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Substrate-Controlled Electronic Properties of Perovskite Layer in Lateral Heterojunction Configuration

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Abstract— In this work, we fabricated halide perovskite-based lateral heterojunction devices with nickel oxide/titanium oxide all back contacts, allowing us to access the perovskite surface directly for analysis with various advanced techniques, including ultraviolet and X-ray photoemission spectroscopy (UPS/XPS), Kelvin probe force microscopy (KPFM), and surface photovoltage (SPV), to discern the role of selective contacts. Specifically, by tuning of the selectivity of the contacts, e.g., through varying the level of nickel oxidation, we show that the selectivity of the contacts induces a gradient in carrier concentration across the surface of the active layer that is connected to carrier extraction at the buried interface and hence to device functionality.

Keywords—lateral heterojunction, perovskite solar cell, carrier concentration, selectivity

I. SUMMARY OF THE MAIN FINDINGS

In this study, lateral heterojunction (LHJ) perovskite devices were fabricated and used as an experimental platform to study the impact the substrate has on the perovskite properties in both the vertical and lateral directions (Figure 1). These all back-contact devices have n-type TiO_x as the electron extraction layer on one side of the substrate, p-type NiO_x as the hole extraction layer on the other side, a continuous perovskite (MAPbI₃) film on top of the patterned substrate, and a 110–120 μm gap between the two contacts that defines the channel length of the device. This architecture is ideal for studying the role of the contacts, as it allows us to directly probe the energetics of a formed perovskite device using surface sensitive X-ray photoemission spectroscopy (XPS) and Kelvin probe force microscopy (KPFM) measurements.

Herein, we first utilize the surface sensitive XPS technique, which is ideal for probing the energetics at the top surface but renders us blind to what might be happening between the top surface and the buried contacts. By tracking the binding energy of the main I 3d and Pb 4f core levels of perovskite film (which

can be viewed as existing a set distance away from the valence band maximum using Kraut method [1]) as a function of the lateral position on the LHJ structure, we obtain the perovskite energetics in lateral direction across the junction. Then, we alter the selectivity of the NiO_x contact by employing a shorter duration anneal such that the conversion from nickel (metallic) to NiO_x (strongly p-type) was less complete [2,3], and repeated measurements. Results show that while both samples produce smooth carrier gradients across the junction, suggesting a rather intrinsic perovskite with low defect concentrations, the core levels of the perovskite on top of the less oxidized Ni/NiO_x shift to higher binding energy than the well oxidized NiO_x contact, resulting in a smaller potential drop (~120 vs 600 meV) across the junction.

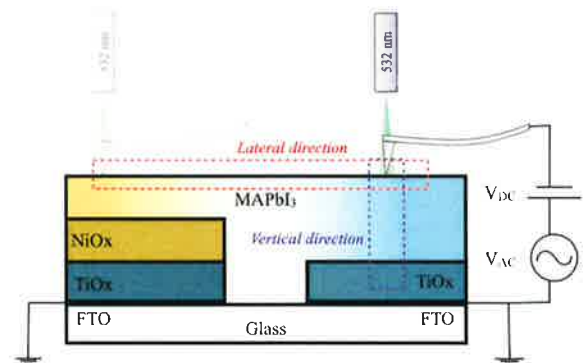


Fig. 1 Schematic of the device architecture in a KPFM set up. The sample is grounded on both sides, both for KPFM and PES measurements. KPFM provides information of MAPbI₃ energetics in vertical direction (purple rectangle), while we use PES to assess this information in lateral direction (red rectangle).

To better understand how the selective contacts may be impacting this carrier gradient, we then complement these measurements with KPFM measurements in dark and under

illumination that provide the surface potential value and the surface photovoltage (SPV) created upon illumination. This SPV can be related to the redistribution of photogenerated charge carriers in space, caused by the superposition of band flattening at the interface due to carrier extraction and surface band bending due to the filling of defect states. Thus, it can provide information on perovskite energetics in the vertical direction (from the top surface to the back interface), revealing the role of the bottom contacts in determining the energetics at the top and showing that much of the loss in this gradient for the less oxidized case is due to large rates of recombination/poor carrier extraction at the less oxidized NiO_x contact.

II. RESULTS

A. Gradual Fermi level shift in lateral direction

The main XPS core level in MAPbI₃ (iodine I 3d) shows a shift of ~600 meV when scanning across the channel (Fig. 2) of a device with TiO_x and well oxidized NiO_x. This is comparable to the ~700 meV shift reported in the literature for the same kind of substrates [4, 5]. Such a shift in the iodine core level is representative of a change in the electrostatic potential across the channel. Moreover, similar shifts can be obtained for samples made with altered stoichiometry, indicating that compositional changes in the perovskite film can be excluded as the origin of the observed behavior.

In contrast, for the device with less oxidized NiO_x, we observe an identical I 3d core level position on top of the TiO_x electrode, but a substantially higher binding energy (w.r.t the oxidized case) on top of the NiO_x electrode, resulting in a smaller shift across the junction (~120 meV). This indicates that the selectivity of the substrate (i.e., its aptitude to provide low recombination current of minority carriers and low resistance of majority carriers) dictates the position of the Fermi level in MAPbI₃. The difference in carrier concentration between the two sides then creates a gradient between them. Moreover, for both samples we observe that the shift in core levels and thus the change in electrostatic potential is gradual and extends over the whole channel in the lateral direction. Such a gradual change is indicative of a low effective doping and defect concentration in the MAPbI₃ [6].

B. SPV-based measurements of perovskite energetics in vertical direction

To investigate the role the bottom contacts may play in setting this carrier gradient, we then conducted KPFM scans on the perovskite surface far away from the channel area in dark and under illumination (we used a 532 nm laser, with an estimated photon flux $\approx 5.5 \times 10^{21} \text{ m}^{-2}\text{s}^{-1}$). Values of the contact potential difference (CPD) between the sample and the tip obtained for the device with poorly oxidized NiO_x are shown in the form of histograms in Fig. 3. These data are extracted from $3 \times 3 \mu\text{m}^2$ CPD maps. The difference in CPD values in the dark measured on top of the NiO_x and TiO_x sides is 110 mV, which correlates well with the difference in core levels measured by XPS for the same LHM sample (~120 meV). This confirms that the substrate controls the position of the Fermi level in MAPbI₃ under equilibrium dark conditions, and that the XPS measurements were not affected by photovoltage effects.

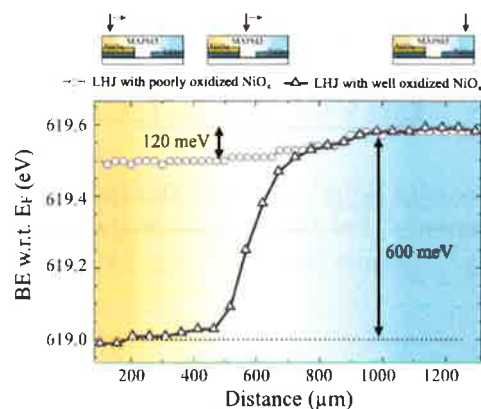


Fig. 2 Gradual shift in I 3d core level as a function of the position on the sample. Markers represent the position of the core level peaks, lines are guides to the eye; grey circles correspond to the data acquired on LHM device with poorly oxidized NiO_x, while black triangles correspond to the data from LHM device with well oxidized NiO_x.

Under illumination, the CPD changes very differently on each side. For MAPbI₃ on top of TiO_x we observe a strong positive change of ~500 mV, while we observe a smaller but negative change of ~320 mV on top of the NiO_x side. This suggests that the carrier extraction and accumulation dynamics on the two sides lead to opposite trends in the overall carrier dynamics. For both samples, we note that reduced lead centers act as donor states at the perovskite surface, making the perovskite appear n-type with the Fermi level position close to the conduction band minimum [7-9]. Therefore, for both samples, downward surface band bending can be expected, which normally contributes negatively to the SPV since illumination tends to flatten the bands and thus decrease the surface potential (and the CPD).

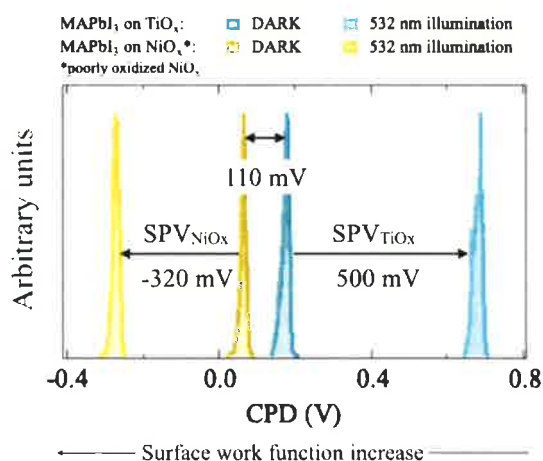


Fig. 3 Normalised histograms extracted from CPD maps showing distributions of CPD values on top of the TiO_x and NiO_x sides for the LHM with poorly oxidized NiO_x.

In addition to these accumulation effects at the surface, SPV is also affected by contributions from interface band bending and charge extraction. Electron extraction at the MAPbI₃/TiO_x interface gives rise to an increase in CPD under illumination,

counteracting electron accumulation at the surface. In contrast, hole extraction at the interface between perovskite and NiO_x also contributes negatively to the SPV, resulting in aligned affects. Thus, one would expect that the SPV magnitude should be larger on top of NiO_x than on top of TiO_x. However, this is not observed, suggesting that the NiO_x side has lower carrier extraction ability/selectivity at the interface compared to the TiO_x.

III. PERSPECTIVES, CHALLENGES AND PENDING ISSUES

Our strategy of combining various advanced characterization techniques to probe the optoelectronic response as a function of the perovskite/substrate interface opens an avenue to tailor the selectivity of the contact materials to enhance the performance in perovskite-based devices. This work also suggests that selectivity in PSCs is related to not only their energetics, but also their terminating groups that affect interface recombination. In this direction, new materials for contact layers, changing the level of oxidation of the extraction layers, and introducing dedicated interface layers for passivation should all provide means to improve selectivity of the interfaces and therefore device parameters.

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