Electrical field profile and doping in planar lead halide perovskite solar cells

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Hybrid lead halide perovskites (PVKs) have emerged as novel materials for photovoltaics and have rapidly reached very large solar to electricity power conversion efficiencies. As occurring with other kind of solar technologies establishing the working energy-band diagram constitutes a primary goal for device physics analysis. Here, the macroscopic electrical field distribution is experimentally determined using capacitance-voltage and Kelvin probe techniques. Planar structures comprising CH3NH3PbI3–xClx PVK exhibit p-doping character and form a p-n heterojunction with n-doped TiO2 compact layers. Depletion width at equilibrium within the PVK bulk has an extent about 300 nm (approximately half of the layer thickness), leaving as a consequence a significant neutral zone towards the anode contact. Charge collection properties are then accessible relying on the relative weight that diffusion and drift have as carrier transport driven forces.

Recently, hybrid lead halide perovskites (PVKs) have reached very large solar to electricity power conversion efficiencies,1,2 with efficiencies 16%.3 In the last two years, many different configurations have been analyzed varying cell configuration, selective contacts, and even the kind of perovskite utilized.1,2 Despite this broad range of variations, probably the most extensively studied has been the CH3NH3PbI3 perovskite (or its analogous but using chlorine precursor: CH3NH2PbI3–xClx) as absorber materials, in combination with electron (TiO2) and hole (spiro-OMeTad) selective contacts. The organic cation CH3NH3+ is mainly responsible for the structural stability of the PVK, while the electronic properties are largely determined by metal and halide hybridized orbitals.4–6 In spite of the spectacular advances in cell efficiency, many aspects of this system are not completely understood. One central piece of information for understanding the photovoltaic operation of these solar cells is the energy-band diagram. In general, the band diagram provides key knowledge of several aspects intervening into the working mechanisms of solar cells, namely, the spatial distribution of the macroscopic electrical field within the absorber layer determining charge collection properties; the direction of electrical field and dipole layer at contacts; the local density of electron and hole carrier at each point of the device. Here, we report on characteristic energy features of PVK solar cells based on the combined use of capacitance-voltage ($C-V$) and Kelvin probe force microscopy (KPFM).

Because of the energetic offset between work functions of the absorber and each contact material, it is expected the formation of a built-in voltage $V_{bi}$ in equilibrium conditions. There are several ways to accommodate $V_{bi}$ depending on the electrostatic characteristics of the bulk materials and interfaces. For undoped absorber materials a rather constant electrical field along the whole bulk is expected as occurring for p-i-n structures. However, doping alters the electrical field distribution by the presence of charged impurities or defects of structural or chemical origin introduced during device processing. Homogeneous defect density gives rise to quadratic band bending profiles, which concentrate the electrical field in the vicinity of the contact and leave large quasi-neutral zones within the bulk layer. Charge transport of minority carriers throughout quasi-neutral zones occurs by diffusion while drift governs the carrier motion within band bending regions. Then collection efficiency is governed by the electrical field distribution which might exhibit several profiles depending on the doping density and applied voltage.

It has been recently suggested that perovskite-based solar cells either with flat or mesoporous electron transport material operate as a p-i-n-type structure.7 Electrical field distribution has been addressed in cells comprising mesoporous TiO2 by capacitive techniques with electron transporting layer electrically modeled as a homogeneous layer.8 Spatially resolved electron beam-induced current has been reported to support that carriers are efficiently collected throughout the whole absorber layer.7 Although high electron beam-induced signal would indicate rather good transport properties, there is no direct determination of the electrical field distribution that allows accounting for the relative weight that diffusion and drift have as carrier transport driven forces. Here, we use planar structures of the type FTO/TiO2/PVK/2,2’,7,7’-tetrakis(N,N-di-p-methoxyphenylamine)-9,9-spirobifluorene(spiro-OMeTad)/Au to show that CH3NH3PbI3–xClx PVK exhibits p-doping character and forms a p-n heterojunction with n-doped TiO2 compact layers. Planar configuration has been chose as it offers a simpler configuration in comparison with samples with nanoporous scaffold, and the reported effect can be just attributed to PVK. We have observed that depletion width at equilibrium within the PVK bulk has an extent about 300 nm (approximately half of the layer...

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thick). When cells are constructed without the hole-transporting layer spiro-OMeTad the amount of PVK doping is dramatically reduced yielding full depletion devices even at voltages below 0.5 V forward bias as in a p-i-n structure.

All the studied cells of structure FTO/TiO\textsubscript{2}/PVK/spiro-OMeTad/Au were prepared\textsuperscript{7} over FTO (Pilkington TEC15, 15 Ω/sq resistance), which were previously etched with zinc powder and HCl (2 M). The FTOs substrates were cleaned with soap (Hellmanex), deionized water, and ethanol, followed by sonication in a mixture acetone/isopropanol (v/v = 1:1). Before the deposition of electron selective contacts, substrates were treated in a UV-O\textsubscript{3} chamber for 30 min. The TiO\textsubscript{2} compact layer was deposited by spin-coating a mildly acidic solution of titanium isopropoxide in ethanol, and heated at 500 °C for 30 min. The mixed halide perovskite was prepared by spin coating 100 µl of perovskite precursor, 40% (w/w) DMF solution of CH\textsubscript{3}NH\textsubscript{3}I, and PbCl\textsubscript{2} \textsubscript{(3:1 molar ratio)}, onto flat TiO\textsubscript{2} substrates at 2000 rpm for 60 s. Then, films were placed on a heated stage at 100 °C under an air stream. The perovskite-adsorbed films were covered with a hole transporting material (HTM) layer by spin coating at 4000 rpm for 30 s outside of the glovebox. The HTM recipe was prepared dissolving 72.3 mg of spiro-OMeTad, 28.8 µl of 4-tert-butylpyridine, and 17.5 µl of a stock solution of 520 mg/ml lithium bis-(trifluoromethyl)sulfonylimide in acetonitrile in 1 ml of chlorobenzene. Other set of cells were prepared without HTM. Finally, 60 nm of gold was thermally evaporated in the vacuum chamber on top of the device to form the electrode contacts. An active area electrode area of 0.224 cm\textsuperscript{2} per pixel is defined by the FTO and the Au contacts. The device fabrication was carried out under controlled atmospheric conditions and a humidity of <0.5 ppm, and the HTM layer deposition was carried out at room conditions. Current density–voltage, J – V, curves were recorded under AM1.5 100 mW cm\textsuperscript{-2} simulated sunlight (ABET Technologies Sun 2000) previously calibrated with an NREL-calibrated Si solar cell. The J – V measurements were performed using a 0.08 cm\textsuperscript{2} mask. Impedance spectroscopy measurements were carried out with a PGSTAT-30 from Autolab, in dark conditions and at different forward biases, by applying a 20 mV AC voltage perturbation over the constant forward DC applied bias, between 0 and 1 V, with the frequency ranging between 1 MHz and 0.05 Hz. Capacitance values are obtained at frequencies of 600 Hz as a plateau is observed in the capacitance vs frequency plot at frequencies in the range of 100 Hz– 10 kHz. KPFM was performed using a Nano-Observer Atomic Force Microscope (Concept Scientific Instruments).

Typical J – V curves are presented in Fig. 1 for cells with and without spiro-OMeTad as HTM. Figure 2(a) shows energy levels of TiO\textsubscript{2} and PVK layers. TiO\textsubscript{2} forms a good electron contact that blocks hole extraction because of the deep laying valence band. As next discussed the measured built-in voltage V\textsubscript{bi} at the TiO\textsubscript{2} side is always quite large (∼1 V) indicating that after equilibration the device accommodates a large potential drop. The model assumes an ideal anisotype heterojunction formed at the contact between the TiO\textsubscript{2} and perovskite flat layers. V\textsubscript{bi} corresponds to the difference in work function (Fermi levels) between the two sides. Since V\textsubscript{bi} is large, one possibility is having a p-n (perovskite-TiO\textsubscript{2}) type heterojunction. Other combinations as n-n isotype function can be ruled out as lower V\textsubscript{bi} values would result. The basic band diagram is displayed in Fig. 2(b) which does not consider interface traps forming a dipole contact layer. Interface dipoles can be discarded as they reduce the flat-band voltage accommodating part of the work function offset. The diagram is still valid provided that the PVK work function is placed deeper than the TiO\textsubscript{2} work function, irrespective of the n or p character.\textsuperscript{10} Depletion zones are formed both at p and n side of the junction, w\textsubscript{PVK} and w\textsubscript{TiO\textsubscript{2}} which are modulated by the applied voltage provided that FTO and spiro-OMeTad/Au form good ohmic contacts. Perovskite presents p-doped character with an acceptor defect density N\textsubscript{PVK}, while TiO\textsubscript{2} is n-doped with donor defect density N\textsubscript{TiO\textsubscript{2}}, which will be considered as position-independent. The total built-in voltage is divided...
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TABLE I. Photovoltaic parameters of CH$_3$NH$_3$PbI$_3$-Cl$_x$ PVK-based devices measured under 1 sun illumination using different processing conditions. Doping density $N$ of TiO$_2$ and PVK layers and built-in voltage $V_h$ extracted from capacitance-voltage measurements in dark conditions.

<table>
<thead>
<tr>
<th>Device structure</th>
<th>$J_a$ (mA cm$^{-2}$)</th>
<th>$V_m$ (mV)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>$N$($10^{19}$) (cm$^{-3}$)</th>
<th>$V_h$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FTO-TiO$_2$</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>620</td>
<td>...</td>
</tr>
<tr>
<td>FTO-TiO$_2$-PVK-spiro-Au</td>
<td>15.77</td>
<td>913</td>
<td>70</td>
<td>10.0</td>
<td>18.0</td>
<td>1.19</td>
</tr>
<tr>
<td>FTO-TiO$_2$-PVK-Au</td>
<td>2.02</td>
<td>544</td>
<td>54</td>
<td>0.6</td>
<td>3.2</td>
<td>0.94</td>
</tr>
</tbody>
</table>

*aVoltage vs. Ag/AgCl.
zero bias relies on Eq. (3). Interestingly, the depletion zone only extents a few nm within the bulk of the TiO₂ layer because of the relatively high doping level. In the PVK side the depletion zone reaches around 300 nm, approximately half of the layer thickness (∼450 nm). Hence, the absorber layer is not fully depleted at zero bias existing as a consequence a significant neutral zone towards the anode contact. More importantly, the electric field is restricted to the space-charge zone made up by immobile acceptor defects near the electron contact. In the rest of the bulk (neutral zone) free hole carriers efficiently shield electrical fields. Since the built-in voltage at the PVK side is relatively large free hole carriers efficiently shield electrical fields. Since the built-in voltage at the PVK side is relatively large $V_{bi_{PVK}} = 0.89$ V, it occurs that the Fermi level crosses midgap energies yielding a thin inversion layer near the interface.

To support the electrical field profile derived from $C - V$ techniques, alternative measurements have been carried out using KPFM methods [see Fig. 2(c) and supplementary material for details]. KPFM allows investigation of the cross-sectional potential distribution in complete devices. Very recently, the enormous potential for characterization of Kelvin probe has been employed to investigate the role of selective contacts in perovskite solar cells, exploring the surface of the samples. Here, KPFM has been employed for the characterization of the cross-sectional potential distribution in complete devices. Fig. 2(d) displays contact potential difference average values over several lateral tracks. It is observed that a potential step in the PVK bulk contacting the TiO₂ layer extends about 300 nm inside the absorber bulk, while a flat profile appears in the rest of the layer. KPFM is not able to resolve with sufficient spatial accuracy the voltage drop in the TiO₂ side occurring in just 5 nm. It should be noted that the average voltage step measured by means of KPFM (∼0.2 V) is below the internal $V_{bi}$ calculated from $C - V$ techniques. A reason for this discrepancy might be found in the different measuring setup that each technique uses. For $C - V$ the junction capacitance is extracted which scales with the active surface area. On the contrary, KPFM allows determining the contact potential following a lateral, external cross-section path as drawn in Fig. 2(c). Here potential distribution not only depends on transversal, bulk properties, but it is certainly distorted by longitudinal effects. As previously addressed by Ottinger et al. there is a difference between the thickness-dependent surface potential and the bulk potential caused by an inherent potential drop at the substrate/semiconductor interface. Specially, doped semiconductors can show deviations that are not negligible. In any case, potential profile derived from KPFM qualitative agrees with that extracted from Mott-Schottky analysis. Despite the inherent limitation in spatial resolution KPFM, it is found again that the electrical field is confined near the cathode with typical size of 300 nm, with a bulky region of the absorber to be nearly field-free. The electrical field profiles derived from our experiments allows drawing a featured picture concerning the driving force for carrier transport, which is governed either by diffusion or drift mechanisms depending on voltage-dependent PVK depletion zone extent.

As commented before, ionized defects play a crucial role in establishing space-charge regions which ultimately withstand the band bending at the contact between absorber and selective layer. In order to provide deeper insight into the origin of PVK impurities responsible for depletion zones, different device processing conditions have been checked and analyzed by $C - V$ techniques. Devices not including the hole transporting spiro-OMeTad layer have been prepared by evaporating Au contacts directly onto PVK layers. Although these devices exhibit lower power conversion efficiency than those obtained with the standard structure (see Table I), it permits to discern how preparation conditions might alter potential distributions. Fig. 3 shows that the Mott-Schottky linear relation is still observed although with larger slope. Lower defect density level is then found when spiro-OMeTad layer is suppressed, which results in $N_{PVK} \approx 3.2 \times 10^{16}$ cm$^{-3}$ (see Table I). As observed in Fig. 3(a), a plateau in capacitance occurs at voltages below 0.4 V. This constant capacitance corresponds to the capacitance $C = 0.24$ μF cm$^{-2}$ that can be related to the series combination of the TiO₂ layer and PVK layer capacitances, $C^{-1} = C_{TiO2}^{-1} + C_{PVK}^{-1}$. Since $C_{TiO2}$ can be independently measured in the FTO/TiO₂/Au diode in reverse bias, perovskite relative permittivity $\varepsilon_{PVK} = 230 \pm 10$ is extracted in full-depletion conditions taking into account the absorber thickness of ∼200 nm in the cell FTO/TiO₂/PVK/Au. In contrast, it has been recently pointed out that $\varepsilon_{PVK}$ is highly dependent on the density of free carriers, either intrinsic or photogenerated. It was found an unprecedented behavior in which the low-frequency permittivity measured below 1 Hz increases under illumination or by charge injection. $\varepsilon_{PVK}$ increases nearly linearly with the illumination intensity from ∼2000 in the dark up to 10$^6$ under 1 sun. The photogenerated carriers in a deformable polar medium exhibit polaronic features, and their slow motion, which drags the lattice distortion, is denoted polaron hopping. An excess of localized charge, with a relative ability to move under external or thermal force, would modify the ionic bonding balance of the unit cell and cause local distortion. This process involves the macroscopic rearrangement of dipolar domains, and it will influence the long-range carrier transport. Indeed, it can be observed that in the low frequency conductivity decreases by 2 orders of magnitude with respect to the intermediate frequency (1 kHz) conductivity. The junction capacitance, which is measured at much higher frequencies (600 Hz as explained in Ref. 13), is related to depletion zones which are built by the presence of immobile charged impurities with majority carriers removed. This explains why $\varepsilon_{PVK}$ extracted from the Mott-Schottky analysis is only 230. On the contrary, low-frequency (1 Hz) capacitances is influenced by the response of quasi-neutral zones in which the carrier density is not negligible then enlarging $\varepsilon_{PVK}$. It is then consistent that the static permittivity found here results below typical values of ∼2000 observed at low frequencies in the dark. More importantly, for this configuration PVK layer undergoes full depletion for $V < 0.4$ V recovering the electrical field distribution extending over the whole bulk as expected for an intrinsic absorber layer.

The preceding experimental data conclude that the electrical field profile along the PVK bulk is dictated by the amount of defects responsible for the perovskite doping. A simple calculation using Eq. (1a) situates the doping level of $N_{PVK} \approx 8.5 \times 10^{16}$ cm$^{-3}$ as the limit below which the occurrence of full-depletion is achievable at 0 V-bias. It is
interesting to note that the growth method can affect significantly the doping level.\textsuperscript{4, 5} The presence and extent of electrical fields are known to change dramatically the charge collection efficiency by varying the relative weight of carrier drift and diffusion mechanisms on the overall transport driving force. Although more extended electrical fields are encountered when spiro-OMeTad layer is not deposited, the solar cell performance suffers from poor contact selectivity. It should be stressed here that precisely the inclusion of the spiro-OMeTad layer promotes carrier extraction at the contact, but at the same time it increases PVK doping. This might be related to the incorporation of light additives such as Li salts usually employed during layer processing and it is an interesting point to be explored in future work.

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\textsuperscript{13}See supplementary material at http://dx.doi.org/10.1063/1.4896779 for experimental details.