

INTRODUCTION TO IN-SITU PRODUCED PEROVSKITE SOLAR CELLS; A NEW CONCEPT TOWARDS LOWEST MODULE MANUFACTURING COSTS

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ABSTRACT

Starting from the glass frit procedure developed to seal dye solar cells, research is being conducted at Fraunhofer ISE on optimizing and upscaling the principle of perovskite solar cells by an in-situ coating method. A process is proposed, in which the porous substrate films can be filled in sequence with the dissolved active materials of the perovskite solar cell. By varying the porosity and the particle size in the substrate films, the active materials can be deposited in a self-organised process by capillary forces, and form the solar cell after drying. Specially designed structures in the glass substrate make the transport and inert drying of the solvent feasible. The procedure will enable future perovskite solar modules to be produced with minimal consumption of resources and at very low costs. In this paper, we report and comment on our results from proof of principle and about the on-going work in this new area.

Keywords: Perovskite solar cell, Stability, In-situ concept, Photoluminescence

1 INTRODUCTION

Perovskite solar cells (PSC) [1-3] are still at the stage of university research. However, after a certified laboratory efficiency value of 17.9% [4] was attained in 2014 for solution deposited perovskite solar cells (PSCs), this concept has attracted strong research interest around the world [5]. A further increase in efficiency is anticipated as the underlying photovoltaic principles become better understood. Parallel to fundamental research, it is now necessary to develop suitable concepts for up-scaling the cells in a cost-effective process.

The fundamental working mechanism of PSC has still to be fully understood. A most recent step in this direction is the explanation of the low exciton binding energies through the presence of high dielectric constants and the occurrence of ferroelectric domains in the crystals [6]. In the physical device picture, PSCs can be regarded as a typical PIN structure (figure 1).

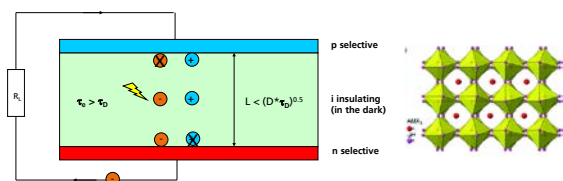


Figure 1: Generalized device principle of a perovskite solar cell. The maximum thickness L of the photoactive (i) layer is approximately limited by the diffusion length $(D_{diff} \cdot \tau_D)^{0.5}$ in this case, assuming that the charge carrier lifetimes $\tau_{e,p}$ are larger than the effective diffusion time τ_D .

The device performance is determined by the selectivity of the contacts towards the up-take of electrons and holes (photovoltage) and the diffusion length of the electron-hole pair (photocurrent). An estimated diffusion length for electrons and holes was reported to be approx. 1 μm in case of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ and higher than 100 nm in the case of $\text{CH}_3\text{NH}_3\text{PbI}_3$ [7, 8] which can be taken as a

design rule for the photoactive layer thickness in PSC devices, so far. The most performing perovskite devices so far have been fabricated in a $\text{CH}_3\text{NH}_3\text{Pb}(\text{I}_{1-x}\text{Br}_x)_3$ / TiO_2 material combination. Recently also for the non-lead containing material combinations $\text{CH}_3\text{NH}_3\text{SnI}_3$ / TiO_2 [9-11] comparable values for carrier diffusion length were reached. For the p-selective contact material highest efficiency values have been reached with the organic conductor spiro-OMeTAD [12] and poly(triarylamine) [13], but also for inorganic materials like NiO [14] and graphite / carbon black [15] promising photovoltages and efficiencies have been reported.

Also, non-inverted and inverted cell set-ups on TCO glass substrates and on foils have been recently studied for PSC. This gives a rather broad choice of possible cell and module designs for up-scaling in the future. One important design rule for PSC modules which originates from the salt-type properties of the halogen perovskites, i.e. their sensitivity towards humidity and the solid-state mobility of ionic charges, can already be drawn today.

Although a good stability at mild temperatures has already been reported by several groups [15, 16], the negative effects on PSCs by humidity have also been remarked [17]. It is well known that the international standard for PV devices are more restrictive since stability tests have to be performed i.e. at elevated temperatures (85°C) and 85% relative humidity (damp heat tests) and under long-term light soaking tests (1,000 h at 1 sunlight). For what studied so far on long-term stability of metal halide PSCs, it emerges that performance degradation under humid environments or high temperatures makes excellent sealing properties crucial for upscaling.

For long-term outdoor operation, both a very good encapsulation to prevent decomposition and (!) a very effective diffusion barrier between neighboring series interconnected cells have to be guaranteed to prevent additional degradation by potential driven ion diffusion. Here the experience gained from the development of stable dye solar modules can be used.

Over the past years, large-area dye solar modules (60 cm x 100 cm, 6.6% active area efficiency) on glass substrates have been successfully developed at Fraunhofer ISE and the associated in situ production method has been established [18]. The solar cells are fabricated from solutions within a module which is hermetically sealed by low-melting glass frits; vacuum processes and module lamination steps are not required. Figure 2 shows the basic concept, which in principle is widely adaptable to other photovoltaic materials too. As our conceptual work demonstrates, this cost-effective technology can be transferred very well to the emerging research field of perovskite solar cells.

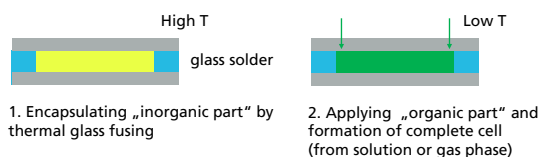


Figure 2: Schematic cross section drawing of the basic in-situ solar cell concept which is in particular applicable for the manufacturing of PV modules containing temperature and moisture sensitive photovoltaic materials which either can be applied from solution and / or from the gas phase through openings and micro-channels in the glass.

Starting from the glass frit procedure developed to seal dye solar cells, research is being conducted at Fraunhofer ISE on optimizing and upscaling the principle of perovskite solar cells by an in-situ coating method. Thin porous substrate films are deposited by screen-printing onto two TCO-coated ($\text{SnO}_2:\text{F}$) glass substrates and are thermally sealed with glass frit in a so-called fusing step with a very narrow gap (figure 3). A gap below $5 \mu\text{m}$ with a constant distance over large areas has been achieved with this method. The up-scalability of this fusing process can be taken for granted as the fusing is carried out by firing the TCO glass plates for several minutes to a temperature of approx. 150°C above the transformation point of the glass. This process results in a stress free leveling of the plates and the fusing of the melted glass solder which keeps the distance constant during cooling and solidifying. A similar temperature treatment and handling is well known in the flat glass industry for the bending and the thermal hardening of architectural glass.

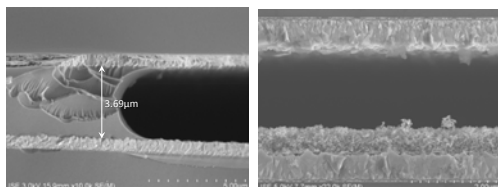


Figure 3: SEM cross sections (exemplary) of fused TCO coated glass substrates using low-melting glass solder (frit). The glass frit solder is visible in the left micrograph, an additional $0.5 \mu\text{m}$ nano-porous TiO_2 layer which has been designed for the uptake of perovskite from solution, is shown in the right micrograph.

A process is proposed, in which the porous substrate films can be filled in sequence with the dissolved active materials of the perovskite solar cell. By varying the porosity and the particle size in the substrate films, the active materials can be deposited in a self-organised process by capillary forces, and form the solar cell after drying. Specially designed structures in the glass substrate make the transport and inert drying of the solvent feasible. The procedure will enable future perovskite solar modules to be produced with minimal consumption of resources and at very low costs.

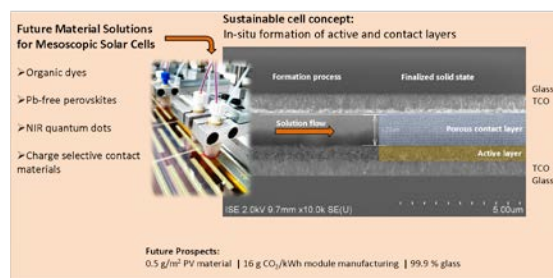


Figure 4: Conceptual approach for the development of mesoscopic in-situ solar cells. The PIN structure of the mesoscopic (e.g. PSC) cell is formed between the lower TCO glass, containing a very thin electron selective layer like for example dense TiO_2 , and the interface between the mesoscopic (photo active) layer and the porous contact layer. The porous contact layer has two functions; transport of the solutions and allowing the subsequent drying as well as providing the electron contact to the second TCO glass. In the ideal case, the material used for the porous contact layer has also hole selective properties.

In this paper, we report and comment on our results from proof of principle and about the on-going work in this new area.

2 EXPERIMENTAL

TCO glass substrates (TEC-8, Nippon Sheet Glass) have been scribed and small filling holes (1 mm) have been drilled both with the appropriate lasers. Five individual cells (2.0 cm^2 active area) have been manufactured by screen printing on a common plate (figure 5). Before the printing steps a thin (10 – 30 nm) layer of dense TiO_2 has been deposited on the working electrode side (WE) by spray coating a commercial solution of a titanium diisopropoxide bis(acetylacetonate) solution (75% in 2-propanol, Sigma-Aldrich) diluted in ethanol (1:42, volume ratio) as precursor and nitrogen as carrier gas on the TCO glass held at a temperature of 450°C . The glass frit paste has been provided by Pröll GmbH, Germany. For depositing the mesoscopic TiO_2 layer the paste 18NRT (Dyesol) has been diluted further by adding two parts of terpineol and screen printed. The paste used for the electrically isolating ZrO_2 is based on primary particles of approx. 150 nm (Tosoh, Japan). These pastes are already rather optimized whereas the graphite containing paste is still far from optimal. The graphite paste contains flakes of approximately $25 \mu\text{m}$ (TIMREX, surface area $< 5 \text{ m}^2/\text{g}$) and much smaller graphite particles which originate from the dispersion process. Also the paste contains a small amount of glass frit binder for enhancing the mechanical contact to the

TCO at the counter electrode (CE) side. After sintering of the plates the WE and CE side have been positioned and stacked for the fusing. The fusing step has been carried out for several minutes at a temperature between 650 – 700 °C. The fusing has taken place in air, as under full inert atmosphere an unwanted increase of the TCO resistance by a factor 3 has been seen. During the fusing, the intension is also to achieve an electronic contact between the graphite layers on the CE and WE side.



Figure 5: Photos of the screen-printed in-situ PSC test cells during manufacturing; The layer sequence and the approximate layer thickness after sintering have been the following: Working electrode (WE): glass - TCO – 10 nm TiO₂ n-selective layer – 400 nm nano-TiO₂ mesoscopic layer – 300 nm porous ZrO₂ isolation layer – 10 μm porous graphite layer composition. Counter electrode side (CE): glass -TCO – 10 μm porous graphite layer composition. During the sintering the glass frit layer has been molten (glazed) as can be seen by the transparent appearance (photo on the right side).

The cell was filled with PbI₂ dissolved in N,N-dimethylformamide (DMF) at a concentration of 1M and kept at 95 °C. The filling process was performed by injecting the PbI₂ solution into the sealed cell from an inlet hole and applying under-pressure on the outlet hole. The device was also kept at 95 °C. In the following step the DMF was removed by under-pressure visibly causing the PbI₂ crystallization (figure 6). The cell was left on the hot plate at 95 °C for 10 min. After cooling down to room temperature a solution of CH₃NH₃I in 2-propanol (10 mg ml⁻¹) was infiltrated into the cell following the same technique used for PbI₂. The complete perovskite transformation occurred in a time scale of seconds while the solution continued to flow towards the outlet hole (figure 6). Finally, the 2-propanol solvent was removed from the cell by under-pressure and then kept at 95 °C for 30 min.

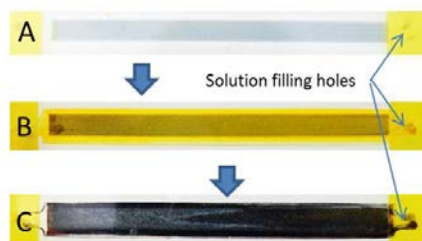
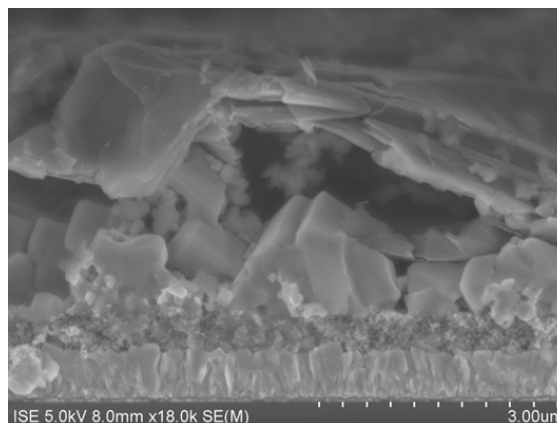


Figure 6: Photo of in-situ PSC test cells showing the formation of the photoactive layer by recrystallization. After application of the PbI₂ / DMF solution through the filling holes and the subsequent drying a homogenous deposition of the PbI₂ (yellow) is seen. In the second step, the purging through of CH₃NH₃I in isopropanol is

causing the fast (< 1 s) recrystallization to the black perovskite. (Top-view from WE side, the graphite contact layer appears already dark in the unfilled case as the TiO₂ and the thin ZrO₂ layers are partially transparent.)

3 RESULTS AND DISCUSSION

After completion of the cells as described in the experimental section, samples were cut and examined under SEM for their layer built-up (figure 7). A general problem is, that the cells are still overfilled with perovskite which can be seen by the formation of large (1 – 2 μm) perovskite crystals on top of the nano-porous layers. Such a behavior is often also observed in spin-coated devices and can lead to a decrease of electron transport. More severe is, that only a very low mechanical contact between the perovskite crystals and the porous contact layer, i.e. the graphite flakes is achieved. Therefore only a localized exchange of holes at the interface and therefore only point currents can be expected in these samples. This is also confirmed by LBIC measurements (figure 8) and the very low average current density which resulted still in < 1 mA/cm². A positive aspect is, that the transformation of the PbI₂ to the perovskite seems to be complete, as no residual needle like crystals which are typical for PbI₂ can be observed.



Figures 7: SEM cross section of a complete in-situ PSC test cell as described as proof-of-principle in this paper. The WE side is shown. Visible are, in the order from below, the TCO crystals, the nano-porous TiO₂ filled partially with perovskite and the particles from the thin isolating ZrO₂ layer, larger crystals of perovskite on top of this layer and the graphite flakes from the porous contact layer.

The analysis of the perovskite layer formation, and the control of crystal growth during cells processing inside the in-situ concept device, was followed and investigated through the photoluminescence (PL) signal. Properly crystallized perovskite layers give high PL intensity and well defined spectra with a peak wavelength at 775 nm for the perovskite under study CH₃NH₃PbI₃ [16]. As it shown from the PL spectrum in figure 8, the in-situ perovskite formation can be confirmed for our samples, which is in correlation to the observation gained by SEM. The intensity of the PL signal is strong meaning that

small non-radiative recombinations occur. This can be seen as an indication for a high obtainable photovoltage which actually has been measured in the samples (up to 1 V under full sun illumination). The PL signal is related to the volume amount of crystals, among other factors like surface recombinations, therefore the PL mapping on our sample shows that the perovskite crystals are distributed over the whole cell area, although without homogeneous morphology. Further information can be obtained by combining the PL intensity and spectral shift with the area-resolved photocurrent (LBIC) (figure 8). The LBIC mapping provides a very low current density clearly pointing to a spot-type behavior as predicted already from the SEM image.

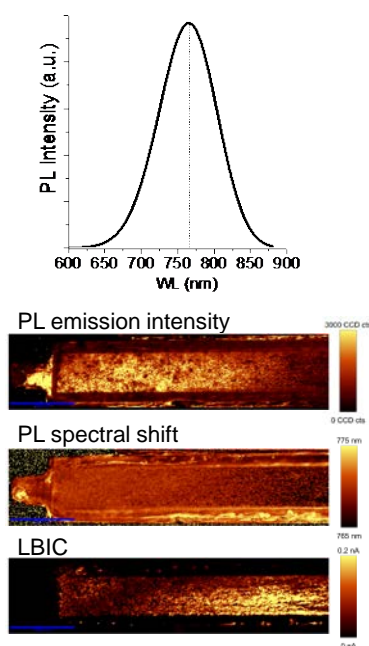


Figure 8: (from top to bottom) Photoluminescence spectrum (centered at 770 nm) obtained from an in-situ perovskite cell. For the same cell spatial resolved imaging of PL emission intensity, spectral shift and Light-Beam-Induced-Current are shown.

4 CONCLUSIONS

The in-situ perovskite solar cell concept has been introduced and our first investigations to transfer this concept from the well-established glass frit sealed dye solar cell technique to the perovskite topic, has been presented.

Complete test cells have been manufactured by screen printing taking into account the solid state P-i-N device structure and a first round of new pastes has been formulated for this purpose.

For the in-situ perovskite solution processing a conductive porous graphite layer has been introduced which also serves as the hole selective contact.

We could show the formation of PbI_2 without the occurrence of large unwanted crystals which is the

necessary condition for the complete and fast reaction with CH_3NH_3I and the subsequent re-crystallization into the perovskite.

Only very low photocurrent has been achieved in this proof of concept which has been explained by SEM, photoluminescence and photocurrent mapping with the small contact between the graphite flakes and the crystals of the photoactive layer.

The ongoing work is focusing in particular on reducing the graphite particle size and the minimization of the electrode distance.

The observation, that with the present proof-of-concept cells already a high photovoltage of up-to 1 V has been reached means that the chance for creating ohmic shunts during cell manufacturing seems rather low which will facilitate the later up-scaling. The coating techniques for the in-organic layers which are acting as a host for the photoactive material do not have to be restricted to screen-printing, also technical ink-jet printing (with e.g. integrated lasers) and combinations with spray coating or even magnetron-sputtering are conceivable.

The only critical thermal step in the fusing process is the short moment (several minutes) where the plates have to be homogeneously heated and cooled down above the transformation point of the glass. Some existing oven techniques will have to be adopted here. The remaining thermal handling is very much straight forward. Also a combination of the sintering and fusing step can be imagined. In this case, the energetic input during module manufacturing will mostly be determined by the heating up of the glass to 650 – 700 °C which still only is half the temperature necessary during the flat glass production.

The materials used in the presented in-situ perovskite solar cells concept, including the TCO glass are readily available already nowadays in large quantities at low price per m^2 .

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