Modifying the ZnO workfunction by adsorption of F4TCNQ

Hybrid inorganic/organic semiconductor (HIOS) heterojunctions have opened up new opportunities for (opto-) electronic devices due to their potential for combining the favorable properties of two distinct material classes. In project A8 we employ molecular acceptor interlayers to tune the work function of the substrate and thus change the energy level alignment (ELA) between the Fermi-level of the substrate and the energy levels of an organic semiconductor. This allows to adjust the ELA to favor e.g. energy or charge transfer across the interface.

We demonstrate, that the work function of ZnO can be controlled over wide ranges (up to 2.8 eV) by adsorbing the molecular electron acceptor F4TCNQ in the (sub-) monolayer regime. Although this is phenomenologically similar to what was observed for metal surfaces, the mechanism of the Φ increase differs markedly for the inorganic semiconductor.
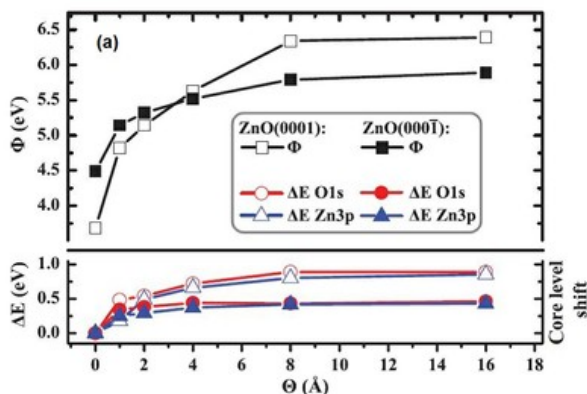

Fig. 1: Evolution of the work function (Φ) as a function of F4TCNQ nominal thickness (Θ) on the ZnO(000-1)-O and ZnO(0001)-Zn surfaces and relative binding energy shifts ΔE of the O1s and Zn3p core levels upon adsorption of F4TCNQ.

$\Delta\Phi$ relies on two complementary mechanisms due to electron transfer to the surface-adsorbed acceptor, i.e., band bending in the inorganic semiconductor

and an interface dipole, yielding $\Delta\Phi_{BB}$ and $\Delta\Phi_{ID}$, respectively (see Fig. 1). We find, that minute electron transfer is sufficient to induce significant $\Delta\Phi$s (see Fig. 2).
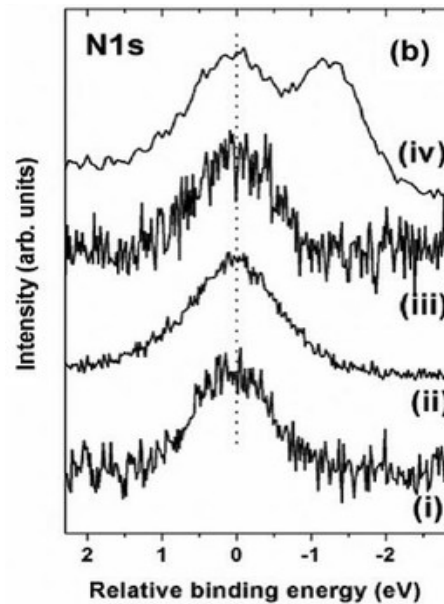

Fig. 2: N1s core-level spectra of (i) 0.5-Å F4TCNQ on ZnO(0001), (ii) 8-Å F4TCNQ on ZnO(0001), (iii) 0.5-Å F4TCNQ on ZnO(000-1), and (iv) 60-Å F4TCNQ on Au. The low-binding energy component in spectrum (iv) is from F4TCNQ chemisorbed on Au with a net electron transfer of approximately 0.3-0.4 eV.

Controlling the work function of ZnO and the energy-level alignment at the interface to organic semiconductors with a molecular electron acceptor

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