CHEOPS	Title **Demonstration of improved front electrode opto-electrical and morphologic properties leading to a 1 mA/cm² current gain**	Deliverable Number **D1.4**
Project Number **653296**		Version **1**

CHEOPS – Production technology to achieve low Cost and Highly Efficient phOtovoltaic Perovskite Solar cells

Deliverable 1.4

Demonstration of improved front electrode opto-electrical and morphologic properties leading to a 1 mA/cm² current gain

WP1 - Perovskite single junction development

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Revision History

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HM Yates (USAL), JL Hodgkinson (USAL), M Afzaal (USAL)	Draft deliverable	05.01.2018
S. Nicolay (CSEM), A. Walter (CSEM)	Revision 1	24.01.2018
HM Yates (USAL)	Final version	29.01.2018

Contents

Acronyms and abbreviations

CHOSE	Università degli Studi di Roma Tor Vergata *(CHEOPS Beneficiary 4)*
CSEM	Centre Suisse d'Electronique et de Microtechnique *(CHEOPS Beneficiary 1)*
TYNDALL-UCC	Tyndall National Institute *(CHEOPS Beneficiary 2)*
UOXF	University of Oxford *(CHEOPS Beneficiary 3)*
USAL	University of Salford *(CHEOPS Beneficiary 8)*
AACVD	Aerosol Assisted Chemical Vapour Deposition
APCVD	Atmospheric Pressure Chemical Vapour Deposition
CTL	Carrier transport layer
CVD	Chemical Vapour Deposition
ETL	Electron transport layer
FF	Fill factor
FTO	Fluorine doped tin oxide
HTL	Hole transport layer
Jsc	Short circuit current
MPP	Maximum power point
PECVD	Plasma Enhanced CVD
PK	Perovskite
SEM	Scanning electron microscope
TCO	Transparent conductive oxide
Voc	Open circuit voltage
WP	Work Package

Executive Summary

This deliverable reports on the development of APCVD and sputter thin films to achieve more transparent and conductive front electrodes. The front electrode includes both the transparent conductive contact (FTO, usually deposited by APCVD) and the electron transporting layer (ETL, conventionally made of spin coated TiO$_2$). The FTO layer properties as defined in Task 1.3 are total transmittance > 85%, sheet resistance <10 Ω/□ and surface roughness < 30 nm. The optimised front electrode opto-electrical and morphological properties should lead to a 1mA/cm^2 photo-generated current gain for 1cm^2 single junction devices. In addition, we will report on work carried out in Task 1.3 on APCVD deposition of CTL layers (Titania and Nickel Oxide) with comparison to sputter coated titania.

Improved FTO thin films achieved the required lower roughness, sheet resistance and a higher transmittance than the reference FTO (TEC 7) especially in the visible spectrum range, despite being generally thicker. The in-line APCVD process was capable of depositing FTO's with a wide range of characteristics, which when combined with a suitable ETL led to cell results which competing closely with the commercial reference. **Front electrodes of optimised FTO with TiO$_2$ ETL produced via vacuum sputtering or by spray pyrolysis produced cells with current gains of > 1mA/cm^2 over that of the reference FTO (TEC7)/spin coated ETL**. The reference cells were the standard reported literature NIP structure. Use of spray pyrolysis to produce the TiO$_2$ ETL led to the highest current, with a gain of 0.87 mA/cm^2 over that of the sputtered ETL. Although this achieved high power conversion efficiencies (MPP 17.64%) for 1 cm^2 cells, similar values were obtained with lower current gain on sputtered ETL layers (MPP 17.76%).

A solution to further increase cell current could be to deposit an anti-reflection coating (ARC) via APCVD. Indeed, a gain of 0.3 mA/cm^2 using such ARC, has been previously demonstrated by USAL and CSEM in the framework of previous FP/ EU project PLIANT (FP7 NMP.2012.1.4-1 309530 PLIANT).

To further demonstrate the quality of the USAL deposited FTOs in an alloyed perovskite FA$_x$MA$_{1-x}$Pb(I$_x$Br$_{1-x}$)$_3$ system (UOXF), median power conversion efficiency improved by 1.5% over that of a cell fabricated with industry standard TEC7. Improved cell characteristics with in particular reduced hysteresis were evident.

An in-line atmospheric pressure PECVD process demonstrated uniform deposition of TiO$_2$ over 20 cm x 20 cm. This was shown to match the cell efficiencies of sputtered TiO$_2$ when used in the fabrication of mesoporous (scaffold) cells. Planar cell architecture gave variable results for the APCVD deposited ETL, in comparison to that of the sputtered reference. Preliminary results on the planar cells indicated that the initially poor efficiencies may be dramatically improved by an annealing cycle. Annealing was shown to reduce structure defects in the APCVD deposited film. This suggests the poor cell results could be due to chemical or structural issues associated with the low temperature deposition process.

We also present a short study of APCVD deposition of nickel oxide as an alternative charge transport material. The availablity of suitable precurors led to use of Flame Assisted CVD (FACVD), which produced adhesive, polycrystalline films of nickel oxide. The FACVD process led to island growth and hence discontinuous films, which would not be suitable as CTL's, so has been discontinued.

Need for the Deliverable

- Electrodes with higher transparency and better conductivity are needed in order to achieve devices providing higher photo-generated current and higher FF on module scale. In addition the morphology of the deposited layers will have to be carefully controlled as a too rough surface

(e.g. from the naturally formed pyramidal shape in FTO deposited by APCVD) could lead to non-uniform PK layer coverage and hence lead to shunt formation.

- Investigate the possibility to use APCVD to deposit thin compact TiO_{2-x} layers acting as ETL and hole blocking layer directly on top of the FTO electrode. This will represent an important simplification of the process flow as both the electrode and electron transport layer could be deposited using the same tool, possibly directly integrated on glass production lines.
- The large scale exploitation of PK based photovoltaics depends not only on the advancement of cell performance but also the cost effective large area production of all component layers. High performing cells described in the literature often use wet processing to produce the ETL's. A more scale-able PVD approach has been adopted under Task 1.1. However vacuum requirements impose batch operation and significant costs, hence the parallel development of a continuous, atmospheric pressure (APCVD) approach may yield significant advantage.

Objectives of the Deliverable

- FTO films with total transmittance > 85%, sheet resistance < 10 Ω/□ and surface roughness < 30 nm.

- The optimised front electrode stack to lead to a 1mA/cm² photo-generated current gain for 1cm² single junction devices.

- A report on work carried out in Task 1.3 on APCVD deposition of carrier TL layers (Titania and Nickel Oxide) with comparison to sputter coated titania.

- To demonstrate a continuous, scalable low temperature, atmospheric pressure process for the production of TiO_x ETL.

Outcomes

The main APCVD factors influencing the FTO properties are the film thickness and dopant level. Reduced thickness increases transmittance, surface smoothness and sheet resistance. While increased dopant levels reduce sheet resistance and the transmittance. By adjusting fluorine doping levels and the number of passes (under the coating head) in the APCVD process, films of desired characteristics were successfully deposited. A correct combination of thickness dependent mobility and carrier concentration, and surface related transmission and haze are required to make significant contribution towards power conversion efficiencies. It was found that the sheet resistance of the FTO has a greater influence on the cell performance than its roughness within the range of 18 nm − 27 nm (RMS). **FTO films with sheet resistance < 8 Ω/□ and transmission > 85% (@650 nm) led to cells with the observed steady-state efficiency of 17.64% and a photo-generated current gain of 2.49 mA/cm² (compared to industry standard TEC7) for cells fabricated using spray pyrolysis for TiO_{2-x} deposition.** Although the current gain was not quite so high (2.14 mA/cm²) when using sputtered ETL layers similar MPP efficiencies values could be obtained of 17.76%. The increase in efficiency over that of the standard TEC7/spin-coated TiO_2 is predominantly due to an improved FF of 77.5% driven by the low Roc (4.86 Ω.cm²) of the cells.

To further demonstrate the quality of the USAL deposited FTOs in an alloyed perovskite $FA_xMA_{1−x}Pb(I_xBr_{1−x})_3$ system (UOXF), median power conversion efficiency improved by 1.5% over that of a cell fabricated withTEC7 (16.8% with TEC7 to 17.4% with USAL deposited FTO). Improved cell characteristics with in particular reduced hysteresis were evident with the cell on TEC7 with an average difference between PCE of forward and reverse scans was 9.8%, while with the APCVD substrate the difference was 4.4%.

The AP PECVD in-line process has proved capable of producing device quality films over 10 cm x 10 cm substrates, with the capability to extend further indicated by the growth demonstrated on 20 x 20 substrates. AP PECVD derived TiO_{2-x} on TEC7 gave cell peak efficiency of 15.09 % compared to 16.54 % achieved for the PVD TiO_{2-x} reference when used in mesoporous (scaffold) cell architectures. The lower efficiency is mainly due to the roughness of the underlying FTO leading to pinholes in the TiO_{2-x} film, as use of a smoother FTO (Solaronix TCO22-15) gave more compatible values (AP PECVD 14.53% and sputtered 14.11%).

Planar architectures proved more challenging with very variable results for the APCVD ETL in comparison to that of the sputtered reference. These preliminary tests indicated that the initially poor efficiencies may be dramatically improved by a 500°C annealing cycle, to the extent of exceeding the reference with a maximum of 13.9 % (7.69 % mpp) compared to 13.1 % (5.13 % mpp) for the PVD (non-annealed) reference. Initial results (via XPS) suggested that deposition of the ETL at room temperature leads to a higher concentration of structural defects in the films than in the sputtered films. These are reduced on annealing, so the apparent cell improvement could be due to chemical or structural issues.

Next steps

FTO - Use of optimised results for APCVD homogeneous FTO for NIP modules within T1.4.

$FA_xMA_{1-x}Pb(I_xBr_{1-x})_3$ system - The initial results showed an increased transparency in the NIR as well as reduced haze over the reference TEC7, which should help gain more current. Ellipsometry is currently being used at UOXF to obtain optical constants and hence model the optimum thickness for absorption in the device stack. Based on this data new CVD FTO samples of optimum thickness will be deposited and used to make new devices, which should demonstrate a further efficiency improvement.

CTL - Improved planar cell properties via –

Reduction of defects and cleaner precursor reaction for TiO_{2-x} by an annealing process or deposition under a pulsed DC power supply (rather than audio frequency). The pulsed supply delivers a higher transient power density at a very low duty cycle to minimise thermal load and control the level of activation. To use nitrogen rather than argon as the plasma gas as more commercially viable.

The surface texture of FTO is a factor in ETL performance. USAL developed APCVD FTO combines high conductivity with a smoother topography compared to the commercial TEC 7. The performance advantage already demonstrated by the USAL FTO may be complemented by improved compatibility with the AP PECVD TiOx process, supporting the envisaged combined on-line processing.

Further investigation with the development of the CVD NiO (HTL) process using AACVD which is expected to produce continuous films.

1 Deposition of APCVD F-doped tin oxide

1.1 Discussion of FTO film properties

Task 1.3 focuses on developing high quality $F:SnO_2$ (FTO) on with high transparency (> 85 %), low sheet resistance (< 10 $\Omega/\square$) and reduced surface roughness (< 30 nm). By adjusting fluorine doping levels and the number of passes (under the coating head) in the APCVD process, films of desired characteristics are successfully deposited. See summary in Table 1.

Table 1. Growth parameters and properties of CVD FTO thin. A growth temperature of 600 °C and water:monobutyltin trichloride ratio of 5:1 was fixed during the deposition process.

	TFAA conc. (M)	No of Passes	R_{sh} ($\Omega/\square$)	$\rho/x10^{-4}$ (Ω cm)	Mean Thickness (nm)	μ (cm²/Vs)	$N/x10^{20}$ (cm⁻³)	Transmission % 450 (nm)	531 (nm)	650 (nm)	800 (nm)	RMS (nm)
Set 1	1	8	7.6	4.66	614 ± 10	25	4.9	80	84	85	86	27
Set 2	1	6	11.2	5.29	473 ± 22	21	5.4	83	81	85	88	13
Set 3	1	8	8.8	4.49	510 ± 14	28	4.7	83	86	87	99	23
Set 4	1	6	13.7	4.94	360 ± 21	23	6	81	88	81	88	18
Set 5	0.8	8	7.5	6.21	828 ± 9	30	3.7	81	85	87	86	26
Set 6	1	8	7.7	5.66	736 ± 7	32	3.8	82	84	85	87	23
	0.6	10	7.9	7.54	955 ± 37	33	2.8	81	83	82	81	
Set 8	1	8	6.6	5.53	807 ± 20	24	5.33	80	84	86	86	27
Set 10	0.8	10	10.1	8.4	832 ± 38	26	2.8	82	84	85	87	
TEC 7	N/A	N/A	7.1	3.2	600 ± 16	27	7.2	77	80	83	81	33

By reducing the film dopant level and increasing their thickness, it was possible to preserve a comparable R_{sh} to the commercial reference FTO. A lower dopant level reduced the carrier concentration and hence led to less free carrier absorption and increased transmittance. However, the increased thickness tended to increase the surface roughness and hence optical haze.

A range of different samples were produced (10 cm x 10 cm) on borosilicate glass and their properties assessed against the cell results. Samples were sent to partners to assess the effects of different ELT application methods (ALD, spin coating, sputtering and spray pyrolysis).

## 1.2 Discussion of results on single junction Perovskite cells

1.2.1 Titania ETL's

Early on in the project it was realised that spin coating lacked the ability to deposit uniformly over large areas and required a high temperature sintering step. This was reflected in the cell data which showed improved characteristics on use of more conformal methods such as ALD and vacuum sputtering. Although, ALD led to the production of highly efficient cells (see Table 2 sets 3 and 4), some collection issues were recorded using this BL, leading to much lower current in particularly for the planar arrangement (see Table 2 - set 8, ALD). This may be related to the higher level of

impurities in ALD derived films than in sputtered ones. An optimum ETL (BL) thickness for both sputtered and spray pyrolysis was found to be 20 -30 nm, as seen by improved cell performance with both USAL deposited and reference FTO's. Higher carrier concentrations in the FTO generally led to lower FF as can be seen with Set 4 (high carrier concentration) against that of Set 3 or 5 (lower carrier concentration).

To demonstrate how the CVD deposited FTOs performed in the perovskite scaffold solar cells[1] current-voltage hysteresis (forward and back scans) and MPPT scans of the champion device using set 5 FTOs are demonstrated in Figure 1. Despite showing a small hysteresis, high PCE of 17.8% under MPPT is obtained. The observed steady-state efficiency in our champion data is predominantly due to an improved FF of 77.5% driven by the low Roc (4.86 $\Omega.cm^2$) of the cells. After integrating the external quantum efficiency (EQE) curve of the device, J_{sc} was found to be 20.88 mA/cm² which is consistent with the measured J_{sc} determined by J-V measurements (see Table 2, set 5). **Use of spray pyrolysis deposited TiO_{2-x} (CHOSE) on USAL FTO led to scaffold cells with the observed steady-state efficiency of 17.64% and a photo-generated current gain of 2.49 mA/cm² compared to TEC7/spin coated TiO_{2-x}.** The solar cell results in general indicate that a single FTO property for example, having low sheet resistance alone does not influence power conversion efficiencies. A correct combination of thickness dependent mobility and carrier concentration, and surface related transmission and haze are required to make significant contribution towards better power conversion efficiencies.
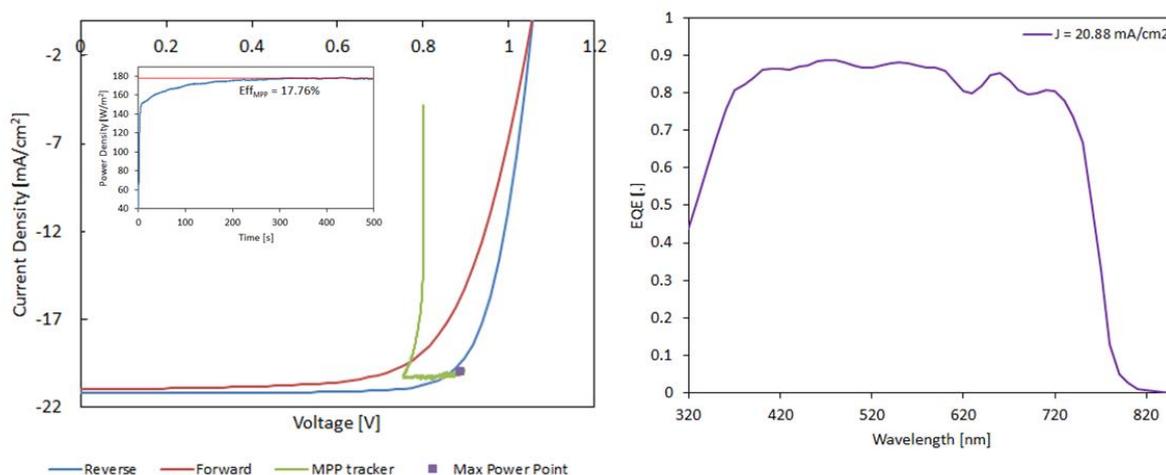
Figure 1. (right) Photocurrent-voltage curve and maximum power point tracking of champion device. (left) corresponding external quantum efficiency spectrum.

Ideally a planar architecture would simplify the fabrication process, but tends to give overall lower cell efficiencies as any imperfections within the FTO and subsequent layers are accentuated within the perovskite which (with the lack of a mesoporous transport layer) needs to act both for charge generation as well as charge extraction. However, CHEOPS partners have strongly improve the efficiencies of planar devices by various improvements in fabrication and optimisation, from early efficiency values around 9% to 16.7% (see Table 2, set 8) and have a fractionally higher median value than the results from the reference FTO used with sputtered ETL. The cell characteristics although similar between reference and CVD FTO, show a slightly higher V_{oc} possibly due to a reduction in non-radiative losses and better charge transport.

Table 2. Summary of significant photovoltaic properties of the cells using USAL FTO films

	Blocking layer	Cell architecture	V_{oc} [mV]	J_{sc} [mA/cm²]	FF [%]	Eff. [%]	R_{oc} [Ωcm²]	R_{sc} [Ωcm²]	Eff. MPP [%]
Set1	Spray Pyrolysis	Scaffold	1081.59	21.54	74.47	17.35	5.22	22139.69	17.64
	Spray Pyrolysis	Planar	1056.62	21.33	61.96	13.97	9.23	2528.18	9.65
Set2	ALD*	Scaffold	1053.47	21.18	56.53	12.61	7.96	454.3	*No stable output*
	ALD*	Planar	1008.77	17.67	52.3	9.32	10.84	526.64	3.42
	Spray Pyrolysis	Scaffold	1101.83	21.48	76.38	18.08	5.07	-11164.41	17.74
Set3	ALD	Scaffold	1106.43	20.27	71.70	16.08	7.79	-6762.81	15.18
	Sputtering	Scaffold	1076.99	20.67	70.15	15.62	7.02	450.56	10.57
Set4	ALD	Scaffold	1059.73	21.22	61.33	13.79	14.11	-3527.98	15.52
	Sputtering	Scaffold	1091.75	20.65	53.47	12.06	11.63	239.29	7.65
Set5	Sputtering	Scaffold	1055.70	21.19	77.52	17.34	4.86	150908.90	17.76
Set6	Sputtering	Issue with cell fabrication – neither cells or reference cells viable							
		See section 1.3							
Set8	Sputtering	planar	1114.59 ±20.85	20.33 ±0.42	62.56 ±6.76	14.21 ±1.78	8.99 ±1.38	1186.57	
	ALD	planar	989.45 ±75.74	11.96 ±1.51	42.23 ±12.31	5.19 ±2.15	28.18 ±16.36	234.62 ±144.13	
TEC7	Sputtering	planar	1082.01 ±27.72	20.49 ±0.29	63.62 ±8.41	14.13 ±2.09	9.68 ±2.85	7488.77	
Set 10	Sputtering*	planar	917.89 ±51.40	19.23 ±1.07	50.44 ±7.32	8.96 ±1.77	14.63 ±1.00	1052.60	
TEC 7	Sputtering*	planar	957.92 ±52.30	19.48 ±1.79	56.83 ±8.04	10.75 ±2.51	12.04 ±3.24	1511.0	
TEC 7	Sputtering	Scaffold	1098.59	20.73	75.6	17.22	5.95	24128.98	17.27
TEC 7	**Spin coating reference**	**scaffold**	**1052.00**	**19.05**	**72.62**	**14.55**	**6.30**	**748.40**	**14.21**

* Possible issue with cell fabrication as use of standard TEC7 gives lower efficiency from same perovskite solution.

1.2.2 Nickel Oxide charge carrier layers

As an alternative approach sputtered NiO has been used as a charge carrier layer directly deposited on the front electrode. By doing so, the cell structure is inverted from the standard NIP scheme to a PIN structure. This allows more choice in the p-type transport material to replace the standardly used spiro-METAD, which opens promising prospects in terms of upscalability and stability. The cell structure was $FTO/NiO/Cs_{0.05}(MA_{0.17}FA_{0.83})_{0.95}Pb(I_{0.83}Br_{0.17})_3/C_{60}/Cu$. The averaged results (over 8 cells, including both forward and back values) showed very similar efficiency results for both Set 8 and the reference TEC7 related cells, despite the differences in the properties of the FTO layers. (cell size $1\ cm^2$).

Table 3. Comparison of cell results for NiO based cells.

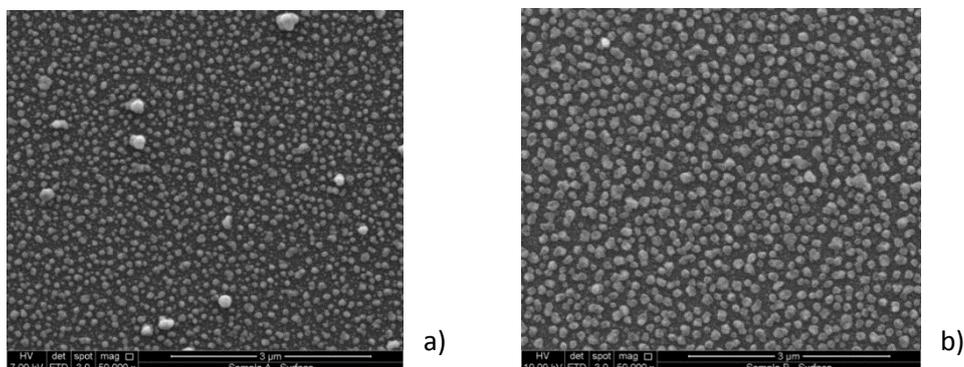|	NiO CTL	Cell architecture	V_{oc} [mV]	J_{sc} [mA/cm²]	FF [%]	Eff. [%]	R_{oc} [Ωcm²]	R_{sc} [Ωcm²]	Eff. MPP [%]
Set 8	Sputtering	planar	994.72 ±61.30	19.40 ±0.54	53.30 ±10.00	10.39 ±2.37	10.70 ±4.08	450.37	
TEC 7	Sputtering	planar	1000.98 ±76.4	18.95 ±0.17	53.66 ±10.37	10.33 ±2.50	11.17 ±5.04	461.03	

1.2.2.1 The Deposition of NiO as an alternative Hole Transport Layer

Recent advances reported in the literature suggest that the use of NiO as an alternative or in conjunction with the organic materials commonly used as the HTL (e.g. spiro-MeOTAD) may significantly improve long term stability. It is also reported that the use of NiO combined with such materials may yield additional benefit in terms of increased efficiency. As with the TiO_x ETL, the reported work focuses on wet chemical or vacuum based processes, and so the provision of a continuous, low cost, large area process would hold similar advantage.

To this end, we have extended our work to investigate the deposition of NiO via flame assisted CVD (FACVD). This process allows the use of readily available water soluble precursors and is compatible with both on and off line processing. Initial tests, with a substrate temperature of 400 °C, demonstrated the production of a clear adherent film when a small addition of oxygen (0.1 l.min⁻¹) was made to the Air/Propane mix. Weak X-ray diffraction maxima at 37.2° and 43.3° were observed, showing the production of NiO (JCPDS-47-1049) with some degree of crystallinity, which could be increased with annealing at 500 °C. Incremental increases in the additional oxygen resulted more defined peaks.

SEM Images of the surface (Figure 2) suggested a largely particulate film, with the level oxygen addition impacting the size distribution. Cross sectional images showed film thicknesses in the order of 80 nm with apparent coverage of the glass.

Figure 2. SEM image of the NiO surface a) 0.1 l.min^{-1} O$_2$ b) 0.6 l.min^{-1} O$_2$

The FACVD process led to island growth and hence discontinuous films, which would not be suitable as CTL's, so has been discontinued. Instead this work will concentrate on AACVD which is expected to produce continous films.

1.3 FA$_x$MA$_{1-x}$Pb(I$_x$Br$_{1-x}$)$_3$ planar system

One major hurdle in producing commercially viable PK solar cells is their lack of long term stability. A possible solution, beside working on the replacement of organic based charge transport material, is to work with alternative active material, notably perovskite with mixed cations such as formamidinium (CH(NH$_2$)$_2^+$, (FA) lead halide which is known to produce cells with both enhanced efficiency and greater stability compared to the often used CH$_3$NH$_3$PbI$_3$. In addition FAPbI$_3$ has a broader optical absorption band and reduced band-gap (1.48 eV compared to 1.57 eV of CH$_3$NH$_3$PbI$_3$). To test this mixed cation perovskite material, set 6 FTO was used (see Table 1). It has similar sheet resistance, lower carrier concentration and is smoother than TEC7. The difference in roughness is reflected in the increased optical scattering for rougher TEC7. The CVD FTO films displayed a high transmission in the NIR (Figure 3).
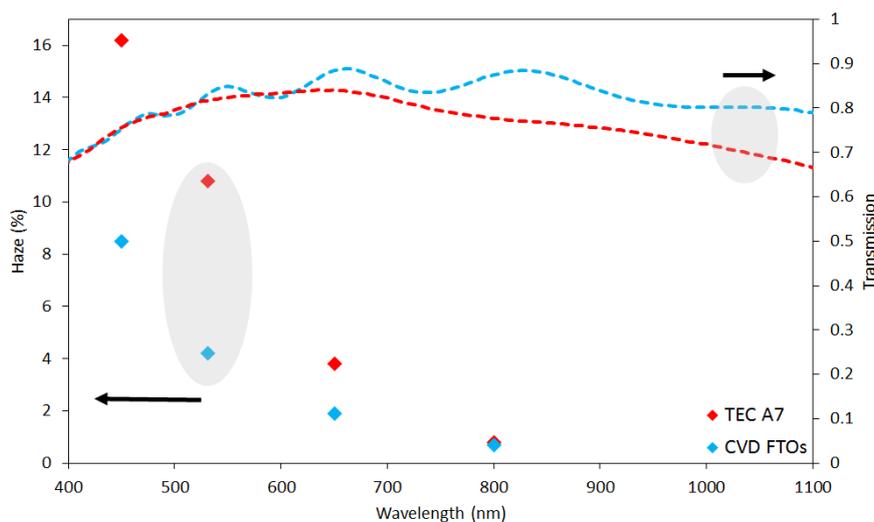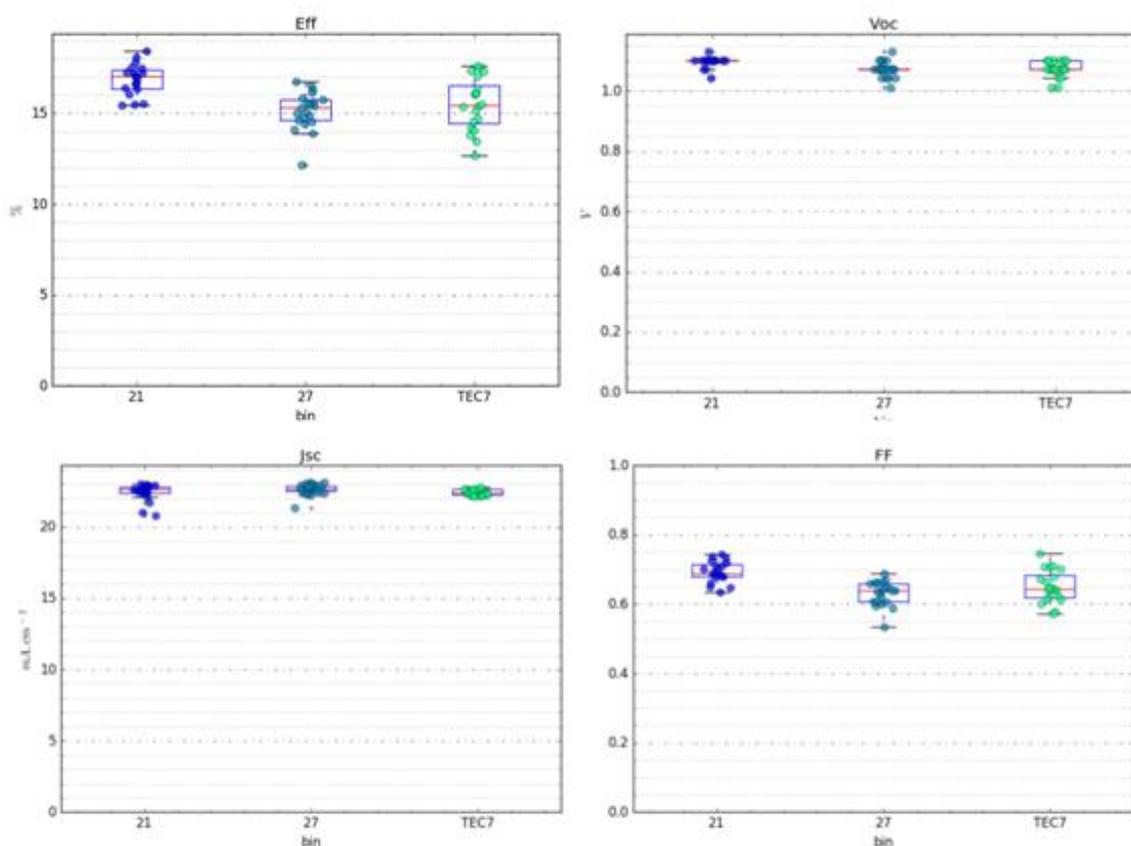

Figure 3. Dependence of optical haze and transmission of FTOs on wavelengths.

Results for the cells (0.09cm^2) were plotted showing a narrow distribution for all cell characteristics (Figure 4). The greatest improvement for the CVD FTO (bin 21) was seen in the V$_{oc}$, while smaller increases for FF and limited variation in J$_{sc}$, led to the enhanced PCE values. It is likely that the

additional smoothness of the CVD film reduces the amount of light lost by scattering and its lower carrier concentration leading to less free carrier absorption (as seen with transmission values). The $FA_xMA_{1-x}Pb(I_xBr_{1-x})_3$ system demonstrated that the median power conversion efficiency improved by 1.5% , relative, once deposited on USAL FTO over that of a cell fabricated with TEC7 (16.8% with TEC7 to 17.4%). Improved cell characteristics with in particular reduced hysteresis were evident with the cell on TEC7 with an average difference between PCE of forward and reverse scans was 9.8%, while with the APCVD substrate the difference was 4.4%.


Figure 4. Cell characteristics comparing cells fabricated via APCVD USAL FTO and TEC7.

2   Deposition of AP PECVD Titania

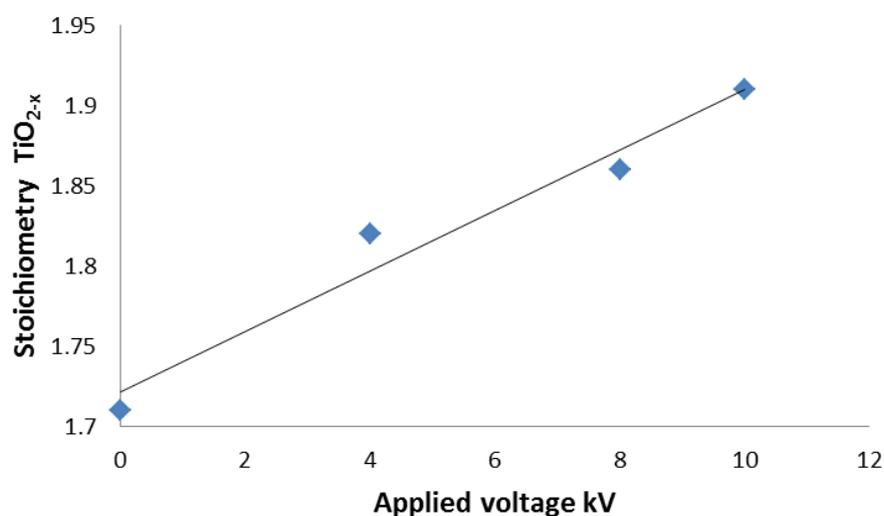### 2.1   AP PECVD as a large area deposition method for TiOx ETL

The TiO_x films were deposited using a scale-able, roll to roll system to convey substrates under a dual flow AP PECVD coating head at room temperature. In-situ activation of the precursor was achieved by a barrier discharge system driven by a purpose built audio frequency power supply.
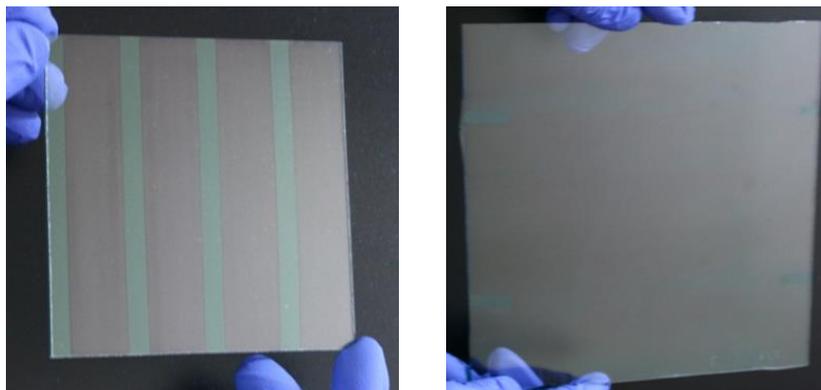
Figure 5. Photographs showing the AP PECVD TiOₓ ETL on FTO substrates. On left, 10 x 10 cm masked for cell construction, on right coating over 20 x 20 cm.
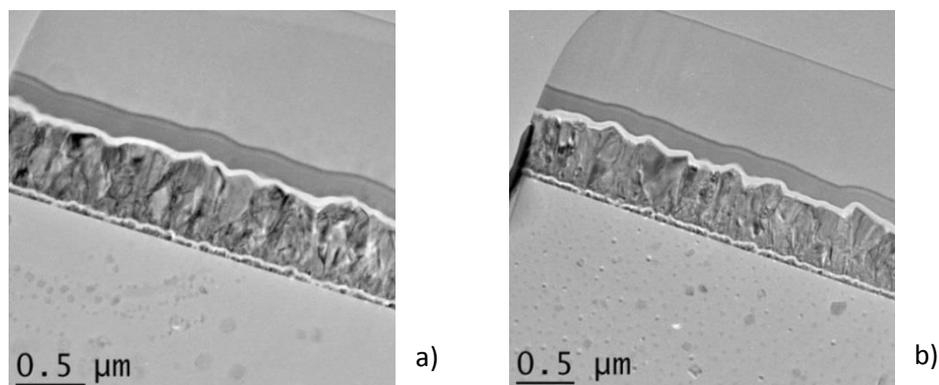
In this work the lab scale system proved capable of depositing compact, sub 100 nm, TiO_{2-x} films with sufficient uniformity over the 10 x 10 cm substrates to allow cell construction and evaluation of ETL performance compared with the established PVD ETL. The scale-ability of the system was further emphasised by demonstrating coating on 20 x 20 cm substrates. Example films are shown in Figure 5.

The films appeared dense and adherent, with controllable stoichiometry over a range comparable to the established PVD process which resulted in a ratio of $TiO_{1.76}$ according to XPS analysis. The stoichiometry of the AP PECVD films was most directly influenced by the applied voltage, and hence the energy applied to the gas phase, inducing decomposition of the precursor as shown in Figure 6.

Figure 6. The influence of applied voltage on film stoichiometry during the AP PECVD process.

Figure 7. TEM cross sections showing the TiO$_{2-x}$ films deposited by a) AP PECVD and b) sputtering.

Comparison of the films via TEM cross-section (TYNDALL-UCC) showed good conformal and continuous growth in each case with no obvious difference between the AP PECVD film (Figure 7a) and the sputtered reference (Figure 7b).

In addition, this could provide the basis for a continuous large area process to replace existing wet chemical or vacuum based technologies. For the initial cell tests the films were deposited using an applied voltage of 4 kV with an audio frequency supply, to drive the argon plasma. The lack of stoichiometry was not an issue as the successfully applied sputtered reference film was also non-stoichiometric (TiO$_{1.73}$). To further enhance the viability of cost effective scale up, we have also explored the use of nitrogen plasma. However, the higher breakdown voltage required and the increased tendency to form a filamentary, rather than diffuse discharge, risk compromising film quality.

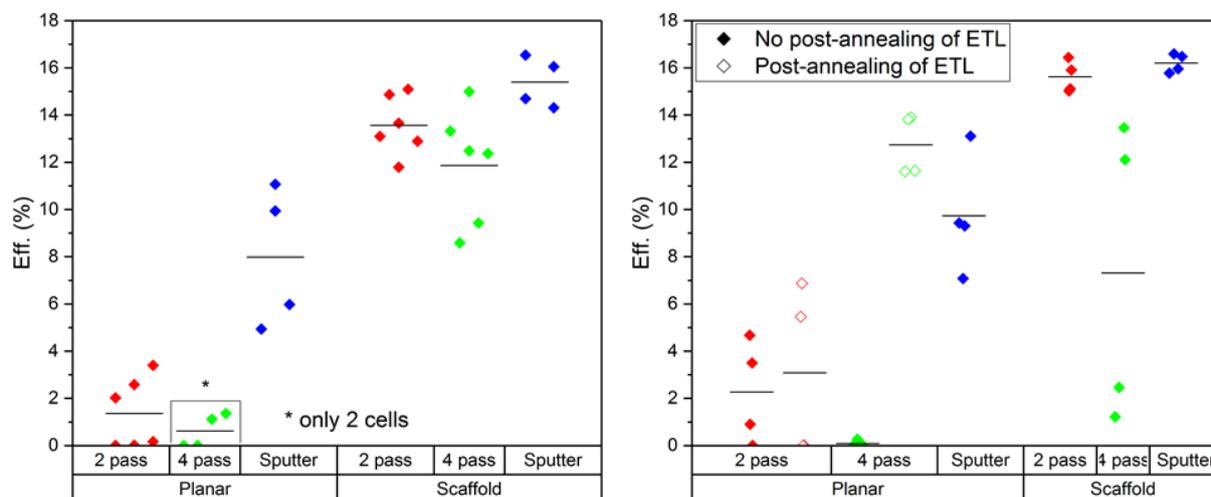## 2.2 Viability of AP PECVD TiOx films for use in perovskite based PV systems

2.2.1 AP PECVD TiOx ETL performance

In previous work (EU FP7 PLIANT), selected films deposited on Solaronix TCO22-15 FTO were used to construct multiple 1 cm^2 mesoporous scaffold cells using a well characterised method at CSEM. These cells were compared to reference cells which used PVD TiO$_{2-x}$ ETL. Measurements of performance parameters conducted by CSEM demonstrated the suitability of the AP PECVD ETL, showing improved V$_{oc}$ and notable increases in fill factor leading to improved overall efficiency, with the 40 nm films showing maximum values of 14.53% and 13.57% MPP compared to 14.11% and 13.15% achieved using the PVD ETL (23nm). External quantum efficiency (EQE) measurements suggested that further advantage may be gained by resolving interface issues alongside further optimisation of film thickness and properties.

2.2.2 The application of AP PECVD TiO$_x$ to planar cells

In this project AP PECVD TiO$_{2-x}$ films were used as a BL (ETL) to produce both planar and scaffold 1 cm^2 cell architectures on FTO. The thickness was determined by the number of passes of the substrate under the CVD coating head. Two different commercially available FTOs were used as substrates: TEC 7 (7 Ω/□) and TCO22-15 (15 Ω/□), the former being rougher than the latter. TiO$_{2-x}$ deposited by sputtering served as reference. Note that the mesoporous TiO$_2$ used for the scaffold cells requires sintering at 500°C. On the contrary, in the planar cells, the sputtered TiO$_{2-x}$ is used as deposited.

Figure 8. Cell efficiency comparing AP PECVD ETL and PVD (sputtering) reference on TEC7 (left) and TCO22-15 (right). The data include forward and reverse measurement. The black line represents the average value.

Figure 8 shows typical efficiencies for 2 pass AP PECVD TiO_{2-x} (ca. 15nm), 4 pass (ca. 30nm) and sputtered TiO_{2-x} (20nm), in planar and scaffold architecture, on TEC 7 (left) and TCO22-15 (right). It was observed that the use of TEC7 rather than the smoother TCO22-15 reduced the efficiencies achieved for the deposited cells. In this case, although reasonable efficiency values for the AP PECVD derived scaffold cells were obtained they were lower than those obtained from the equivalent sputtered derived reference. A more significant discrepancy was noted for the planar cells. For both scaffold and planar cells the thinner 2 pass TiO_{2-x} films led to better cell results than the 4 pass. The planar cells accentuated any issues with the ETL and with the PECVD ETL gave poor results. This may relate to the challenge of producing pinhole free PECVD TiO_{2-x} films over the rough TEC 7 surface, which would be especially testing with the 2 pass TiO_{2-x} film. To test the influence of FTO roughness on planar cells, the experiment was repeated using the smoother TCO 22-15 (rather than TEC 7) as the substrate (Figure 8, right).

When using a smoother FTO (TCO 22-015), the scaffold cells showed similar efficiency for the thinner 2 pass AP PECVD ETL and the PVD reference. The corresponding IV curves for the best performing samples supported this observation with MPP tracking giving peak efficiency values of 15.15 % for the cells derived from the 2 pass AP PECVD ETL compared to 15.61 % for the PVD reference. This result is supporting previous observations.

Planar cell architecture (again using TCO 22-015 rather than the rougher TEC 7), gave lower and more scattered efficiencies for both APCVD and sputtered ETLs. In the case of the APCVD ETL gave poor, variable results in comparison to that of the sputtered reference. However, an annealing at 500°C of the TiO_{2-x} layers prior to PK deposition led to a significant improvement of the cells performances, with some cells surpassing the reference. It is important to note that only a few cells were compared so much more data is required to support this single test. Whilst, it does imply that some of the observed interface issues could be assigned to chemical or structural issues associated with the low temperature deposition process.

The change in structure was confirmed by XPS, which established that annealing does reduce the defect level. The FWHM of the Ti 2p $_{3/2}$ peak could be seen to reduce on annealing, from 1.36 eV to 1.16 eV for the AP PECVD film, sugesting a reduction in defects, possibly explaining the improved performance.

It is possible that an excess of defects or impurities in the AP PECVD film may arise from incomplete conversion of the precursor and removal of waste products at room temperature. This may be addresssed via increased plasma density, whilst taking care to avoid hetrogeneous nucleation and powder formation. This is supported by the XPS that showed changing from low (4 kV) to higher (< 8kV) applied voltages reduced the Ti $2p_{3/2}$ FWHM from 1.36 eV to 1.28 eV in each case.

This is currently being addressed by application of an advanced sub microsecond pulsed DC power supply, which delivers high transient power density at a very low duty cycle to minimise thermal load and control the level of activation. Initial work with this unit showed that the use of 5 kV, 10 µs, DC pulses, separated by 500 µs periods to drive the argon plasma, could result in a narrower Ti $2p_{3/2}$ FWHM of 1.17 eV under otherwise similar conditions. This value matches that achieved by anealing the film produced using the audio frequency supply, with the sugestion that further work may identify a route to more effective performance in the planar cell structures.