In-situ growth rate monitoring during perovskite physical vapor deposition

Previously, we have introduced LayTec's InspiRe metrology system for the in-situ monitoring of thin film formation processes by means of spectral reflectance measurements. In this note we go beyond the mere visualization of growth kinetics by extending its capabilities to in-situ real-time growth rate and thickness monitoring.

Perovskites have shown an unprecedented progress in efficiency in photovoltaics (PV) and even outperformed all thin film PV technologies in terms of record lab cell efficiency (25.7%) [1]. In tandem configuration with a crystalline silicon solar cell even the best silicon solar cell was surpassed (29.8%) [1]. Besides wet-chemical deposition methods such as spin-coating and doctor-blading, also vapor-based processes such as physical vapor deposition (PVD) bear the potential of reaching even higher efficiencies as they allow depositing the perovskite films on textured silicon cells and precise control of deposition rates and composition using well-established vacuum technology.

Previously, we demonstrated the capability to visualize even complex film formation processes like the anti-solvent-drip 3-cation deposition [2, 3] based on spectral reflectance spectroscopy using LayTec's InspiRe metrology system (https://www.laytec.de/inspire/).

The InspiRe metrology system employs a halogen lamp and a fiber-optical head for reflectance measurements and can detect the visible or near-infrared region (or a combination of both). The spectral data obtained from these measurements can then be used for further analysis and modelling. In this application note it will be demonstrated how constant growth rates, film thickness and film properties like refractive index can be determined in-situ in real-time.

Since 2019, LayTec closely cooperates with the HySPRINT Helmholtz Innovation Lab of Helmholtz-Zentrum Berlin (HZB) in the field of in-situ monitoring of perovskite formation processes [2-4]. In 2022 a second InspiRe metrology system was installed at HZB. This system was installed at a PEROvap thermal evaporation chamber and is designed for in-situ reflectance measurements in the wavelength range from 450 nm to 1100 nm. The system is shown in Fig 1.

HZB Helmholtz Zentrum Berlin HySPRINT Helmholtz Innovation Lab

Fig. 1: Photographs of the InspiRe metrology system installed at a PEROvap evaporation chamber at HySPRINT - A Helmholtz Innovation Lab of Helmholtz-Zentrum Berlin.
Left: Optical measurement head mounted to the chamber; Right: Glove box containing the chamber with the measurement PC and controller (in black rack compartment) next to it.

At HZB the InspiRe system was used for monitoring several perovskite evaporation processes. In Fig. 2 (upper left), the spectrogram obtained during a deposition process on ITO-coated glass is shown (duration ≈ 90 min). An excellent signal-to-noise ratio is achieved and the oscillations evolving during film growth are clearly resolved. In order to determine the growth rate and film thickness, a proprietary algorithm developed by LayTec was used which fits the reflectance transients (intensity vs. time) of distinct wavelengths with an optical model, in which the refractive index n(λ), the extinction coefficient k(λ) and the growth rate are chosen as variables. For spectral measurements as conducted by the InspiRe the user can choose the wavelengths to which the fit is applied. By this fit, the precise growth rate and absorber thickness of the perovskite can be deduced. In this example, two wavelengths (800 nm, 900 nm, see Fig. 2 lower left) were chosen for which the deposited film was transparent ($k = 0$). Note that identical rate and thickness values were obtained for both wavelengths, thus confirming the reliability of the fit.

The application of this fitting algorithm for growth rate and thickness calculation in real-time during the run has just been implemented in LayTec's EpiNet software, which thereby allows determining both parameters directly during deposition. Thus, maximum control of the growth process is possible, which further facilitates the development of advanced perovskite processes and fine-tuning the properties of this complex but highly promising class of materials. In Fig. 2 (right) the results of a real-time fit of the same deposition process is shown. Besides the actual reflectance signal at 950 nm (blue trace), the growth rate (orange trace), the film thickness (brown trace), the refractive index (green trace) and the extinction coefficient (red trace) are displayed. The real-time fitting was started after ~1000 s, when sufficient reflectance information for reliable fitting had already been gathered. After an initial period of change all values rapidly converge to a reasonable and fairly constant value, thus again demonstrating the robustness of the method.

HZB and LayTec will continue to join forces for expanding the capabilities of in-situ monitoring for these processes.

The contribution of HZB / HySprint is gratefully acknowledged.

References:

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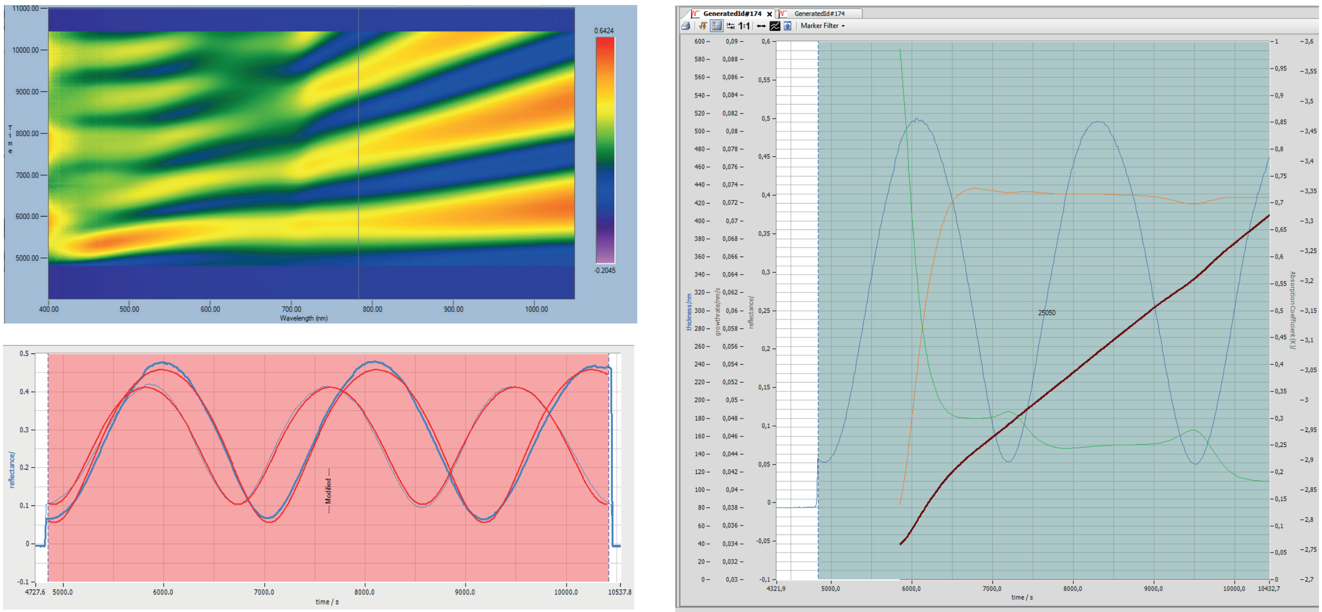

Fig. 2: Upper left: Reflectance spectrogram as obtained with the InspiRe metrology system during in-situ monitoring of a perovskite deposition run on ITO-coated glass. Lower left: Fit of the 800 nm and 900 nm transients of the same run for deducing film thickness, growth rate, refractive index and extinction coefficient simultaneously. Right: Result view of the real-time fitting of the same quantities for the identical deposition process.

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