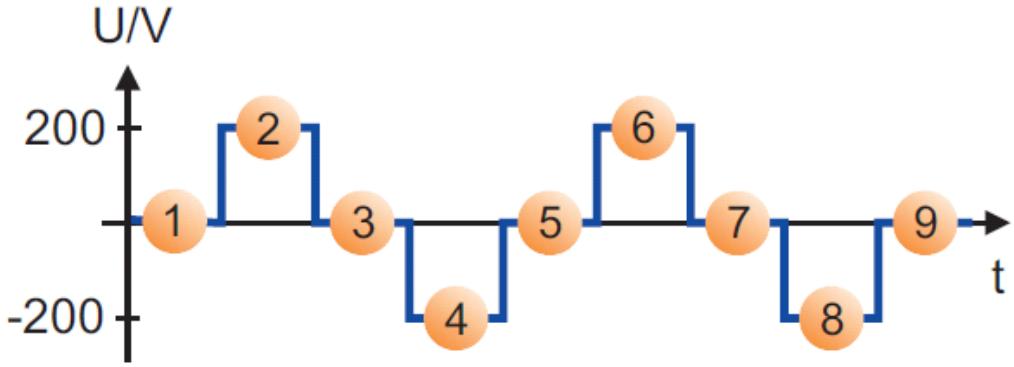
→ **Pb- and Bi-containing materials have high E_{VB}**

→ **Pb- or Bi-free materials have low E_{VB}**

Phys Rev B 88 (2013) 045428

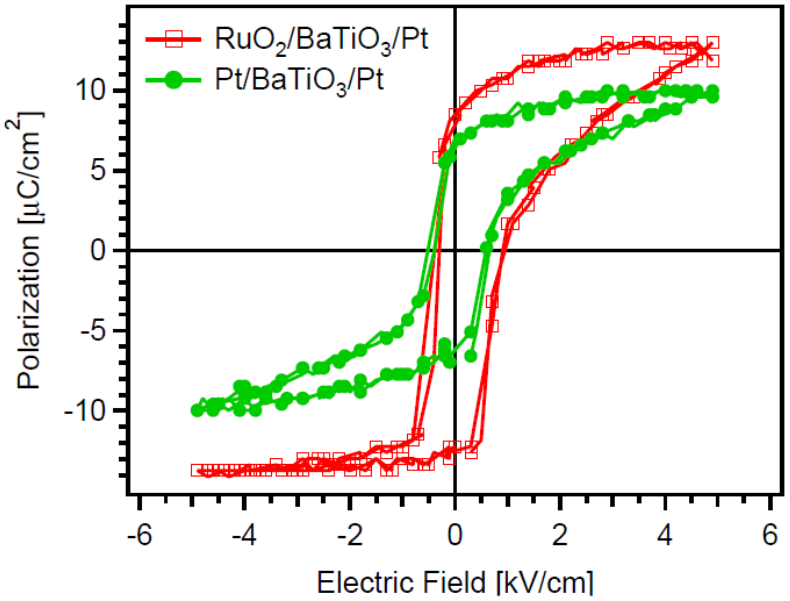
Polarization dependence of barrier



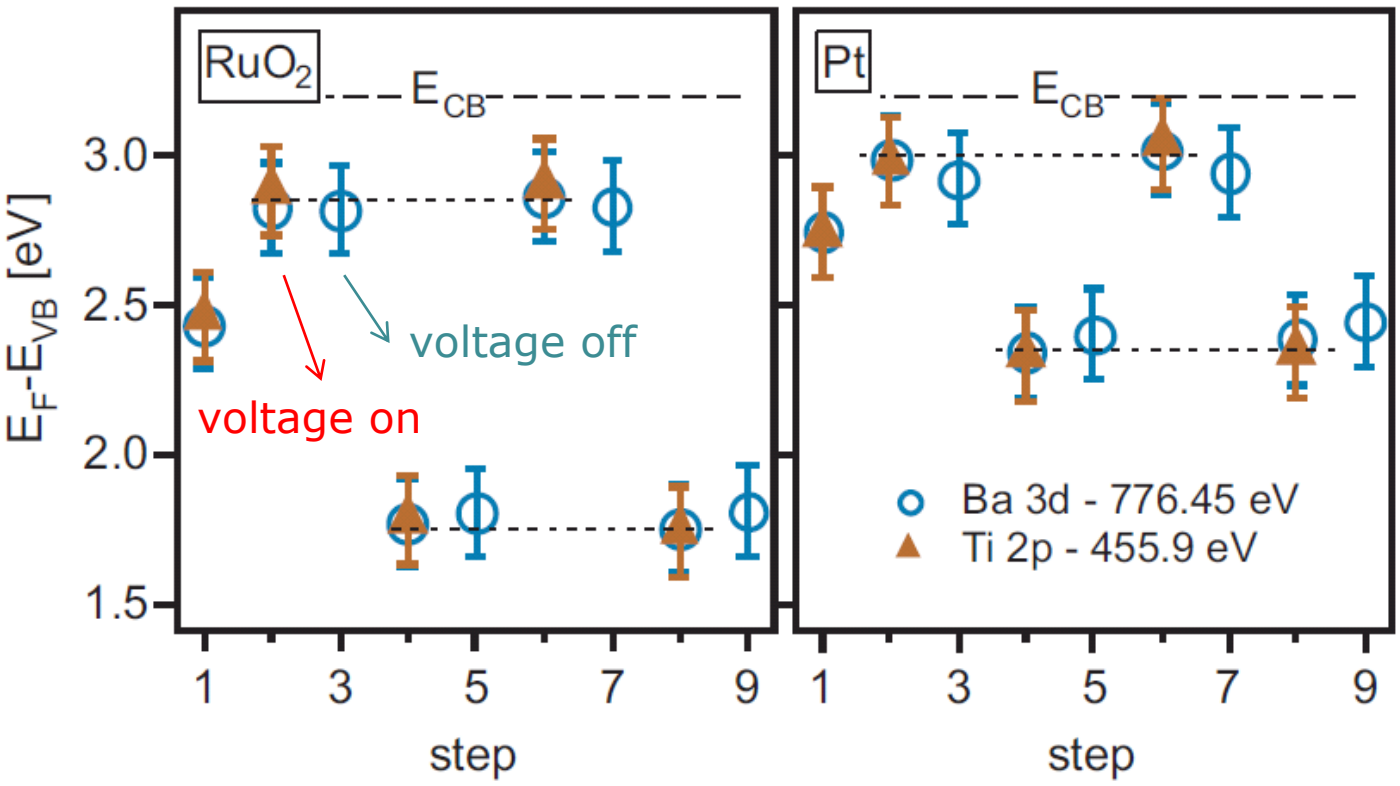


experiments

- sc-BTO/RuO_2
  sc-BTO/Pt
- pc-PZT/RuO_2
  pc-PZT/ITO
  pc-PZT/Pt
- pc-PLZT/ITO



Schottky barrier heights

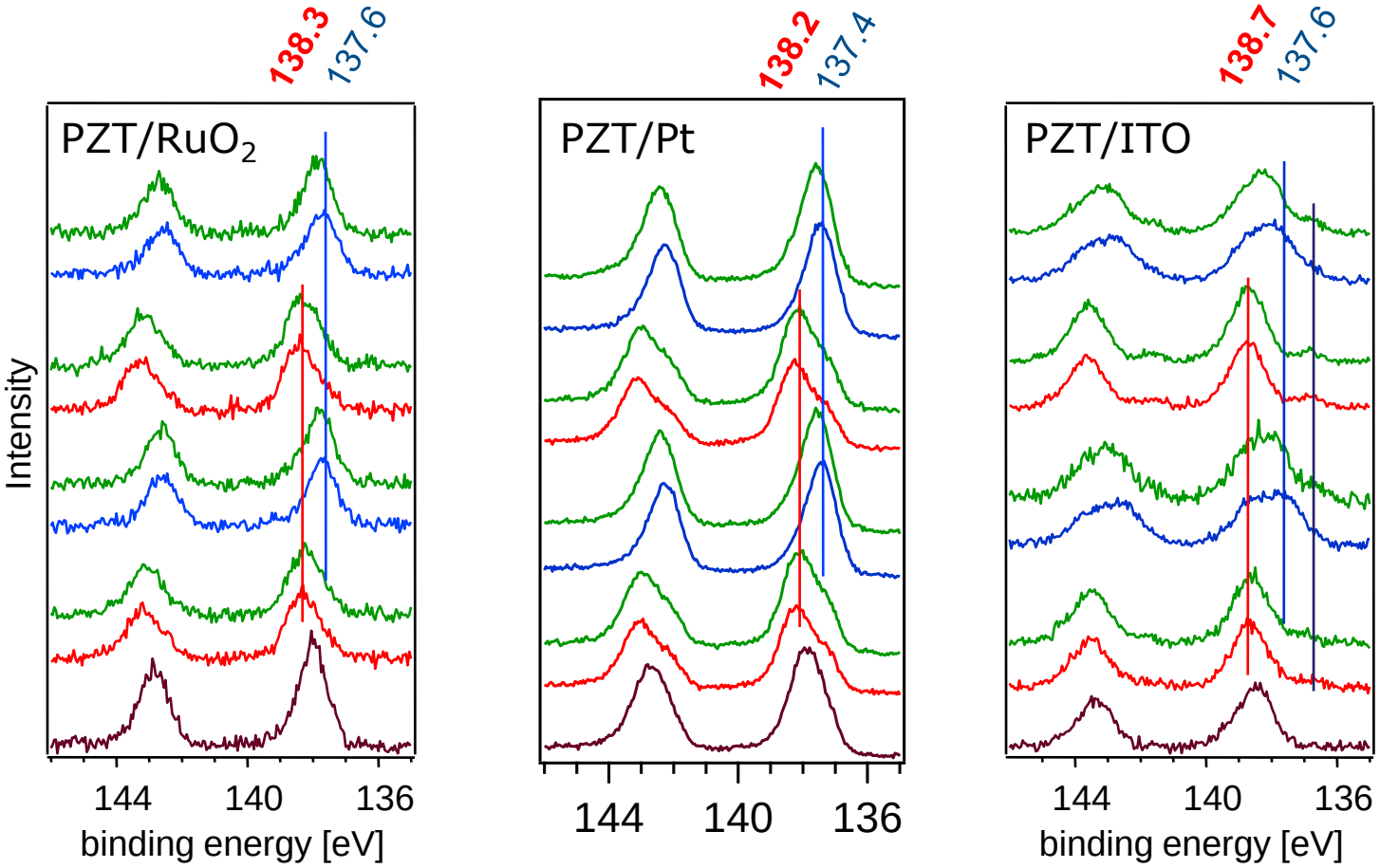


$\Delta\Phi_B \sim 1.1$ eV $\Delta\Phi_B \sim 0.65$ eV

→ **Barrier heights reproducibly shifted with polarization**

PRB 86 (2012) 094105

Stability of PZT during poling

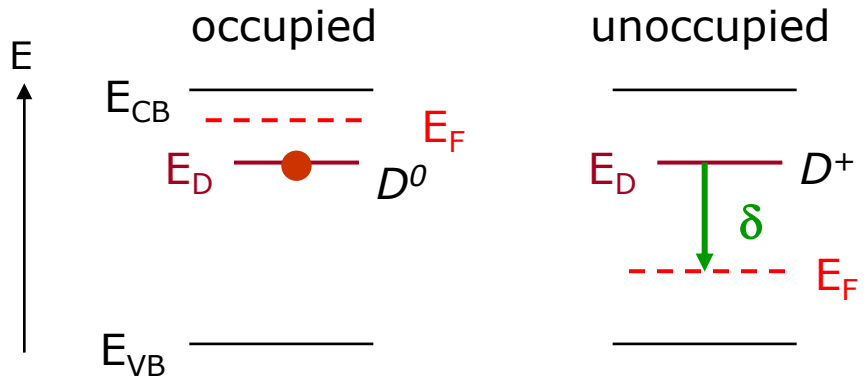


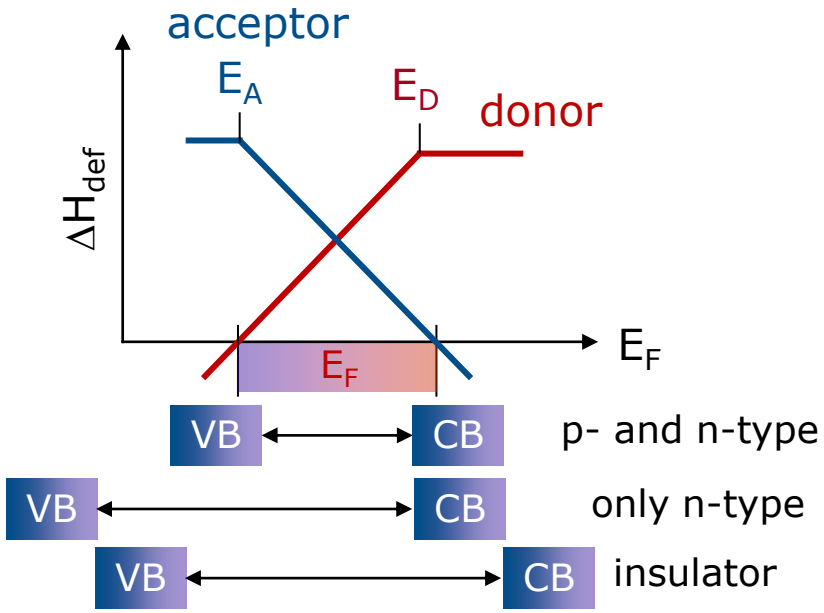
→ Formation of secondary phase during poling

Defect formation and Fermi energy

- **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 $D \rightarrow D^+ + e^-$





Fermi level changes too much

→ defects form and material decompose → fatigue appears

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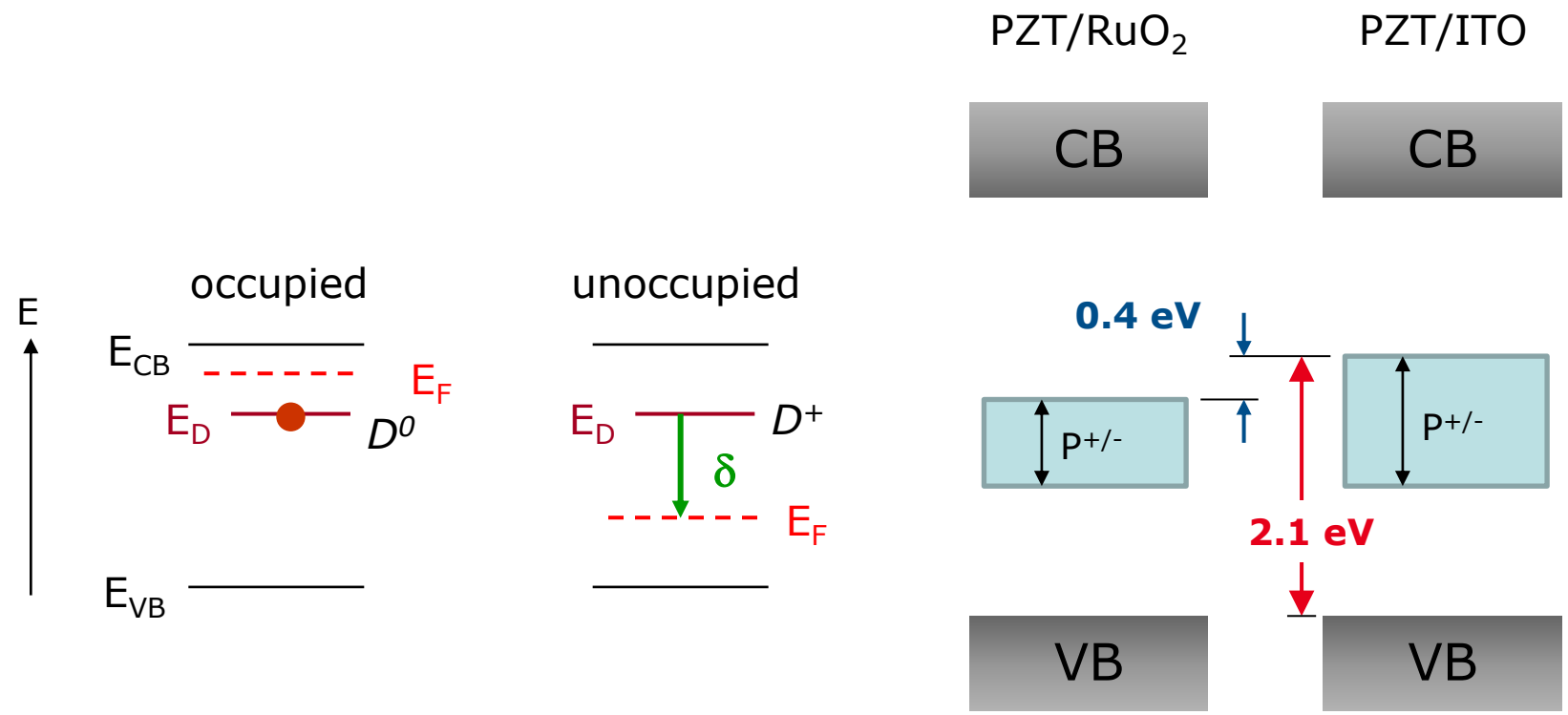
Defect formation and Fermi energy



Fermi level changes too much

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Stability of PZT – growth of thin films

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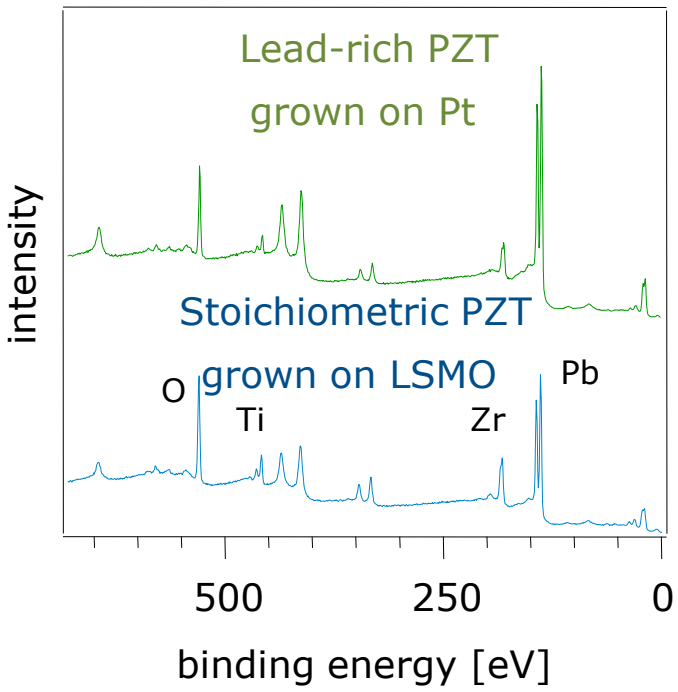
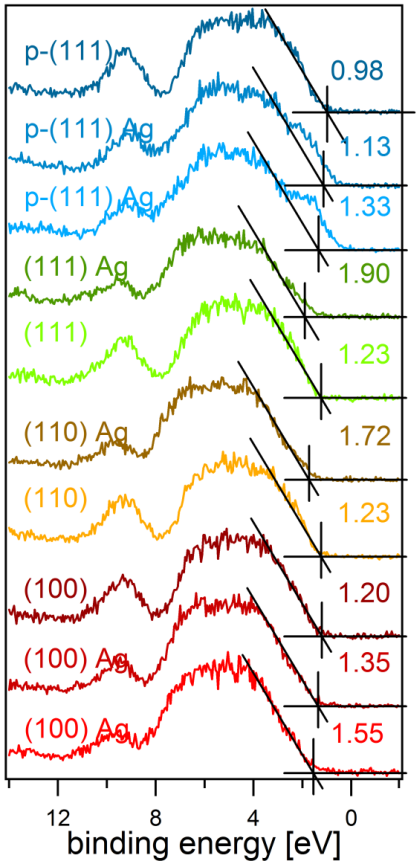
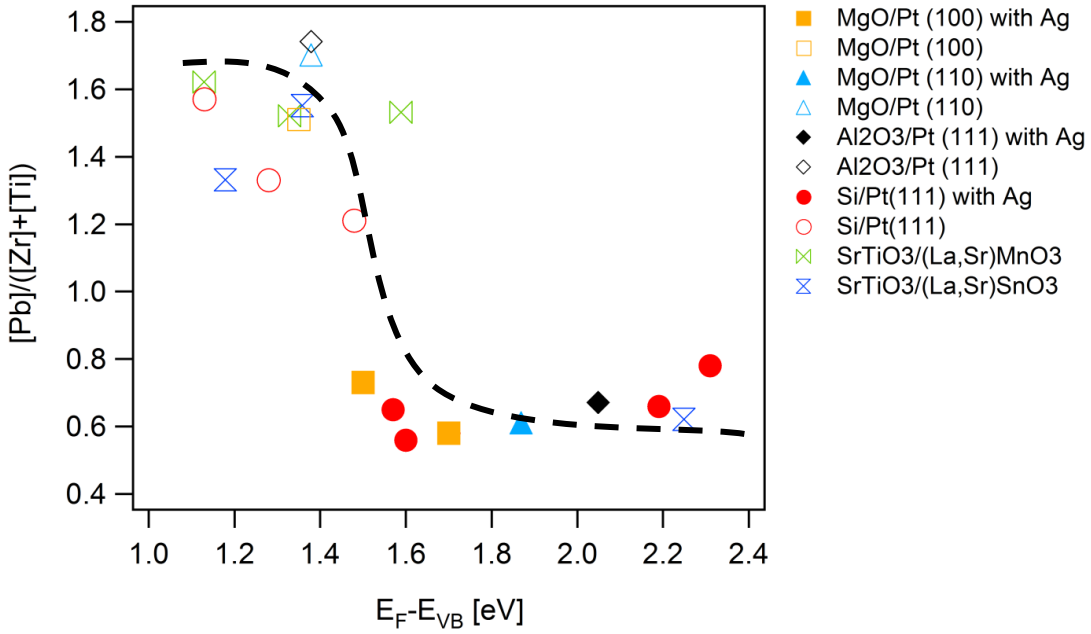
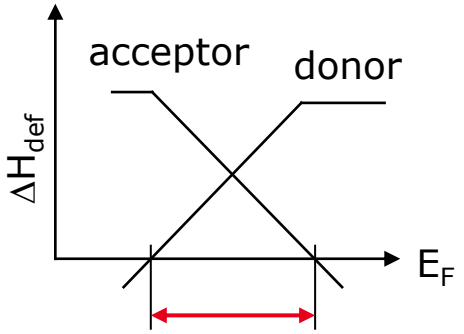


valence band E_{VB} of PZT



Fermi level position and composition





region of stability

→ The composition and phase of PZT films depends on the Fermi level position at the substrate/film interface

Summary

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- Defect formation at ferroelectric-metal interfaces
  - Reversible change of the Schottky barrier height
- Distinct energy level of ferroelectric materials
  - $BaTiO_3$, $SrTiO_3$ and $(K,Na)NbO_3$ show relatively low E_{VB}
  - Pb- and Bi-containing ferroelectrics show higher E_{VB}
  - Very different behavior for defect formation
- Dependence of barrier height on ferroelectric polarization
  - In-situ measurement with XPS
- Dependence of composition on Fermi level position
  - (Ir)Reversible defect formation during switching
  - Chemical destabilization while E_F approaches the limit

Publications since 2007

TECHNISCHE UNIVERSITÄT DARMSTADT

- Invited conference presentations: 6
- Total number of publications: 15
- Highlights:
  - *Barrier heights, polarization switching and electrical fatigue in $Pb(Zr,Ti)O_3$ ceramics with different electrodes*
    J. Appl. Phys. 108, 104106 (2010)
  - *$PbTiO_3/SrTiO_3$ interface: Energy band alignment and its relation to the limits of Fermi level variation*
    Phys. Rev. B 84, 045317 (2011)
  - *Polarization dependence of Schottky barrier heights at interfaces of ferroelectrics determined by photoelectron spectroscopy*
    Phys. Rev. B 86, 094105 (2012)
  - *Energy Band Alignment Between Anatase and Rutile TiO_2*
    J. Phys. Chem. Lett. 4, 4182-4187 (2013)
  - *Influence of orbital contributions to valence band alignment of Bi_2O_3, Fe_2O_3, $BiFeO_3$, and $Bi_{0.5}Na_{0.5}TiO_3$*
    Phys. Rev. B 88, 045428 (2013)

Acknowledgement

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- Prof. Dr. Andreas Klein for the guidance

Thank you for your attention