The Influence of Fermi Level Alignment with Tin Oxide on the Hysteresis of Perovskite Solar Cells

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ABSTRACT

We tune the Fermi level alignment between the electron transport layer consisting of SnO_x , and, $\text{Cs}_{0.05}(\text{FA}_{0.83}\text{MA}_{0.17})_{0.95}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$ and highlight that this parameter is interlinked with current-voltage hysteresis in perovskite solar cells (PSCs). Furthermore, thermally stimulated current measurements reveal that the depth of trap states in the ETL or at the ETL-perovskite interface correlates with Fermi level positions, ultimately linking it to the energy difference between the Fermi level and conduction band minimum. In the presence of deep trap states, charge accumulation and recombination at the interface are promoted, affecting the charge collection efficiency adversely, which increases the hysteresis of PSCs.

An astonishing improvement in power conversion efficiency (PCE) of perovskite solar cells (PSCs) from 3.8% up to more than 22% in a few years has brought them to the forefront of photovoltaic research with the goal of producing low-cost and solution-processed yet competitively efficient solar cells.¹⁻³ In spite of the enormous growth in the field, their development is still hampered by anomalous hysteresis in the characteristic current-voltage scan of the solar cells.⁴ This effect has been linked to several processes such as ion migration in the perovskite phase, trapping of electronic carriers at the perovskite - electron transport layer (ETL) or hole transport layer (HTL) interface as well as ferroelectric polarization.⁵⁻⁶ However, none of these processes fully account for the behavior observed: perovskites have poor polarization retention at room temperature⁷; charge trapping and detrapping occurs at a much faster timescale than hysteresis (microseconds vs tens of seconds); and ion migration cannot offer a complete explanation of why changing the interfacial contact materials, i.e. fabrication of inverted solar cells employing PEDOT:PSS and PCBM yield such pronounced differences regarding the hysteretic behavior of the devices.⁶

Despite the limited understanding of hysteresis in PSCs, several studies have demonstrated that the hysteresis can be suppressed by modifying the interface between ETL and perovskite or replacing the contact materials. The first approach was realized with fullerene derivatives with/without self-assembled layers (SAMs), resulting in negligible hysteresis in solar cells by reducing the non-radiative recombination channels due to the reduction in the trap density at this interface.⁸⁻¹⁰ Additionally, ZnO was shown to be a promising alternative to TiO₂ due to better electron mobility, very high transmittance as well as lower fabrication cost.¹¹ However, there are still issues regarding degradation of the perovskite due to the basic surface of ZnO which therefore requires the use of organic interfacial layers to maximize performance and minimize hysteresis.¹²⁻

¹³ Although thermal annealing of the ZnO layers improves the perovskite stability on ZnO, it does not guarantee long-term stability of the system.¹²

More recent efforts by van Reenen *et al.* demonstrated that several mechanisms are at play, where both ion migration and electronic charge traps must be included to achieve hysteresis in the modeled current-voltage characteristics.⁴ Recently, Calado *et al.* confirmed this hypothesis by showing ion migration regardless of whether the devices show hysteresis or not. Their transient optoelectronic measurements as well as device simulations revealed that hysteresis requires the combination of both mobile ionic charge and recombination near the perovskite - contact interfaces.⁶ Furthermore, any built-in field at the ETL-perovskite interface is expected to be screened by mobile ions.¹⁴ Therefore, matching the Fermi levels of the charge transport layers and the perovskite absorber is important to ensure effective charge extraction and to avoid charge accumulation and recombination.¹⁵

Here, we have investigated the influence of the Fermi level alignment between the ETL and the absorber on the hysteresis of multiple-cation mixed-halide PSCs. Our ultra-violet photoelectron spectroscopy (UPS) measurements show that annealing SnO_x layers at different temperatures allows fine tuning of their Fermi level, as schematically shown in Figure 1a. Furthermore, we link the Fermi level position to the presence of energetically deep trap states in the ETL or at the ETL-perovskite interface with the help of thermally stimulated current (TSC) measurements. We show that depth of traps correlates with an increase in hysteresis of PSCs, likely due to increased charge recombination at the interface. Moreover, our measurements show that if the band alignment between the perovskite absorber and SnO_x layer is fulfilled, the resulting device excels due to greatly reduced hysteresis and much better performance.

The solar cell architecture used in this work is shown in Figure 1b in a typical device stack composed of FTO/SnO_x/Perovskite/Spiro-OMeTAD/Gold. Briefly, we deposited SnO_x layers on a fluorine-doped tin oxide (FTO) substrate *via* atomic layer deposition (ALD) at 118 °C.¹⁶ The perovskite absorber, Cs_{0.05}(FA_{0.83}MA_{0.17})_{0.95}Pb(I_{0.83}Br_{0.17})₃, was then deposited according to a procedure published by Saliba *et al.*¹⁷ The solar cells were finalized by spin-coating of 2,2',7,7'-tetrakis-(N,N-dimethoxyphenylamine)-9,9'-spirobifluorene (spiro-OMeTAD) as a hole transport layer and thermal-evaporation of gold (Au) electrodes. The full experimental description of the device fabrication can be found in the Supporting Information (SI).

Solar cells were prepared with as-deposited SnO_x layers as well as layers annealed in air at up to 300 °C. Top-view scanning electron microscopy (SEM) images show that the morphology of the SnO_x (10 nm) layers does not change upon annealing of the substrates (Figure S1d, e, and f). Also, the morphology of the perovskite layers was not affected by the annealing temperature of the ETL (Figure S1a, b, and c).

Figure 1. (a) Schematic diagram of energy level alignment of PSCs used in this work. Gray dashed lines and arrows depict the Fermi level tuning of SnO_x, which depends on the annealing temperature. Red dashed lines represent the trap states. (b) SEM cross-section of a solar cell.

In order to investigate the influence of the annealing temperature of the SnO_x layer on the device performance, we recorded current-voltage (J - V) characteristics (Figure 2a and S2a) of the solar cells and additionally fabricated reference devices incorporating a planar TiO₂ ETL. A summary of the PCEs of the solar cells extracted from the reverse scan of the J - V curves is given in Figure 2b and the corresponding stabilized power output *via* maximum power point tracking is shown in Figure S2b. The PCE of the solar cells slightly increases with the annealing of SnO_x, showing the maximum performance average at an intermediate annealing temperature of 180 °C (Figure 2b). On the other hand, solar cells with layers annealed at higher temperatures lose their PCE from 16.1 % (for 180 °C) to 13.9 % (for 300 °C). The observation of a PCE maximum at an ETL annealing temperature of 180 °C is attributed to the change in fill factor (FF), which shows the same trend as the PCE (see Figure 2c). This key parameter rises up to the optimum annealing temperature (180 °C) and decreases at higher annealing temperature. The drop in V_{OC} at higher annealing temperatures is likely related to an increase in detrimental defect states formed in SnO_x films (Figure S3b).¹¹ Furthermore, external quantum efficiency (EQE) measurements were performed on the solar cells and integrated current densities from these measurements are in good agreement with short circuit current values obtained from J - V scans (Figure S4).

All solar cells exhibit some degree of hysteresis (Figure 2a), which can be quantified by the so-called hysteresis index (HI).⁶ This parameter is extracted from comparing forward and reverse J - V curve scans as:

$$HI = \frac{PCE_{rev}}{PCE_{for}} - 1$$

where PCE_{rev} and PCE_{for} are the PCEs in reverse and forward scan, respectively.⁶ Interestingly, we observed that a minimum in hysteresis occurs at the same annealing temperature as the optimum performance, 180 °C, as shown in Figure 2d. Furthermore, we have measured the solar

cells on TiO_2 and SnO_x (annealed at 180 °C) at different scan rates (Figure S5). We found that the PCE increases with both ETLs while the HI decreases with an increase in scan rate. This behavior is attributed to the charge carrier collection efficiencies at different scan rates which depend on ion accumulation at the interfaces.¹⁴

Figure 2. (a) $J-V$ curve of solar cells fabricated with non- and 180 °C annealed SnO_x , demonstrating a big difference in hysteresis between the samples annealed at different temperatures. (b) PCE, (c) FF and (d) HI of the solar cells fabricated on SnO_x annealed at different temperatures (9-11 devices for each annealing temperature). The values in (b) and (c) were extracted from the reverse scan of the $J-V$ curves. The grey lines are a visual aid to interpret the trend of the results.

In order to understand the observed trends in device performance and to gain insight into the effect of thermal annealing on SnO_x, we first determined the band alignment between the ETL and the perovskite by measuring the work function of both in ultrahigh vacuum via ultra-violet photoelectron spectroscopy (UPS) (Figure 3 and Figure S6). The valence band maximum (VBM) was found by a linear extrapolation of the leading edge of the valence band spectra (Figure 3b). The conduction band minimum (CBM) was determined by subtracting the band gap energies of SnO_x, which do not change at different annealing temperatures and which were estimated via Tauc plots of absorbance measurements (Figure S7 and S8). The Fermi levels were extracted by subtracting the value found by a linear extrapolation of the secondary electron edge from $h\nu$ (Figure 3a). Further experimental and evaluation details of UPS measurements are given in the SI. Our results show that both the SnO_x and perovskite show n-type character with very little gap between their Fermi level and CBM, considering that UPS analyzes only the surface properties. Figure 3c shows a schematic diagram of the band alignment between the ETL and perovskite in the solar cells, where we obtained different Fermi levels (dashed black lines below CBM) from different annealing temperatures of SnO_x.

Figure 3. Linear fittings of (a) secondary electron edge (SEE) and (b) valence band maximum (VBM) of both SnO_x from UPS and XPS measurements, respectively. (c) Schematic diagram of energy band of the ETL and perovskite. The temperatures at the bottom of the band diagram are the annealing temperatures of the SnO_x layers. The energy levels are aligned according to Fermi level. (CB, VB and PK are conduction and valence band, and perovskite respectively. Dashed black line represents the Fermi level.)

UPS measurements highlight a remarkable connection: The smallest energetic distance between Fermi level and CBM corresponds to the lowest HI. Samples annealed at 180 °C, which demonstrate the highest PCE and lowest HI, exhibit the smallest energy offset between the Fermi level and CBM of 0.22 eV. When compared to the Fermi level of the perovskite, it can be seen that the annealing at 180 °C results in the best energy alignment since the Fermi level of SnO_x is the closest to the CBM of perovskite, whereby the photogenerated electrons can be efficiently extracted into the SnO_x layer. At annealing temperatures below or above 180 °C, the Fermi level shifts further away from the respective CBM, where lower PCEs and higher HI values were obtained due to the inefficient charge collection.

The change in Fermi level energy can be explained by means of the defect states formed in the metal oxide layer. In a semiconductor, the work function of the material is defined not only by the band structure and the density of states of the pristine material, but also by defects which causes charge carrier trap states within the band gap. Therefore, it is likely that the SnO_x used in this work is defect-rich since the films are not crystalline (Figure S9). In fact, Du *et al.* have shown that the oxygen vacancy defect in TiO₂ causes deep defect levels located 0.4-1.18 eV below the CBM of TiO₂.¹⁸ Analogously, the defects in SnO_x layers are attributed to oxygen vacancies,¹⁹⁻²⁰ leading to similar defect distributions below the CBM. Therefore, changing the density and depth of the trap states in the semiconductor allows for Fermi level tuning, which in our case can be achieved by thermal annealing of ETL in air.²¹

In order to fully understand this connection, we investigated the energetic trap landscape in devices fabricated with different SnO_x films via thermally stimulated current (TSC)²² measurement, which we applied successfully to PSCs in previous work.²³⁻²⁴ As TSC is performed on fully processed solar cells (as described above), it enables probing of electronic trap states and

allows linking the results to the device performance directly. The devices are first cooled down to very low temperatures (here: 30 K) in dark conditions. The illumination with white light LED then generates free charge carriers without heating the solar cell. After the light is turned off, charge carriers relax into the deepest trap states during a certain dwell time. During this limited timeframe, charge carriers populate available trap states in the bulk and at the interfaces with the charge extraction layers. Due to the low thermal energy available, the charge carriers cannot be released from these states. Subsequently, the device is heated up to room temperature at a constant rate (here: 3 K/min), which initiates a gradual release of the trapped charges as soon as they gain enough thermal energy to escape. The current flow originating from trap release is precisely monitored and is used to determine the trap depth as well as density of the electrically active defect states in the probed system. Further details on the measurements technique can be found elsewhere.²³

Figure 4a shows the resulting TSC signals for solar cells, where the SnO_x ETL was annealed at temperatures of up to 225 °C. Starting at approximately 180 K, a strong current was detected in all investigated devices, with a distinct shoulder at around 240 to 250 K (marked by shaded area). The TSC signal is the largest for the device with non-annealed SnO_x layer (Figure 4a, red curve) and dramatically decreases upon annealing of the SnO_x layer with a minimum in TSC signal for the 180 °C annealed device for which we observed also the best device performance and minimum HI. We note, for higher temperatures than 225 °C, the occurrence of leakage current due to a decrease in shunt resistance prevented reliable detection of very small TSC signals. As the layout is identical for all devices studied, we ascribe the decrease in TSC signal to a reduction in the density of trap states in the ETL or at the ETL-perovskite interface. Interestingly, the density of traps increases again for device with SnO_x above the annealing temperature of 180 °C. This increase in trap

density could be due to the surface of SnO_x annealed at higher temperatures which might trigger the formation of perovskite decomposition products.²

Figure 4. (a) TSC signals of solar cells fabricated on SnO_x annealed at different temperatures. (b) Corresponding Arrhenius plot of the TSC signals with the activation energy peak marked with an arrow for all devices. (c) Comparison of energetic difference between CBM and Fermi level of SnO_x and trap depth energies of solar cells.

In order to extract the activation energy of the trap states, the slope of the initial rise of the TSC current, which was attributed to the start of trap release, is fitted in the Arrhenius plot (Figure 4b) for each annealing temperature according to the following equation:

$$I_{TSC} \propto \exp\left(-\frac{E_A}{k_B T}\right),$$

where E_A , k_B , and T are the activation energy, Boltzmann constant and temperature, respectively.²⁵⁻²⁶ The values of the activation energies to release electrons from trap states are summarized in Table S1. These energies follow a remarkably similar trend with one we observed in UPS measurements as well as for the HI: The activation energy decreases with increasing annealing temperature, where a significant drop is observed from 275 (non-annealed ETL) to 202 meV for ETLs annealed at only 125 °C. The activation energy of the trap states reduces further to 187 meV with annealing of SnO_x layer at 180 °C. Interestingly, for annealing temperatures above 180 °C, the trend reverses, showing even higher activation energy (307 meV) than the non-annealed sample.

The results from UPS and TSC, summarized in Figure 4c are in noticeably good agreement: Annealing of as-prepared SnO_x films leads to a significant reduction in the trap density as well as energetic depth of the trap states in the ETL or at the ETL-perovskite interface, resulting in a shift of the ETL Fermi level closer to the CBM. Particularly, we find the trap depth plays a significant role in charge accumulation at the interface since charge transport in metal oxides such as the SnO_x layers relies on a trapping-detrapping mechanism.²⁷ The photogenerated electrons are transferred from absorber into SnO_x layer where they relax and localize in sub-band gap states. The electron transport occurs *via* thermal detrapping, diffusion in the conduction band and again retrapping. In this way, charge transport is limited by the detrapping events, which is highly dependent on the energetic depth of the trap state.²⁷ Ultimately, the highest PCE and lowest HI are found for the solar cell with the ETL annealed at a temperature of 180 °C, where the shallowest trap states result in the best Fermi level matching. Additionally, we point out that these trap states in SnO_x are unlikely to cause a light-soaking effect in PSCs. This effect has previously been assigned to light-

induced ion/defect migration in the perovskite lattice.²⁸ In fact, in other solar cell systems, UV-light soaking effects are reduced when TiO₂ is exchanged by SnO_x.²⁹

Based on this, we propose that charge accumulation occurs at the interface and is determined by the energy gap between the electron acceptor's Fermi level and its CBM. Essentially, deeper traps, given by the Fermi level position in the SnO_x layer, cause more charge accumulation at the interface between ETL and perovskite due to the lack of available thermal energy required to release electrons from these states. This, in turn, leads to enhanced recombination as can be observed by (i) an increase in HI (Figure 2d) and (ii) a loss in open circuit voltage (V_{oc}) (Figure S3b), which are in good agreement with the literature.^{6, 30} Furthermore, the stabilized power output demonstrates that the solar cells with a high HI show a larger loss in performance than those one with a lower HI (Figure S2b).

In this work, we unveil the influence of Fermi level alignment between the SnO_x ETL and perovskite absorber as well as associated trap depth on the PCE and hysteresis of PSCs. We were able to tune the Fermi levels of ALD SnO_x layers by thermal annealing. We obtained the maximum PCE and the smallest HI at the optimum annealing temperature of 180 °C. We find a strong correlation between the Fermi level positions of SnO_x and the trap depth deduced from the UPS and TSC measurements, respectively: Based on the trapping-detrapping charge transport mechanism in SnO_x layers, deep trap states likely trigger charge accumulation at the interface, which in turn leads to enhanced charge recombination at the SnO_x-perovskite interface, causing a higher HI in solar cells. Therefore, a decrease in the trap energy, partially eliminating trap states in the ETL or at the ETL - absorber interface, results in a better Fermi level alignment and hence in more efficient and hysteresis-free PSCs.

ASSOCIATED CONTENT

The following files are available free of charge.

Experimental details of solar cell fabrication, SEM top-view images of SnO_x and perovskite films, characterization of solar cells, absorbance spectra and Tauc plots of perovskite and SnO_x films.

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Notes

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ABBREVIATIONS

PSCs, perovskite solar cells; PCEs, power conversion efficiencies; ETL, electron transport layer; CBM, conduction band minimum; UPS, ultra-violet photoelectron spectroscopy; TSC, thermally stimulated current; HTL, hole transport layer; ALD, atomic layer deposition; FTO, fluorine-doped

tin oxide; spiro-OMeTAD, 2,2',7,7'-tetrakis-(N,N-di-pmethoxyphenylamine)-9,9'-spirobifluorene; SEM, scanning electron microscopy; HI, hysteresis index; VBM, valence band maximum; SI, Supporting Information.

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TOC Figure