Tapered Cross-Section Photoelectron Spectroscopy of State-of-the-Art Mixed Ion Perovskite Solar Cells: Band Bending Profile in the Dark, Photopotential Profile Under Open Circuit Illumination, and Band Diagram

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The purpose of this article is twofold. On the one hand the method of spatial resolved photoemission spectroscopy on small angle tapered cross-sections (TCS) of complete devices is introduced to analyze simultaneously the chemical and electronic structure. On the other hand, a specific working principle of the analyzed cell type is revealed. Solar cells of 18% efficiency are prepared from a single precursor (FAPbI$_3$)$_{0.85}$(MAPbBr$_3$)$_{0.15}$ with excess of 15% PbI$_2$. It is shown that TCS-phototoelectron spectroscopy allows to determine the chemical composition as well as the potential distribution across the full device in the dark and in operation. The energy converting contact is the hole extraction back contact. Interestingly the photopotential in the analyzed cell type is predominantly created within the hole extraction layer and not in the n-doped perovskite absorber. With the addition of measured core level to valence band maximum positions of the respective layers, TCS line scans lead to the band diagram for the full device. In addition, depth variations of the chemical composition are found: the bromide concentration increases while the iodide concentration is reduced near and within the mesoporous TiO$_2$ layer.

1. Introduction

Interfaces play a major role in semiconductor device functionality. For halide perovskite devices this was reviewed, e.g., in ref. [1]. Photocurrent spectroscopy (PES) is a powerful tool to analyze the electronic structure of semiconductor interfaces. Decisive electronic properties as doping level, band line up, and band bending are directly accessible, in addition to the chemical information concerning chemical element distribution and their oxidation states due to interface reactions as shown by numerous publications and authors and summarized, e.g., in one of our publications.[2] Interfaces may be analyzed, using synchrotron hard X-ray photoelectron spectroscopy (several keV) to increase the escape depth of the photoelectrons, as was also applied to halide perovskites.[3] Due to the small escape depth of the photoelectrons, when using lab sources, interface analysis is usually conducted by interface experiments of step-by-step deposition of the contact material onto the respective substrate. Contamination free results are obtained when using a vacuum deposition chamber that is vacuum-connected to the PES spectrometer chamber in an “integrated system.” Shining light onto interfaces that show band bending in the dark leads to a shift of the photoemission spectra due to an induced photovoltage.[4–9]

Care has to be taken not to underestimate band bending without bias light in the “dark” due to stray light, unthought illumination, e.g., by UHV pressure sensors, or to X-ray or UV source induced photovoltage.[10]

Interface experiments helped to enlighten the role of selective contacts in the performance of perovskite solar cells. MAPbI$_3$ has been intensively studied via PES to investigate not only its synthesis[11] and degradation[12,13] but also the contact formation to several different hole transporting materials (HTMs) like 2,2′,7,7′-tetakis(N,N-di-p-methoxyphenyl-amine)9,9′-spirobifluorene (spiro-MeOTAD),[14] copper phthalocyanine (CuPC),[15] or MoO$_3$.[16,17] Other studies also investigate the interface alignment of methylammonium lead iodide to different ETMs like C$_{60}$[18–20] or phenyl-C$_{61}$-butyric acid methyl ester,[18] but also to Au.[19,21]
It has also been shown that spiro-MeOTAD is suited for hole extraction from MAPbI\(_3\) (CH\(_3\)NH\(_3\)PbI\(_3\)), but not from MASN\(_3\) (CH\(_3\)NH\(_3\)SnI\(_3\)).\(^{[22,23]}\)

For multilayer devices, the electronic structure has to be composed from analysis of single interface experiments. Unfortunately, such interface experiments are hard to perform with perovskites as they cannot be deposited from a single evaporation source. Alternatively sputter depth profiles can be acquired on ex situ prepared contacts. Thus X-ray photoelectron spectroscopy (XPS) depth profiling of the chemical composition showed storage time dependent variations of the I/Pb ratio in planar (MAPbI\(_3\)) solar cells.\(^{[24]}\) Variation of photoelectron escape depth by varying excitation energies using hard synchrotron radiation allowed for nondestructive analysis of composition variations within a depth of around 20 nm of multiple cation perovskite layers.\(^{[25]}\)

Electronic information of ex situ prepared contacts can be obtained using hard X-rays. Thus an energy level diagram of the valence and conduction band edges of TiO\(_2\) and MAPbI\(_3\) was derived from hard X-ray (4 keV) valence band spectra of and through a thin CH\(_3\)NH\(_3\)PbI\(_3\) layer on a TiO\(_2\) substrate.\(^{[26]}\)

Several other attempts have been undertaken to analyze perovskite devices using PES. A lateral device model of a contacted MAPbI\(_3\) layer was used to measure iodine migration under applied voltage.\(^{[26]}\)

An alternative route to obtain information of a complete and operating device is to analyze its cross-section. As perovskite solar cells are thin film devices consisting of layers in the range of several hundred nanometers, while XPS lateral resolution at best is in the range of 10 μm, Kelvin probe microscopy is often used to study local resolved electronic properties. Kelvin probe force microscopy (KPFM) has been applied successfully to perovskite device cross-sections normal to the layer structure in the dark as well as under operation and different working principles have been derived. A p–i–n structure with band bending and photopotential in the CH\(_3\)NH\(_3\)PbI\(_3\) perovskite at the hole extraction p-contact was found.\(^{[27]}\) Later it was shown with KPFM that the position of the main photopotential drop depends on the doping type of the perovskite.\(^{[28]}\) The authors found on planar cells, that the main photopotential drops in the perovskite in front of the HTL for n-type (excess PbI\(_3\)) and in front of the ETL for p-type (excess methylammoniophotopotential iodide (MAI)) material. The n- and p-type self-doping properties of excess PbI\(_3\) and MAI have been demonstrated with UPS on MAPbI\(_3\) samples produced from solutions with respective concentration ratios by Wang et al.\(^{[29]}\) and for samples prepared from solution and coevaporated by Olthof et al.\(^{[30]}\) A shift of the photopotential drop into the HTL has been observed with KPFM for TiO\(_2\) ETL but not for a C\(_60\) ETL, which was proposed to be due to a higher concentration of mobile iodide in MAPbI\(_3\) in the TiO\(_2\) cell, which led to the formation of a neutral spiro-MeOTAD–iodide HTL layer.\(^{[31]}\)

The advantage of KPFM is to provide the high local resolution to analyze normal cross-sections of thin film devices. However, the primary electronic information measured by KPFM is restricted to the work function and its variation for different materials and by induced contact potentials. Although material specific in principle, the work function is most sensitive to cross contamination and contamination by adsorbed species from the ambient air, which has to be considered in the interpretation.

Electron beam induced current (EBIC) is a further method to analyze full devices using (normal) cross-sections and was applied to derive dynamic information on currents in perovskite solar cells. For a CH\(_3\)NH\(_3\)PbI\(_3\) solar cell cleaved normal to the layer structure a p–i–n working structure with the photopotential inside the perovskite in front of both the ETL and the HTL contact was suggested.\(^{[32]}\) However, EBIC measurements do not represent typically working conditions that is illumination with a broadband light source normal to the device layers. In addition dark measurements are not possible. For [FAPbI\(_3\)]\(_{0.85}\)MAPbBr\(_{0.15}\) devices the EBIC signal increased for the first 2–5 scans and then it decreased again. The initial increase was suggested to be due to passivation of defect states on the cleaved perovskite surface (reducing recombination), while for later scans the reduction of the EBIC signal was explained by damage induced with the electron beam.\(^{[33]}\)

In contrast to KPFM that measures contact potentials differences between the probe and the sample vacuum level, photoemission measures directly the energetic position \(E_g\) of spectroscopically resolved states and bands versus the Fermi level reference at \(E_F = 0\), which is defined experimentally by reference measurements of the Fermi edge of a grounded metal (e.g., Au) layer. With additional reference measurements of the valence band maximum position the energy difference between core level and valence band maximum \(\Delta E_{BCV}\) is accessible, which is a material specific property. Thus interface band diagrams including valence band and conduction line up and band bending are classically derived by following binding energy variations in step-by-step deposition experiments of a contact material onto a substrate.\(^{[34]}\) In addition tapered cross-sections (TCS)-PES delivers spectroscopic information from which the different layers can be discriminated and details on the chemical composition, e.g., of the complex perovskite that is investigated here can be gained, even within the m-TiO\(_2\) layer. The simultaneous combination of electronic and spectroscopic information is unique for TCS-PES in comparison to other cross-sectional analysis methods.

In this work we introduce photoelectron spectroscopy on TCS as a novel technique to analyze electronic devices. A small angled wedge is prepared by mechanical polishing the device to enhance the nm scale of the normal cross-section to the mm scale on the TCS, which is accessible to laterally resolved XPS and UPS. Spatially resolved XPS line scans of representative element core level emissions along the TCS allow deriving locally resolved information on the chemical composition and the induced interface potentials in thermodynamic equilibrium and under operating conditions. We demonstrate that with TCS-XPS and TCS-UPS measurements, the chemical composition across the device structure, as well as the band energy diagram can be derived for a wet chemically produced state of the art mixed ion perovskite solar cell of 18% efficiency.

The perovskite of the 18% efficient devices used in this study were prepared with 15% PbI\(_2\) surplus in the precursor solution and is therefore expected to be self-doped n-type.\(^{[35]}\) We have proven n-type doping by measuring the valence band maximum position directly against the Fermi level reference using PES and considering the energy gap of the material. The energy gap \(E_g\) of MAPbI\(_{3−x}\)Br perovskites increases linearly with Br concentration from 1.60 of pure MAPbI\(_3\) to 2.23 of pure...
MAPbBr$_3$.[34] On the other hand the energy gap varies only by 0.07 eV when the organic molecule is changed from MAPbI$_3$ to FAPbI$_3$.[35] Considering the precursor Br/I ratio of 0.15/0.85 we derive an energy gap of 1.7 eV for our samples using the findings by Park et al.[34] and the VBM at 1.1 eV (i.e., 0.25 eV above the Fermi level) using a logarithmic plot of the valence band spectra in Figure S5b (Supporting Information) that emphasizes low density of states (DOS) at the valence band onset as suggested for perovskites in literature.[36] Although the time consuming TCS-XPS measurements induce some degradation, a photopotential induced binding energy shift of 0.64 eV was observed as demonstrated in Figure 3. In the quick and more gentle TCS-UPS measurements on a different sample shown below in Figure 7, the observed photoinduced shift was 1.2 eV, which compares well to $V_{oc} = 1.1$ V of the pristine and 1.05 V of a freshly tapered cell sample (see I–V curves in Figure S3 in the Supporting Information).

Making use of respective $\Delta E_{BCV}$ and with the addition of the energy gaps $E_g$ we are able to derive the band diagram concerning band bending and band line up of valence band maxima and conduction band minima of our complete solar cell system (displayed in Figure 7). The cell architecture is from front to back contact: SnO$_2$:F|compact-TiO$_2$|mesoporous-TiO$_2$|FA$_{0.85}$MA$_{0.15}$Pb$_{2}$I$_{8.75}$|Spiro-MeOTAD|Au with MA and FA being methylammonium and formamidinium.

2. Results and Discussion

A wet-chemically prepared state-of-the-art mixed ion perovskite solar cell of 18% efficiency was analyzed for its chemical composition and induced potentials, i.e., the course of band bending in the dark and photopotentials under illumination at open circuit conditions (OC) throughout the full device. Along the TCS spatially resolved scans of XPS core level spectroscopy of all elements present in the solar cell were performed in darkness and under white light illumination of 100 mW cm$^{-2}$ intensity. Element specific core level spectroscopy is used at first to identify the respective device layers and interfaces. In addition, the bromine and iodine element spectral intensity reveal concentration gradients. Especially near and within the mesoporous TiO$_2$ layer the Br/I ratio increases strongly as becomes obvious directly in the 1 and Br intensity contour line scan maps displayed in Figure 2 and in the associated atomic ratio plots Figure S1 (Supporting Information). The exposure of the perovskite to vacuum for the PES measurements has negligible effect on the chemistry of the perovskite. In our previous study we have shown that the iodine ratio does not change after 14 h of PES measurements in the dark.[28] As we have observed higher concentrations of Br near and within the meso-TiO$_2$ in several samples we assume this is an inherent film property. A detailed discussion of these self-organized halide concentration ratio variations will be given elsewhere. Here we concentrate on the electronic structure derived from the TCS-XPS measurement.

To reveal the working mechanism, i.e., to identify the photoactive interface(s) of a microelectronic device, it is desirable to collect relevant data during active operation. For surface sensitive methods the closest approach would be to analyze a normal cross-section of a device and KPFM exhibits the necessary local resolution on the nm scale. In order to apply the chemical and simultaneously electronic analytical abilities of PES, we prepared the tapered cross-section to surmount PES inherent insufficient local resolution. Using a small angle cut of 0.02° the nm scale of the normal cross-section is projected to the nm scale of the tapered cross-section. To take a line scan, the tapered cross-section is then moved under the analyzer focus with a step width of 50 μm as schematically shown in Figure 1c. During the measurements the gold back contact was grounded while the SnO$_2$:F (FTO) front contact was left floating. A SEM micrograph of the cross-section prepared by cracking and a photograph of the tapered cross-section prepared by mechanical polishing are shown in Figure 1a,b. Figure 1b shows three of the four solar cells each of an area 3 × 10 mm$^2$ (before TCS polishing) that is defined by the Au back contact layers that appear bright on the left in the photography. To the right deeper layers up to the FTO front contact appear on the TCS as sketched in Figure 1c. Importantly, a part of the cell stack is kept undisturbed by TCS polishing and forms the

![Figure 1.](image-url)

**Figure 1.** a) SEM micrograph of the normal cross-section of the cell architecture with the composition SnO$_2$:F|compact-TiO$_2$|mesoporous TiO$_2$|FA$_{0.85}$MA$_{0.15}$Pb$_{2}$I$_{8.75}$|Spiro-MeOTAD|Au. b) Photograph of the tapered cross-section showing 3 of the 4 cells on one sample each of area 3 × 10 mm$^2$ defined by the gold back contact. The undisturbed part of the cells appears bright (Au) the polished part dark (TiO$_2$). c) Schematic representation of the cell architecture and the tapered cross-section XPS arrangement. The scans were taken in 60 steps of 50 μm width along the tapered cross-section.
The cell architecture as schematically shown in Figure 1c consists of electron extracting front contact to hole extracting back contact of SnO₂:F|compact-TiO₂|mesoporous-TiO₂|FA₀.₈₅MA₀.₁₅Pb(I₀.₈₅Br₀.₁₅)₃|spiro-MeOTAD|Au. In Figure 2 the contour maps of the respective core level spectra are displayed for one line scan consisting of 55 points across the TCS. On each position Au₄f₇/₂, C₁s, N₁s, Pb₄f₇/₂, I₃d₅/₂, Br₃d, Ti₂p₃/₂, and Sn₃d₅/₂, XPS spectra have been measured and are displayed as intensity contour plots. Exemplarily an Au spectrum and its color contour plot are shown at the top left in Figure 2. In addition in Figure 2, the direct C₁s spectra of pure spiro-MeOTAD taken at position 6 and of pure mixed ion perovskite taken at position 22 are shown together with the molecular structures of MA, FA, and spiro-MeOTAD. The body of element intensity contour maps displayed in Figure 2 allows for the identification of interfaces on the TCS as indicated by brown horizontal lines. In accord to these lines, a schematic of the device layer structure as it appears on the TCS is shown on the left in Figure 2. The assignment of interfaces on the TCS is hampered by three factors related to 1) the XPS process, 2) the electron analysis system, and 3) the roughness of TCS preparation: 1) The rather small but finite escape depth λ of the photoemitted electrons leads to superposition of spectra from overlapping layers at ideal interfaces on the TCS. According to the universal escape depth versus kinetic energy curve, λ is in the range of 1.0–1.5 nm for the analyzed core levels depending on the emitted electron kinetic energy. 2) The finite local resolution (in the direction normal to the interface) of the XPS electron analyzer at best in the 10 µm range leads to superposition of spectra from neighboring materials at ideal interfaces on the TCS. 3) The finite local resolution (in the direction parallel to the interface) leads to superimposed emissions of the top and bottom layer due to roughness induced by the preparation process of the tapered cross-section using silk cloth type 9450. Further details on the TCS preparation are given in the experimental.

Spiro-MeOTAD extends from position 6 to 10, while fringes extend over Au in positions 6 to 0 as discussed in detail later (see Figure 4). A sharper interface is formed between spiro-MeOTAD and the perovskite with a clear onset of strong Pb and I emissions at position 10. While bromine is present throughout the perovskite, its intensity increases while iodide intensity decreases near the position when Ti₂p₃/₂ emission of the mesoporous TiO₂ layer sets in. A similar gradient of iodine and bromine, with increasing Br concentration towards a TiO₂ blocking layer was already observed before by photoemission sputter depth profiling. Titanium shows a clear 2p₃/₂ line intensity starting at position 36 indicating mesoporous titania. Ti₂p₃/₂ intensity becomes strong at position 46 indicating the TiO₂ blocking layer. Finally, Sn₃d₅/₂ emission of the front contact sets in at position 49. Based on their specific C₁s spectra carbon emission of the hole conductor and of the perovskite can be discriminated as demonstrated by displaying the C₁s spectra of pure perovskite and pure spiro-MeOTAD.
of a pure spiro-MeOTAD and of pure FA + MA of the perovskite at the top of the C1s line scan in Figure 2. The spiro-MeOTAD C1s emission has a strong maximum at 284.6 eV binding energy and a shoulder at 286.1 eV while FA + MA show maxima at 285.4, 286.9, and 288.7 eV. For each position in the line scan, the binding energy of the maxima of the fits to the core level emission lines of the respective elements are indicated as dots which are threaded to dotted lines. Deviations from a constant binding energy value $E_B$ of a certain core orbital indicate band bending as the binding energy is measured with reference to the sample Fermi level at $E_B = 0$. On the other hand, changes of binding energy are given by changes of chemical composition as, e.g., the Br/I ratio and the perovskite to TiO$_2$ ratio in the m-TiO$_2$.

Comparison of PES measurements under dark (no bias light) and light (bias light on) condition helps to discriminate contact induced electronic shifts from shifts resulting from chemical composition. While band bending is reduced in the nonequilibrium measurement under illumination, composition induced binding energy variations are persistent. Interestingly the maximum positions of the Pb4f$_{7/2}$, I3d$_{5/2}$, and Br3d, spectra show a bowing to higher binding energy while Ti2p$_{3/2}$ shows a bowing to lower binding energy within the meso-porous TiO$_2$ where the concentration of iodide decreases while bromine concentration increases. As these binding energy changes are preserved under illumination as displayed for Pb4f$_{7/2}$ and Ti2p$_{3/2}$ in Figure 3, we conclude that they are not due to induced

![Figure 3](image_url)  
**Figure 3.** Intensity Contour plots of Au4f$_{7/2}$, Pb4f$_{7/2}$, Ti2p$_{3/2}$, and Sn3d$_{5/2}$ spectra in direct comparison in dark and illuminated under open circuit condition. At the bottom, the cell layer structure is sketched. While the Au4f$_{7/2}$ emission of the back contact is fixed due to grounding, already Pb4f$_{7/2}$ emission of the perovskite layer shows a positive shift of 0.64 eV due to illumination. This photopotential appears for all following layers as indicated for Pb4f$_{7/2}$ and Ti2p$_{3/2}$ in the meso-porous TiO$_2$, for Ti2p$_{3/2}$ in the compact TiO$_2$, and for Sn3d$_{5/2}$ in the FTO front contact. As the maximum position binding energy shifts of Pb4f$_{7/2}$ and Ti2p$_{3/2}$ are conserved under light, those are addressed to chemical shifts in Pb4f$_{7/2}$ due to Br/I concentration variation and to variation in the Fermi level position in the mesoporous TiO$_2$ particles due to increasing TiO$_2$ content in the composite when approaching the TiO$_2$ blocking layer.
potentials but rather to the change of the chemical composition of the perovskite with increasing Br/I concentration within the mesoporous TiO₂ layer. The larger electronegativity of bromine induces a chemical shift of the Pb4f⁷/₂ spectrum of the perovskite species to higher binding energy as measured for the pure iodine and bromine spectra before.[5] For the shift of the TiO₂ spectra, a tentative explanation can be given considering a variation of the Fermi level within the TiO₂ energy gap due to an increasing TiO₂/perovskite concentration ratio approaching the TiO₂ blocking layer. The Fermi level position in composites is established by charge transfer at the internal interfaces of the host and guest materials.[19] In addition, increasing Br/I concentration in the perovskite may lead to changes in the electronic structure, which may induce a respective change in the resulting Fermi level of the mesoporous TiO₂ in the composite, again according to ref. [39]. Thus, the doping level found in m-TiO₂ in the composite with the perovskite may deviate from doping levels measured on pure m-TiO₂ reference samples.

The direct comparison of dark and open circuit illuminated XPS spectra of Au4f⁷/₂, Pb4f⁷/₂, Ti2p₃/₂, and Sn3d₅/₂, the representatives of the respective device layers back contact, perovskite, mesoporous and compact titania, and FTO front contact is displayed in Figure 3. While the Au4f⁷/₂ emission of the grounded back contact does not change, the Pb4f⁷/₂ emission of the perovskite layer already shows a 0.64 eV shift due to illumination. This photopotential appears throughout the perovskite and all following layers as indicated for Ti2p₃/₂ and Pb4f⁷/₂ in the perovskite/m-TiO₂ compound, for Ti2p₃/₂ in the compact TiO₂, and for Sn3d₅/₂ at the floating FTO front contact.

Clearly the photopotential arises at the hole extraction back contact. But in the dark no band bending has been observed in the perovskite at this contact as the constant binding energy of Pb4f⁷/₂ in Figure 3 indicates. Under light the Pb4f⁷/₂ emission in the complete perovskite layer on the TCS is shifted by the photopotential. A closer look to the CIs emission is necessary to further locate the induced potential and the photopotential as displayed in Figure 4.

A closer look to the CIs emission is necessary to further locate the induced potential and the photopotential as displayed in Figure 4. Detailed considerations due to superimposed electrical shifts due to band bending and chemical shifts due to transition from spiro-MeOTAD to the organic molecules FA and MA are needed. In addition, artificial effects due to fringing of spiro-MeOTAD in the polishing process have to be considered too. Under light exposure the maximum of the leading spiro-MeOTAD CIs emission in the positions 0–6 on top of Au is lower than in the dark measurements, indicating that within the spiro-MeOTAD fringe a downward band bending (labeled “ΔE₈ = 0.4 eV Au per spiro fringe per vacuum dark” in Figure 4) from the very gold contact to the spiro-MeOTAD/vacuum interface at the top of the fringe exists in the dark, which is removed under light. Assuming flat band under illumination the spiro-MeOTAD position under light can be taken as binding energy reference in the dark directly at the interface to gold (labeled “ΔE₈ = 0 eV Au per spiro fringe per vacuum light”). This interpretation is supported by the fact, that the leading spiro-MeOTAD CIs emission shows a much more clear maximum thread line under light, when all locally integrated emission stems from flat band spiro-MeOTAD independent of the locally varying fringe thickness with locally varying band bending in the dark. Towards the contact to the perovskite, the band bending increases further to an overall “ΔE₈ Au/spiro/pero dark” of 0.74 eV between the interface to gold and to perovskite. As the TCS Pb emissions of the underlying perovskite layer show constant binding energy up to the spiro-MeOTAD interface as indicated by the horizontal line Figure 3, the 0.74 eV band bending must fully drop in spiro-MeOTAD. This effect is supported by a band bending downward in the p-doped spiro-MeOTAD toward the perovskite as was observed in a classical interface experiment displayed in Figure S4 (Supporting Information) in which spiro-MeOTAD and p-dopant LiTFSI were stepwise coevaporated onto a spin-coated MAPbI₄ layer in the integrated UHV deposition and XPS analysis system. In this case the band bending of 0.3 eV was divided to 0.2 eV in spiro-MeOTAD and 0.1 eV in MAPbI₃. In the line scans under illumination (Figure 4 on the right) the band bending in spiro-MeOTAD is mostly removed leaving 0.1 eV (ΔE₈ Au per spiro per pero light).

The lowest energy CIs emission of the perovskite due to carbon atoms in MA and FA called “CIs pero” shifts by 0.64 eV to lower binding energy due to the photovoltage “U/photo” as do the perovskite CIs emission maxima “CIs pero.” But already the bright leading spiro-MeOTAD CIs emission at the interface to the perovskite shows the shift of 0.64 eV. The binding energy difference of the lowest energy spiro-MeOTAD CIs emission and the lowest energy perovskite CIs emission indicates the chemical shift between the C–H groups in spiro-MeOTAD and the C–N bonds of the organic molecules in the perovskite.

The electronic properties band bending in the dark ΔE₈ dark (x), residual band bending under illumination ΔE₈ light (x) and resulting photopotential U/photo(x) are draw schematically in Figure 5 through the tapered cross-section of a full device according to equation

\[ U_{\text{photo}}(x) = (\Delta E_{\text{B,light}}(x) - \Delta E_{\text{B,dark}}(x)) / e^- \] (1)

with x being the position number on the tapered cross-section and e the electron charge. ΔE₈ dark (x) is the change of binding energy of the respective layer-representative elements representing the band bending in the dark (without the chemical shifts due to variation of composition) and ΔE₈ light (x) the respective change of binding energy under light. Thus U/photo(x) represents the spacial distribution of the photovoltage in the solar cell monitored by the PES emissions from the TCS.

In addition to the induced contact potentials and their change on illumination that may be accessible by KPFM on the cross-section as well, TCS-PES has the power to derive the band diagram of the full device in one measurement as displayed in Figure 6. With the addition of the material specific value of the energetic difference ΔE₈CV between the respective core level and the valence band maximum a complete band diagram including doping level, band bending and band line up of the valence band maximum VBM can be derived. With the addition of the respective energy gaps also the conduction band minimum CBM line up can be derived. We have measured the core level to valence band energy difference ΔE₈CV on spin coated spiro-MeOTAD with 284.1 eV for CIs-VBM (see Figure S5a in the Supporting Information) and on (FAPbI₃)₀.₈₅(MAPbBr₃)₀.₁₅ perovskite with 137.₃₉ eV for Pb₄f⁷/₂-VBM (Figure S5b,
Supporting Information). For perovskites the derivation of the valence band maximum from photoemission spectra has to consider low DOS at the onset of the valence band. As suggested by comparison of UPS spectra with DFT calculated DOS,[36] we use in Figure S5b (Supporting Information) a logarithmic plot of the valence band spectra. The samples for these reference measurements have been produced using the same precursor solution as used for the solar cells measured by TCS-PES. For titania we use the value of 456.0 eV published before for anatase.[40] The simplification concerns binding energy variations due to the measured change of Br/I concentration ratio and due to the change of the perovskite to TiO₂ ratio within the mesoporous TiO₂ layer, which are ignored at this stage.

For the energy gap $E_g$ of spiro-MeOTAD the electronic gap of 3.5 eV for individual charges is used instead of the optical gap which is reduced by the exciton binding energy to 3.1 eV.[1] For the perovskite one common value of $E_g = 1.7$ eV is used for the Br/I concentration ratio of the precursor solution according to published halogen ratio dependent values.[14] For Titania the optical gap of 3.2 eV is used for $E_g$. The core level values are taken from the dark measurements in Figure 2 except for spiro-MeOTAD where the flat band value measured for spiro-MeOTAD on gold under illumination is used taken from Figure 4. The dashed part of the CBMs and VBMs in Figure 6 shall illustrate decreasing perovskite and increasing TiO₂ concentration within the perovskite + m-TiO₂ layer when going from the perovskite to the blocking TiO₂ layer.

Using UPS on a freshly prepared tapered cross-section of a new device, direct information on the valence band line up can be measured. A light induced shift of the valence band maxima by around 1.2 eV was observed in TCS-UPS displayed in Figure 7 and in Figure S2 (Supporting Information). This value is near the $U_{oc}$ from $I-V$ measurements Figure S3 (Supporting Information).

In Figure 7 the contour plots of the UPS spectra along a line scan of the tapered cross-section are mapped. The respective
valence band spectra on positions 1 (Au), 20 (perovskite), 35 (perovskite in TiO₂), and 46 (TiO₂/FTO) in the dark and illuminated are displayed in Figure S2 (Supporting Information). In Figure 7, the intensity was cut at 10,000 (dark) and 7500 counts s⁻¹ (light), which roughly indicate the valence band maximum positions that shift to lower binding energy under illumination. In the Au area the edge is at $E_B = 0$ indicating the Au Fermi level as expected for metallic Au. Also, the spiro-MeOTAD VBM starts near the Fermi level indicating p-doping, and then bends to higher binding energies. In the area of the FA₀.₈₅MA₀.₁₅Pb(I₀.₈₅Br₀.₁₅)₃ perovskite the cut off is found at around $E_F - E_B = 1.7$ eV, which does not represent the onset VBM value $E_B = 1.11$ eV we derived from the core level TCS-XPS data and the reference measurement of $\Delta E_{BCV}$ in Figure S5b (Supporting Information) for the band diagram Figure 6. The difference is due to the difference of the cut off at a reasonable value and the actual VBM position, which has to take low DOS at the valence band onset into account. In both cases n-doping of the perovskite is indicated. In the m-TiO₂ layer we find a continuous transition from the perovskite VBM around 1.7 eV to the TiO₂ VBM at around 3.5 eV. The continuous transition is not an electronic property, but is rather due to the continuous decrease of perovskite VBM intensity and increase of TiO₂ VBM intensity in the perovskite + m-TiO₂ layer. Electronically the two

Figure 5. Schematic representation of the electronic binding energy shifts due to band bending in the dark and under OCP of the respective layer-representatives (without chemical shifts) and the resulting open circuit photovoltage course along the tapered cross-section.

Figure 6. Schematic band diagram for the complete SnO₂:F|compact-TiO₂|mesoporous-TiO₂|FA₀.₈₅MA₀.₁₅Pb(I₀.₈₅Br₀.₁₅)₃|spiro-MeOTAD|Au solar cell in the dark derived from the TCS-XPS core level contour plots of Figure 2. Band bending $\Delta E_B$ in the spiro-MeOTAD VBM is indicated as measured in the CsTs core level. Spiro-MeOTAD and perovskite VBM almost perfectly line up with the perovskite VBM $\Delta = 0.02$ eV below the spiro VBM. Measured values for the Au$_{4f/2}$, CsTs, Pb$_{4f/2}$, Ti$_{2p3/2}$, and Sn$_{3d5/2}$ are given in the figure; in addition material specific core level to VBM differences $\Delta E_{BCV}$ for spiromeOTAD and FA₀.₈₅MA₀.₁₅Pb(I₀.₈₅Br₀.₁₅)₃ perovskite measured on spin coated layers (see Figure S5 in the Supporting Information) and published for anatase TiO₂ are used to draw the VBM line up. Published values of the energy gaps of spiro-MeOTAD and of TiO₂ are used to draw the conduction band line up. The gap for the perovskite is derived from paper for the Br/I concentration ratio of the precursor solution. The core energy levels as well as the VBM and CBM are drawn to scale but on two different scales. For simplification the change of the Pb$_{4f}$ and of Ti$_{2p}$ binding energies within the mesoporous TiO₂ layer are ignored. The dashed part of the CBMs and VBMs shall illustrate decreasing perovskite and increasing TiO₂ concentration within the perovskite + m-TiO₂ layer when going from the perovskite to the blocking TiO₂ layer.
A mechanical polishing technique is used to prepare tapered and electronic structure of 18% efficient perovskite solar cell. PES measurements have been applied to analyze the chemical and interfaces. Element spectroscopy is used to identify the respective layers in the full device architecture. Locally resolved information on the chemical composition and density contour plots of the XPS core level emissions allow to draw µm resolution of the undisturbed part of the device from the respective core levels measured by the open circuit photovoltaic of $V_{oc} = 1.2$ V.

VBM coexist as drawn in the band diagram Figure 6. A small amount of elemental Pb$^0$ indicates the metallic Fermi edge at binding energy $E_B = 0$ eV in the dark even in the perovskite part of the cell by an intensity step from dark brown to light brown. The Pb$^+$ Fermi edge shifts by around 1.2 eV to negative binding energy values in the illuminated non-equilibrium open circuit case corresponding to a photovoltage $V_{oc} = 1.2$ V. Full undisturbed solar cells made by the same recipe showed a photovoltage of 1.1 V as evident from the $I-V$ curve displayed in Figure S3a in the Supporting Information. The discrepancy may be due to the less defined illumination spectrum in the electronic properties of the complete device structure in the dark and under illumination can be deduced from TCS-XPS. It is shown that the course of the built-in potential in the undisturbed part of the solar cell stack can be monitored on the TCS by following the continuous energetic shifts of the layer representative element spectra. The difference of the electronic shifts in the dark and under illumination directly represents the photopotential throughout the solar cell. For the cell type analyzed, the photopotential is created in the hole extraction contact. No band bending is found in the dark within the perovskite in contact to spiro-MeOTAD as is generally expected. Instead the induced potential in the dark completely drops inside the hole extraction spiro-MeOTAD layer and the photovoltage actually is created within the mesoporous TiO$_2$ scaffold. In addition, the perovskite/TiO$_2$ ratio decreases within the m-TiO$_2$ layer. The composition induced energy shifts remain under illumination. Simultaneously to the chemical information detailed information on the electronic properties of the complete device structure in the dark and under illumination can be deduced from TCS-XPS. It is shown that the course of the built-in potential in the undisturbed part of the solar cell stack can be monitored on the TCS by following the continuous energetic shifts of the layer representative element spectra. The difference of the electronic shifts in the dark and under illumination directly represents the photopotential throughout the solar cell. For the cell type analyzed, the photopotential is created in the hole extraction contact. No band bending is found in the dark within the perovskite in contact to spiro-MeOTAD as is generally expected. Instead the induced potential in the dark completely drops inside the hole extraction spiro-MeOTAD layer and the photovoltage actually is created within the hole extraction layer. Although the time consuming TCS-XPS measurements lead to some degradation we still find a photopotential of 0.64 V, while in the quick and more gentle TCS-UPS measurements the photon-induced shift was 1.2 eV, which compares well to $V_{oc} = 1.1$ V of the undisturbed cell.

The analyzed perovskite solar cells show 18% efficient. Although prepared from a single mixed ion precursor solution of (FAPbI$_3$)$_{0.85}$(MAPbBr$_3$)$_{0.15}$ composition the Br/I ratio is found to vary in the perovskite and is increased within the mesoporous TiO$_2$ scaffold. In addition, the perovskite/TiO$_2$ ratio decreases within the m-TiO$_2$ layer. The composition induced energy shifts remain under illumination. Simultaneously to the chemical information detailed information on the electronic properties of the complete device structure in the dark and under illumination can be deduced from TCS-XPS. It is shown that the course of the built-in potential in the undisturbed part of the solar cell stack can be monitored on the TCS by following the continuous energetic shifts of the layer representative element spectra. The difference of the electronic shifts in the dark and under illumination directly represents the photopotential throughout the solar cell. For the cell type analyzed, the photopotential is created in the hole extraction contact. No band bending is found in the dark within the perovskite in contact to spiro-MeOTAD as is generally expected. Instead the induced potential in the dark completely drops inside the hole extraction spiro-MeOTAD layer and the photovoltage actually is created within the hole extraction layer. Although the time consuming TCS-XPS measurements lead to some degradation we still find a photopotential of 0.64 V, while in the quick and more gentle TCS-UPS measurements the photon-induced shift was 1.2 eV, which compares well to $V_{oc} = 1.1$ V of the undisturbed cell.

Making use of core level and valence band reference measurements on surfaces of single material layers, the binding energy difference $\Delta E_{BCV}$ between core level and valence band maximum can be derived. With the help of the respective material specific $\Delta E_{BCV}$ the valence band line up can be derived for a full device from the respective core levels measured by the TCS line scan (see Figure 6). With the valence band maximum found 1.11 eV below the Fermi level as shown

![Figure 7. UPS valence band spectra intensity contour plots across the tapered cross-section taken on a freshly prepared full device in the dark (left) and under illumination (right). The intensity was cut at 10 000 and 7500 counts s$^{-1}$ in the dark and illuminated TCS-UPS (dark green line), which is used as the respective valence band maximum course that shifts by 1.2 eV to lower binding energy under illumination. A small amount of elemental Pb$^0$ indicates the metallic Fermi edge at binding energy $E_B = 0$ in the dark by an intensity step from dark brown to light brown that shifts by roughly 1.2 eV to negative binding energy values in the illuminated nonequilibrium case corresponding to an open circuit photovoltaic of $V_{oc} = 1.2$ V.](Image 119x545 to 479x711)

3. Summary

The purpose of this publication is twofolds: 1) the new method tapered cross-section photoelectron spectroscopy TCS-PES is introduced and 2) the power of this method is exemplified by revealing simultaneously chemical and electronic properties of a state-of-the-art mixed ion perovskite solar cell.

Tapered cross-section photoelectron spectroscopy TCS-PES is introduced for the investigation of full and operating electronic thin film devices. TCS-PES allows for locally resolved spectroscopy on devices consisting of thin layers in the range of 100 nm although the analysis spot size is in the range of several 10$\mu$m. Point by point line scan intensity contour plots of the UPS core level emissions allow to draw locally resolved information on the chemical composition and electronic structure throughout the solar cell. Element spectroscopy is used to identify the respective layers and interfaces.

The tapered cross-section photoelectron spectroscopy TCS-PES measurements have been applied to analyze the chemical and electronic structure of 18% efficient perovskite solar cell. A mechanical polishing technique is used to prepare tapered cross-sections at a very low angle to stretch out the thin layers in the 100 nm range to the mm scale which is within the lateral resolution of the PES analyzer of several 10$\mu$m.
in Figure S5b (Supporting Information) clearly n-type doping of the MAPbI$_3$/Br$_x$ perovskite is indicated. TCS-PES shows that in our samples the built-in potential drops inside the hole extraction spiro-MeOTAD layer. As a consequence, the photovoltage actually is created within the hole extraction layer and not in the perovskite. This result is consistent with the KPFM results for MAPbI$_3$ cells with similar n-doping by PbI$_2$ surplus. Thus the perovskite in our analyzed cell type is measured to be n-type and the device system shows a n–n–p structure with the photovoltage arising within the HTL. The n–n–p working structure is in contrast to the often assumed n–i–p structure with the photovoltage arising in front of the ETL and HTL within the intrinsic perovskite.

In addition to the induced potentials and photopotentials that can be accessed by KPFM also, the band diagram of the device can be derived. The band diagrams derived with this method may then be compared to the direct TCS-UPS measurements (Figure 7), which are more surface sensitive and thus more sensitive to cross contamination induced in the TCS preparation process. Forming a cross-section for KPFM or a tapered cross-section for TCS-PES introduces an additional interface toward the vacuum at the cross-section surface. At the semiconductor surfaces, surface potentials and photopotentials induced by respective material specific surface states cannot be excluded in general. As in the case shown here the photopotential is of a constant value for all layers on top of spiro-MeTAD, we conclude, that surface potentials and photopotentials at the vacuum interface play a minor role in our measurements, as these would be expected to be different for different materials.

TCS-UPS directly shows the valence band line up similar to the valence band line up derived from core level scans in TCS-XPS using $\Delta E_{BCV}$. In the perovskite/m-TiO$_2$ compound a continuous valence band maximum shift from the perovskite VBM at 1.5 eV to the TiO$_2$ valence VBM at 3.5 eV below the Fermi level. TCS-XPS rather suggests a continuous change from perovskite to TiO$_2$ valence band emission intensity.

4. Conclusion

With this study we have shown that tapered cross-section photoelectron spectroscopy TCS-PES proves to be a powerful method for the investigation of full and operating electronic thin film devices. Point by point XPS core level line scans allow to draw locally resolved information on the chemical composition. Using intensity contour plots of the emissions the electronic structure throughout the full device architecture is mapped. Ex situ prepared samples and even the individual parent materials within composite layers of, e.g., a mesoporous matrix and a wet chemically incorporated semiconductor become accessible to local resolved PES analysis. Approaching interfaces, built in contact potentials are quantitatively mapped by measuring local variations of respective core level emission binding energy shifts. In addition, binding energies variations under operating conditions can be mapped. For case of solar cells as investigated here, binding energy variations induced by operation under open circuit illumination directly map the course of the photopotential throughout the part of the device left undisturbed by the TCS preparation.

Induced contact potentials shift all energy levels and bands of a specific contact material in parallel with respect to the Fermi level, which is the reference energy position of all PES measurements. Using material specific energy differences $\Delta E_{BCV}$ of the core level to valence band maximum, the valence band maxima positions with respect to the Fermi level can be derived from TCS-XPS. Specific $\Delta E_{BCV}$ can be taken from core level and valence band reference PES measurements of the different device materials. Adding published values for the semiconductor energy gaps $E_g$ the device band diagram containing band bending and valence band and conduction band line up at all interfaces can be derived. Complementarily TCS-UPS allows to directly map the valence band line up to be compared with valence band line up derived from core level line scans in TCS-XPS using the $\Delta E_{BCV}$, which showed to be similar. Future experiments are planned to apply TCS-PES to devices under different operating conditions as, e.g., applied potentials and for solar cell in short circuit.

Furthermore, the TCS-PES experiments shown here for perovskite solar cells are in principle also possible with other devices used for many different applications as LEDs, transistors, solid state batteries, and so on.

5. Experimental Section

The samples used for the experiments were prepared at EPFL in Lausanne as described previously. In short: conductive FTO glass (NSG10) was sequentially cleaned by sonication in a 2% Helmanex solution and isopropanol for 15 min respectively. A 20–50 nm titania blocking layer was deposited onto the substrates by spraying a solution of 200 µL titanium disopropoxide bis(acetylacetonato) in 5 mL ethanol at 450 °C. For the 200–300 nm mesoporous TiO$_2$ layer, 30 NR-D titania paste (Dyesol) diluted in ethanol (ratio 1:8 by weight) was applied by spin-coating at 2000 rpm for 10 s followed by a sintering step at 500 °C for 30 min. After cooling down the substrates, a Li-treatment was applied by spin-coating 60 µL of a solution of bis(trifluoromethylsulfonyl)amide-lithium-salt (Li-TFSI) in acetonitrile (15 mg mL$^{-1}$) onto the mesoporous layer, followed by a sintering step at 500 °C for 15 min to decompose the Li-salt as previously described. The perovskite layers were fabricated by a single step spin-coating procedure reported by Seok et al. For the perovskite precursor solution 556 mg of PbI$_2$ (TCI), 68 µg PbBr$_2$ (TCI), 180.5 µg formamidinium iodide (Dyesol), and 20.7 µg methylammonium bromide (Dyesol) were dissolved in a 1:4 mixture of dimethyl sulfoxide:dimethylformamide. This resulted in a precursor solution having an excess of PbI$_2$ of around 15%. The perovskite solution was spun at 1000 rpm for 10 s followed by 5000 rpm for 30 s using a ramp of 3000 rpm s$^{-1}$. 15 s prior to the end of the spin-coating sequence 100 µL chlorobenzene were poured onto the spinning substrate. Afterward the substrates were transferred onto a heating plate and annealed at 100 °C for 45 min. Spiro-MeOTAD was used as a HTM and applied using a 70 × 10$^{-5}$ mol solution in chlorobenzene. tert-butylpyridine (TBP), triis(2-(2H-pyrazol-1-yl)-4-tert-butylpyridine)cobalt(III) (FK209), and Li-TFSI were added as additives: 330 mol% TBP, 50 mol% Li-TFSI from a 1.8 µL stock solution in acetonitrile, and 3 mol% FK209 from a 0.25 µL stock solution in acetonitrile. The HTM solution was spin-coated dynamically onto the perovskite layers at 4000 rpm for 20 s. The gold electrodes were deposited by thermal evaporation of 80 nm gold using a shadow mask under high vacuum conditions.

For TCS-PES the samples were transferred from EPFL Lausanne to TU Darmstadt. No measures were taken to avoid ambient air contact. The tapered cross-section was prepared using a metallographic polishing
machine. For polishing a silk cloth type 9450 was used at 80 rpm. The sample was kept at low angle with the polishing wheel. Great care has been taken to minimize the cross-contamination during TCS preparation. After polishing the devices are transferred to the vacuum chamber for TCS-PES measurements.

The XPS/UPS system (Escalab 250) is equipped with monochromatic Al-K\textalpha\ source (1486.6 eV), in combination with a magnetic collector lens system with a low field of view angle and acceptance angle to have higher spatial resolution. For bias illumination a 50 W high-intensity discharge lamp, with a spectrum close to AM 1.5G was shone on the sample. X-rays of 250 \mu m spot size were used for photoexcitation. The Au contact of the device was grounded to the spectrometer during measurements. The number of scans at each position of the line scan was kept low and was adapted to the respective core level signal intensity to obtain a sufficient signal to noise ratio to identify the core level or valence band maximum energy positions. The spectra were recorded using a concentric hemispherical analyzer with a pass energy of 10 eV. The system was calibrated to gold emission lines (Au4f7/2 at 83.98 eV, Au4d5/2 at 335.17 eV, and Au4p 3/2 at 546.44 eV) and the Fermi-edge at 0 eV as reference.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements
This work was supported by the Federal Ministry of Research and Development (BMBF) under the Project title “Perosol” project number 03SF0483A and by the German Research Foundation (DFG) under the Project title “Interrogate” project number MA 2104/3-1 within the priority program SPP 2196. The spelling error in the name of C.P. was corrected on July 2, 2020 after initial online publication.

Conflict of Interest
The authors declare no conflict of interest.

Keywords
band diagrams, open circuit potentials, perovskites, photoelectron spectroscopy, photopotential

Received: December 24, 2019
Revised: April 2, 2020
Published online: May 18, 2020

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