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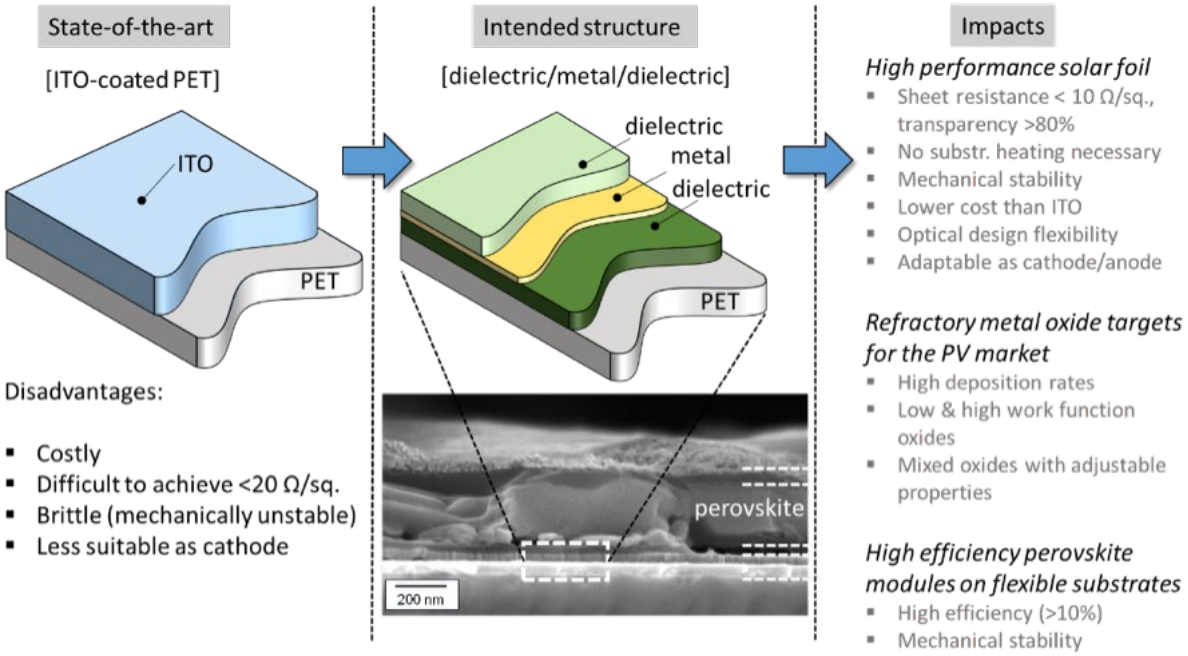
Final report

NEXT-FOIL

Next generation conductive solar foil for flexible photovoltaics (SOLAR-ERA.NET ID : 44)



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Summary

The perovskite solar cell is a fairly new thin-film technology that nevertheless boasts high efficiencies. The technology is based on substrates coated with a transparent electrode. For flexible modules, ITO-coated PET is by far the most common (ITO: indium tin oxide), despite high costs, poor mechanical stability and limited applicability as a cathode. The project NEXT-FOIL – carried out within the framework of the European call Solar Era.net – aimed at the realization and validation of a flexible substrate having a transparent electrically conductive layer formed by a thin metallic film enclosed between two metal oxide layers, forming a dielectric/metal/dielectric (DMD) stack. The partners in this Era.net project were the Austrian Institute of Technology (AIT) in Vienna, acting as the coordinator, the company PLANSEE (Reutte, Austria) making tailored mixed metal oxide sputtering targets, and SOLARONIX (Aubonne, Switzerland) preparing the perovskite solar cell devices together with the AIT.

Such DMD coated polymer foils (PET) have been evaluated for their conductivity, their mechanical properties, and their fitness to serve as substrate in low-temperature processed perovskite solar cells. Apart from its economic competitiveness, the unique benefit of a DMD based substrate is that it keeps its excellent electrical conductivity during repeated bending on small radii of a few millimetres, impossible with the conventional flexible transparent electrically conductive substrates, as their ceramic ITO layer is very fragile upon deformation. Thanks to a low temperature processed mesoporous titanium oxide layer, it was possible to make perovskite solar cells on DMD substrates, having similar electrical performance than cells made on ITO coated glass. In the same time, this validated the outer niobium-titanium oxide DMD layer to act directly as the key ‘hole blocking layer’ in such perovskite based solar devices.

Résumé

La cellule solaire pérovskite est une technologie en couche mince assez récente qui se distingue néanmoins par son haut rendement. Cette technologie est basée sur des substrats recouverts d'une électrode transparente. Pour les modules flexibles, le PET revêtu d'ITO est de loin le plus courant (ITO : oxyde d'indium et d'étain), malgré son coût élevé, sa faible stabilité mécanique et son applicabilité limitée en tant que cathode. Le projet NEXT-FOIL - réalisé dans le cadre de l'appel européen Solar Era.net - visait la réalisation et la validation d'un substrat flexible ayant une couche transparente électriquement conductrice formée par un mince film métallique enfermé entre deux couches d'oxydes métalliques, formant un empilement diélectrique/métal/diélectrique (DMD). Les partenaires de ce projet Era.net étaient le Austrian Institute of Technology (AIT) de Vienne, qui agissait en tant que coordinateur, la société PLANSEE (Reutte, Autriche) qui fabriquait des cibles de pulvérisation d'oxyde métallique mixte sur mesure, et SOLARONIX (Aubonne, Suisse) qui préparait les dispositifs de cellules solaires à base de pérovskite en collaboration avec l'AIT.

Ces feuilles de polymère revêtues de DMD ont été évaluées pour leur conductivité, leurs propriétés mécaniques et leur aptitude à servir de substrat dans les cellules solaires pérovskites réalisées à basse température. Outre sa compétitivité économique, l'avantage unique d'un substrat à base de DMD est qu'il conserve son excellente conductivité électrique lors de flexions répétées sur de petits rayons de quelques millimètres, ce qui est impossible avec les substrats conventionnels souples et transparents électriquement conducteurs, car leur couche céramique d'ITO est très fragile lors de la déformation. Grâce à une couche d'oxyde de titane mésoporeux déposée à basse température, il a été possible de fabriquer des cellules solaires en pérovskite sur des substrats DMD, ayant des performances électriques similaires à celles des cellules fabriquées sur du verre revêtu d'ITO. En même temps, cela a permis de valider que la couche DMD extérieure en oxyde de niobium-titane agissait directement comme la "couche de blocage des trous" dans ces dispositifs solaires à base de pérovskite.

Zusammenfassung

Die Perowskit-Solarzelle ist eine relativ neue Dünnschichttechnologie, die hohe Wirkungsgrade aufweist. Die Technologie basiert auf Substraten, die mit einer transparenten Elektrode beschichtet sind. Für flexible Module ist ITO-beschichtetes PET mit Abstand am gebräuchlichsten (ITO: Indium-Zinn-Oxid), trotz hoher Kosten, schlechter mechanischer Stabilität und begrenzter Anwendbarkeit als Kathode. Das Projekt NEXT-FOIL - durchgeführt im Rahmen des europäischen Calls Solar Era.net - zielte auf die Realisierung und Validierung eines flexiblen Substrats mit einer transparenten, elektrisch leitfähigen Schicht, die aus einem dünnen Metallfilm besteht, der zwischen zwei Metalloxidschichten eingeschlossen ist und eine Schichtfolge aus Dielektrikum/Metall/Dielektrikum (DMD) bildet. Die Partner in diesem Era.net-Projekt waren das Austrian Institute of Technology (AIT) in Wien, das als Koordinator fungierte, die Firma PLANSEE (Reutte, Österreich), welche massgeschneiderte Mischmetalloxid-Sputter-Targets herstellte, und SOLARONIX (Aubonne, Schweiz), die zusammen mit dem AIT die Perowskit-Solarzellenbauteile herstellte.

Solche DMD-beschichteten Polymerfolien (PET) wurden auf ihre Leitfähigkeit, ihre mechanischen Eigenschaften und ihre Eignung als Substrat in niedrigtemperaturverarbeiteten Perowskit-Solarzellen untersucht. Abgesehen von der wirtschaftlichen Wettbewerbsfähigkeit besteht der grosse Vorteil eines DMD-basierten Substrats darin, dass es seine hervorragende elektrische Leitfähigkeit bei wiederholtem Biegen auf kleinen Radien von wenigen Millimetern beibehält, was bei den herkömmlichen flexiblen transparenten elektrisch leitfähigen Substraten unmöglich ist, da ihre keramische ITO-Schicht bei Verformung sehr zerbrechlich ist. Dank einer mesoporösen Titanoxidschicht, die bei niedrigen Temperaturen verarbeitet wurde, war es möglich, Perowskit-Solarzellen auf DMD-Substraten herzustellen, die eine ähnliche elektrische Leistung aufweisen wie Zellen, die auf ITO-beschichtetem Glas hergestellt wurden. Gleichzeitig bestätigte dies, dass die äussere Niob-Titanoxid-DMD-Schicht direkt als die entscheidende «Lochsperrschicht» in solchen Perowskit-basierten Solargzellen fungiert.

Main findings

- Fast DMD (dielectric/metal/dielectric) production: Sputtering process time is below 3 minutes for the entire DMD stack, thus allowing a for competitive roll-to-roll manufacturing.
- DMD on PET (polymer foils) outperforms ITO (indium tin oxide) on PET by a factor of 1.5, allowing for higher electrical conductivity for the same transparency, this is important for solar cell and display applications.
- Mechanically robust DMD foil, achieving >100 bending cycles on a 5 mm radius with no change in electrical conductivity. In contrast, ITO on PET sees a 50-fold decrease in conductivity in the same conditions. This robustness against deformation is a unique property of DMD foils, opening novel applications where flexibility and robustness is key.
- First low temperature processed (< 120°C) perovskite cell on DMD foil with 9 % PCE, having similar performance than on ITO glass. Proof-of-principle of the DMD foil's top metal oxide to act as charge selective electrode, greatly simplifying the low-temperature and energy efficient solar cell manufacturing process.

Contents

Abbreviations

AIT	Austrian Institute of Technology in Vienna, Austria
c-TiO_2	Compact TiO_2, acting as hole blocking layer
Cl:MALI	Chlorine doped methylammonium lead iodide perovskite
DMD	Dielectric/Metal/Dielectric
ETL	Electron transporting layer
FF	Fill-factor
FTO	Fluorine-doped tin oxide
HTL	Hole transporting layer
I-V	Current voltage (plot)
I_{sc}	Short-circuit current
ITO	Indium tin oxide
m-TiO_2	or meso-TiO_2, mp-TiO_2, mesoporous TiO_2
MALI or MAPI	Methylammonium lead iodide perovskite ($CH_3NH_3PbI_3$)
MPP	Maximum power point
MTO	Molybdenum-titanium oxide (MoO_3-TiO_2)
N-I-P	n-type / intrinsic / p-type semiconductor layering
OPV	Organic photovoltaics
P-I-N	p-type / intrinsic / n-type semiconductor layering
PCE	Power conversion efficiency
PET	Polyethylene terephthalate
PSC	Perovskite solar cell
PV	Photovoltaic
SEM	Scanning electron microscope
spiro-OMeTAD	2,2',7,7'-Tetrakis-(N,N-di-4-methoxyphenylamino)-9,9'-spirobifluorene, a hole transport material
TCO	Transparent conducting oxide
TNO	Titanium-niobium oxide (TiO_2-Nb_2O_5)
UPS	Ultraviolet photoelectron spectroscopy
V_{oc}	Open-circuit voltage
W_F	Work function
XRD	X-ray diffraction

1 Introduction

1.1 Background information and current situation

So called “next generation photovoltaics” based on organic, inorganic or hybrid absorbers can be fabricated as thin, lightweight and flexible modules. This makes them attractive for integration in building façades and consumer products. From these technologies, organic photovoltaics is the most mature, pursued by a number of companies and marking efficiencies up to 16%[1]. Hybrid perovskite cells, on the other hand, is a new technology but with soaring efficiencies, above 25% on cell level[2]. These technologies rely on substrates coated with a transparent electrode. For flexible modules, ITO-coated (ITO = indium tin oxide) PET is by far the most common despite its high cost, poor mechanical stability and limited applicability as cathode.

1.2 Purpose of the project

The project NEXT-FOIL aimed at the development of an alternative to ITO-coated PET, based on dielectric/metal/dielectric (DMD) multilayers, sputtered at industry-compatible deposition rates, while offering a sheet resistance below 10 ohm/sq. and an excellent mechanical robustness. Single and mixed oxides based on TiO_2 and MoO_3 (intrinsic and doped) will be used as dielectric layers, being abundant and affordable materials. While TiO_2, with a low work function, is suited for electron extraction (cathode), MoO_3, a high work function oxide, is employed to extract holes (anode). In mixed oxides, the work function can be adapted to fit the specific device energetics. As metals, Cu, Au and Ag offer optimal performance/cost ratio.

The competitive edge of the DMD-based foils was demonstrated with the fabrication of first hybrid perovskite modules processed at low temperatures.

1.3 Objectives

The project conforms with the Strategic Targets of the European SET-Plan of the “Initiative for Global Leadership in Photovoltaics”, since it contributes to: (a) the advancement in efficiency of new PV concepts, namely PSC (perovskite solar cell) and OPV (organic photovoltaics)[3], which will mainly profit from the developed solar foil, and (b) the advancement in manufacturing, through the reduction of cost and the simultaneous improvement of the performance and functionality of transparent electrodes on flexible substrates.

The project objectives were:

1. To replace the ITO-coated PET foil, currently used for flexible PV modules, with dielectric/metal/dielectric (DMD) electrodes, featuring better electrical (5 ohm/sq), optical (> 75% transmission in visible light) and mechanical properties (no change of electrical conductivity upon multiple bending cycles), lower cost by avoiding indium, and top oxide work-function adaptability to different device architectures.
2. To develop oxide targets of refractory metals (like TiO_2 and MoO_3), which are compatible with high throughput sputter processing and yield stoichiometric oxide films with the desired opto-electronic properties on large area substrates with high homogeneity.
3. To demonstrate the superiority of the developed DMD-foil against the standard ITO-foil, through the fabrication of efficient and mechanically stable low temperature processed perovskite cells.

The project objectives reflect following industrial needs:

a) High throughput processing without modification of existing equipment (no new capital expenditure required). In the project, the new DMD electrodes will be deposited by DC magnetron sputtering, being currently used to deposit the state-of-the-art ITO.

b) Penetration to new, high potential markets. This will be the case for the refractory metal oxide targets for the flexible PV market, as well as other high-volume applications, especially flat panel displays / light emitting diodes and smart windows.

c) Increasing the performance/cost figure of the products, namely the transparent electrically conductive foil itself, as well as the PV module fabricated with the use of that foil.

d) Easy product adaptation to meet diverse customer requirements. The DMD foil can be easily adapted to different solar cell architectures ("conventional" or "inverted") and types (organic, perovskite, dye-sensitized) through the choice of the dielectric and the adjustment of layer thicknesses.

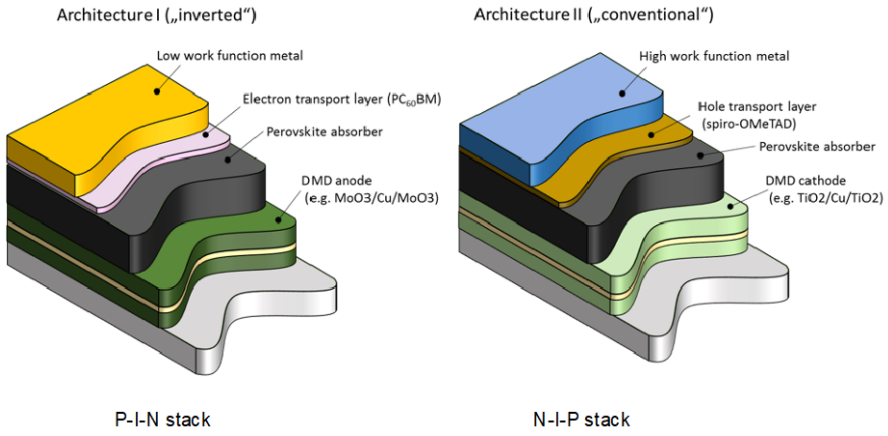


Figure 2. Sketches of the P-I-N and N-I-P types of perovskite solar cell stacks, showing the top high work-function MoO_3 oxide layer acting as electron-blocking layer for the P-I-N devices, respectively the low work-function TiO_2 of the DMD stack working as the hole blocking layer needed in the N-I-P architecture.

2 Procedures and methodology

The project involved 3 complementary partners:

1) AIT took care of the DMD electrode layer design including target layer thickness modelling, the low temperature perovskite solar cell development, and the corresponding characterization works.

2) PLANSEE, manufactured the customized metal oxide based sputtering targets needed for the experimental coating of PET foils (and glass) with metal-oxide / metal / metal-oxide layers forming the transparent electrically conductive DMD stack. The last metal oxide is chosen to have the appropriate energy level to act either as ETL such as with TiO_2 or TiO_2-Nb_2O_5 alloys, or as HTL with MoO_3 and its alloys with TiO_2.

3) SOLARONIX provided the materials for low temperature deposited perovskite solar cells. The solar cell samples have been manufactured in the AIT premises in Vienna, as this type of perovskite solar cell needed an inert gas filled glovebox during the spin-coating of the perovskite precursor. At the end of the project, SOLARONIX intended to commercialize the DMD foils manufactured during this project.

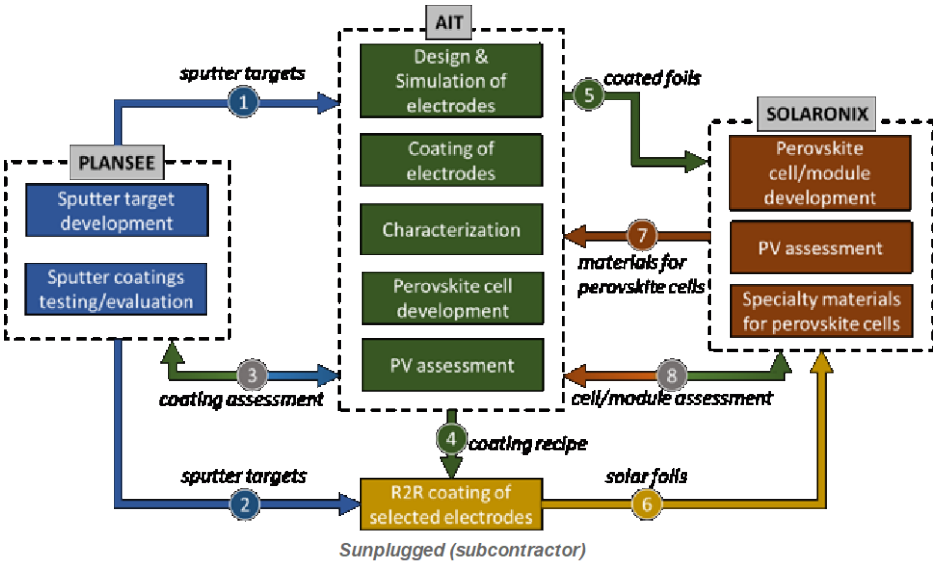


Figure 3. Overall project partner interactions with key partner contributions.

The project comprised the steps of

- Manufacturing at PLANSEE of sputtering targets composed of either single or mixed oxides, based on TiO_2 and MoO_3 (intrinsic and doped). As metals, Cu, Au and Ag offer optimal performance/ cost ratio.
- Sputtering at AIT of the DMD layers on glass and PET foils, with the respective metal oxide and metal layer thicknesses being based on optical modeling to target highest electrical conductivity for a given visible light absorption. Average optical transmittance in the visible range is realistically expected to be 80-85% (based on our previous results and the existing literature), with sheet resistance well below 10 ohm/sq.[4,5]
- Characterization at AIT and PLANSEE of the DMD-layers in terms of chemical and mechanical stability. MoO_3 proved to be unstable in presence of moisture and alloying with TiO_2 enabled a robust mixed oxide. The mechanical stability of the DMD-layers on PET were investigated by stress tests where the sample is periodically bent around a small radius of ca. 5 mm, while monitoring the electrical conductivity of the sample once at rest.
- Low-temperature perovskite solar cells investigations at AIT and SOLARONIX. AIT worked on the air-sensitive deposition process requiring a glovebox, and at SOLARONIX worked on alternative air-tolerant perovskite solar cell architectures (N-I-P and P-I-N types).
- Selection, assembly, and characterization of the most promising solar cell architecture - being an N-I-P device with a low-temperature deposited mesoporous TiO_2 and a perovskite processed in the glovebox at AIT.
- Manufacturing of demonstration DMD-foils at a subcontractor, achieving 20 meter long and 30 cm wide DMD-PET rolls having the structure TiO_2:Nb_2O_5 / Ag / TiO_2:Nb_2O_5 and MoO_3:TiO_2 / Ag / MoO_3:TiO_2.

Two workshops held at AIT Vienna enabled SOLARONIX to contribute to the assembly of low-temperature deposited perovskite solar cells requiring access to a glovebox for the of air-sensitive step of the perovskite film formation.

3 Results and discussion

3.1 Sputter target development (PLANSEE + AIT)

3.1.1. Powder Metallurgical Process Development for Manufacturing MoO_x Targets

A manufacturing process for Molybdenum-Oxide (MoO_x) sputtering targets was developed, based on the following process steps:

1. Powder processing / mixing,
2. compaction of the powder mixture by vacuum hot pressing to a solid blank,
3. machining the blank into a sputtering target, and
4. bonding the target onto a Cu backing plate (cooling plate), to be installed into a sputter coater.

As pure MoO_3 is insulating, thus prohibiting the fast DC-sputtering, sub-stoichiometric $MoO_{2.9}$ and $MoO_{2.7}$ materials were developed. For hot pressing, a powder mixture with high flowability and high tap density is required and powder mixtures of MoO_2 and MoO_3 (both oxides are readily available and stable in ambient conditions) were prepared.

In PLANSEE's PVD Application Lab, basic sputtering tests with ∅100 mm targets were performed; all $MoO_{2.7}$ material could be readily sputtered in DC mode. Depending on the Ar pressure and DC power, deposition rates between 70 and 170 nm/min could be achieved in pure Ar.

3.1.2 Powder Metallurgical Process Development for Manufacturing $MoTiO_x$ Targets

Unfortunately, tests revealed poor stability of MoOx-based films in aqueous solution. To overcome this issue, it was decided to add Ta or Ti into the molybdenum oxides, and to prioritize the development of a MoTi-oxide target material. Subsequently, a powder mixture of Mo-oxide and TiO_2 (or Ta_2O_5) was developed, using classification and mixing technologies. A vacuum hot-pressing process was developed to consolidate the powder mixture into a solid blank with a density of >98%, in an analogue manner as described above for $MoO_{2.7}$. MoTa-oxide and MoTi-oxide sputtering targets were indium-bonded onto Cu backing plates and shipped to AIT (**Fig. 4**). DC sputtering capability was confirmed at PLANSEE in basic sputtering tests.

Figure 4. MoTa-Oxide and MoTi-Oxide sputtering targets.

To assess the fitness of the newly developed mixed metal oxide targets, a long-term test over $^1/_3$ of the whole target lifetime was successfully conducted at the company SUNPLUGGED (subcontractor) using an industrial scale $MoTiO_x$ target in their roll-to-roll sputtering equipment.

3.2 DMD-foil development (AIT + PLANSEE)

3.2.1 Electrodes with Mo-Ti-O_x (MTO)

A sputter target of $MoTiO_x$ (50 at.% Ti, 71 at.% O_2) was employed in the DC magnetron mode, and optically transparent MTO layers, having an indirect bandgap of ~3.2 eV, were obtained when reactively sputtering with Ar/O_2 (6.6% O_2) mix. The optical modeling done AIT gave an optimal MTO thickness of

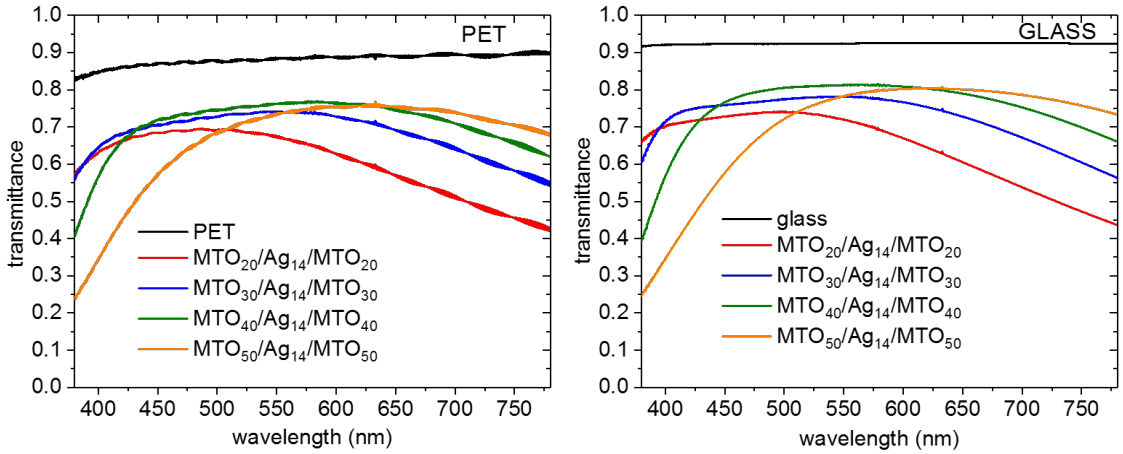


Figure 5. Transmittance spectra of MTO/Ag/MTO electrodes on PET and glass with different thickness of dielectrics (in nm) and 14 nm of Ag. The sheet resistance for all electrodes is 5 Ω/sq. The maximum average visible transmission (AVT) on PET is obtained for the $MTO_{40}/Ag_{14}/MTO_{40}$ electrode (green colored plot).

~40 nm for both dielectric layers when combined with Ag (or Au) metal, resulting in a broad transmittance maximum on glass and PET, as shown in **Fig. 5**.

Most importantly, the MTO films are very stable in all solvents (Table 1), including tap and DI water exposure for 17 hours. This offers process flexibility for the fabrication of perovskite solar cells, using also water-based material formulations.

Table 1. Stabilities of the pure MoO_x and MTO electrodes in different solvents.

DMD electrodes with:	Tap water	DI water	DMSO	DMF	toluene	chlorobenzene	IPA
MoO_3 (reactive sputt.)	Very low	Very low	high	high	high	high	high
MoO_{3-x} (non-reactive)	high	low	high	high	high	high	high
MTO (reactive sputt.)	high	high	high	high	high	high	high

The UPS investigation showed that the work function of the sputtered MTO is 5.0-5.2 eV, making such layers suitable for use as anodes.

3.2.2 Electrodes with Nb:TiO_x (TNO)

A Nb-doped TiO_x (9.4 rel. at.% Nb to Ti, TNO) target served for the fabrication of DMD cathodes, suited for N-I-P architecture perovskite solar cells. DC sputtering at a rate of 8 nm/min in a pure Ar atmosphere afforded highly transparent TNO films, both on glass and PET. The optically determined indirect bandgap determined is 3.3 eV and the direct bandgap is at 3.8 eV.

Thanks to optical modelling done at AIT, the optimal layer thickness for the TNO dielectric is 35 nm for both sides, when having a 10 nm thick Ag layer in-between. Such DMD stacks achieved the highest average visible light transmittance (AVT, taken between 400 and 700 nm) of 77% on glass and 73% on

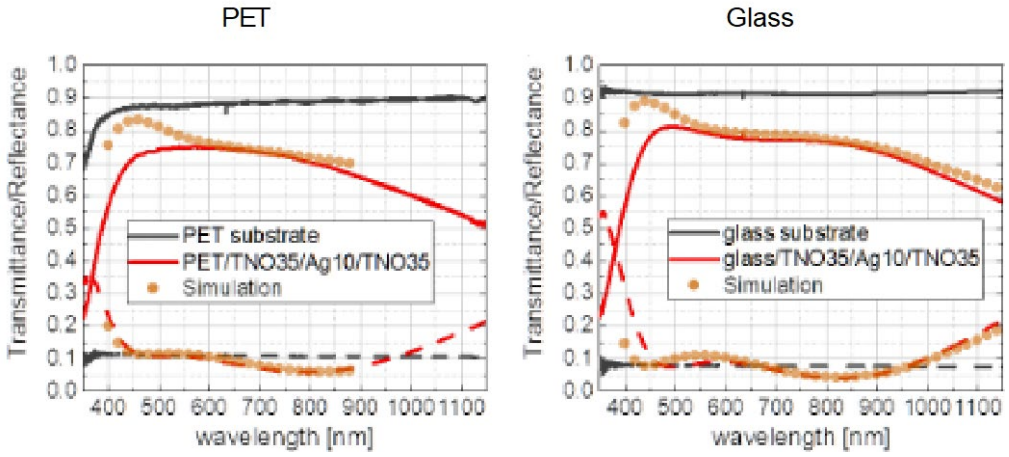


Figure 6. Simulated and experimental transmission and reflectance spectra for TNO(35 nm) / Ag(10 nm) / TNO(35 nm) DMD electrodes on glass and on PET. There is increased absorption in the DMD with respect to the calculated spectrum, especially below 500 nm.

PET (**Fig. 6**) with a sheet resistance of 8 ohm/sq., though a small absorption in the higher photon energies portion of the spectrum somewhat reduced the observed AVT with respect to the modelled values.

The UPS investigation showed that the work function of the sputtered TNO is 4.2 eV, making such layers suitable for use as cathodes.

3.2.3 Mechanical stability of the DMD electrodes

The mechanical stability of the DMD electrodes compared to ITO on PET, was tested using bending cycling tests, applying compressive or tensile stress on the layers, and varying the bending radius in the range between 10 and 3.2 mm, with a constant bending speed of 1000 mm/min. The resistance of the electrode was measured at the electrode's relaxed state. **Fig 8.** shows the bending stress result of a MTO/Ag/MTO electrode passing over 2000 bending cycles at a bending radius of 4.5 mm, both for tensile (coating outside the curvature) and compressive (coating inside the curvature) tests.

While the resistance of ITO is dramatically increased after only a few bending cycles[6,7], the resistance of the DMD electrode remains stable until >500 cycles. For compressive stress the DMD electrode increases its resistance by a factor of ~5 after 2000 cycles and for tensile stress by a factor of ~20. We note that the resistance is measured along the direction of the stress, using electrical contacts made with Ag paste and Cu adhesive tape at the two edges of the sample. The resistance increase is due to the development of cracks in the films. While such cracks in the ITO are fatal for the electrode's resistance, the ductility of the metal in the DMD allows the current to flow almost undisturbed, despite having cracks in the dielectric layer.

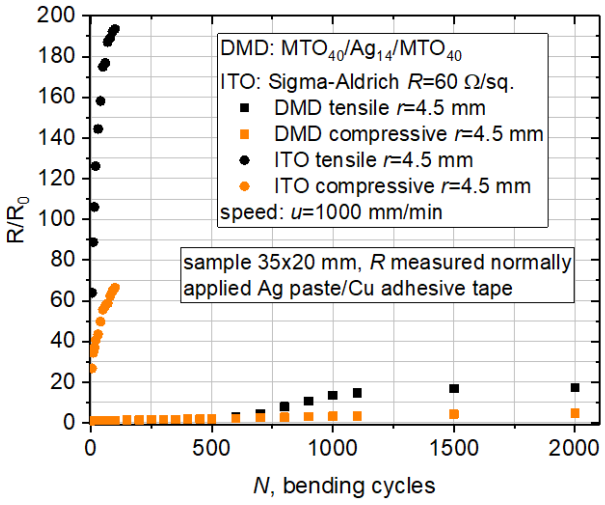


Figure 8. Relative change of the surface resistivity of commercial ITO and MTO/Ag/MTO electrodes in bending test.

3.2.4. Upscaling of the DMD electrodes

The upscaling of the electrode fabrication also took place in the second project period. For this, two targets were fabricated by PLANSEE with a length of 300 mm, one Nb:TiO_x (TNO) and the other Ti:MoO_x (MTO) for the cathode and the anode respectively. All targets were delivered to the company SUNPLUGGED in Tirol, Austria, which was subcontracted by AIT for the roll-to-roll depositions. AIT transmitted the deposition recipes to SUNPLUGGED and a close coordination was established to optimize the depositions of the electrodes. It is reminded that due to the pandemic-related travel restrictions, it was not possible to have the presence of a researcher from AIT at SUNPLUGGED for the deposition optimization. It was, however, possible to optimize and deposit the two DMD architectures of MTO/Ag/MTO and TNO/Ag/TNO in rolls of 20 m length and 300 mm wide, with optical and electrical properties similar to the ones of the electrodes deposited at lab scale. A photo of the cathode is seen in **Fig. 9**, therefore showing the industrial feasibility of the DMD production.

Figure 9. Photo of a 300 mm-wide roll of TNO/Ag/TNO DMD, sputtered according to the developed recipe.

3.3 Development of perovskite cells

3.3.1 Low-temperature Perovskite solar cell development at SOLARONIX

a) N-I-P device at SOLARONIX

For NEXT-FOIL, SOLARONIX had to develop from scratch a low-temperature process to deposit perovskite solar cells, first on glass as reference, and later, on the DMD foils once they got available within the project. In order to be compatible with PET substrates, the processing temperature to form the solar cell should not exceed ~ 140°C.

SOLARONIX has knowledge for making N-I-P cells based on high temperature (~450°C) processed TiO_2 layers, where power conversion efficiency (PCE) of up to 12% was achieved in solar cells having the structure FTO-glass/compact-TiO_2/mesoporous-TiO_2/Perovskite/spiro-OMeTAD/Gold.

Experiments have shown that it is possible to make a N-I-P solar cell without the mesoporous TiO_2 layer (requiring high temperature firing), thus forming a 'planar' junction cell, where the $CH_3NH_3PbI_3$ (MALI) perovskite is directly spin-coated onto a flat compact-TiO_2 layer (still deposited at 400°C).

Such devices having the structure FTO-glass/compact-TiO_2/Perovskite/spiro-OMeTAD/Gold achieved a PCE of up to 5.6% at 1000 W/m^2 artificial sunlight irradiation, showing that the planar cell structure fundamentally works, though the obtained photocurrent density is quite low with only 11.4 mA/cm^2, probably due to a too thin perovskite layer of only ca. 200 nm.

As SOLARONIX masters a chemical bath process to deposit the compact-TiO_2 layer at temperatures below 80°C, fully low-temperature processed devices were assembled, giving decent current-voltage (I-V) characteristics and PCE's in the range of 3% (**Fig 11.** and **Fig 12.).**

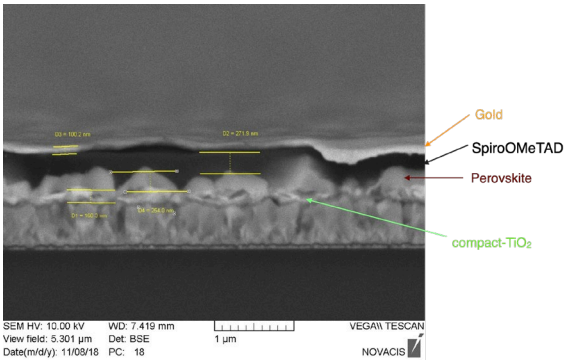
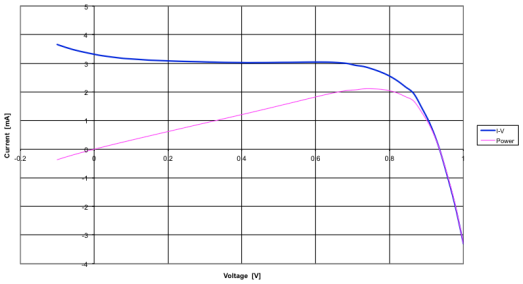


Fig. 11. SEM cross-section, showing that the low-temperature compact-TiO_2 layer is ca. 100 nm thick, and the perovskite layer is very irregular due to large crystals.



Low temperature blocking titania layers :

- Voc: 935 mV
- Jsc: 5.2 mA/cm²
- PCE: 3.29%

- Voc: 925 mV
- Jsc: 5.25 mA/cm²
- PCE: 2.99%

- Voc: 926 mV
- Jsc: 5.25 mA/cm²
- PCE: 2.96%

- Voc: 922 mV
- Jsc: 5.21 mA/cm²
- PCE: 2.60%

Fig. 12. I-V plot example of a low-temperature processed planar N-I-P perovskite cell, and characteristics of four such cells, the best device giving up to 3.2 % PCE.

b) P-I-N device at SOLARONIX

The project partner AIT has also developed a P-I-N perovskite solar cell procedure, which was shared with SOLARONIX to jump-start the low temperature cell development. The proposed cell structure, having PEDOT:PSS (a conductive polymer) as hole transport layer, is given in **Fig. 13**.

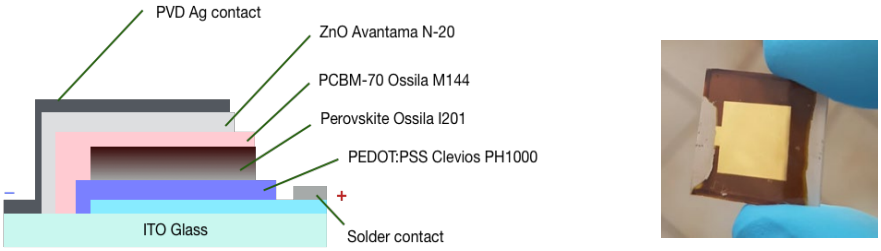


Figure 13. Solar cell structure developed at AIT and proposed to SOLARONIX, and back-side view of the device with its 11 x 11 mm gold electrode.

About 40 of such cells were fabricated in several campaigns (8 cells per run) and the best cell gave a PCE of only 3.4%, the modest performance comes mostly from a low fill-factor of only 0.33 and a reduced short circuit-current of ca. 12 mA/cm^2, whereas 'good' perovskite cells should give ca. 20 mA/cm^2 in short-circuit with fill-factors of ca. 0.65 at least (**Fig.14**).

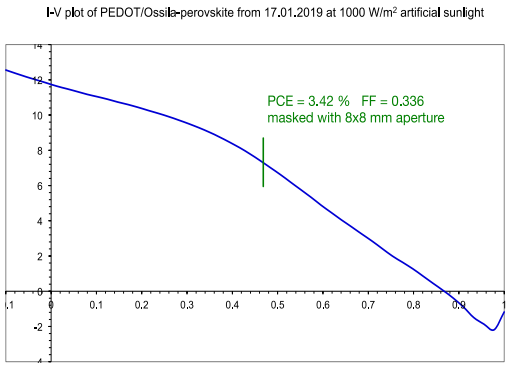


Figure 14. I-V characteristic of the low-temperature processed P-I-N solar cell made according the AIT procedure, though being processed in air at SOLARONIX.

Note: Our actual test cells have an active area of 1.21 cm^2, delimited by the evaporated gold electrode surface, whereas the typical laboratory perovskite test cells reported in the literature have a surface of only 0.09 to 0.16 cm^2! For measuring the current-voltage characteristics, we use a 0.64 cm^2 sized mask made of black tape to delimit an aperture on the cell under test, and to avoid stray light altering the measurement.

3.3.2 Processing of PET foils for module manufacturing

The making of a larger area solar cell module needs separations of the transparent conductive layers sitting on top of the polymer substrate. Typically, such separations are achieved by scribing the conductive layer of the flexible substrate (usually ITO on PET) with a pulsed YAG-laser. This process works well on glass substrates, but unfortunately, we were not able to translate our laser scribing process to the polymer foils, such ITO on PET or DMD on PET (as provided by the AIT).

What happens is that the YAG-Laser starts to char the polymer surface, leaving dark traces and completely damaging the surface getting very rough in these areas, inhibiting any further processing into a solar cell (**Fig. 15**).

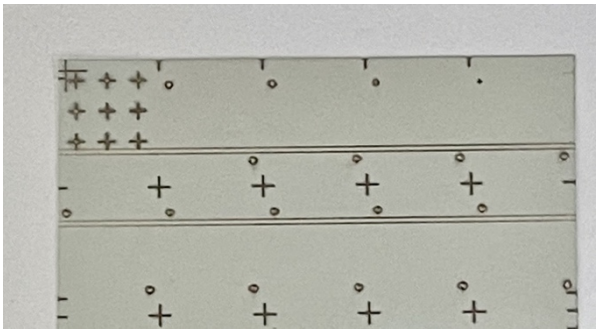


Figure 15. Picture of a 10 x 5 cm sized ITO on PET foil with pulsed YAG-laser scribed areas. Note that the processed surface gets darkened by the laser beam, forming charred areas having a very rough surface. Similarly, the parallel separation lines are also showing substantial damages, making it impossible to fabricate a solar module with such a substrate.

As an alternative to the ill-fated laser scribing process, micro-fabrication techniques with photoresist and subsequent chemical or plasma etching, followed by photoresist stripping might be a better way to pattern these types of substrates – though implementing such a complex technology was out of scope in the short time left in this project.

Despite this setback, SOLARONIX continues to investigate how to increase the size of flexible-substrate- based perovskite solar cells.

3.3.3 Low-temperature Perovskite solar cell development at AIT Vienna

a) P-I-N device at AIT

AIT explored the manufacturing of P-I-N structures having a first layer of water-borne PEDOT:PSS (Clevios PH1000) acting as the hole transport layer, being spin-coated onto the MTO/Ag/MTO coated glass. The air-sensitive perovskite $MAPI_{3-x}Cl_x$ (MAPICl) was deposited by spin-coating in an inert gas filled glovebox, followed by anti-solvent quenching to form a crystalline perovskite layer. The device was completed by covering the perovskite with either PCBM/ZnO-nanoparticles or plain ZnO-nanoparticles, followed by thermally evaporated aluminium as back contact.

It was, regretfully, observed that even with the inclusion of PEDOT:PSS between the DMD and the MAPICl, the electrodes with Ag started degrading fast after the solar cell fabrication, with their resistance increasing to several kΩ in a period of ~2 days. The cause of degradation (as corroborated from electrical and SEM characterization) is that Ag is drawn to and reacting with the perovskite layer (especially with the iodine). In contrast, solar cells with electrodes employing Au were stable even when measured in ambient conditions. Any solar cell degradation was exclusively caused by the degradation of the perovskite but not of the electrode, which retained its low resistance and layer integrity.

Cross section SEM images of solar cells on glass with ITO and MTO/Au/MTO electrodes, respectively, are shown in **Fig. 16**, demonstrating a conformal layer morphology for each layer architecture. It is interesting to note that the thickness of the perovskite layer is <200 nm, and therefore the layer has a high visible transmittance, as can be seen in the photo (inset).

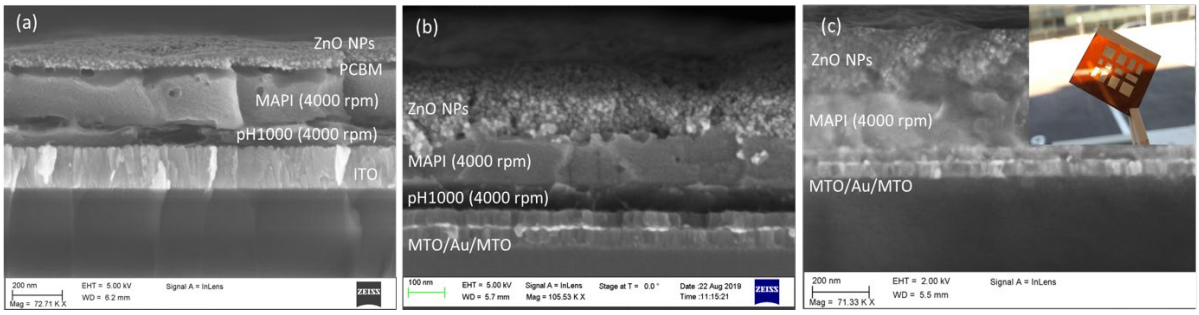


Figure 16. Cross-section SEM images of perovskite layers on (a) glass/ITO/PEDOT:PSS (pH1000), (b) glass/MTO/Au/MTO/PEDOT:PSS and (c) glass/MTO/Au/MTO. The perovskite layers are covered with either PCBM/ZnO-NPs (a), or plain ZnO-NPs ((b) and (c)). As inset is a photo of a perovskite cell on MTO/Au/MTO, showing high transparency.

In **Fig. 17** we present I-V characteristics (dark and under AM1.5G illumination) of solar cells employing the reference ITO and MTO-based electrodes on glass and PET. From the I-V characterization, we conclude that the solar cells on PET present a much lower performance than on glass, which is attributed to differences in the film morphology. After three consecutive runs of optimization, we have concluded that the particular cell architecture does not allow for adequate control of the layer morphology on flexible substrates, and therefore the performance of the solar cells on PET always lag behind the performance of the ones on glass.

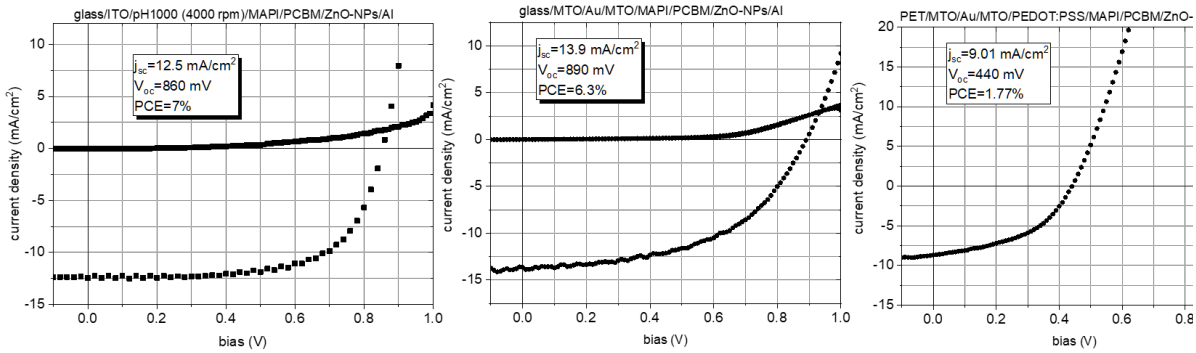


Figure 17. Dark and illuminated I-V curves of solar cells on glass and PET substrates, showing the significantly reduced performance of the cells on the PET substrate (right graph).

b) N-I-P device at AIT

It became therefore clear that an alternative strategy should be developed, which permits the deposition of perovskite layers of high quality without the need of antisolvent step, and which is not so sensitive to small process modifications. For such a strategy, a mesoporous oxide film, acting as a scaffold for the perovskite crystallization, could play a determining role. However, such mesoporous (mp) films need high temperature processing (>400°C) and are therefore incompatible with PET substrates. In contrast to most TiO_2 dispersions for mesoporous films, SOLARONIX has developed a dispersion that can be processed at <120°C. We therefore pursued the idea to combine this mesoporous film with the TNO-based DMD, in a N-I-P architecture of: TNO/Au/TNO/mp-TiO_2/MAPICl/spiro-OMeTAD/Au. The mp-TiO_2 dispersion was spin-coated on the TNO-based electrodes and then annealed at 90°C for 30 min in air. The perovskite layer could be then statically spin-coated on the mp-TiO_2 (in the N_2-filled glovebox). The wetting of the perovskite ink on the mesoporous layer was exceptional and the obtained absorber layer morphology very homogenous and of high crystalline quality, as seen in **Fig. 18**.

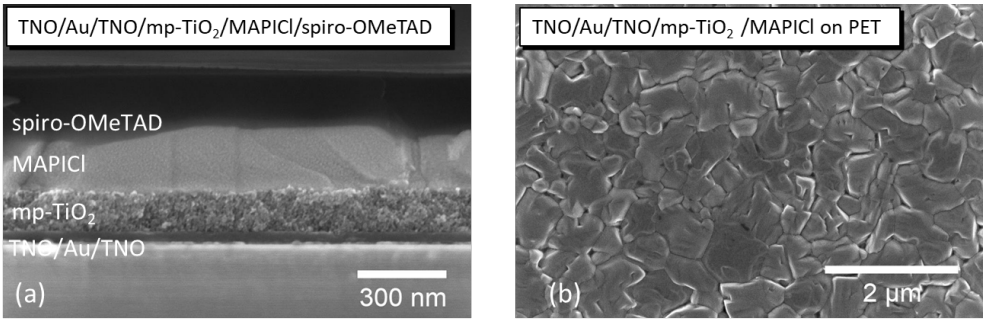


Figure 18. Cross section (a) and plain view (b) SEM images of a perovskite device employing the TNO/Au/TNO/mp-TiO_2 cathode.

As a result of the process improvement, we could, for the first time, fabricate solar cells on PET substrate with the same performance compared to glass and much better than the one achieved with the reference P-I-N architecture with PET/ITO. I-V characteristics of such solar cells are presented in **Fig. 19**, alongside with maximum-power-point (MPP) tracking measurements for a total time of 4 min, showing that the solar cell presents a constant performance.

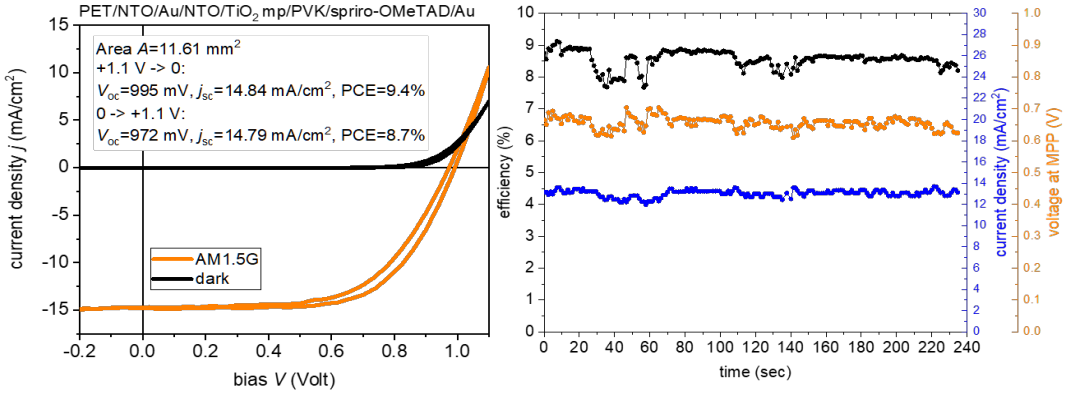


Figure 19. I-Vs in dark and under illumination (AM1.5G) of n-i-p solar cells employing the TNO-based DMD electrode, combined with the mesoporous TiO_2. Also shown on the right are MPP tracking measurements showing the temporal evolution of the efficiency, voltage and current at the MPP.

Coated PET samples with the TNO/Au/TNO and TNO/Ag/TNO electrodes, as well as with MTO/Au/MTO electrodes, with sizes of 5x5 cm were sent to SOLARONIX for process up-scaling.

The **main results** of the project are:

1) The successful fabrication of oxide ceramic targets of MoO_x, $MoTiO_x$, $MoWO_x$, $MoTaO_x$ and $Nb:TiO_x$ with appropriate electrical conductivity for sputtering in direct current (DC) magnetron mode, achieving high sputter rates.
2) The successful optical design and realization of dielectric/metal/dielectric (DMD) electrodes on PET substrates, based on MoO_x, $MoTiO_x$ (MTO) and $Nb:TiO_x$ (TNO) dielectrics, combined with thin layers of Ag and Au. Certain DMDs show performance figure-of-merit (combination of optical transmittance and sheet resistance) that surpasses the commercial ITO-on-PET, as well as evaporated DMDs of similar multilayer structures.
3) We have achieved very fast deposition of DMD electrodes, with total deposition time down to few minutes for the whole electrode and without substrate heating.
4) DMD electrodes based on MoO_x are stable under specific processing conditions applied in the fabrication of perovskite (or organic) solar cells. Specifically, MoO_x is stable for processing with solvents like DMF, DMSO, toluene and chlorobenzene. The MoO_x-based electrodes are, on the other hand, very unstable in water-based processing. It was also shown that the use of Ag in the DMD, combined with methylammonium-lead-iodide perovskite layers, leads to the chemical reaction of the metal and the fast degradation of the electrode over time.
5) Drastic enhancement of the water stability of the DMD electrode was achieved by using $MoTiO_x$ compound instead of MoO_x. This permits the long-term storage of these electrodes in ambient conditions and their processing with water-based dispersions or solutions, such as the water-based PEDOT:PSS (PH1000), a conductive polymer employed in perovskite P-I-N architectures.
6) The electronic properties of the MoO_x and $MoTiO_x$ films were found appropriate for use as anodes in perovskite solar cells, with measured work function of 5.0-5.2 eV.

7) Highly stable DMD cathodes, based on Nb:TiO_x and Ag or Au, were fabricated at high sputter rates, and with suitable work function for a cathode of 4.2 eV.

8) The TNO-based DMDs were successfully combined with low temperature-processed TiO_2 mesoporous layers from SOLARONIX, to obtain a unique, highly conductive, TiO_2-based, mesoporous electrode that facilitates the processing of the absorber in perovskite solar cells.

9) The DMD anode MTO/Ag/MTO and cathode TNO/Ag/TNO were successfully up-scaled to a 300 mm wide roll-to-roll process. For this, 300 mm-long MTO and NTO sputter targets were fabricated at PLANSEE and AIT has transferred the deposition recipes to the industrial subcontractor (SUNPLUGGED).

10) The TiO_2-based cathode, implementing the mesoporous layer, fosters easy and reproducible perovskite absorber processing and efficient solar cells, with power conversion efficiency ~9%.

11) The stability of the electrical resistance of the DMD electrodes (anodes and cathodes) upon cyclic bending, under tensile and compressive stress, is orders of magnitude higher than that of ITO on PET.

4 Conclusions

The challenge of replacing the expensive and mechanically brittle indium tin oxide (ITO) as electrically transparent conductive layer deposited on a polymer substrate (PET) by a low-cost and fast-processable dielectric-metal-dielectric (DMD) stack was met during this Solar-ERA.NET project.

In order to assess the industrial feasibility, a 30 cm wide roll of niobium-titanium oxide / silver / niobium-titanium oxide DMD on PET was realized in the roll-to-roll solar cell factory at SUNPLUGGED. The achieved surface resistivity was 6 ohm/square, with the bonus of being insensitive against bending cycles, in contrast to the currently available ITO coated PET foils.

The very precise layering required for a DMD to work was only possible thanks to the expertise of PLANSEE who manufactured the tailored mixed metal oxide sputtering targets, initially being employed in the making of test samples at the Austrian Institute of Technology facilities, then subsequently transferred to the industrial scale in a roll-to-roll process.

Moreover, the niobium doped titanium oxide dielectric material acts directly as the hole blocking layer for certain types of methylammonium lead iodide perovskite photovoltaic solar cells, thus simplifying their manufacturing when deposited on the flexible DMD PET foil.

At the Austrian Institute of Technology and at SOLARONIX, so called N-I-P perovskite cells were made on FTO glass, on ITO glass, and on DMD PET foils. The best small-sized cells achieved a power conversion efficiency of > 9% when using a gold based DMD foil. This shows that fundamentally, it is possible to manufacture perovskite solar cells on an ITO-free transparent conducting flexible substrate, thanks to a low-temperature mesoporous titanium oxide layer needed to orient the perovskite layer growth.

5 Outlook and next steps

This achievement of a proof-of-concept DMD foil made with industrially relevant roll-to-roll methods, and the mastering of low-temperature processed mesoporous titanium oxide layers opens the doors to manufacture tailored high performance flexible electrodes, addressing the needs for perovskite and OPV photovoltaic cells, OLED displays, as well as other “printed electronics” devices.

At SOLARONIX, the next steps are the realization of perovskite solar cells and mini-modules on DMD/meso-TiO_2 foils to explore the benefits of lightweight and flexible substrates.

The project Partners will engage in discussions to create a business plan to exploit the project’s results on the short, medium or long run, possibly involving other companies like SUNPLUGGED.

Having proven the roll-to-roll feasibility of the process and the success of making devices, is a big advantage for the upcoming exploitation.

6 National and international cooperation

The consortium partners had complementary expertise and depended on each other's knowledge to accomplish the different tasks. The transnational added value was very significant. The Austrian partners had the unique opportunity to collaborate with one of the most innovative companies in the emerging PV technologies - SOLARONIX. At the same time SOLARONIX established a collaboration with one of the major global players in vacuum materials, PLANSEE, while AIT catalyzed the innovation for what concerns the transparent electrode, which is the crucial link between the core businesses of the two industry partners.

Discussions between AIT, PLANSEE (both in Austria) and SOLARONIX are planned to further develop the manufacturing and its related business of flexible DMD electrodes for devices such as 'organic' and perovskite based solar cells, OLEDS, electrochromic displays, photodetectors, etc.

7 Publications

A joint AIT-PLANSEE-SOLARONIX article about TNO/metal/NTO/meso-TiO_2 electrodes for perovskite solar cells is in preparation, led by Theo Dimopoulos at the AIT.

A paper is under review for the performance and stability of MoO_x/metal/MoO_x DMDs in *Journal of Materials Science*.

A patent has been submitted from AIT for the MTO/metal/MTO DMD structures.

8 References

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