Determination of the V_{oc}-generating interfaces within perovskite-based solar cells

Norbert Koch[1,2]

[1] Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, 12489 Berlin, Germany.

[2] Institut für Physik & Center for the Science of Materials Berlin, Humboldt-Universität zu Berlin, 12489 Berlin, Germany.

To this day, the band alignment at perovskite interfaces is of paramount importance to gain a deeper understanding of the device physics, yet it remains as a heavily debated topic in perovskite solar cells. Despite its importance, the band alignment at perovskite/charge transport layer junctions and throughout complete device stacks - under both dark and light conditions - has rarely been mapped to directly locate the built-in field. Some reports interpreted the light-induced shift of energy levels at NiOx/perovskite and SnO_2/perovskite interfaces as evidence of band bending. However, such a shift - known as the (surface) photovoltage (SPV) effect – can stem from two potential mechanisms: textbook band flattening or band realignment due to redistributed photogenerated charge carriers at the junctions. The observed SPV shifts in the full device stacks were mostly considerably smaller than the device open circuit voltage (V_{oc}). These ambiguities underscore the imperative to resolve the band alignment of complete device stacks under both dark and illuminated conditions.

In this work, using *operando* ultraviolet photoelectron spectroscopy (UPS), we unravel the band alignment within a state-of-the-art p-i-n perovskite solar cell employing triple-cation perovskites with self-assembled monolayer (SAM) and C_{60} as charge transporting layers. Sequential in-situ deposition of the electron transport and electrode layers reveals the full energy landscape of the device both in the electronic ground state and under device operating conditions. These *operando* measurements reveal a near flat band alignment across the p-i-n interfaces and a significant illumination-induced energy level realignment of ca. 0.9 eV at the buried SAM/perovskite interface, which gives rise to the observed surface photovoltage shifts in the layers above. The resulting band alignment across the full device stack further reveals a build-in potential of 1.42 eV, determined by the effective work functions of the electrodes, and provide direct insights into dominant energy loss pathways in high efficiency p-i-n perovskite solar cells.