InspiRe – visualization of perovskite deposition kinetics by in-situ monitoring

LayTec's InspiRe metrology system has been designed for the in-situ monitoring of thin film formation processes by means of spectral reflectance measurements. In this note it is demonstrated how InspiRe can be used to visualize the complex kinetics of perovskite formation during spin-coating.

Perovskites have shown an unprecedented progress in efficiency in photovoltaics (PV) [1]. In contrast to other thin film PV technologies, perovskite record efficiencies were obtained with low-cost methods such as spin-coating or doctor-blading. Perovskites even outperformed all thin film PV technologies in terms of record lab cell efficiency (25.7%) [1] and in tandem configuration with a crystalline silicon solar cell even the best silicon solar cell was surpassed (29.8%) [1]. Here, also vapor-based processes bear the potential of reaching even higher efficiencies as they allow depositing the perovskite films on textured silicon cells. Furthermore, perovskites also demonstrated exceptional potential for the fabrication of lasers, LEDs, X-ray detectors and many more.

Despite record-breaking efficiencies, numerous process-related challenges remain for perovskite technology. In particular, wet-chemical low-cost deposition suffers from poor reproducibility and predictability. Similarly, also the optimization of vacuum processes still suffers from a lack of understanding the basic kinetics and reactions of the underlying processes.

Since 2019, LayTec closely cooperates with the HySPRINT Helmholtz Innovation Lab of Helmholtz-Centre Berlin in the field of in-situ monitoring of perovskite formation processes [2-4]. For this application, LayTec recently launched its product "InspiRe" for spectral in-situ reflectance spectroscopy of the formation of perovskite and similar thin films such as CIGS, TCOs or CdTe **(InspiRe)**.

The InspiRe metrology system employs a halogen lamp and a fiber-optical head for reflectance measurements and can be designed for detection either in the visible or near-infrared region or both.

For spin-coating (Fig. 1a), the measurement head is mounted perpendicularly to the sample plane, whereas for annealing monitoring, reflectance was measured with a tilted measurement head (15° off-axis; Fig. 1b) for collecting only diffuse light as no interference patterns were observed in the visible optical spectrum due to the roughness of the untreated perovskite samples when no solution was present.

In order to resolve the details of perovskite formation reactions and their kinetics, the InspiRe system was de-

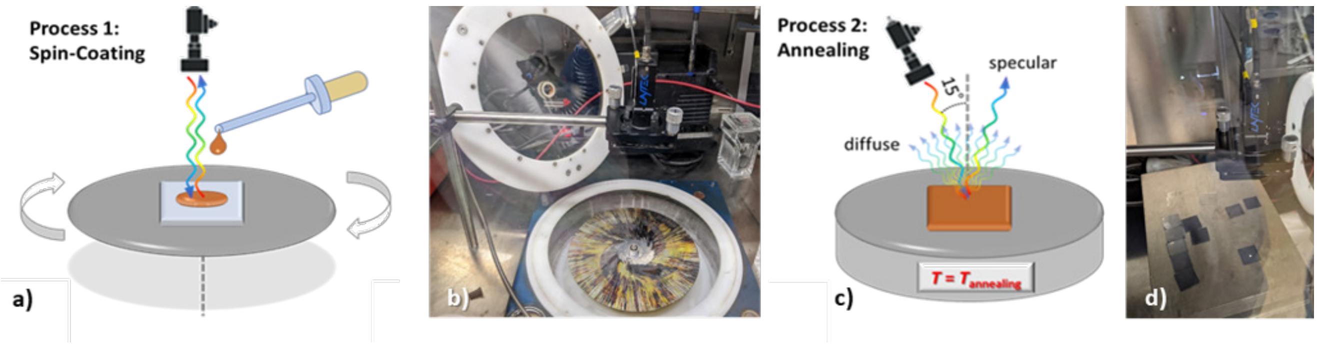

Fig. 1 Schematic sketches and photographs of the experimental setups for perovskite thin film spin-coating (a, b) and annealing (c, d) as they were used at HySPRINT - A Helmholtz Innovation Lab of Helmholtz-Zentrum Berlin.

signed for very high data acquisition speed. Integration times as low as 0.1 ms for spin-coating and 10 ms for annealing could be realized.

In this Application Note recent results on the spin-coating deposition process are presented which highlight the ability of the InspiRe metrology system to resolve the rapid kinetics occurring during this deposition processes. One particular process step, which at the same time increased perovskite material quality as well as the complexity of its formation is the so-called "anti-solvent-drip" (ASD) [5 and references therein]. In Fig. 2, a schematic sketch of the process sequence can be found. The kinetics and exact reaction path are still not well understood and it appears that the exact timing of the process is highly crucial in achieving the highest materials quality and device performance. Here, recent studies of this process by in-situ reflectance spectroscopy using LayTec's InspiRe system as well as a conventional setup using a fiber-probe instead are compared.

A standard spin-coater setup (see e.g. Fig. 1b) was used for deposition at an acceleration from 0 to 3500 or 4000 rpm within 5 s and a subsequent rotation time between 35 and 180 s. For deposition, the solution was pipetted on a glass substrate directly before starting the rotation. A MAPBr:FAPI solution (1:5) + 5% CsI (3CAT) was used as precursor solution. Here, the ASD was deposited 31 s after starting the rotation. Details about the ASD and further experimental details can be found in [2-5].

In Fig. 3, the in-situ reflectance spectrograms as obtained with the InspiRe system during monitoring of the 3CAT process without (Fig. 3a) and with (Fig. 3b, c) ASD are depicted.

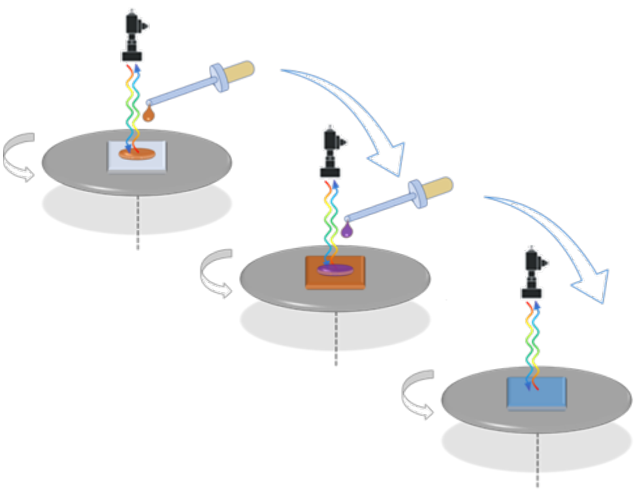

Fig. 2 Schematic sketch of the anti-solvent-drip 3-cation deposition process: Upon dispensing of the original precursor solution an additional anti-solvent is applied for improving the crystallization process.

Without ASD (Fig. 3a), it can be seen that as soon as spinning starts (~20 s), interferences evolve from the liquid precursor film. At an acquisition speed of 100 Hz, the shift of the fringes for the thinning liquid precursor film can be resolved from the very beginning of the rotation. Simultaneously, a steady shift of the absorption edge towards ~440 nm is observed, indicating changes in the solution composition.

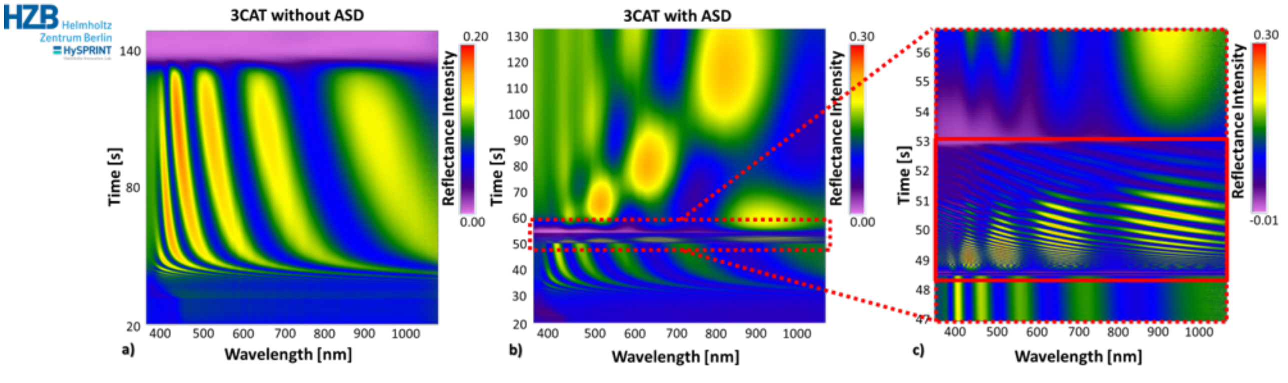

Fig. 3 Reflectance spectrograms as obtained with the InspiRe metrology system during in-situ monitoring of the 3-cation (3CAT) perovskite spin-coating deposition process without (a) and with (b) anti-solvent-drip (ASD). Additionally, the period directly after applying the ASD is shown enlarged in (c).

At t = ~40 s the spectra only show a small number of fringes with a rather constant absorption edge at ~440 nm.

After the complete removal of the liquid film, all interference patterns disappear quite suddenly (purple area in Fig. 3a at ~130 s). This effect can be attributed to the vanishing liquid film as well as to a sudden change in sample roughness upon sample crystallization causing a less intense specular reflex.

In Fig. 3b, the beginning of the process is very similar to the reference process. However, as soon as the ASD is applied (see red box), a sudden and major change in the spectra is clearly evident.

Fig. 3c shows the enlarged segment of the color plot right after applying the ASD. Upon the ASD, a period of about 4 s of highly complex interference patterns forms in the process after which the process starts to become more steady again and interference patterns can be resolved. Interestingly, there seems to be a second, overlaying, interference pattern on top of the interference from the underlying perovskite precursor wet-film. Compared to the interference maxima and minima that can be attributed to the wet-film thinning of the perovskite precursor, the superimposed oscillation of the peak intensities after deposition of the ASD change much more rapidly.

The spin-coating results for the 3CAT ASD process clearly demonstrate the advantages of the rapid InspiRe in-situ reflectance measurements. The high time and spectral resolution of the InspiRe measurements will be extremely helpful for studying the complex kinetics of this process. Fig. 3b and 3c show that the reaction kinetics are completely changed within 4 s after the ASD. This period is highly complex but still exhibits clear spectral features instead of just turbulence-induced noisy signals indicating that the kinetics of this process, which is not yet understood to a large extend, can potentially be deduced from these patterns. The fact that a separated spectral regime seems to form during these 4 s in the color plot already indicates that the ASD process does not occur in a linear manner. The HZB researchers hypothesize that this indicates the intermediate state of two liquid layers with the anti-solvent on top evaporating much more rapidly. First results obtained about this topic with a similar setup will be published in [5].

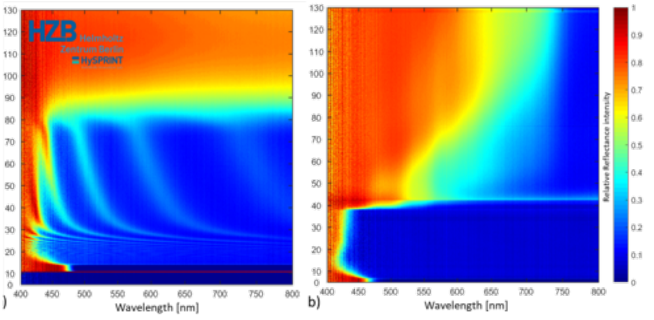

Fig. 4 Spectrograms of the 3-cation (3CAT) perovskite spin-coating deposition process without (a) and with (b) anti-solvent-drip (ASD) as obtained with a conventional probe-based optical setup, i.e. without LayTec's InspiRe metrology system.

Even within this very short period of time the spectrogram obtained with LayTec's InspiRe metrology system clearly resolves numerous superimposed interference fringes which can be considered as a fingerprint of the complete reaction kinetics of this complex perovskite formation process. Accordingly, this set of reflectance data can be used as a basis for modelling the underlying kinetics. This work is currently conducted in the group of Dr. Eva Unger at the HySPRINT Helmholtz Innovation Lab in collaboration with LayTec.

For comparison, Fig. 4 shows in-situ reflectance spectrograms of an equivalent 3CAT process with (Fig. 4a) and without (Fig. 4b) ASD as obtained by monitoring with a conventional fiber-probe-based setup. With this setup, integration times of 500 ms had to be chosen for achieving a sufficient signal-to-noise level. Generally, the spectrogram for the ASD-free process in Fig. 4a agrees well with the one in Fig. 3a. But as soon as the ASD is applied, the shortcomings of this setup become clear. Due to the long integration time, much fewer spectral features and details can be resolved, which will also limit the possibilities for revealing the underlying reaction schemes. In conclusion, the results presented here demonstrate the benefits of a high-speed and spectrally resolved optical method for in-situ monitoring of perovskite formation.

Numerous process features could be resolved that could not have been studied before due to their rapidness. For further reading one may refer to [2-4] in which further results on further precursor as well as the annealing of perovskite thin films are published. Here, particularly the absorption edge shift could be visualized in-situ providing an excellent method for process control of further industrialization of these processes. In the future, the InspiRe metrology system will also be applied to additional reactions and processes in order to gain further insights into the reaction kinetics.
HZB and LayTec join forces for developing a suitable optical model for deducing more quantitative information from the reflectance data obtained.

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For more information please visit: www.laytec.de/inspire/ or contact info@laytec.de.

LayTec AG
Seesener Str. 10-13
10709 Berlin, Germany

Tel.: +49 (0)30 89 00 55-0
Email: info@laytec.de
Web: laytec.de