

Recent advances in *in-situ* and *in-line* monitoring of perovskite thin film formation



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Berlin, Germany

Outline

Company introduction

Metrology methods & monitoring parameters

In-situ monitoring of perovskite formation

In-line monitoring of perovskite formation

Metrology capabilities for entire perovskite stack

Summary & outlook

Outline

Company introduction

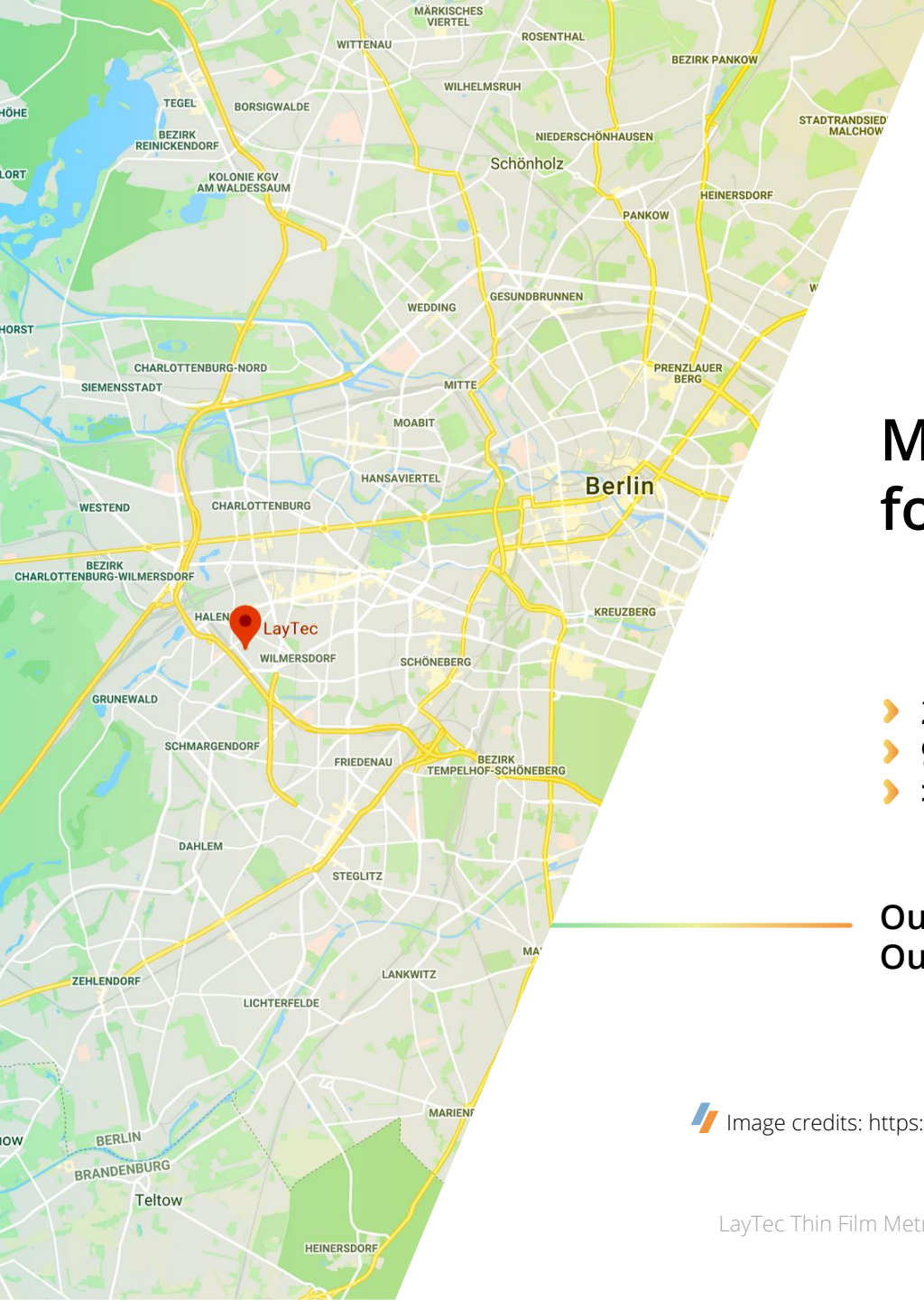
Metrology methods & monitoring parameters

In-situ monitoring of thin film formation

In-line monitoring of thin film formation

In-depth analysis for R&D

Summary & outlook



NYNOMIC
THE PHOTONICS GROUP



Metrology company founded 1999 in Berlin

- › 25 years old
- › 90 employees
- › >3500 systems sold
- › spun-off out of TU Berlin
- › Operating worldwide
- › Member of Nynomic group

Our business: Process-integrated optical metrology
Our markets: Semiconductor and thin-film industry & academia
incl. lighting, laser, PV, glass coating ...

 Image credits: <https://www.google.de/maps>

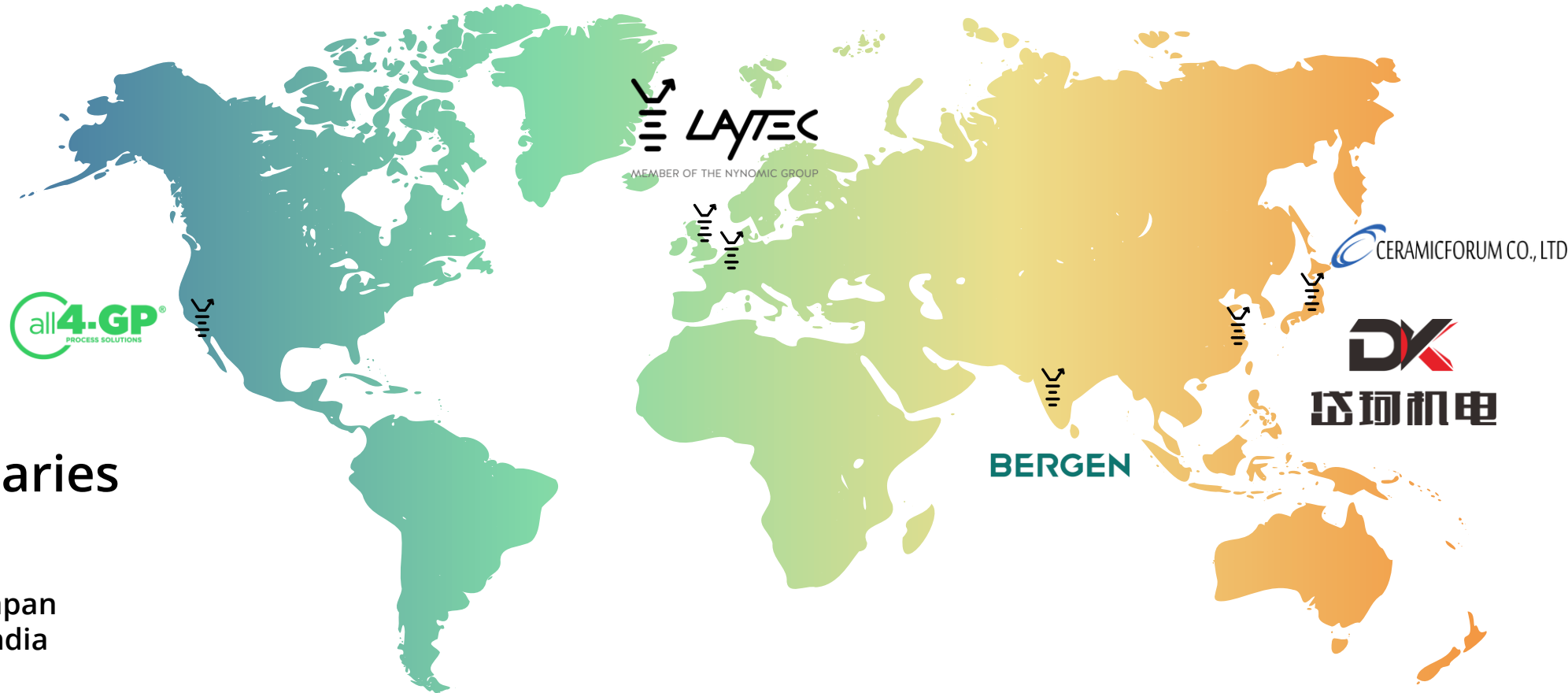
Worldwide network of sales and service partners

Headquarter

- › Berlin, Germany

Sales & service offices, subsidiaries (solar applications)

- › North America
- › Europe
- › China
- › Japan
- › India



PV company & institute references



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Reflectometry – Thickness measurement

› Interference of light reflected

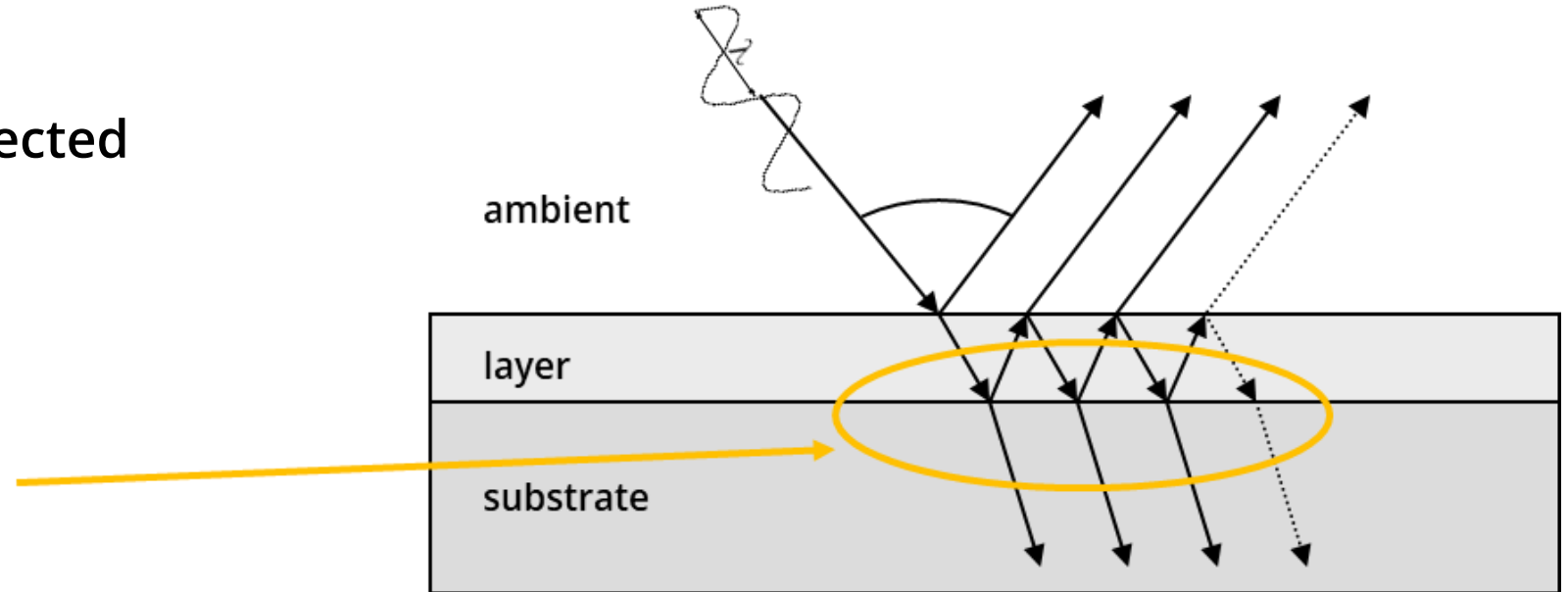
- › at the gas/layer interface
- › at the buried interface

› Interference is

- › constructive at $2 \cdot n \cdot d = m \cdot \lambda$
- › destructive at $2 \cdot n \cdot d = (m + 1/2) \cdot \lambda$

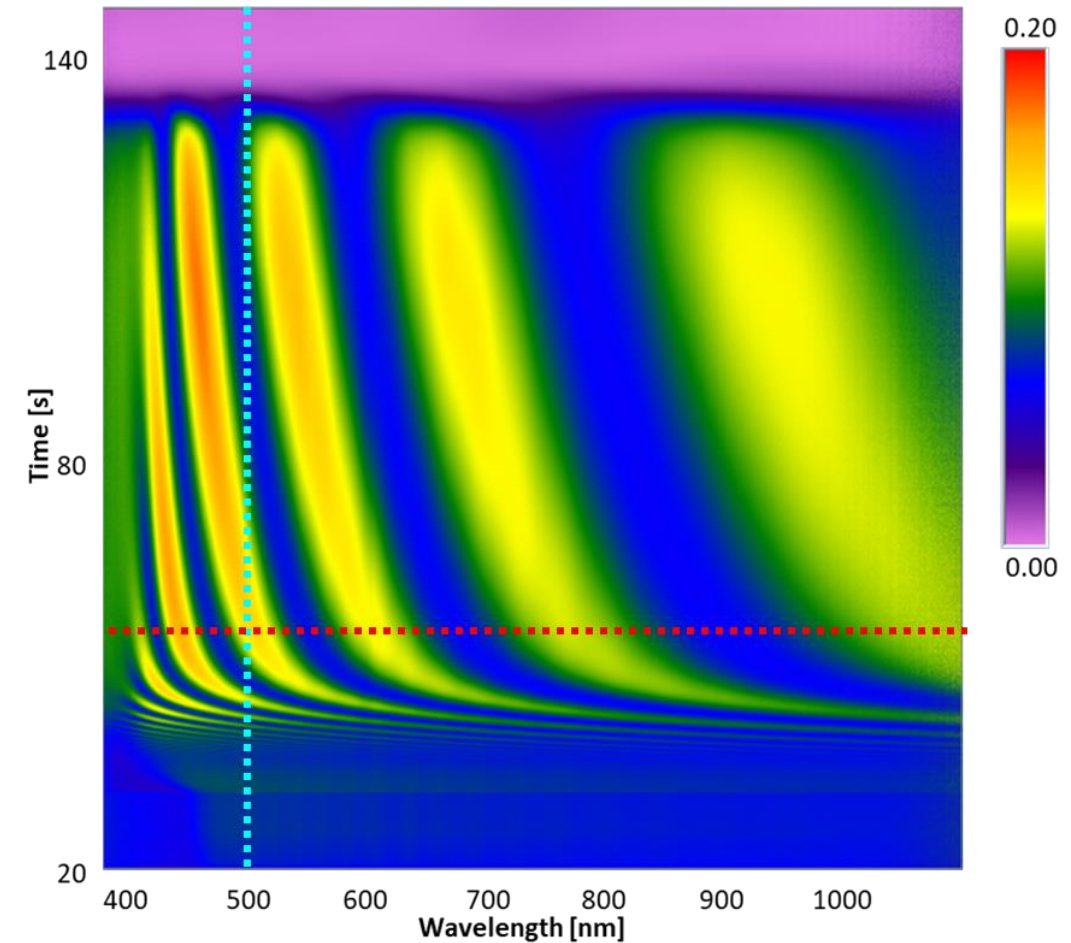
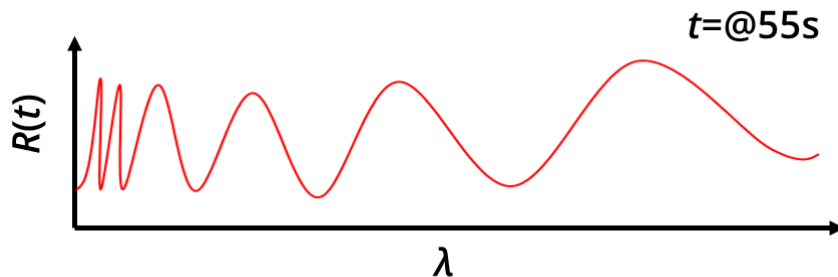
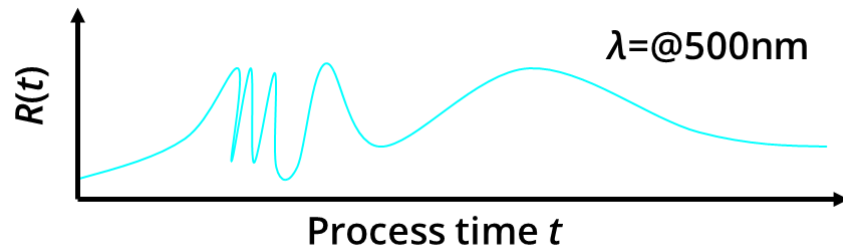
› Oscillations in reflectance spectra (Fabry-Perot)

- › → thickness measurement
- › at specific wavelengths (in-situ)
- › white light reflectance (in-situ or in-line)

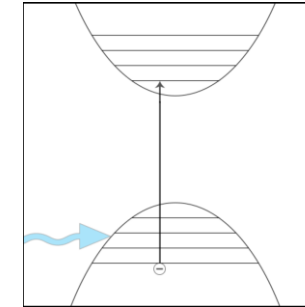
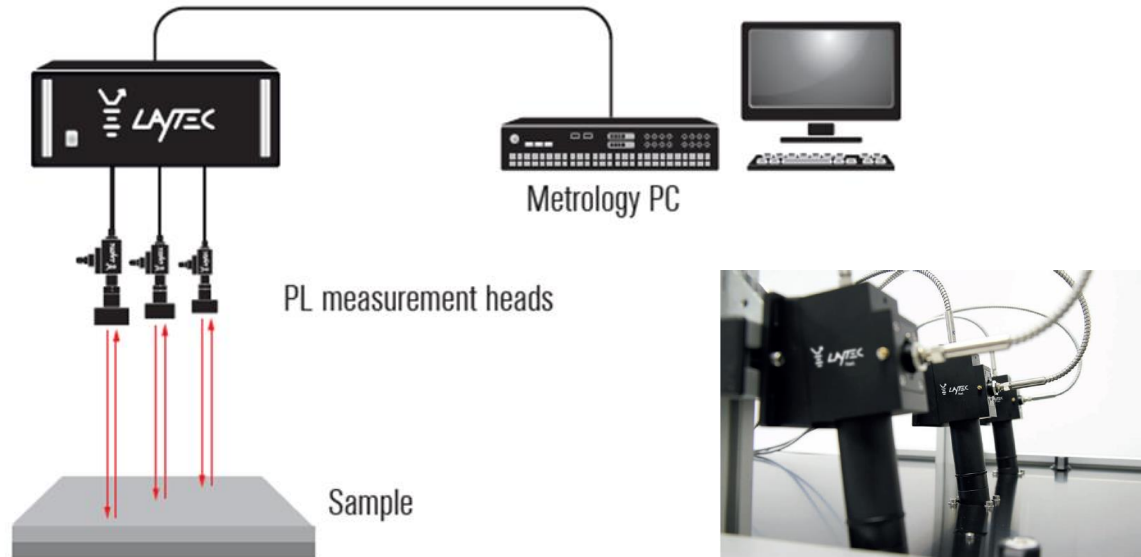


Reflectometry – Thickness measurement

- 1 spectrum per measurement
- 3D data set: λ , R , t ("spectrogram")
- Different ways to analyze:
 - Over time $\rightarrow R(t, \lambda=\text{const.}) \rightarrow$ transient analysis
 - Over wavelength $\rightarrow R(t=\text{const.}, \lambda) \rightarrow$ spectrum analysis

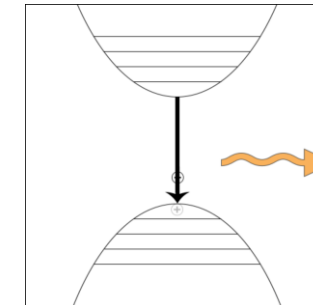


Photoluminescence

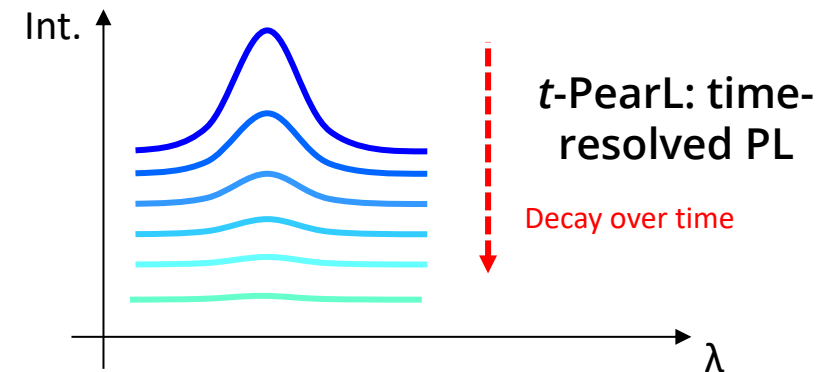
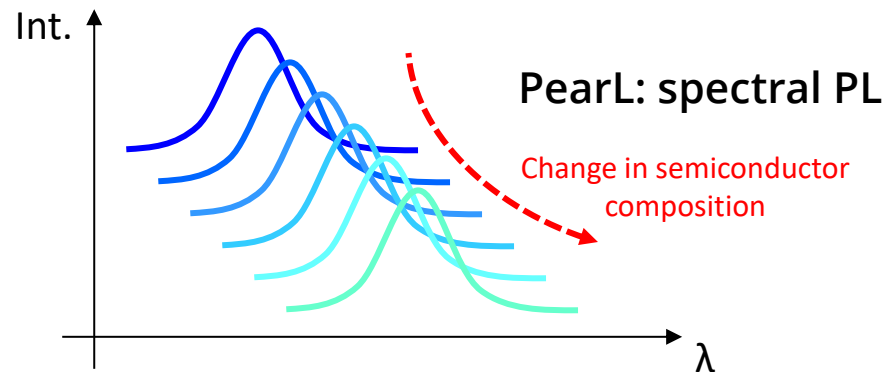


[2]

Excitation:
photon in



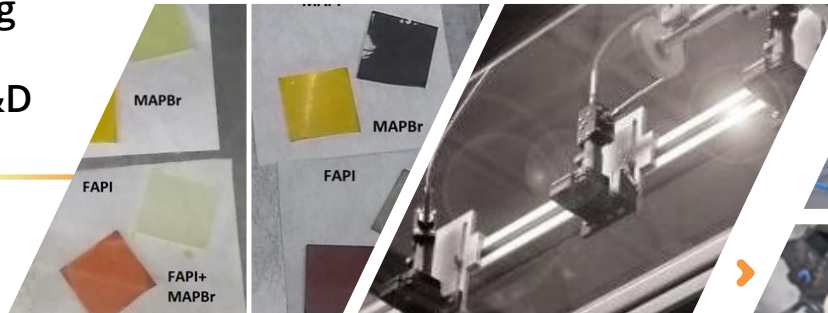
Emission:
photon out



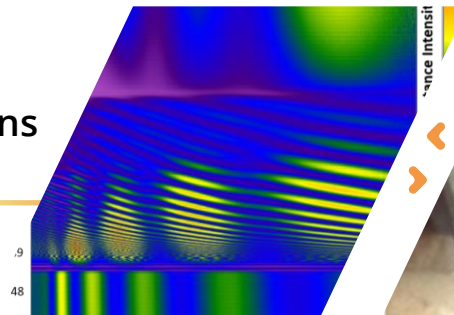
references: see last slide

Metrology for high-efficiency photovoltaics

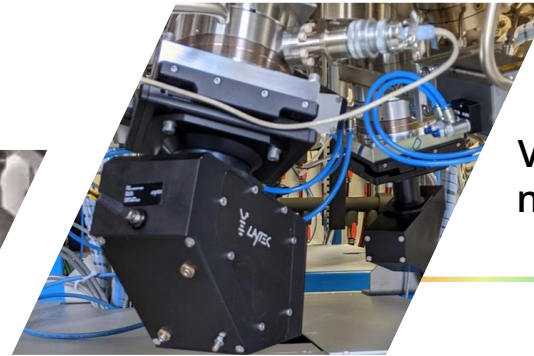
In-situ monitoring
of thin film
deposition for R&D
and production



Visualization of reaction
kinetics and phase transitions
during thin film formation



Vacuum and
non-vacuum
integration



Measurement of

- › layer thickness
- › absorption edge
- › phase transitions
- › reaction kinetics
- › color
- › composition
- › spectral PL
- › time-resolved PL
- › layer homogeneity
- › sheet resistance

Tandem and thin film
photovoltaic modules

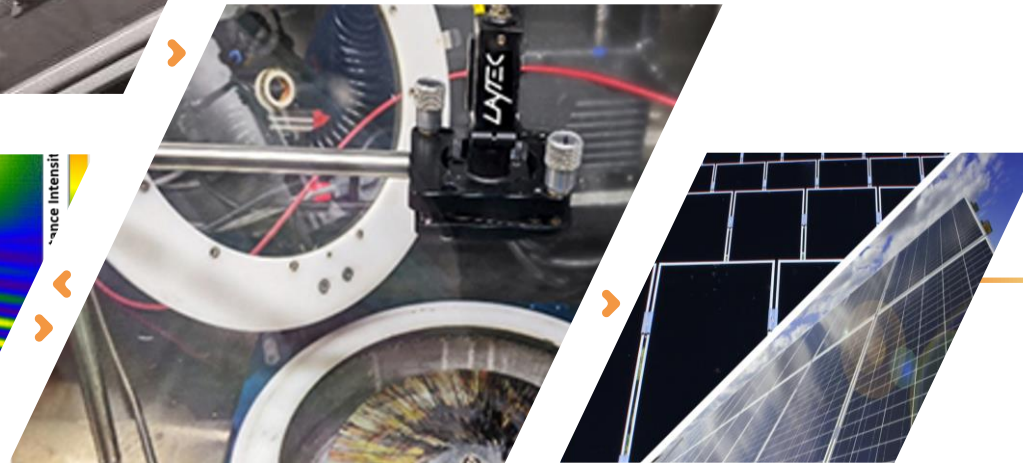


Image credits: see last slide

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In-situ monitoring of perovskite formation

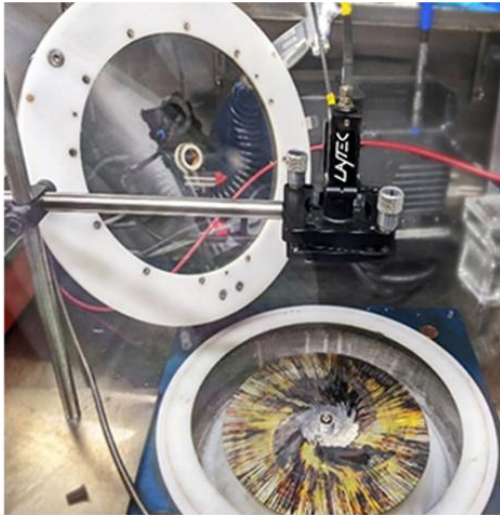
In-line monitoring of perovskite formation

Metrology capabilities for entire perovskite stack

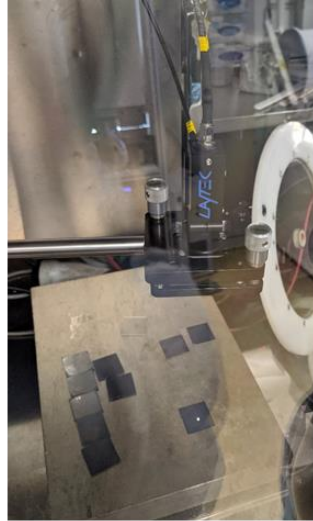
Summary & outlook

In-situ monitoring of perovskite formation

Spin-Coating



Annealing



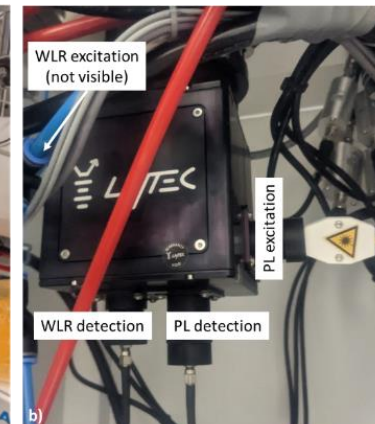
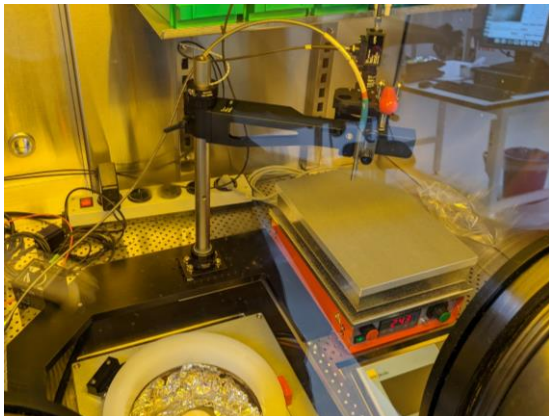
Thermal evaporation



Slot-die coating



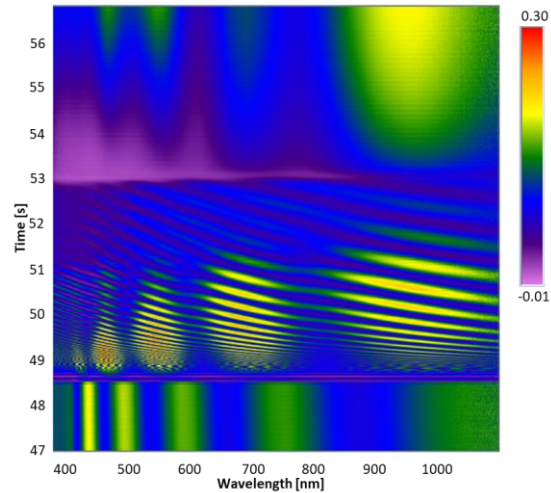
Combined
spin-coating &
annealing set-
up



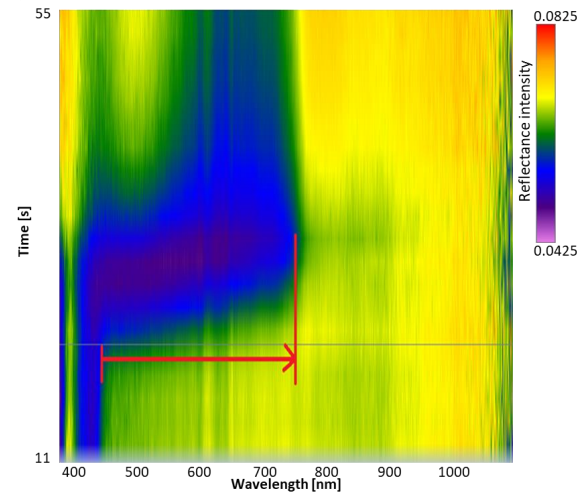
Combined
reflectance &
PL set-up for
PVD

In-situ monitoring of perovskite formation

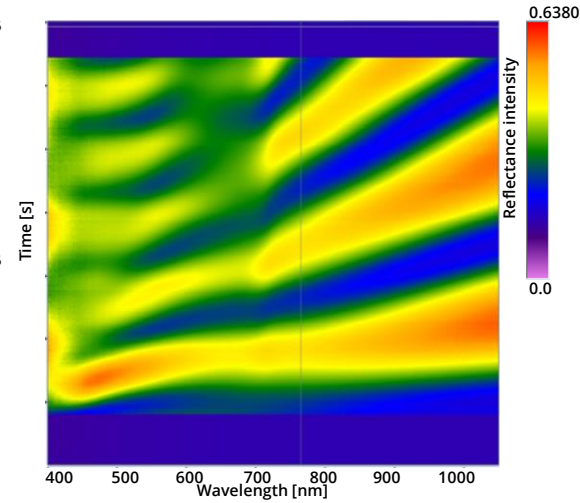
Spin-Coating



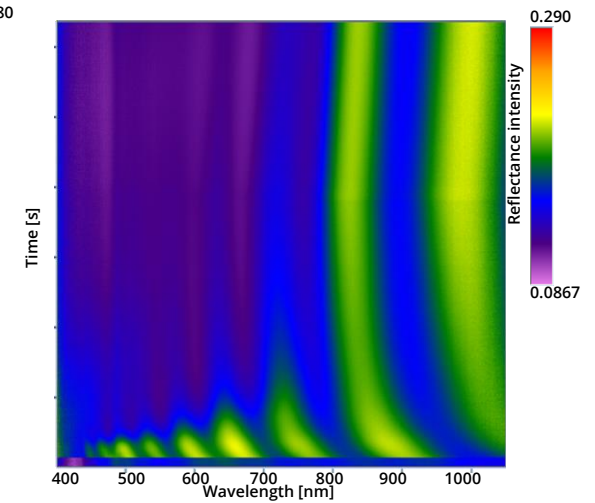
Annealing



Thermal evaporation



Slot-die coating



- Early fringes → wet film thickness
- Late fringes → solid film thickness
- Fingerprint of reaction kinetics
- Late fringes → roughness
- Band gap formation

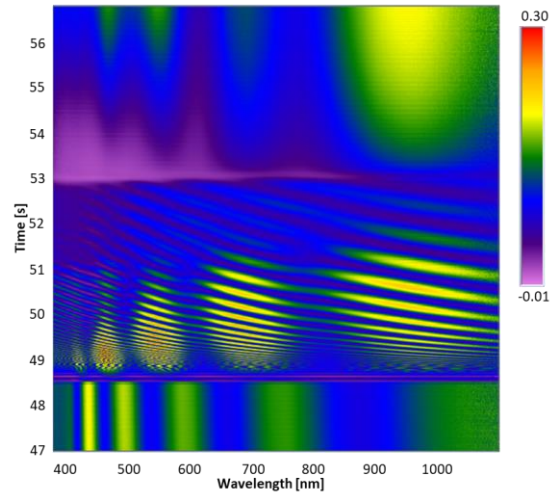
- Band gap formation
- Film degradation by phase transitions

- Fringes → growth rate → thickness
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- Roughness
- For const. growth rate → n, k
- For known n, k → thickness

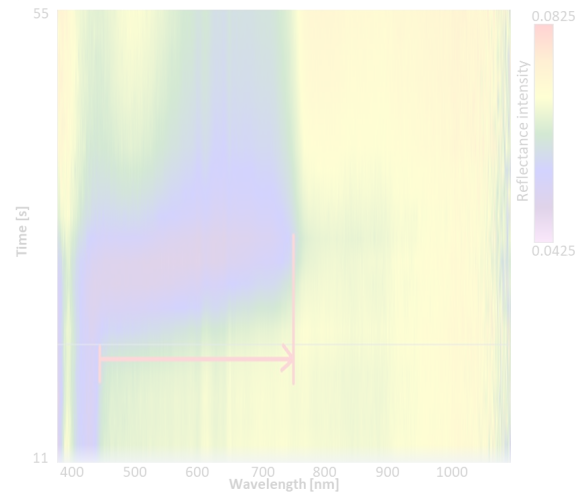
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In-situ monitoring of perovskite formation

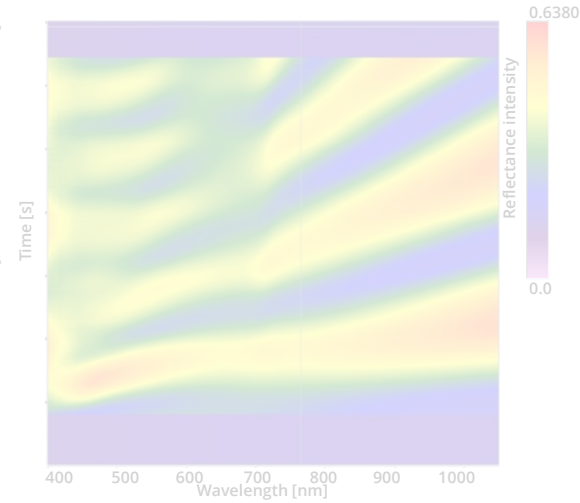
Spin-Coating



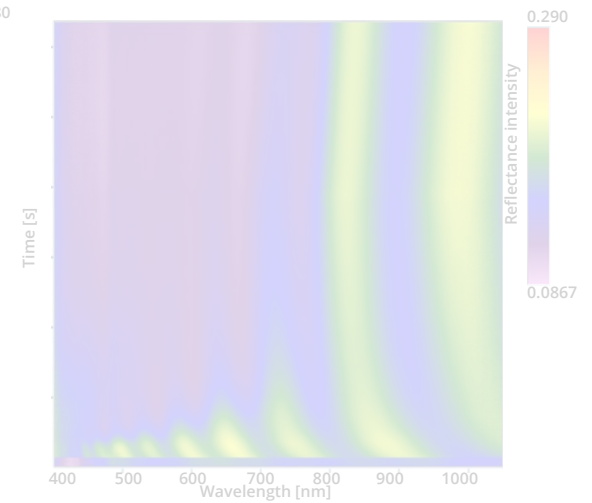
Annealing



Thermal evaporation



Slot-die coating



- › Early fringes → wet film thickness
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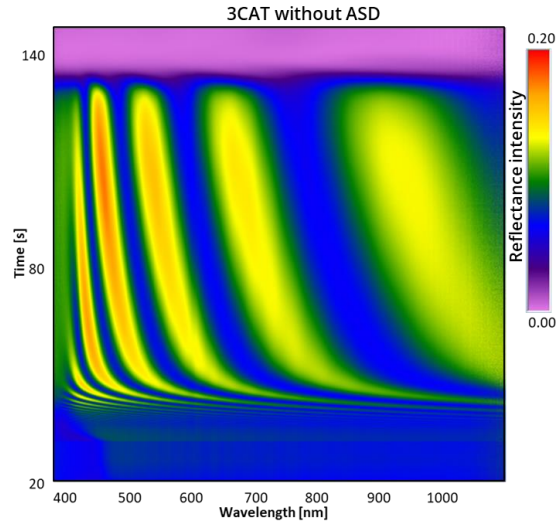
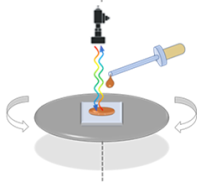
- › Band gap formation
- › Film degradation by phase transitions

- › Fringes → growth rate → thickness
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- › Early fringes → wet film thickness
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- › Fingerprint of reaction kinetics
- › Late fringes → roughness
- › Band gap formation

Anti-Solvent Drip: Spin-Coating for 3CAT

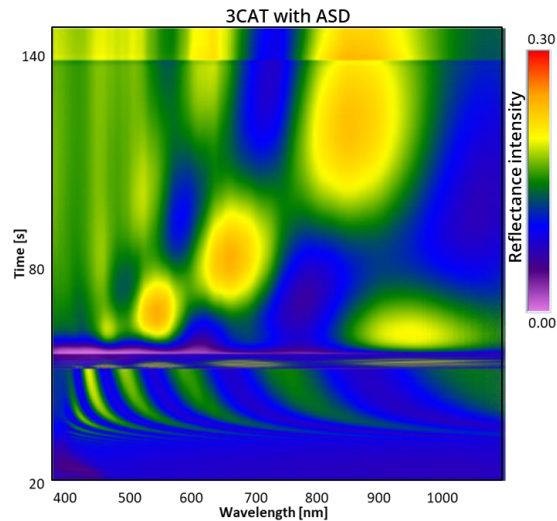
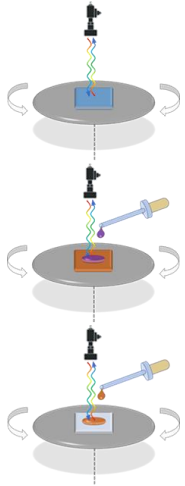
3CAT without ASD



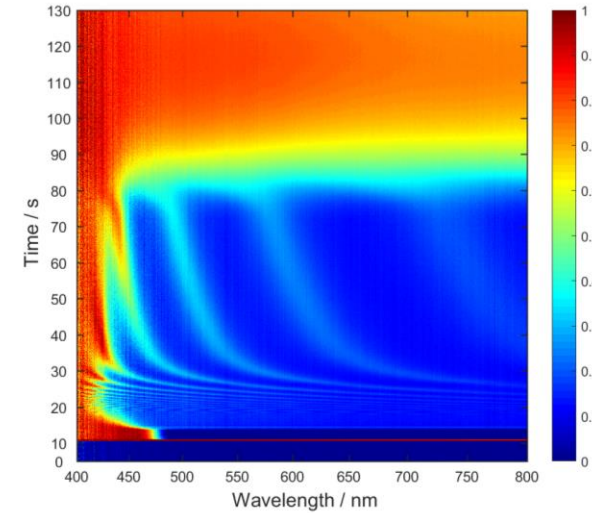
With  LAYTEC



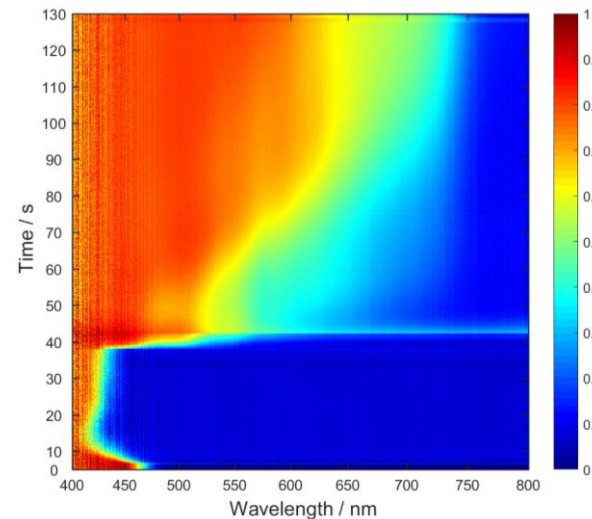
3CAT with ASD



With  LAYTEC



Self-built setup



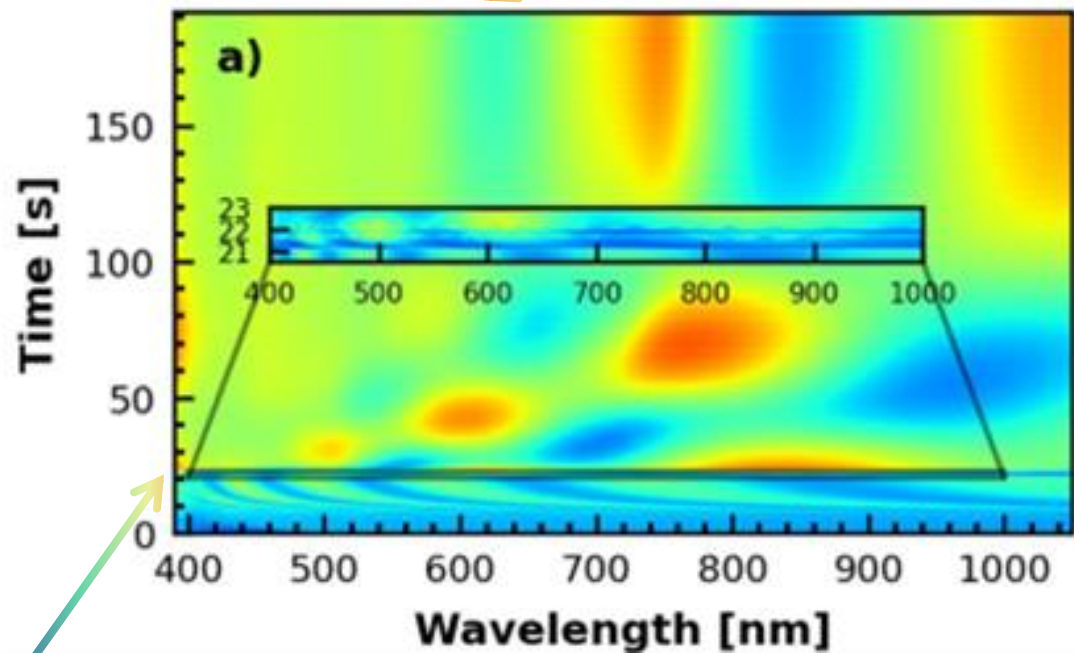
Self-built setup



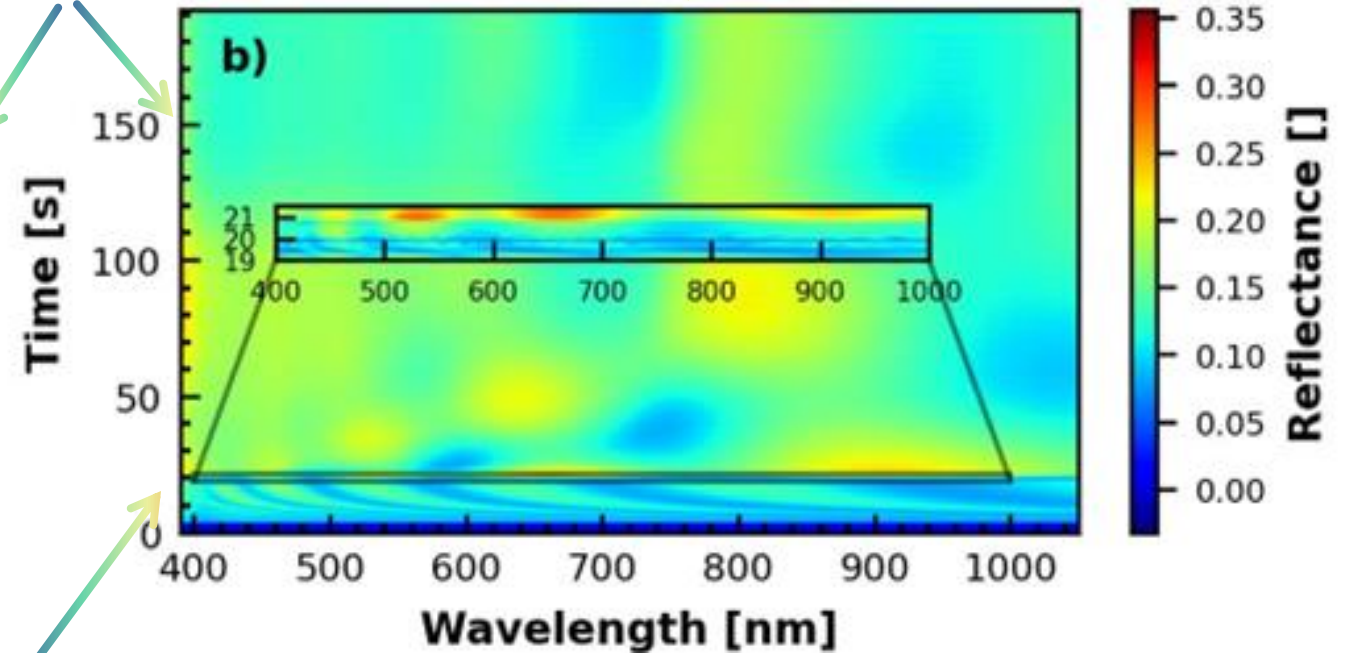
Impact of ASD on 3CAT process

Interference fringes persist →
smooth surface due to ASD

Change in pattern (= film properties)



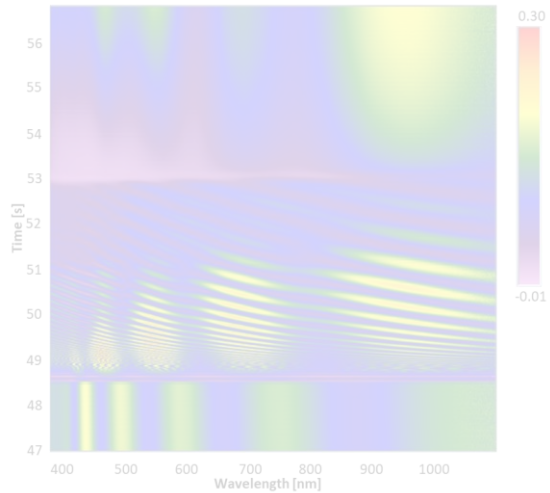
ASD @ $t = 21\text{s}$



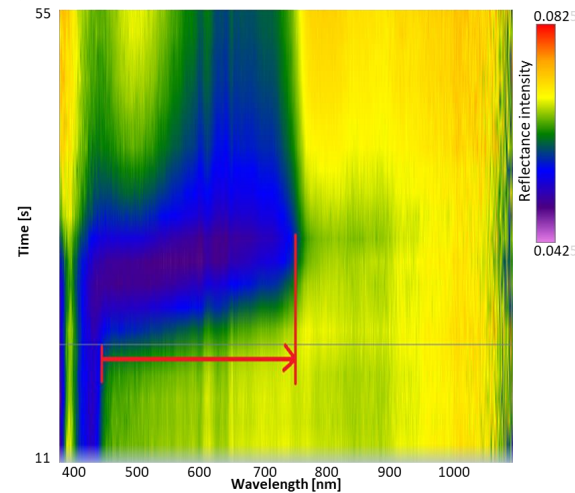
ASD @ $t = 19\text{s}$

In-situ monitoring of perovskite formation

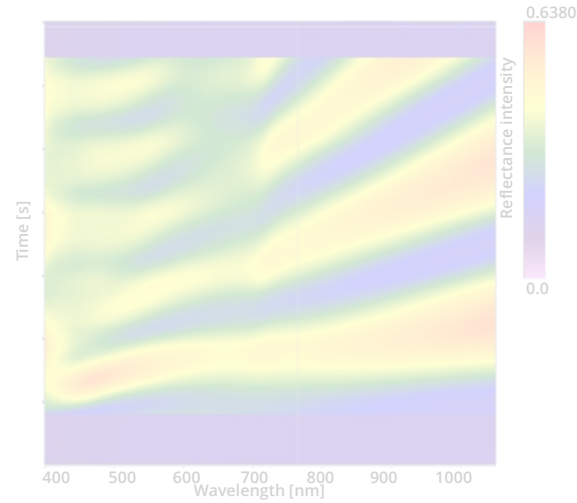
Spin-Coating



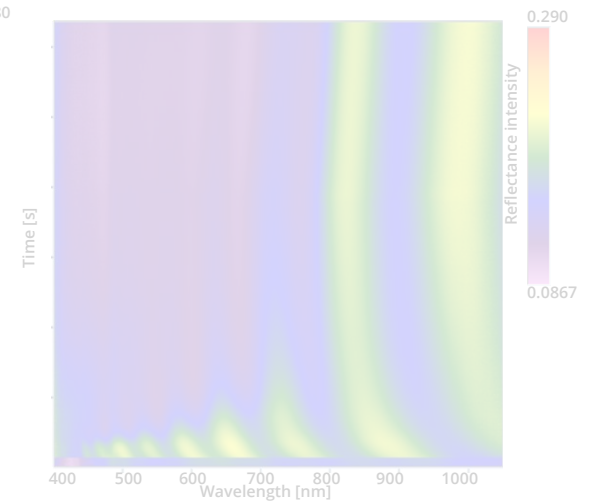
Annealing



Thermal evaporation



Slot-die coating



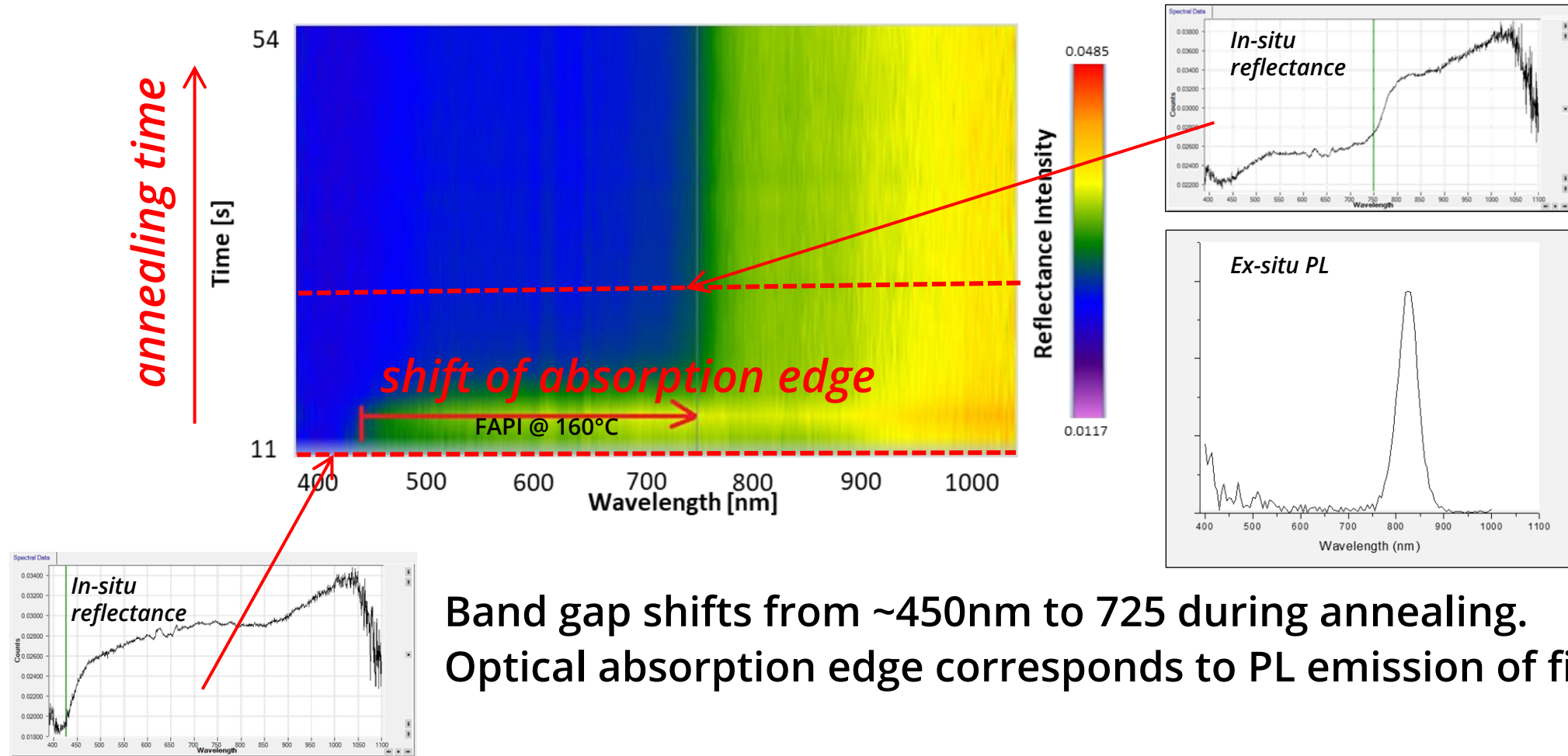
- › Early fringes → wet film thickness
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- › Fingerprint of reaction kinetics
- › Late fringes → roughness
- › Band gap formation

- › **Band gap formation**
- › **Film degradation by phase transitions**

- › Fringes → growth rate → thickness
- › Band gap formation
- › Roughness
- › For const. growth rate → n, k
- › For known n, k → thickness

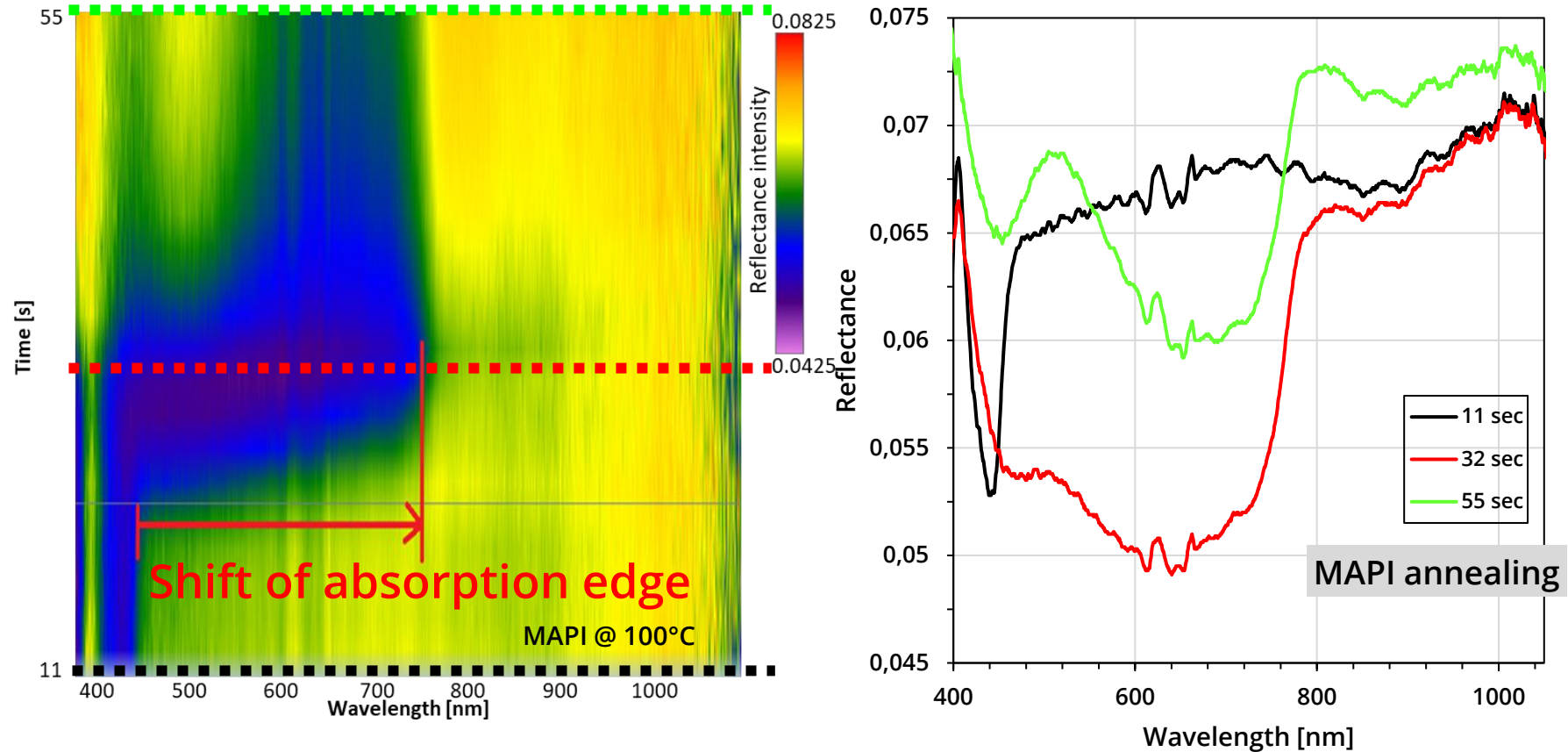
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- › Band gap formation

Annealing: As it is supposed to be...



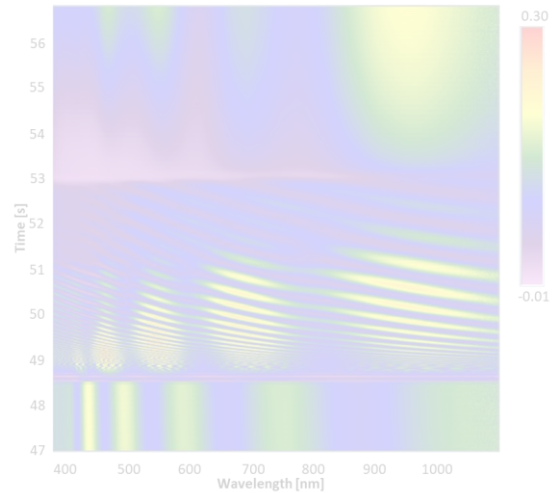
Band gap shifts from ~450nm to 725 during annealing.
Optical absorption edge corresponds to PL emission of final film.

Annealing: As it is NOT supposed to be...

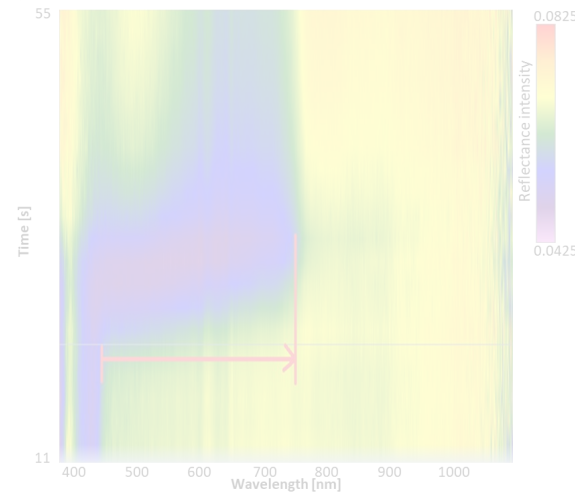


In-situ monitoring of perovskite formation

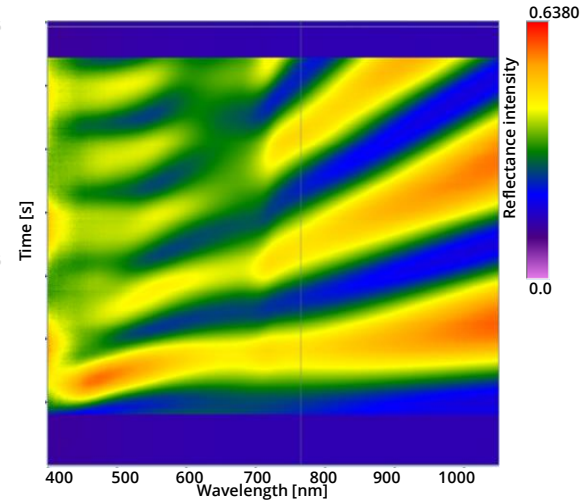
Spin-Coating



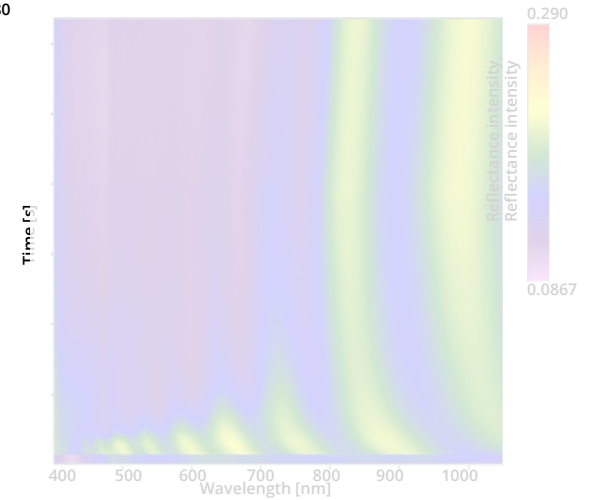
Annealing



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Slot-die coating



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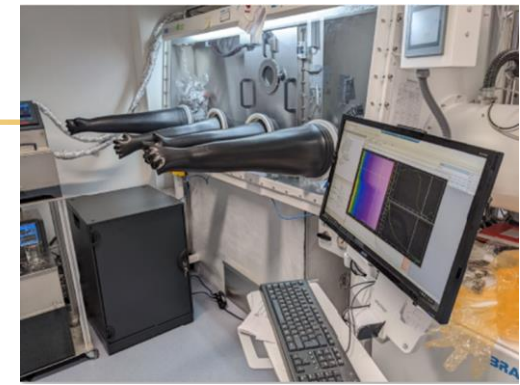
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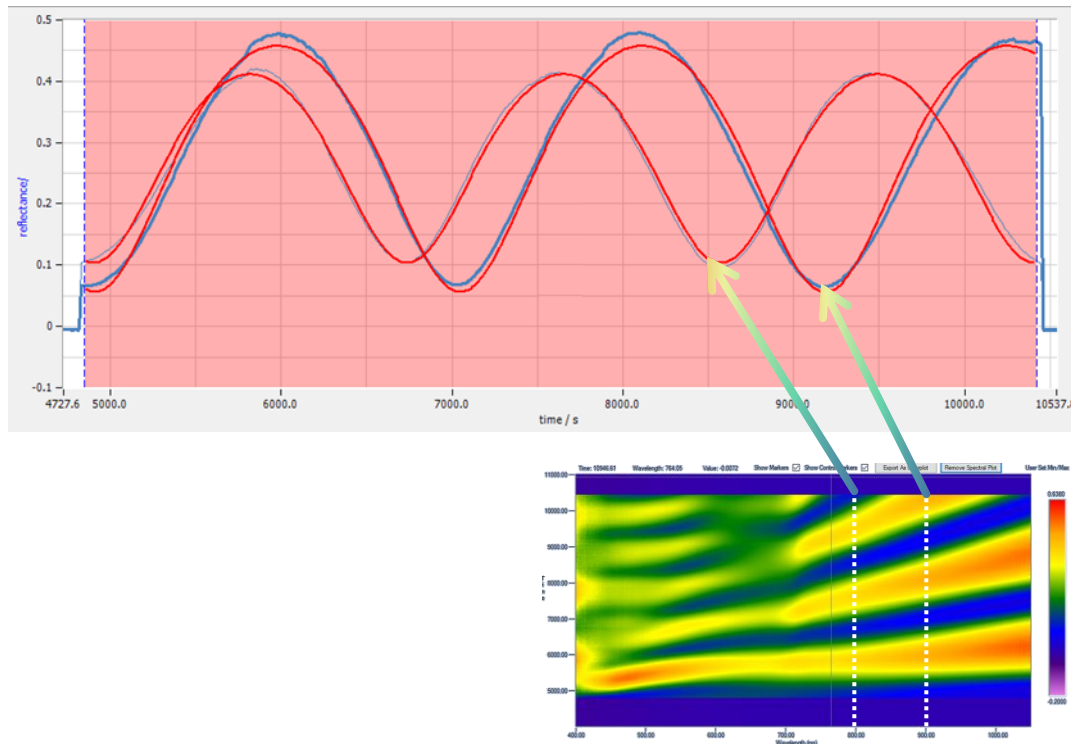
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In-situ monitoring of perovskite formation...

... Quantitative growth analysis...



➤ ...by transient analysis ...

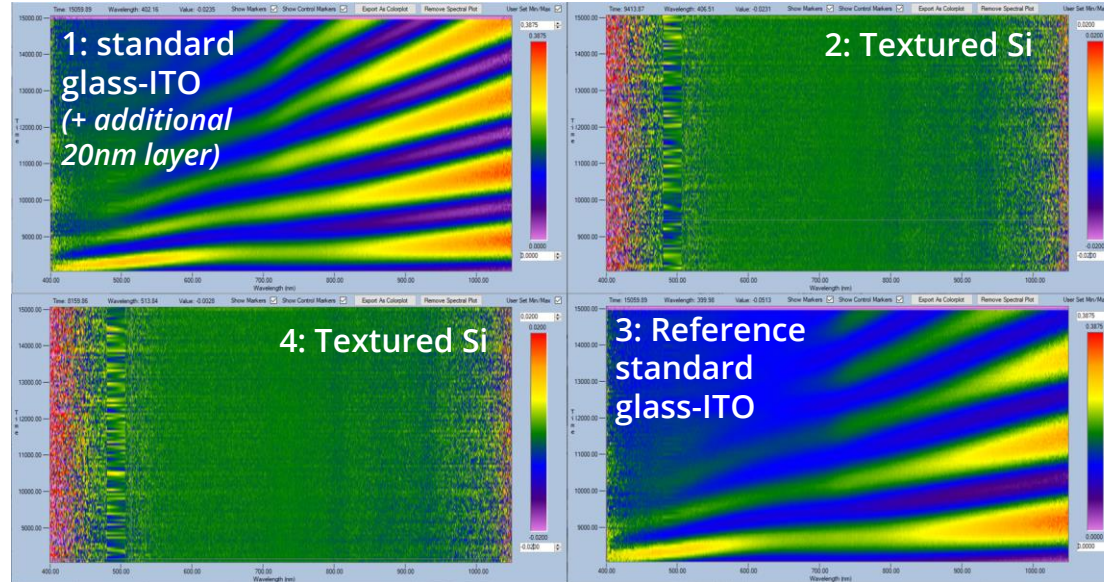
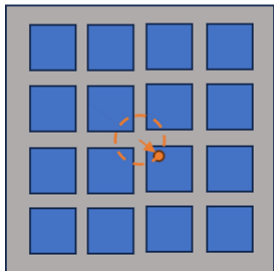
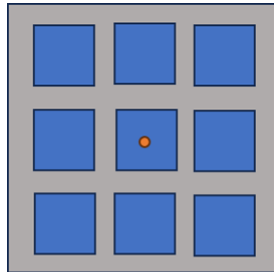


➤ ... for real-time results...

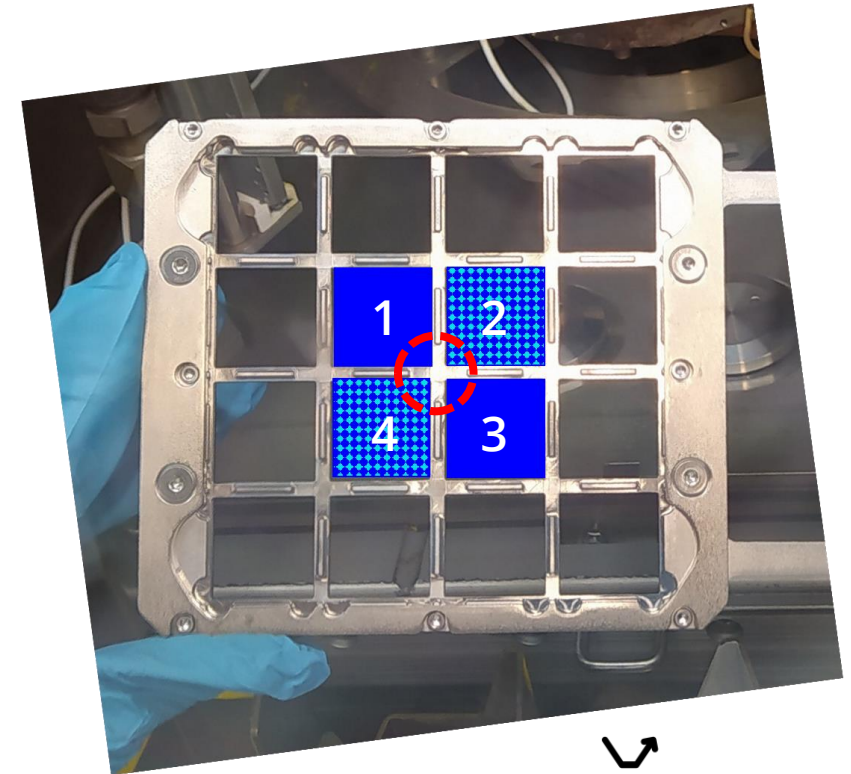


In-situ monitoring of perovskite formation...

... multi-sample analysis...

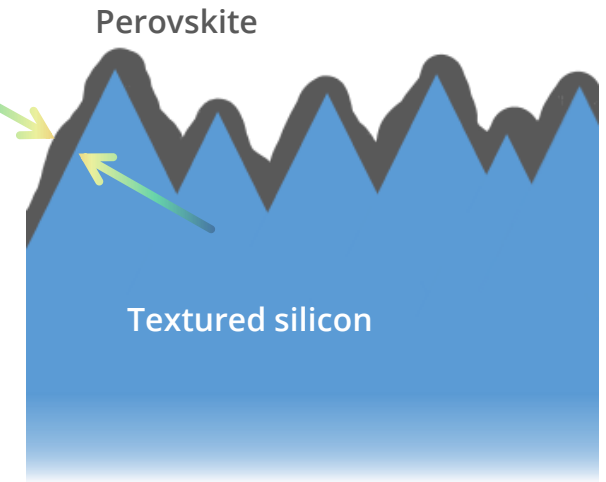
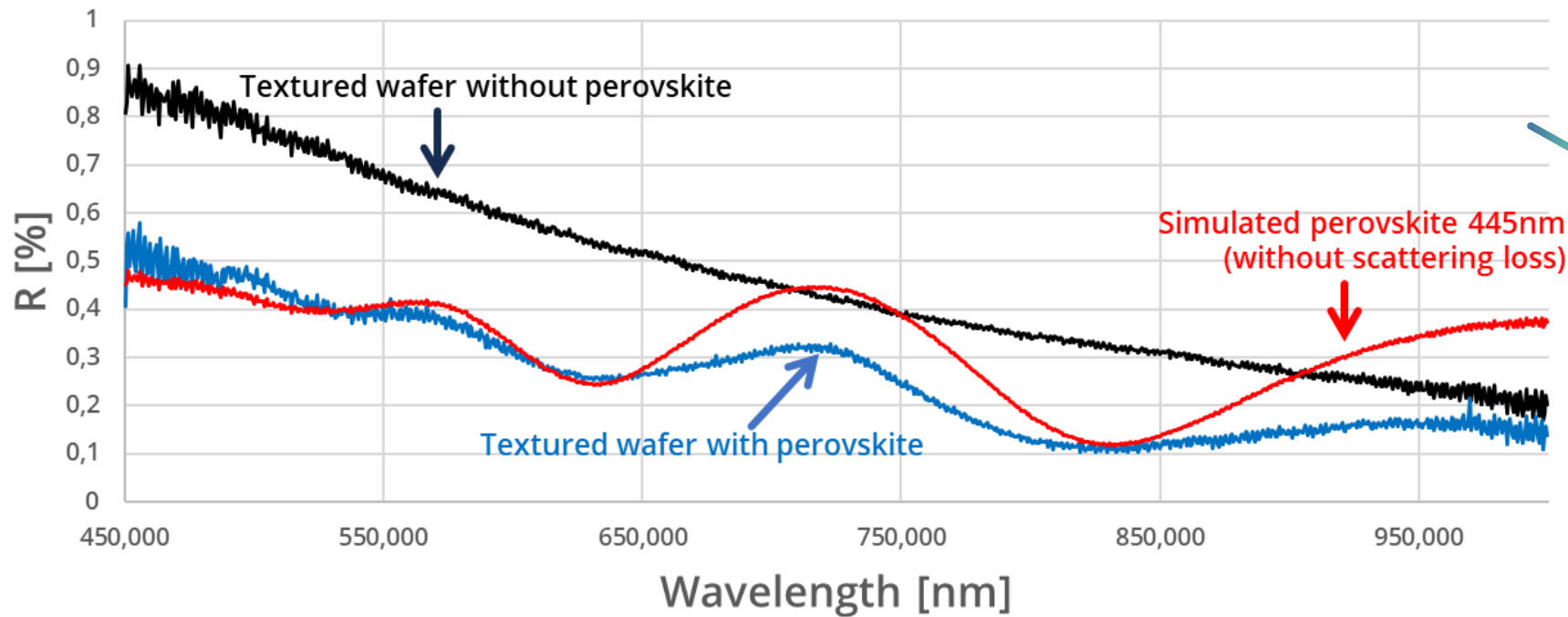


- Each sample is analyzed separately
- Comparative studies possible
- Indirect monitoring of textures samples by planar control samples
 - Almost $R = 0$ on textured samples
 - Full signal and “same” process on planar ones



Outlook: First results with texture-optimized reflectance

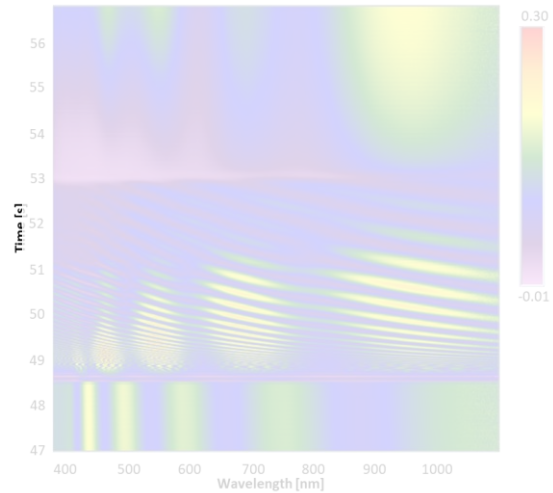
FaCsPb(IBr)₃ on textured silicon (+TCO)



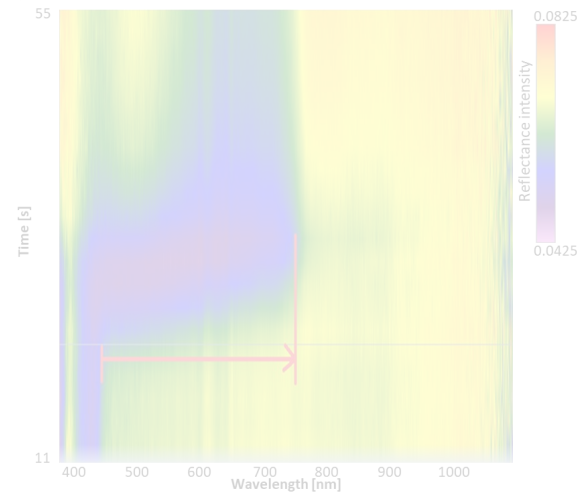
- With texture optimized reflectance, perovskite thickness can be calculated → agrees with SEM thickness
- n, k was deduced from in-situ reflectance data
- Currently being implemented for in-line application

In-situ monitoring of perovskite formation

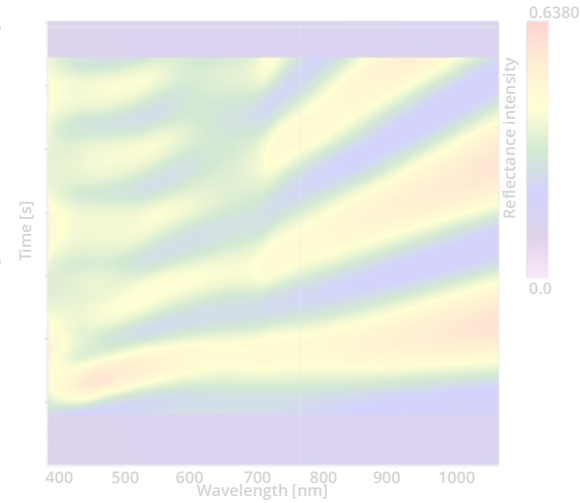
Spin-Coating



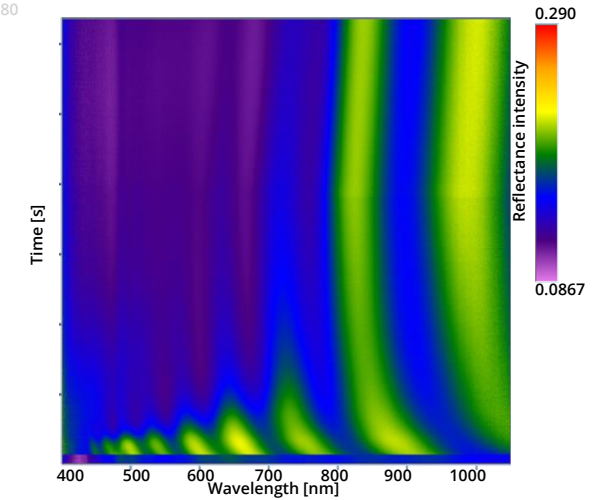
Annealing



Thermal evaporation



Slot-die coating



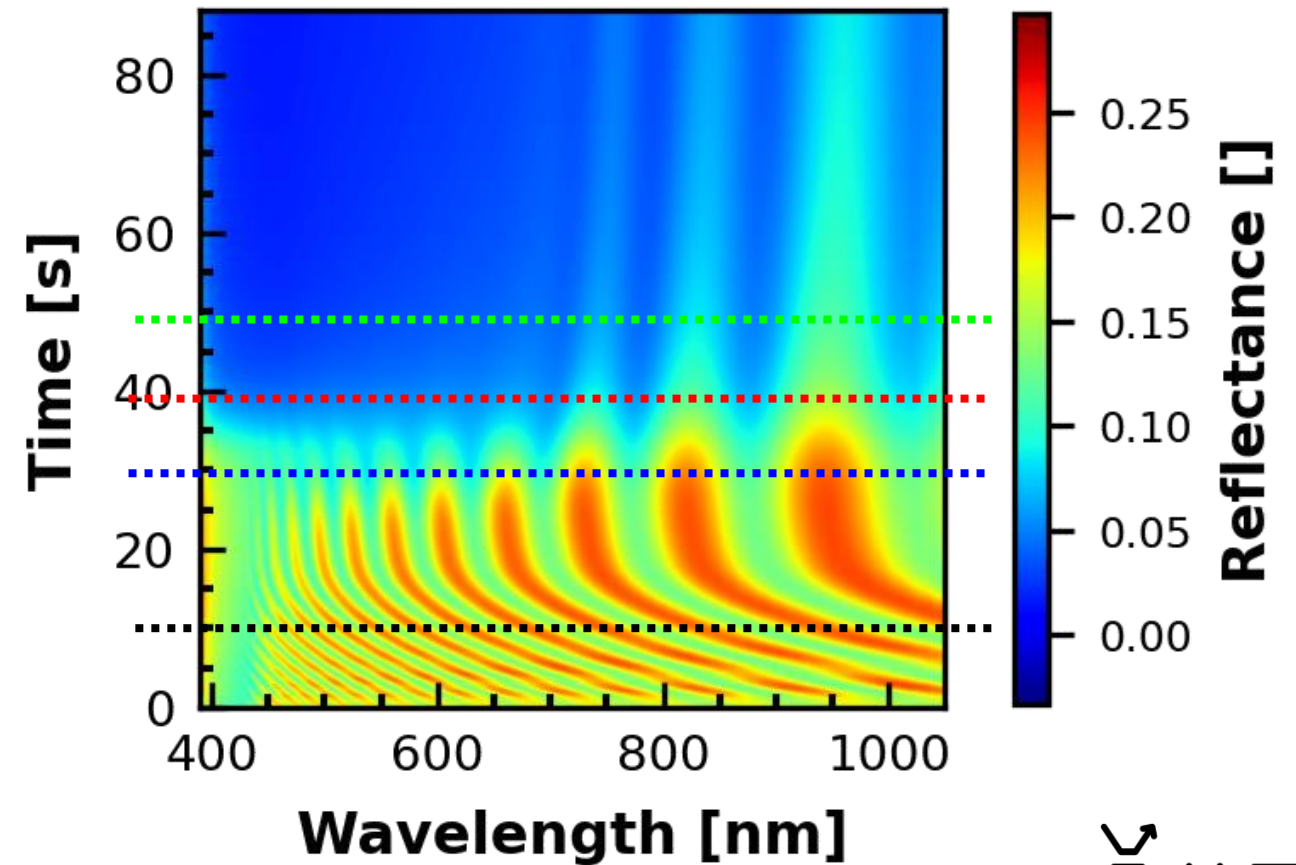
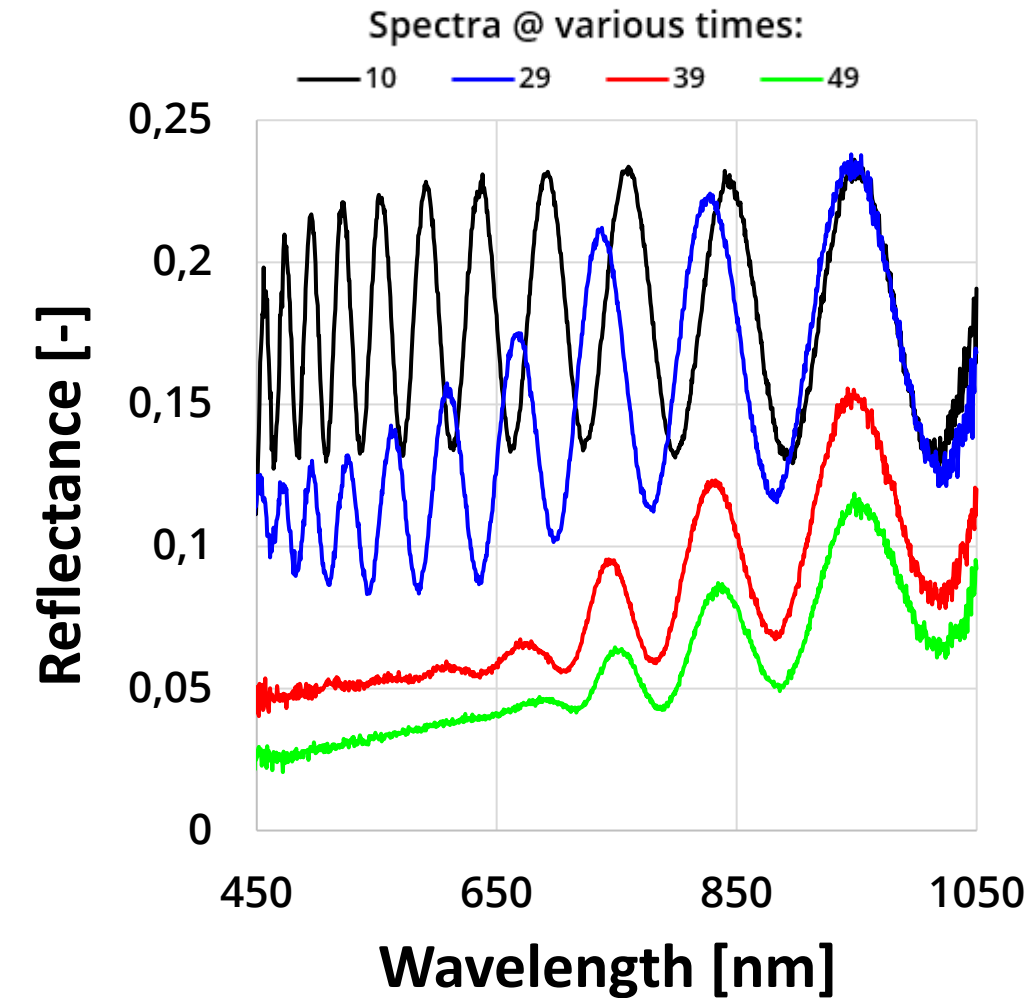
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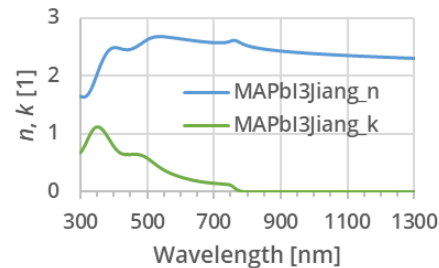
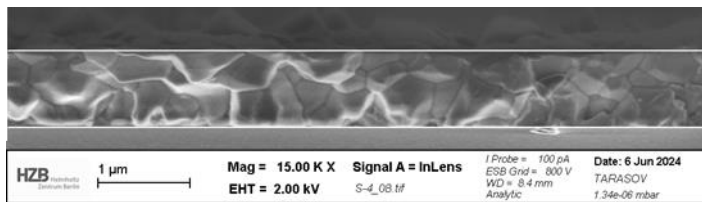
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Analysis of an SDC run (MAPI)

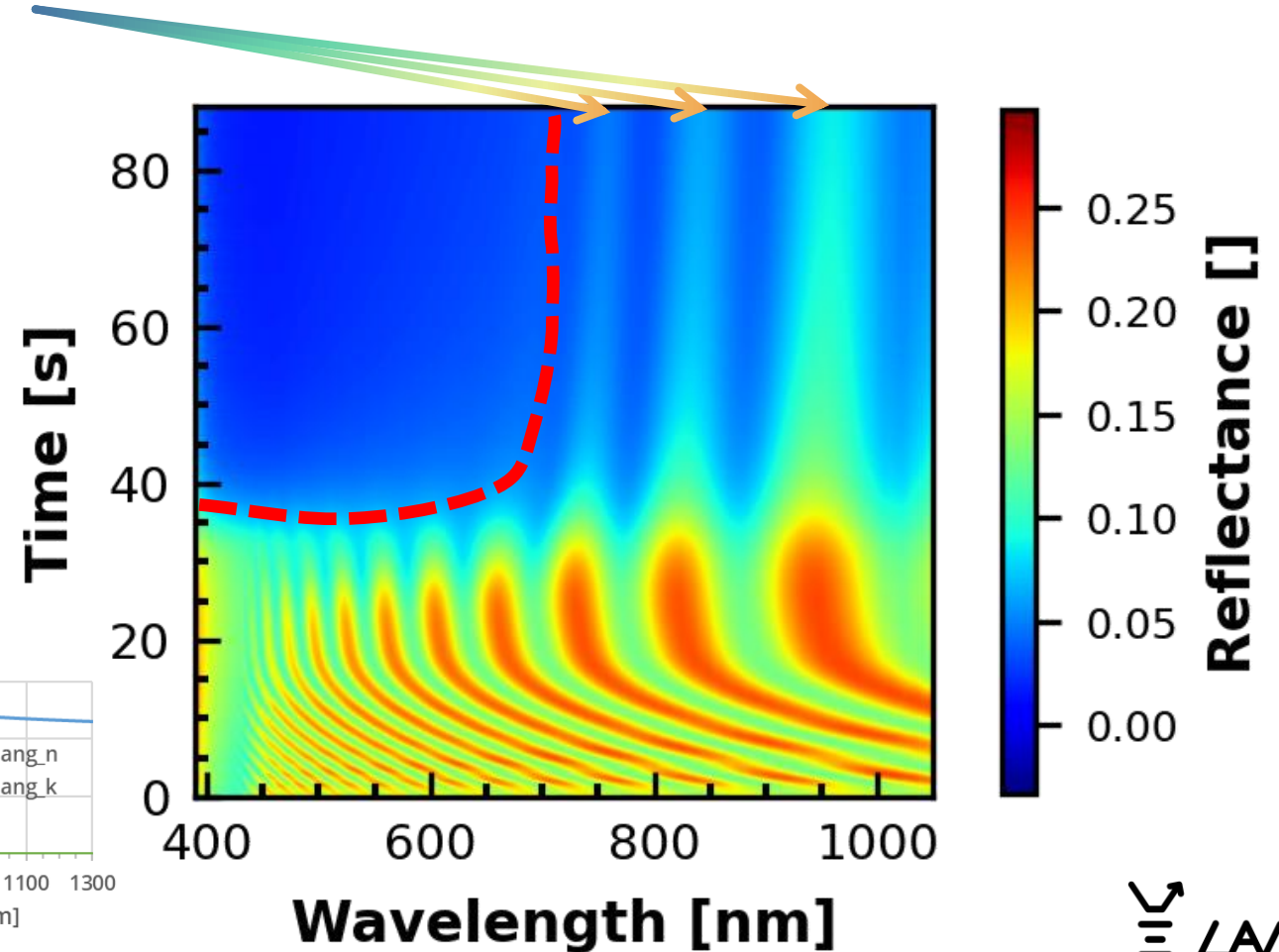


Analysis of an SDC run (MAPI)

- Intensity decreasing due to roughening
- MAPI bandgap evolves
- Stationary long-wavelength fringes indicate const. thickness
- By applying solid state n, k final thickness can be calculated in good agreement with SEM
 - $d \approx 890$ nm

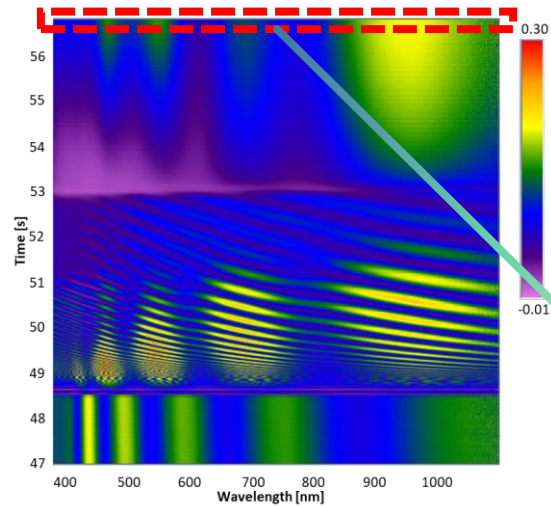


Stationary long-wavelength fringes

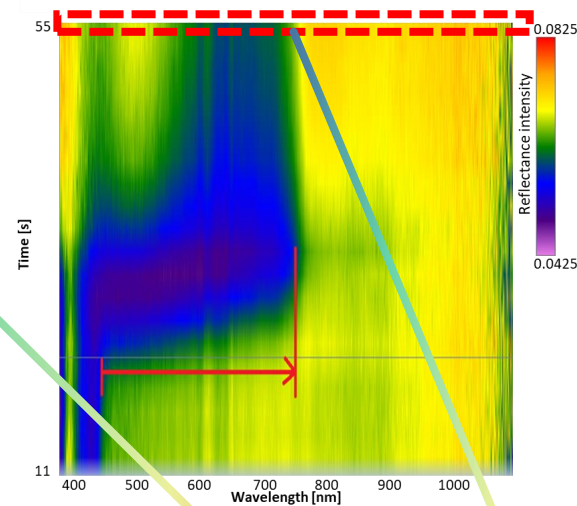


In-situ monitoring of perovskite formation

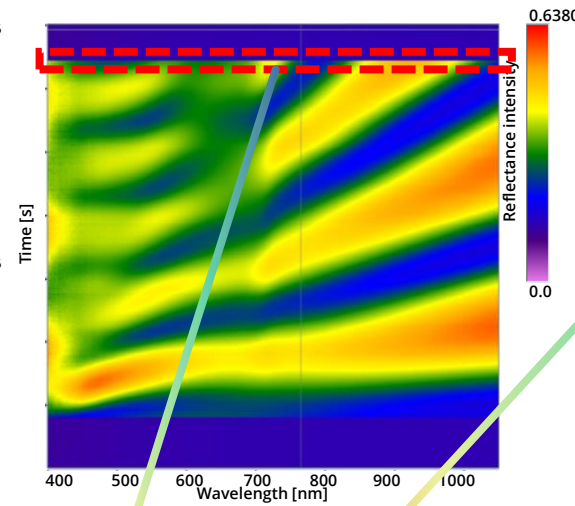
Spin-Coating



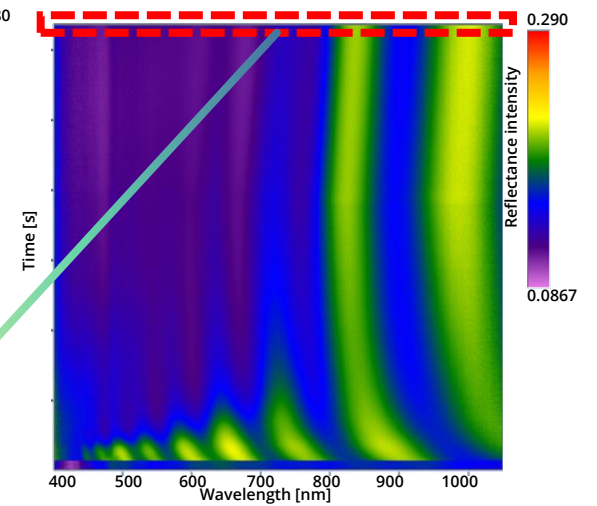
Annealing



Thermal evaporation



Slot-die coating



- › In all cases, "last" in-situ spectrum corresponds to the spectrum obtained in-line**
- › Early fringes → wet film thickness
 - › Late fringes → roughness
 - › Fingerprint of reaction kinetics
 - › Band gap formation
 - › Fringes → growth rate → thickness
 - › For const. growth rate → n, k
 - › For known n, k → thickness
 - › Early fringes → wet film thickness
 - › Late fringes → roughness
 - › Fingerprint of reaction kinetics
 - › Band gap formation

Outline

Company introduction

Metrology methods & monitoring parameters

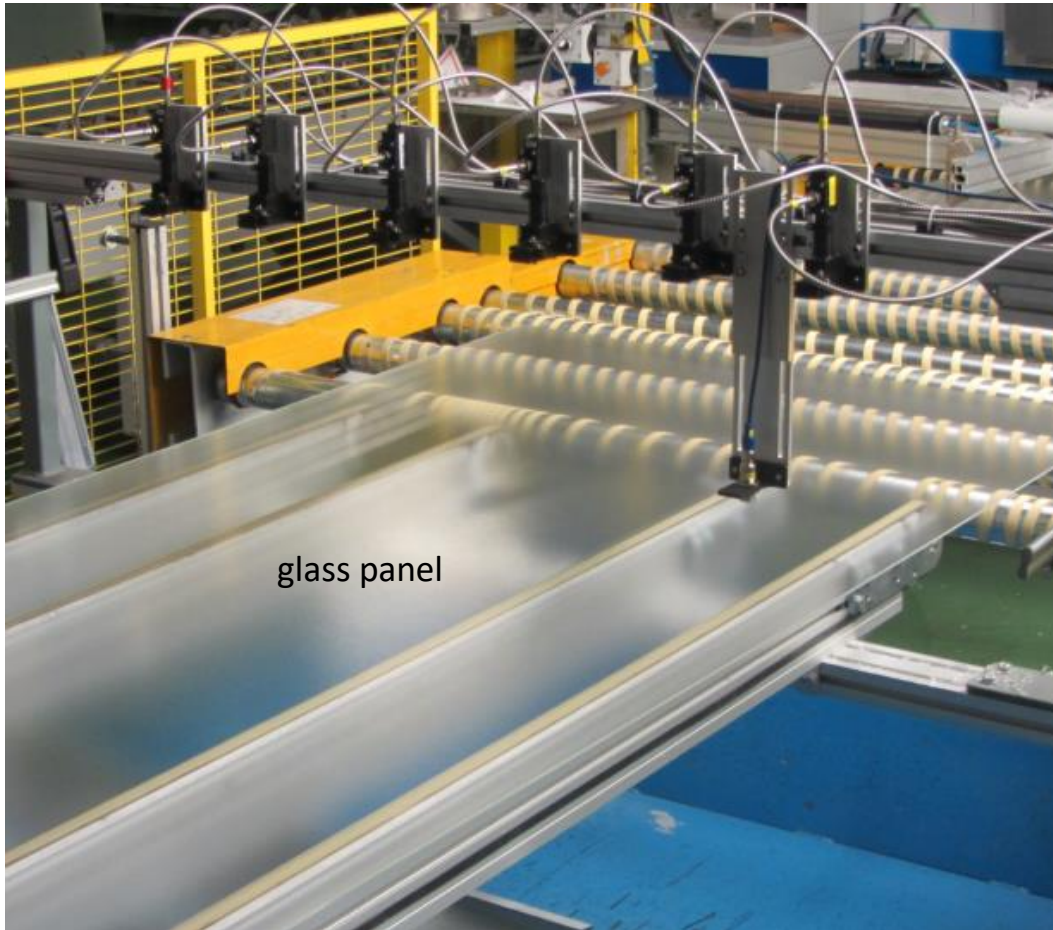
In-situ monitoring of perovskite formation

In-line monitoring of perovskite formation

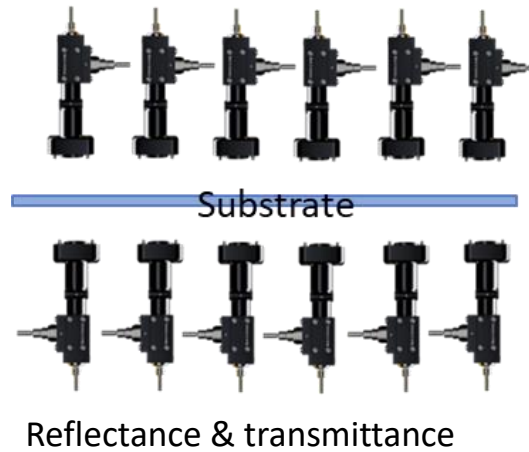
Metrology capabilities for entire perovskite stack

Summary & outlook

Typical in-line setups for in-line TCO monitoring

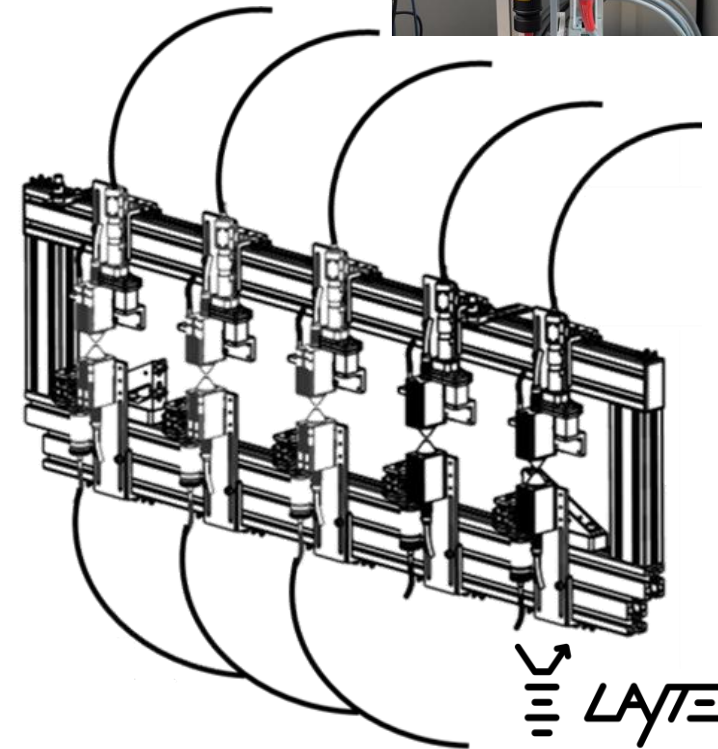
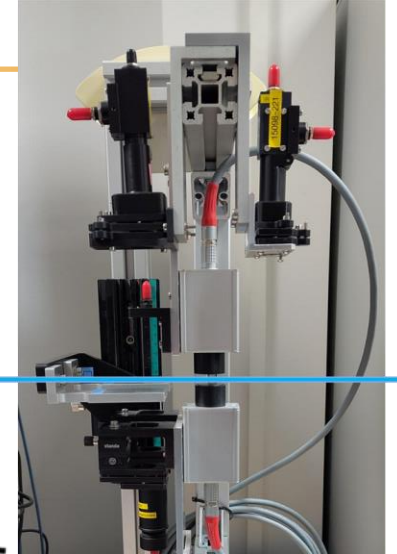


Reflectance setup for
TCO-coated glass

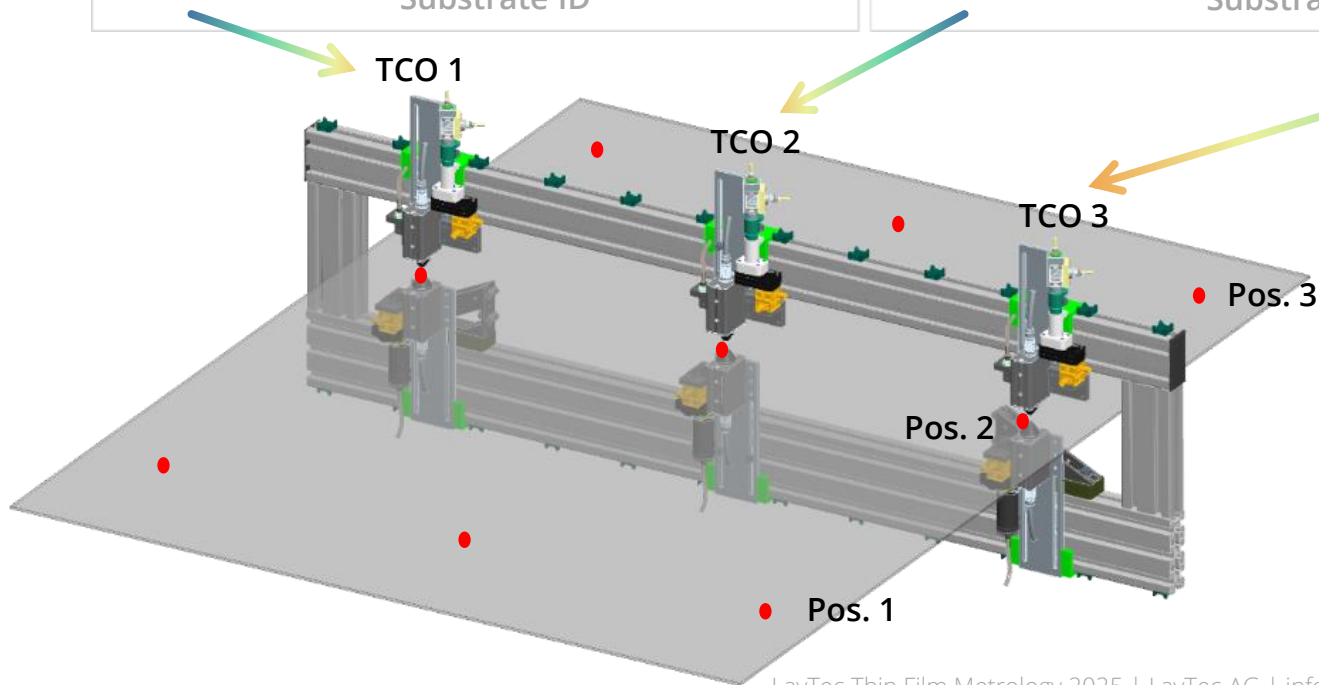
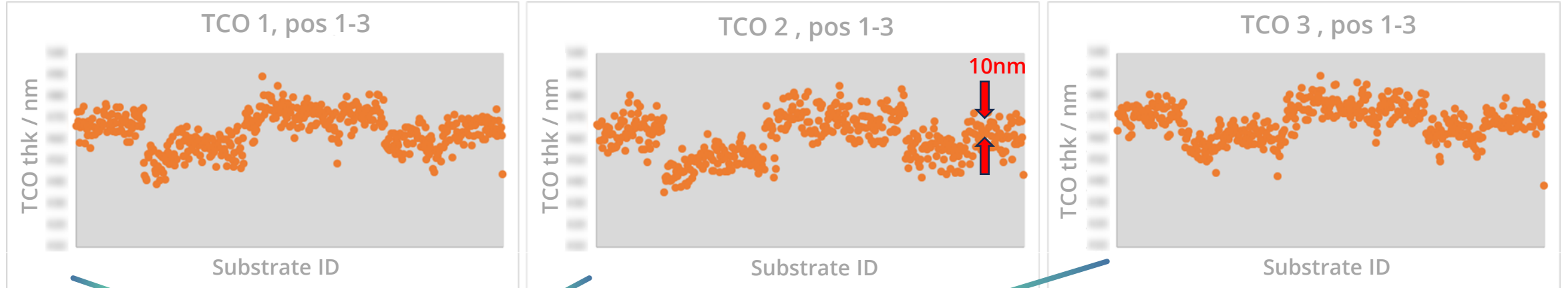


Reflectance &
transmittance &
sheet resistance

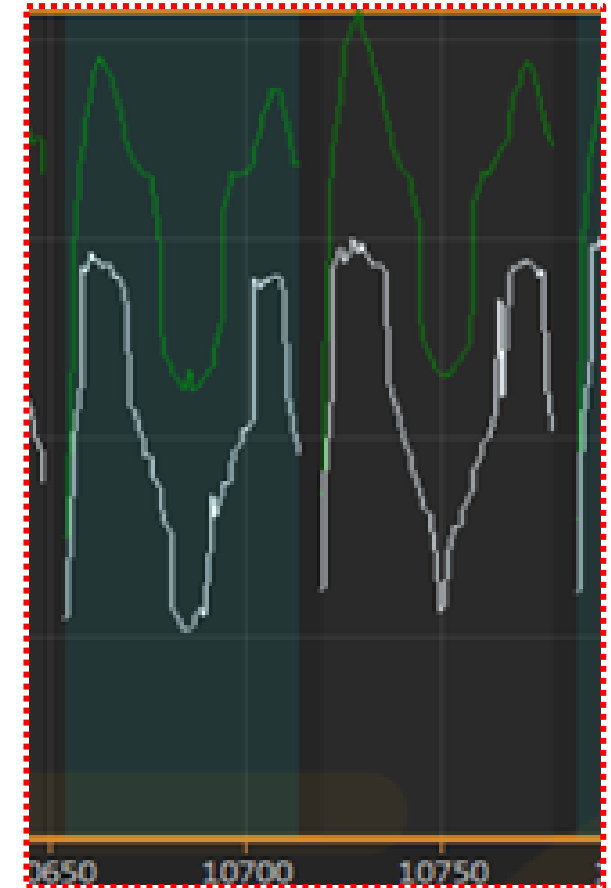
glass panel



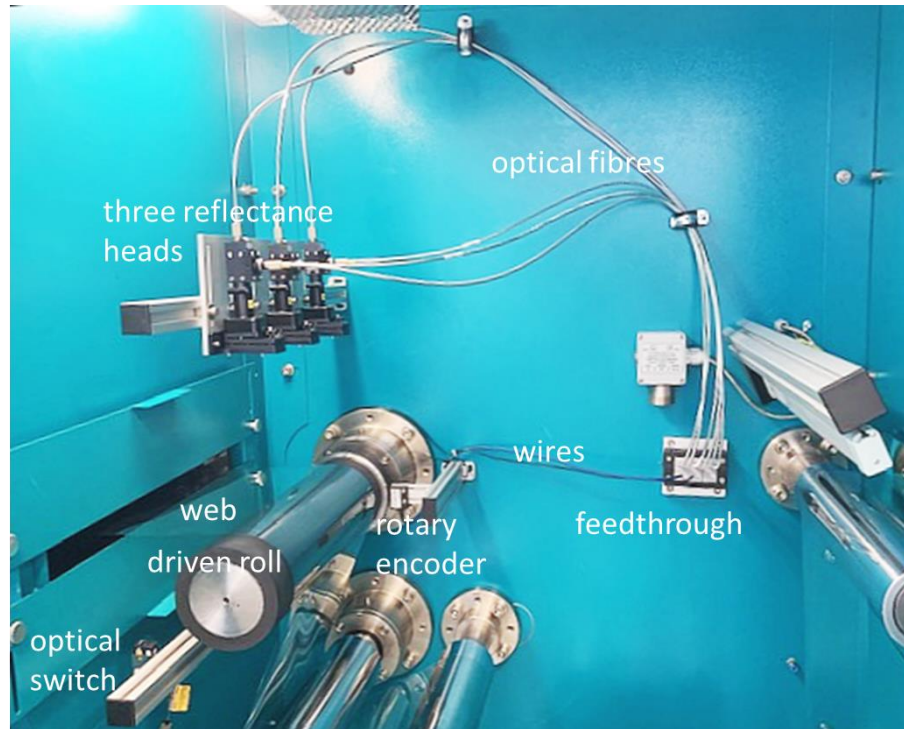
In-line monitoring of TCO / glass substrates from production



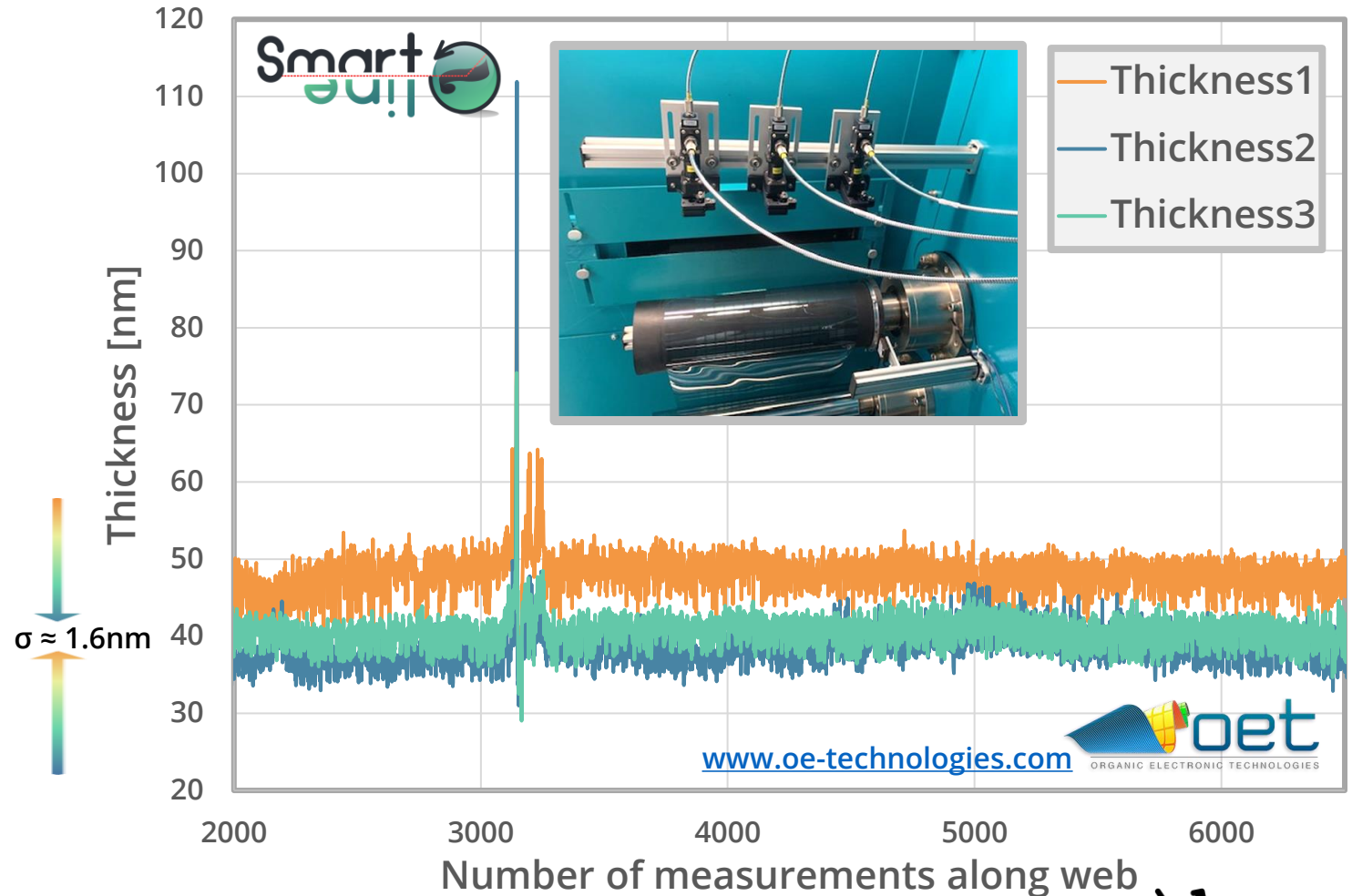
Sheet-2-sheet quality control: Exemplary production data (CIGS)



Roll-2-roll (R2R) quality control

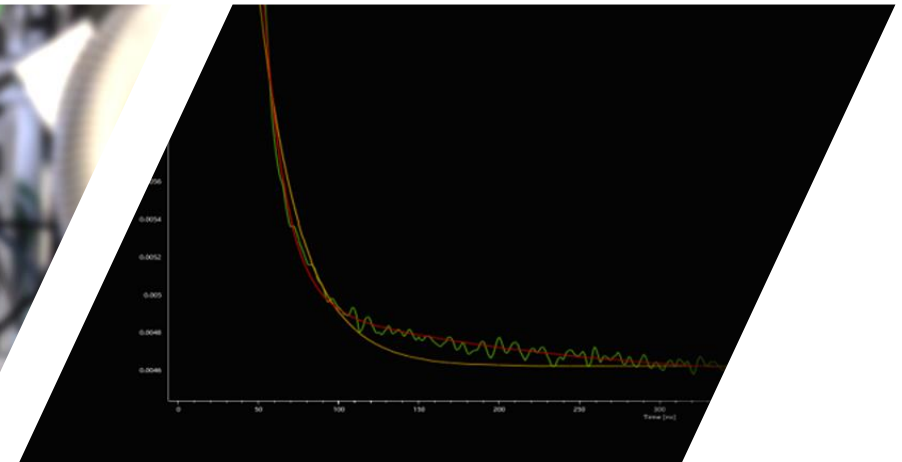
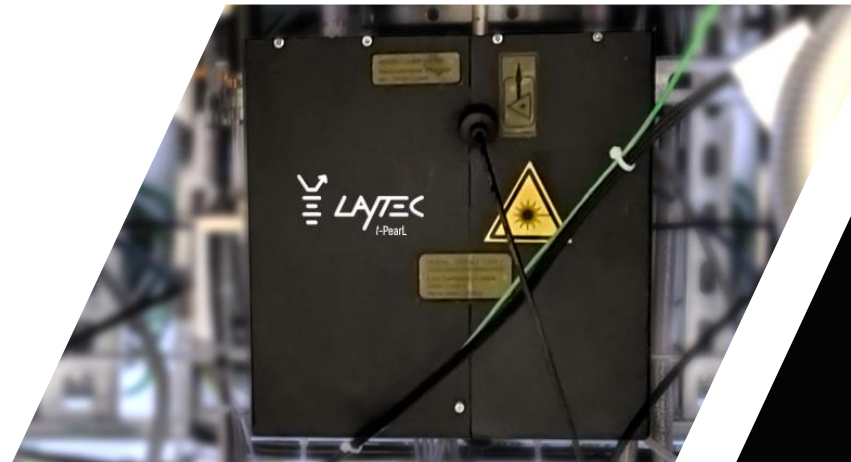
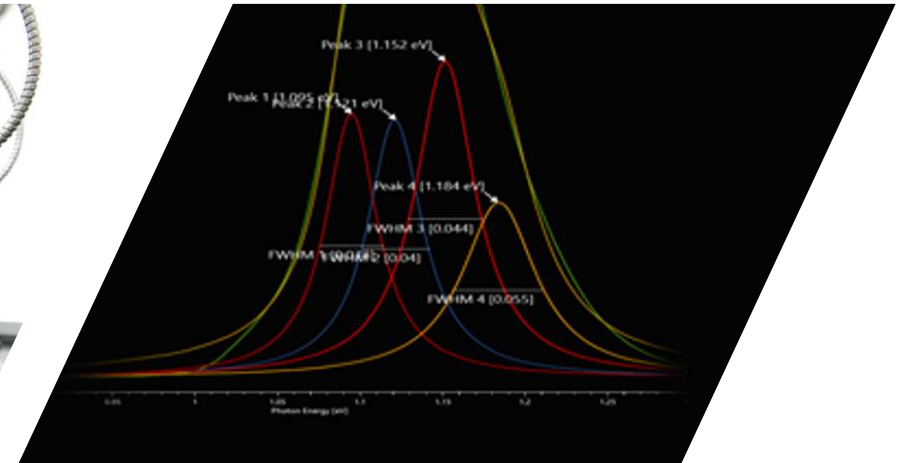
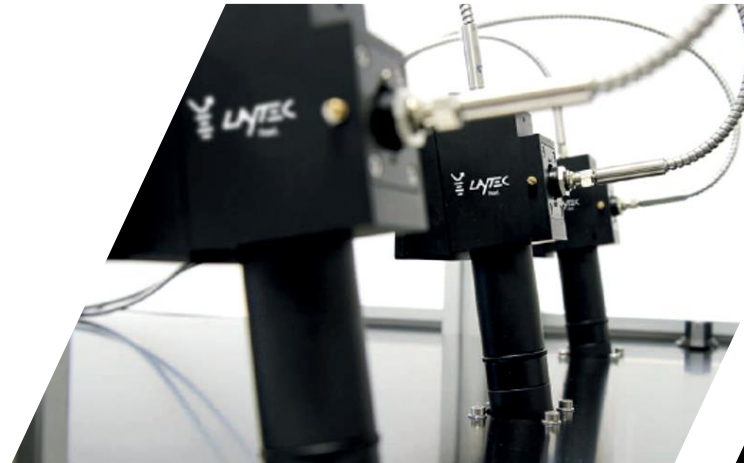


- In-line monitoring of deposition of electron-transport layer on PET / IMI (ITO-metal-ITO)



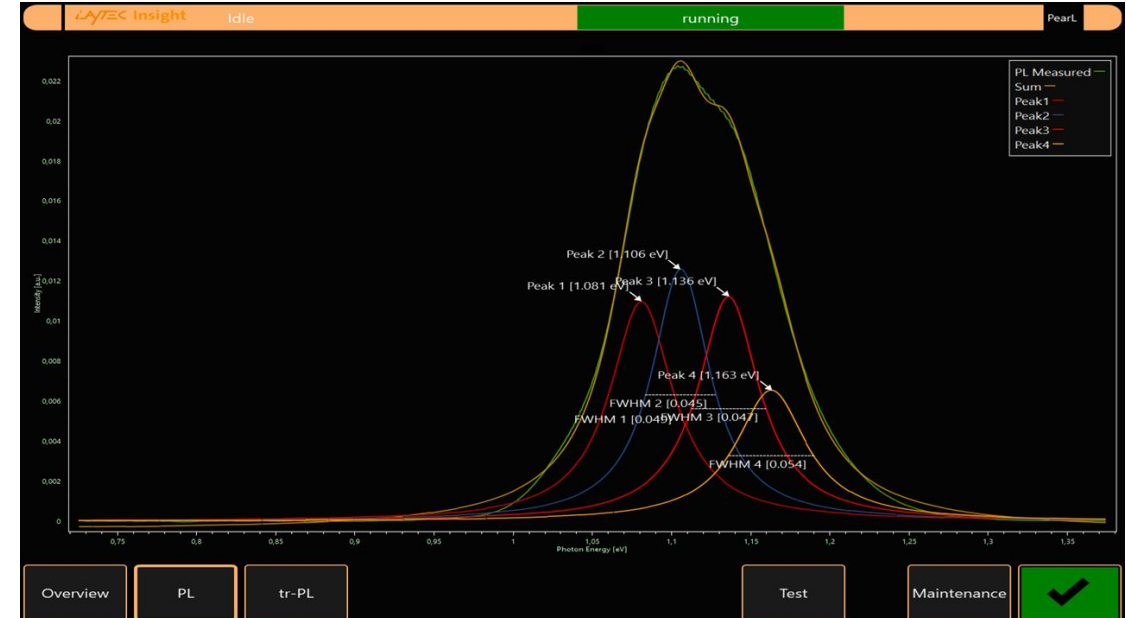
Photoluminescence systems

- › Metrology method portfolio for photoluminescence:
- › Spectral PL
 - › Peak deconvolution
 - › Composition
- › Time-resolved PL
 - › Charge carrier lifetime ($> 20\text{ns}$)
- › Can be combined
- › Laser class $> 3\text{b}$
- › Wide variety of excitation sources



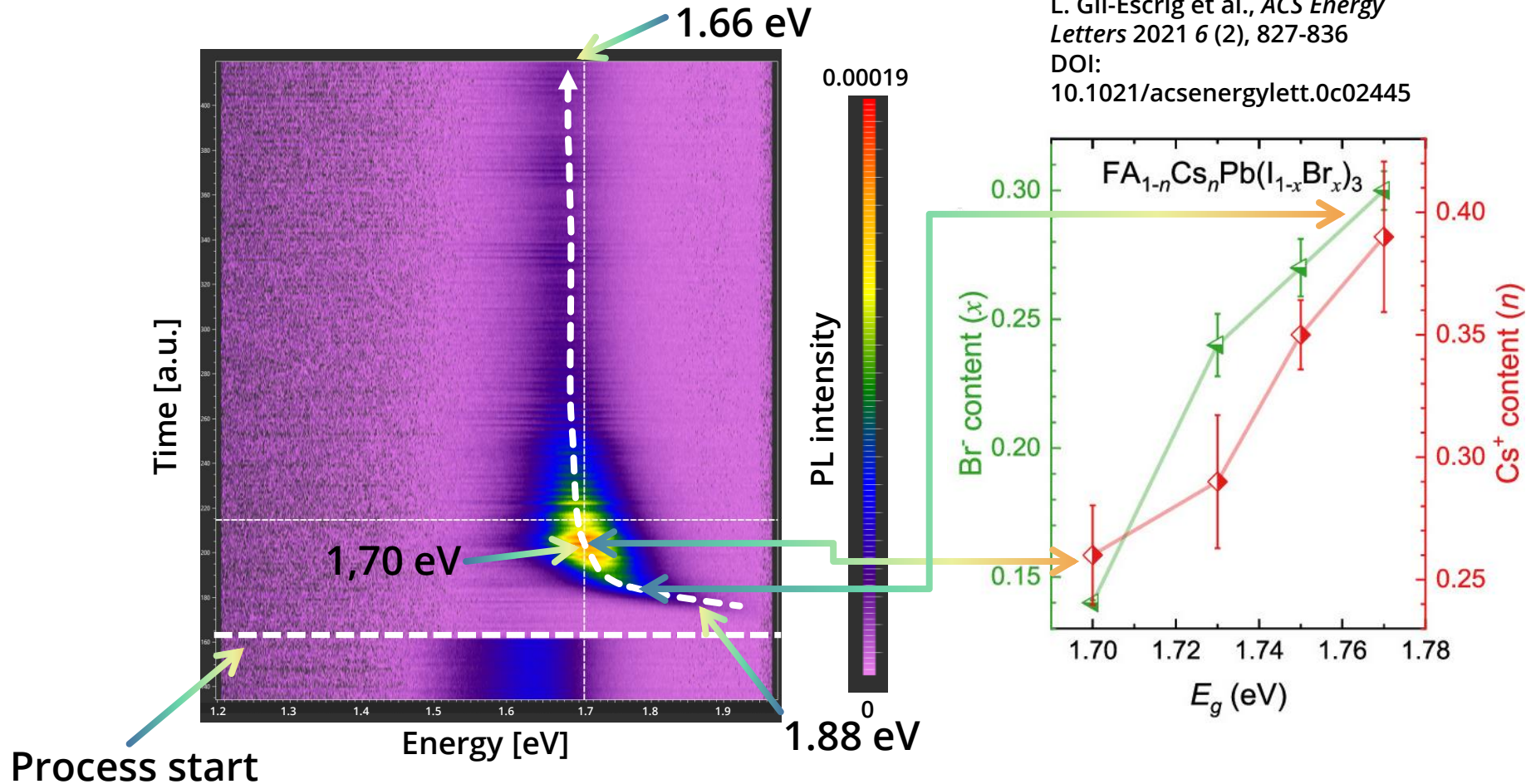
PearL – spectral PL

- Wide range of UV, VIS, NIR wavelengths
- Spectral range for detection:
 - 450nm...1050nm / 1700nm
 - 900nm... 1700nm / 2500nm
- Peak fit with up to 4 peaks
- Usually class 3b - 4 laser is needed for large working distances (vacuum)
- For short working distances, laser-free LED-based system available (slot-die coating etc.)



LAYTEC Insight		Idle		running		Overview	
Photoluminescence							
	Peak 1	Peak 2	Peak 3	Peak 4	TotalPeak		
Peak Pos. [eV]	1.081	1.106	1.136	1.163	1.106		
Intensity [a.u.]	0.012	0.014	0.013	0.007			
FWHM [eV]	0.048	0.044	0.047	0.054			
GGI					21.056		

In-situ monitoring of perovskite formation during $\text{FaCsPb}(\text{IBr})_3$ PVD: Compositional shifts



Supported by:



Partially funded by the Federal Ministry for Economic Affairs and Climate Action (BMWK) under the contract of SHAPE with the reference number of 03EE1123

on the basis of a decision by the German Bundestag

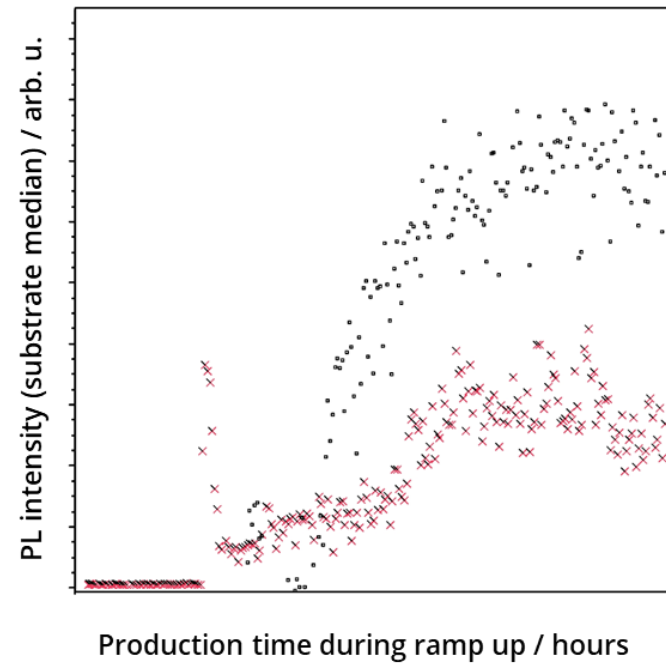
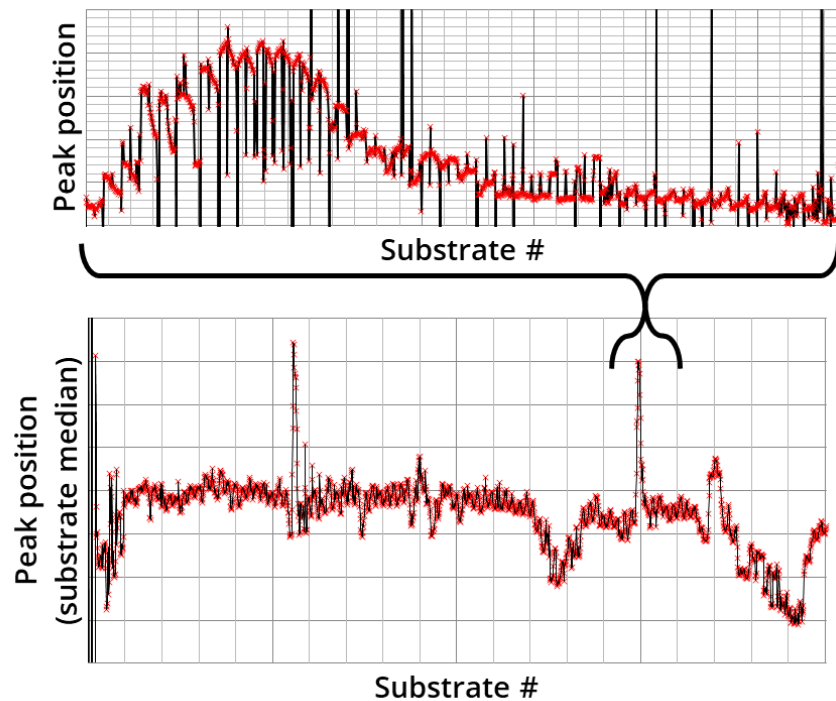
t -PearL – time-resolved PL

- Wide range of UV, VIS, NIR wavelengths
- Mono- and biexponential fit
- Lifetimes $\gg 5\text{ns}$
- Usually class 3b - 4 laser is needed



PearL – spectral PL: Exemplary production data (CIGS)

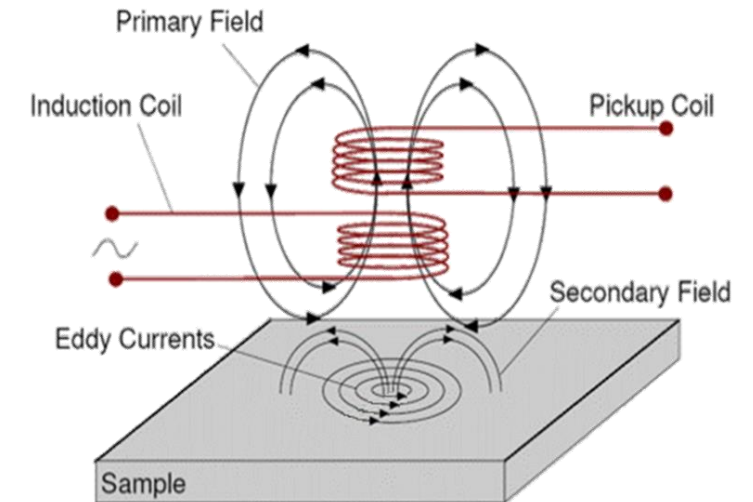
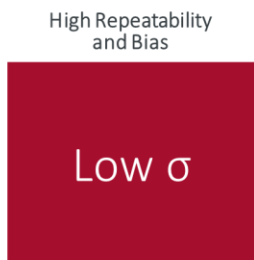
- PearL system installed in a CIGS PVD production line



Sheet Resistance Measurement by Eddy Current Inspection

Technology

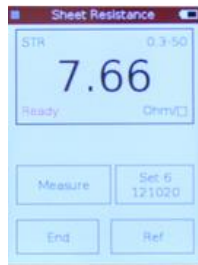
- ▶ Relies on non-contact current induction and electromagnetic field measurement
- ▶ High sample rate, high sensitivity, non-contact, dedicated to conductive materials



- + High sample rate
- + High sensitivity
- + Non-contact solutions
- Limited to conductive materials

Non-contact Eddy Current Testing for Glass Technology

Portable Testing



Single-Point Measurement



Mapping Solutions



Inline / Tool Integrated



- ▶ Real time high-speed measurement – up to 1,000 measurements/sec
- ▶ Scalable fixed sensor installation
- ▶ Process control in atmosphere or in vacuum environments
- ▶ Long term stability by temperature compensated measurements
- ▶ Integration of 1 – 99 monitoring lanes per system

Non-contact Eddy Current Testing for Glass Technology

Portable Testing

Single-Point Measurement

Mapping Solutions

Inline / Tool Integrated

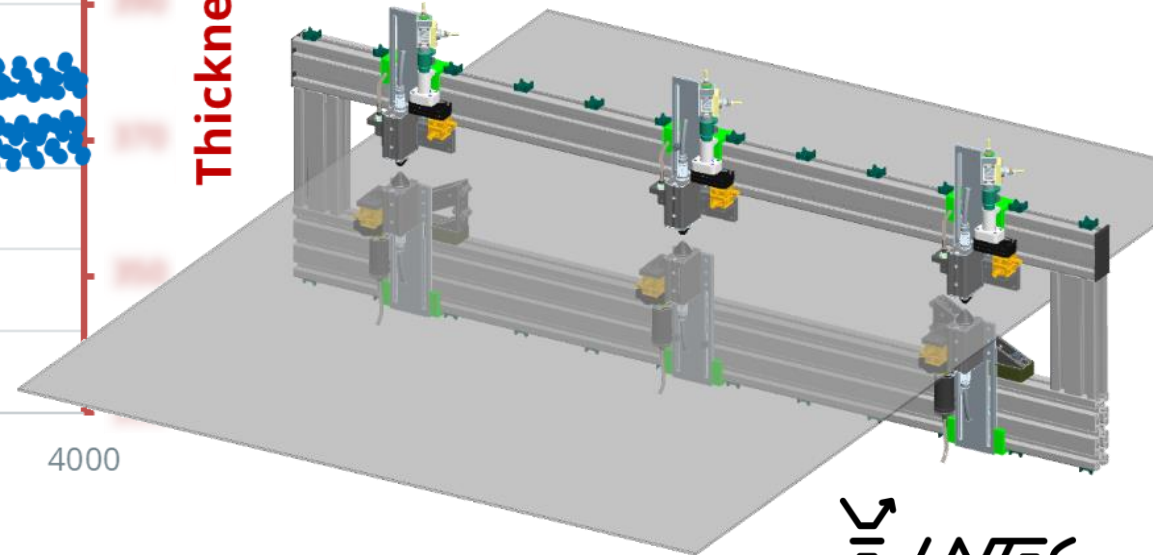
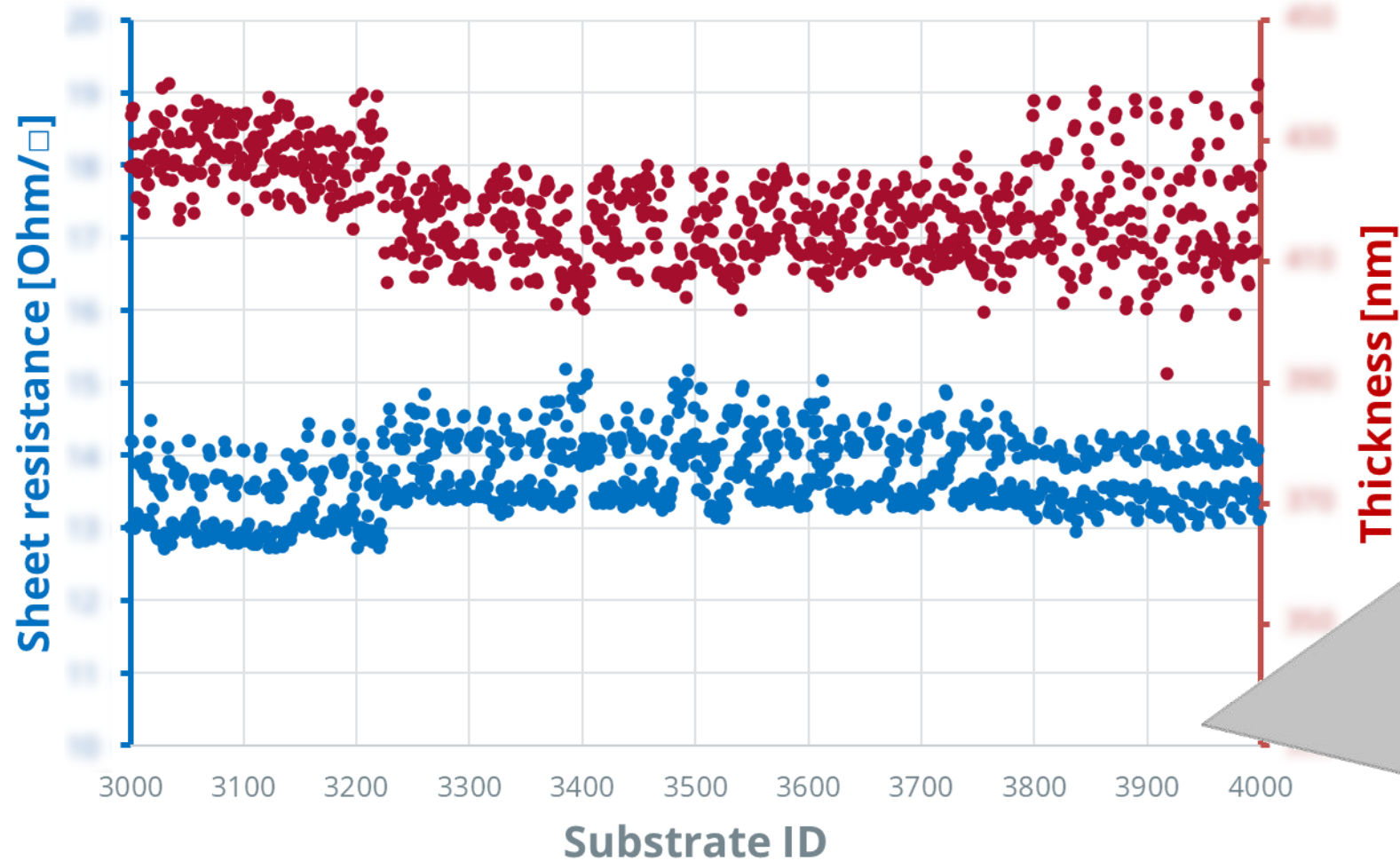
➤ **Suragus' Eddy-current systems can be fully integrated into LayTec's FLAMES metrology systems**



- ▶ Real time high-speed measurement – up to 1,000 measurements/sec
- ▶ Scalable fixed sensor installation
- ▶ Process control in atmosphere or in vacuum environments
- ▶ Long term stability by temperature compensated measurements
- ▶ Integration of 1 – 99 monitoring lanes per system



Combined thickness & sheet resistance monitoring (ITO)



Outline

Company introduction

Metrology methods & monitoring parameters

In-situ monitoring of perovskite formation

In-line monitoring of perovskite formation

Metrology capabilities for entire perovskite stack

Summary & outlook

Metrology capabilities for entire perovskite stack

- Get full insight on your perovskite devices!
 - Anode, Cathode: Thickness, color, transmittance, sheet resistance
 - HTL, ETL: Thickness
 - Perovskite: Thickness, E_{Gap} , roughness

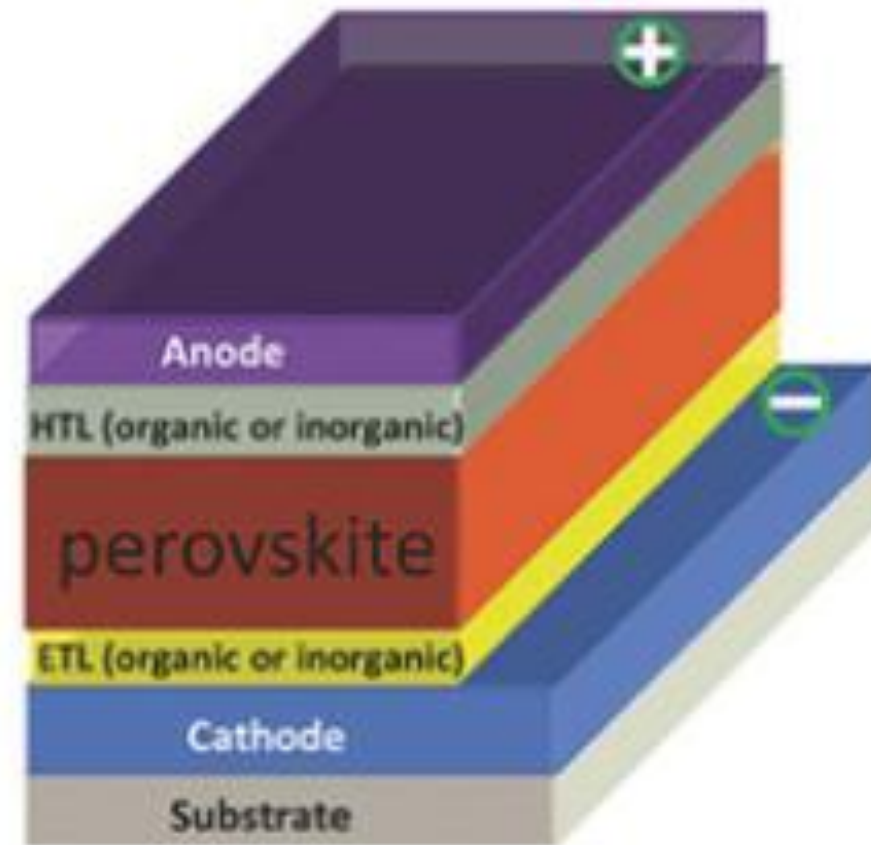


 Image credits: Zhuang et al., 10.1007/s40820-023-01046-0

Outline

Company introduction

Metrology methods & monitoring parameters

In-situ monitoring of perovskite formation

In-line monitoring of perovskite formation

Metrology capabilities for entire perovskite stack

Summary & outlook

Summary & outlook

- Broad spectrum of technologies based on 25 years of in-situ and in-line metrology
- Optical methods are ideally suited for monitoring perovskite formation and related layers in-situ and in-line
- Reflectance spectroscopy allows to assess film thickness, roughness, band gap and many more parameters
- Photoluminescence provides further insights about composition and lifetime
- All methods can be combined freely in one system; Eddy-current can be added for sheet resistance measurements
- In-situ monitoring allows for understanding 100% of the process; in-line monitoring allows for 100% production control

Knowledge is key



扫一扫上面的二维码图案，加我为朋友。



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Acknowledgements

- The Smartline project has received funding from the European Union's HORIZON 2020 research and innovation programme under Grant Agreement No 768707
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- HZB groups headed by E. Unger, S. Albrecht and N. H. Nickel
- ZSW group headed by S. Paetel
- All colleagues at LayTec AG



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by the German Bundestag



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Image credits

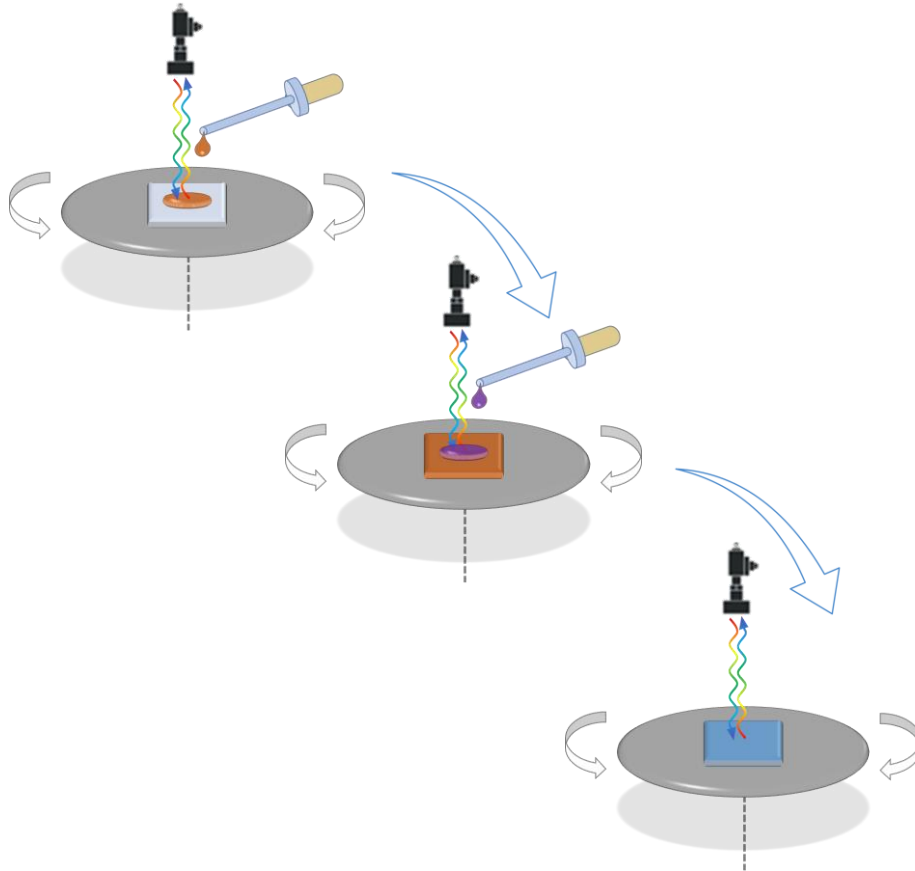
- Fábio Pozzebom/ABr (<https://commons.wikimedia.org/wiki/File:Radaravelocidade20022007.jpg>), „Radaravelocidade20022007“, <https://creativecommons.org/licenses/by/3.0/br/deed.en>
- GaN recess etch: Oxford Instruments Plasma Technology, 2019, White Paper: Atomic Layer Deposition and Atomic Layer Etching for GaN Power Electronics
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- Shutterstock

The background features a dark blue/black area on the left with a glowing white arrow pointing upwards and to the right. Several horizontal light bars in green, yellow, and orange are visible on the left side. A large white diagonal band runs from the top left to the bottom right. A blue parallelogram is positioned at the top, and an orange parallelogram is at the bottom right.

Knowledge is key

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Background: Anti-Solvent Drip



- Initiation of perovskite crystallization
- Anti-solvent:
 - (partially) miscible with the solvent
 - perovskite precursor species are insoluble
- Local region of super-saturation on surface of liquid precursor by:
 - a) excess of a solvent in which the perovskite is insoluble
 - b) removing precursor solvent molecules
- Results in dense and uniform perovskite films.
- Timing is critical for perovskite morphology and device efficiency
- Crystallization is crucial for layer and device quality