

THE FERMI ENERGY IN ACCEPTOR DOPED SrTiO₃ AND BaTiO₃

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In order to evaluate the presence of space charge layers and the magnitude of band bending at electrode interfaces of mixed ionic-electronic conductors we have evaluated the Fermi energies in the bulk and at interfaces of acceptor-doped SrTiO₃, BaTiO₃ and (Ba,Sr)TiO₃. While the interface Fermi energy can be directly obtained using photoelectron spectroscopy (XPS) if conducting electrode materials are deposited, the determination of the bulk Fermi energy is more challenging due to the high resistivity of the samples. One approach is to use XPS on thin films deposited on conducting samples. In general, we observed a good agreement between upper and lower limits of Fermi energies at thin films surfaces and at interfaces. Surprisingly, the Fermi energy is hardly observed below $E_F - E_{VB} \approx 2\text{eV}$ (see Fig. 1), although defect chemistry calculations predict values as low as $E_F - E_{VB} \approx 2\text{eV}$ for acceptor doped samples, such as Fe-doped SrTiO₃ or Mn-doped BaTiO₃.^{c,d} Even at anode interfaces of ionically polarized Fe-doped SrTiO₃ single crystals,^e at which the oxygen vacancy concentration should be very low, we have not observed lower Fermi energies.

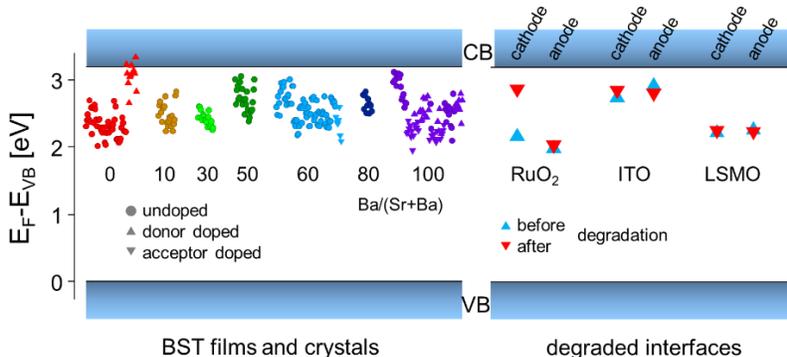


Figure 1 – (left) Fermi energy at surfaces of differently doped polycrystalline (Ba,Sr)TiO₃ thin films. Each data point represents one sample prepared using different parameters and on different substrates; (right) Fermi level positions at anode and cathode interfaces of Fe-doped SrTiO₃ single crystals before and after ionic polarization at 210°C.

The too high Fermi energies might result from the presence of additional defect levels, which pin the Fermi energy. In order to resolve the discrepancy, temperature dependent conductivity measurements have been applied. Starting with electronically highly conducting reduced samples, these are slowly re-oxidized during temperature cycling with permanently recording the conductance. These measurements reveal activation energies in dependence on conductivity, which can be directly compared to defect chemistry calculations. In particular, the activation energy should exhibit a plateau in dependence on conductivity if the Fermi level is pinned at a certain defect level. This approach allows to quantify the energy levels of defects in the relevant temperature regime, in particular those related the 3+/2+ valence change of Fe and Mn. Such levels are clearly observed for single crystal and polycrystalline BaTiO₃ but not for Fe-doped SrTiO₃. In the latter case, the samples directly convert from metallic behavior at resistivities $<10^6$ S/cm to p-type behavior. All measurements being in good agreement with present defect chemistry models. The origin of the too high Fermi energy therefore remains unresolved.

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