SPRAY PYROLYSIS – A VERSATILE TECHNIQUE FOR THIN FILM DEPOSITION IN PV

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Fraunhofer Institute for Solar Energy Systems ISE

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AGENDA

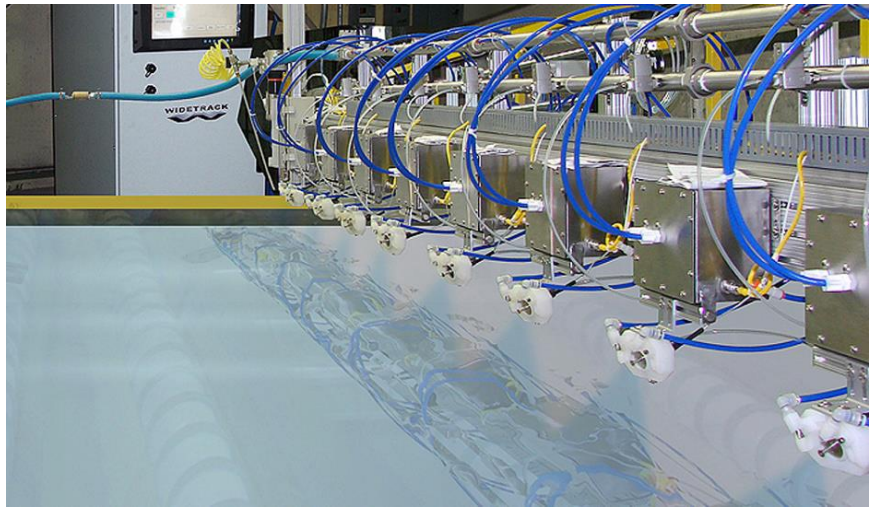
- Spray Coating / Spray Pyrolysis – Introduction
- Materials and Applications
  - Overview and Literature – Bird's eye view
  - Spraying of Dielectric Thin Layers – in more detail
    - TiO_x Layers as Capping Layer for SHJ Solar Cells
    - TiO_x / ZnO Layer Stacks for MorphoColor®
- Summary

Spray Coating / Spray Pyrolysis
Introduction

- Liquid passing through a nozzle → **Spray**
- Directing onto a substrate → **Coating**
- Fast, simple, high volume

Pressure air nozzle[1]

- Adding heat: Liquid precursor evaporates & decomposes over surface → **pyrolysis**
- Usually, substrate is heated
- Very similar to APCVD, but no bubbling of carrier gas, nebulized droplets sprayed directly
- Spray created by ultrasonic (US) or pressure air (PA) nozzle



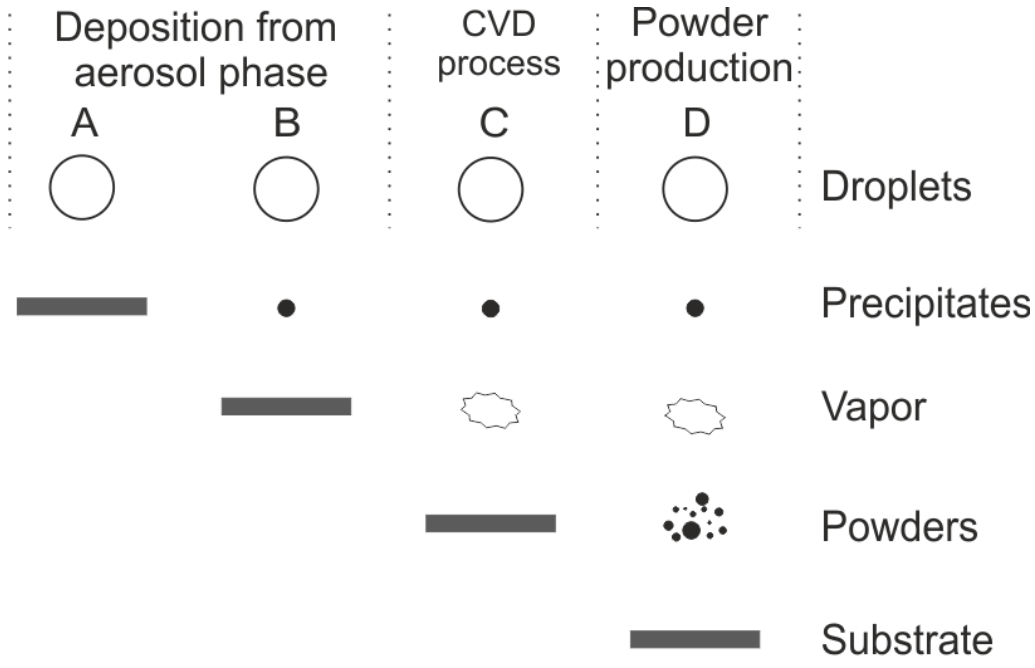
Array of ultrasonic nozzles over substrate[2]

[1]https://www.aquaflex.de/Systeme/SCS/Produkte_SCS_1.html

[2]https://www.sono-tek.com/wp-content/uploads/2019/05/25a_Float-glass-install-Dual-Jet.jpg

Spray Coating / Spray Pyrolysis
Introduction – Spray Pyrolysis

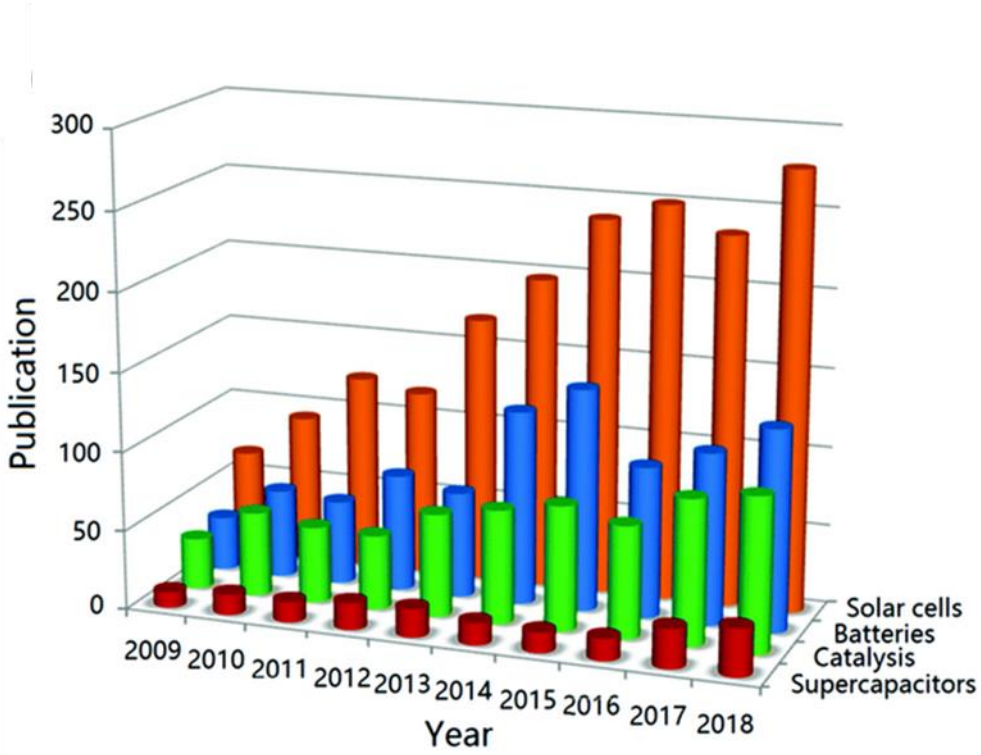
- Spray Pyrolysis:
  - Decomposition of precursor, real CVD desired
  - (Directed) growth of crystalline layer
  - Pre- or post-heating (e.g. for SolGels)
  - Post-treatment (e.g. sulphurization)
  - Also used for nanoparticle fabrication
- Know-How
  - Process (droplet size & distribution, temperature)
  - Machine (flow conditions, homogeneity, material efficiency)
  - Chemistry (precursor chemistry, atmosphere)



Process regimes of spray pyrolysis

Spray Coating / Spray Pyrolysis
Overview and Literature

- Materials deposited by spray pyrolysis in literature (with a focus on PV application)
- Typically oxides (standard atmosphere)
  - TCOs
  - Metal oxides / stacks
  - Mixed phases, Sulfides, Nitrides
    - p-type TCMs
    - Absorbers
  - Organics, e.g. to complete perovskites[2]
- Layer properties and morphology can be tuned
- Surface conformal deposition



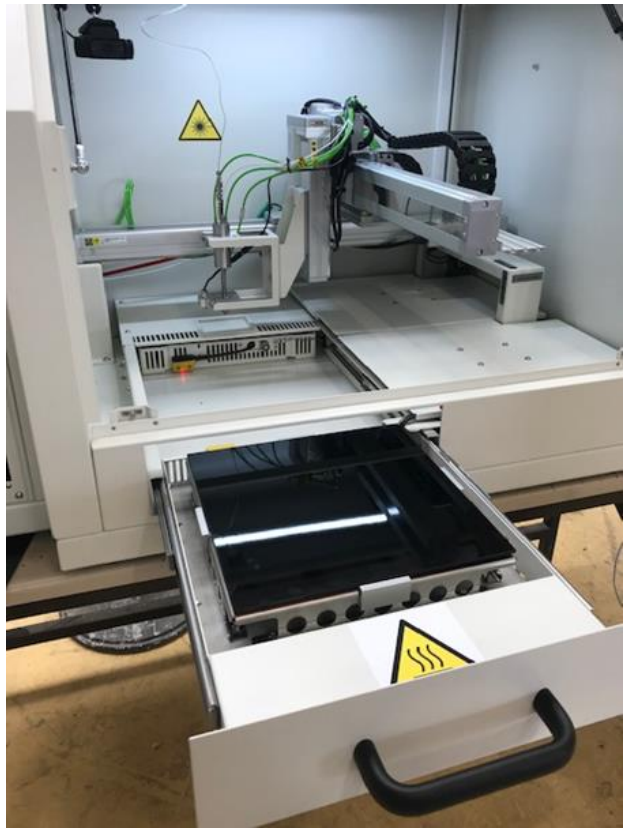
Recent R&D topics associated with spray pyrolysis[1]

→ A really versatile technique

[1] J. Leng et al., Chem. Soc. Rev., 2019, 48, 3015
[2] L. Cojocaru et al., „Hybrid Evaporation/Spray-Coating Process for a Simplified and Controllable Production of Perovskite Solar Cells," IEEE J. Photovoltaics, pp. 1–11, 2019.

Spray Coating / Spray Pyrolysis
Spray Coating @ Fraunhofer ISE

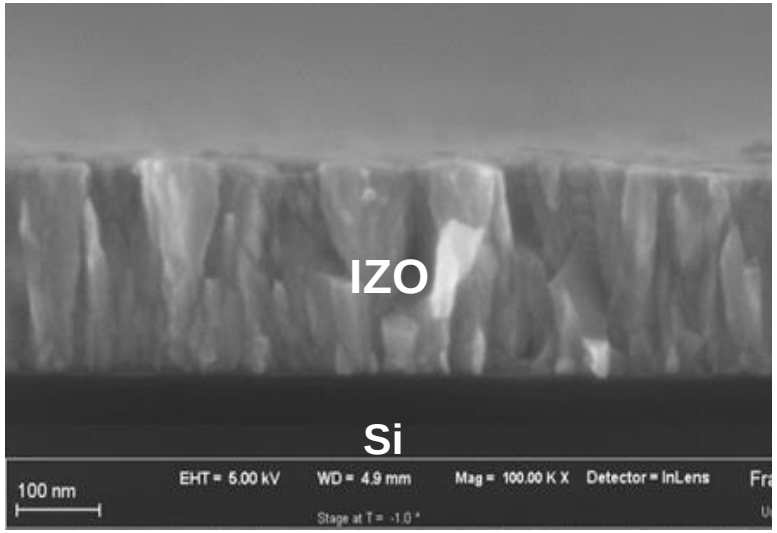
- Lab spray coater / pyrolysis setup
- Up to 500°C substrate temperature
- 3 axis robot moving nozzle over substrate
- Maximum size: 160x160mm²
- Ambient atmosphere



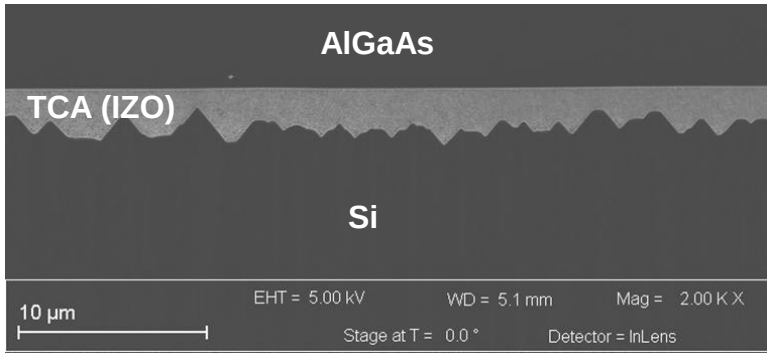
Spray coater @ Fh ISE

Materials and Applications
Overview - TCOs and Application as TCA

- Connect III-V to Si solar cell with TCO[1]
- Contact layer (sprayed IZO or ITO)
  - High mobility, low sheet resistance
  - Directed growth
  - Moderate contact resistivity
- Glue layer – spray coating + post calcination
  - Sprayed IZO yields very low connecting resistivity
- Research ongoing, first solar cells completed



SEM cross section of sprayed IZO on Si[1]

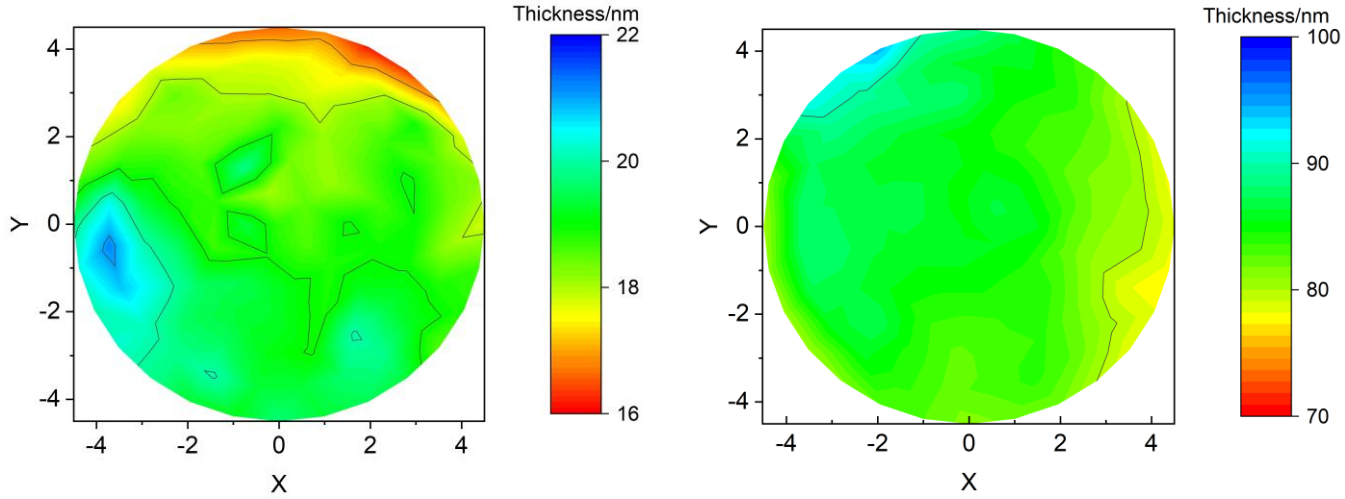


Bond created between III-V and Si solar cell[1]

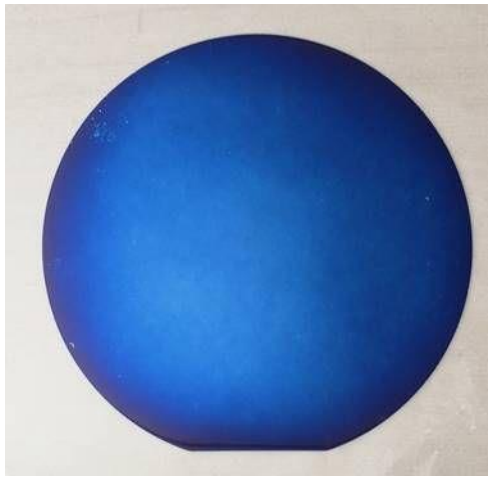
[1]U. Heitmann et al., „The First Glued Tandem Solar Cell Using a ZnO-based Adhesive“, Proceedings of the 47th IEEE PVSC, virtual meeting 2020.

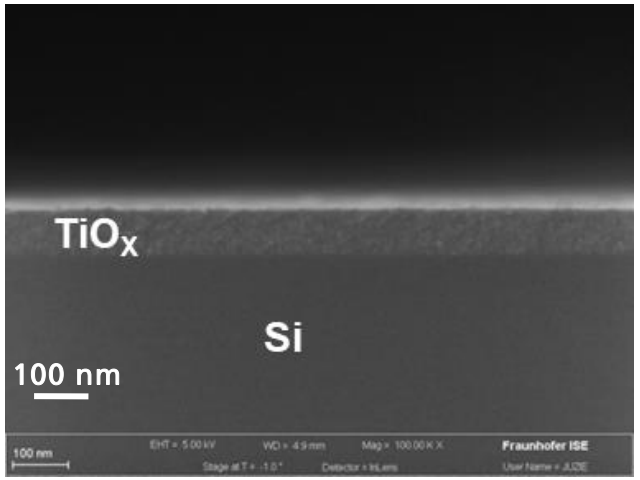
Materials and Applications
Spraying of Thin Dielectric Layers

- Tested Materials: AlO_x, TiO_x, ZnO_x (undoped)
- Homogeneity of ±2 nm around target thickness on 4“ wafer achieved
- Deposition rate up to 50 nm per pass → industrially between **20k and 50k Wafers / hour,** depending on
  - Tool design
  - Application (layer thickness)
  - Material



Ellipsometry maps - Deposition homogeneity of sprayed AlOx on 4“ wafers


Photograph of wafer with sprayed AlOx



SEM cross section of sprayed TiOx

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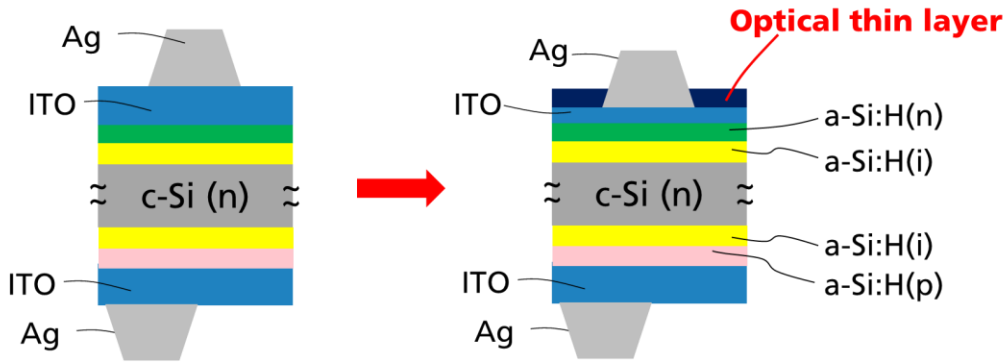
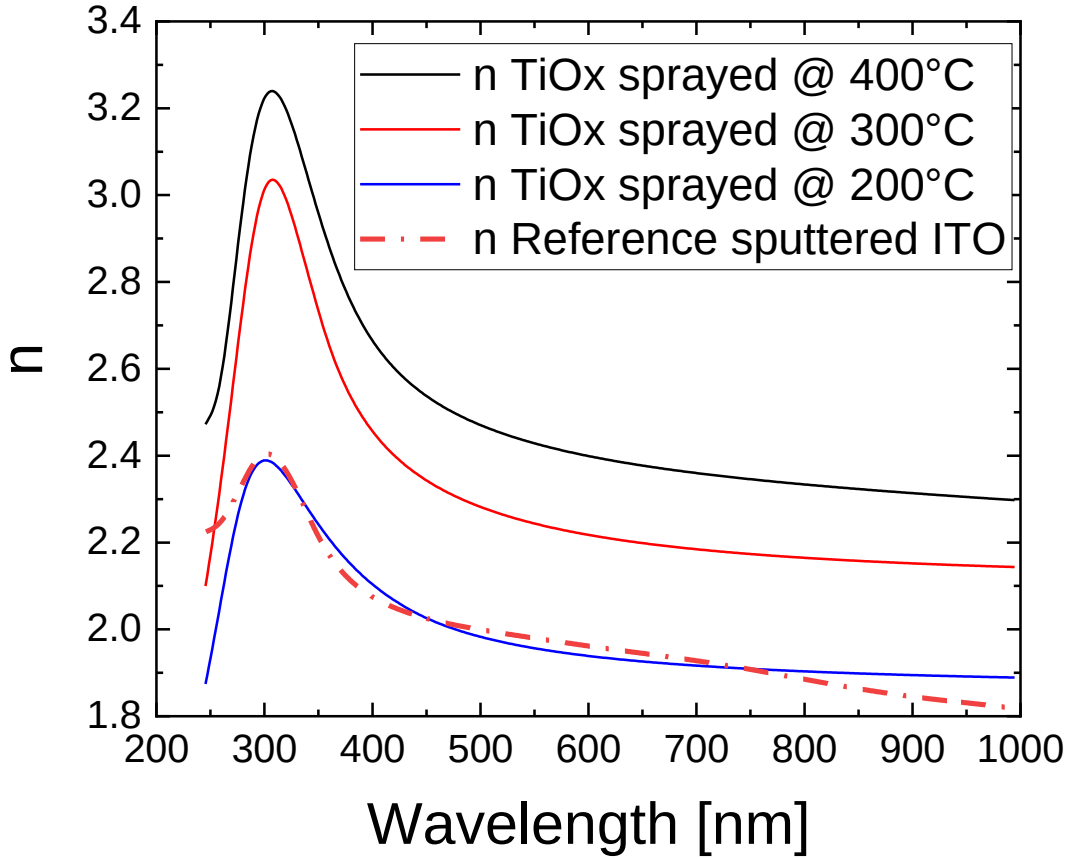
Materials and Applications

Spraying of Thin Dielectric Layers – TiO_x Layer as Capping / ARC for SHJ

- Reduction of ITO layer in SHJ solar cells desired[1]
- Cheap capping layer required for optics
- So far realized by PECVD[1] of SiNx
- Refractive index requirement and thermal budget can be met by sprayed TiO_x



Standard SHJ solar cell SHJ solar cell „2.0“



Refractive index of TiOx layers deposited by spray pyrolysis at different substrate temperatures

[1]D. Bätzner et al., 36th EU PVSEC, Marseille, 2019

Materials and Applications

Spraying of Thin Dielectric Layers – TiO_x Layer as Capping / ARC for SHJ

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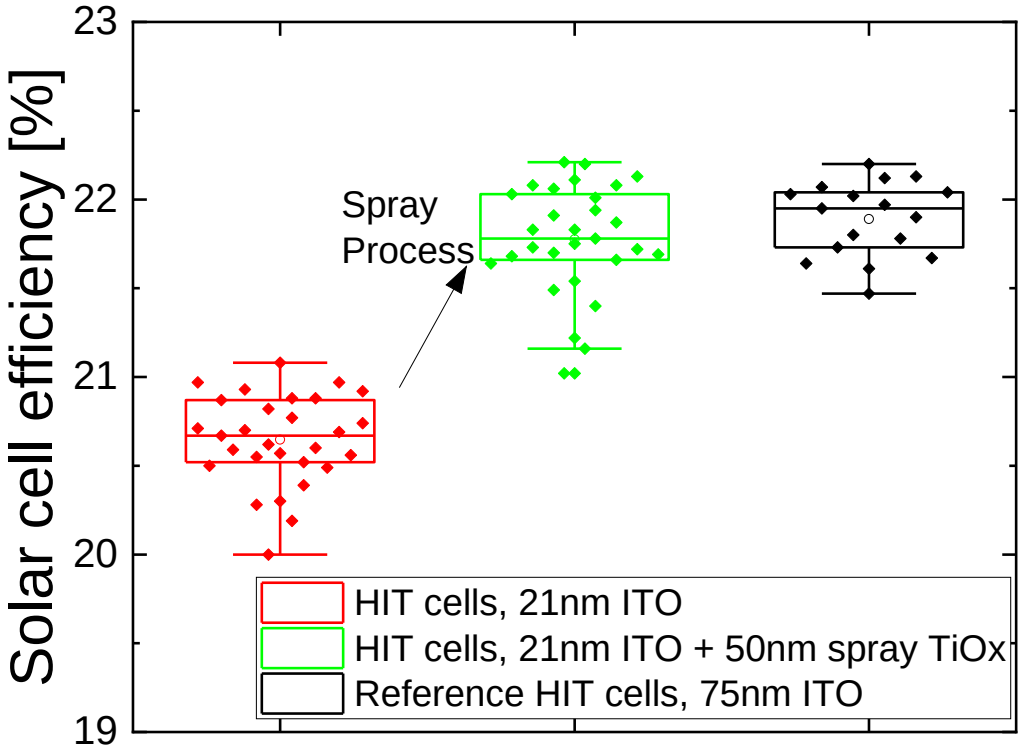
- **Works on cell level, similar efficiency**
- **72% reduced ITO consumption**



Cell efficiencies for SHJ solar cells with thin (21 nm) ITO layer + sprayed TiO_x and for a reference group

[1]D. Bätzner et al., 36th EU PVSEC, Marseille, 2019

Materials and Applications

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2x2 cm² lab cells (average values)	V_{OC} [mV]	J_{SC} [mA/cm²]	FF [%]	Eta [%]	R_S [Ωcm²]
Before TiOx spray	732	34.7	81.3	20.6	0.84
After TiOx spray	733	36.6	81.1	21.8	0.85
Reference 75nm ITO	733	36.5	81.7	21.9	0.73

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[1]D. Bätzner et al., 36th EU PVSEC, Marseille, 2019

Materials and Applications

Spraying of Thin Dielectric Layers – TiO_x / ZnO Layer Stacks for MorphoColor®

- Coloured modules interesting for XiPV (Cars, Facades)
- Morpho Effect yields[1]:
  - Bright colour before dark background
  - High transparancy for incident light, small band reflection
  - Module efficiency 93% of standard module
  - **Currently realized by sputtering**

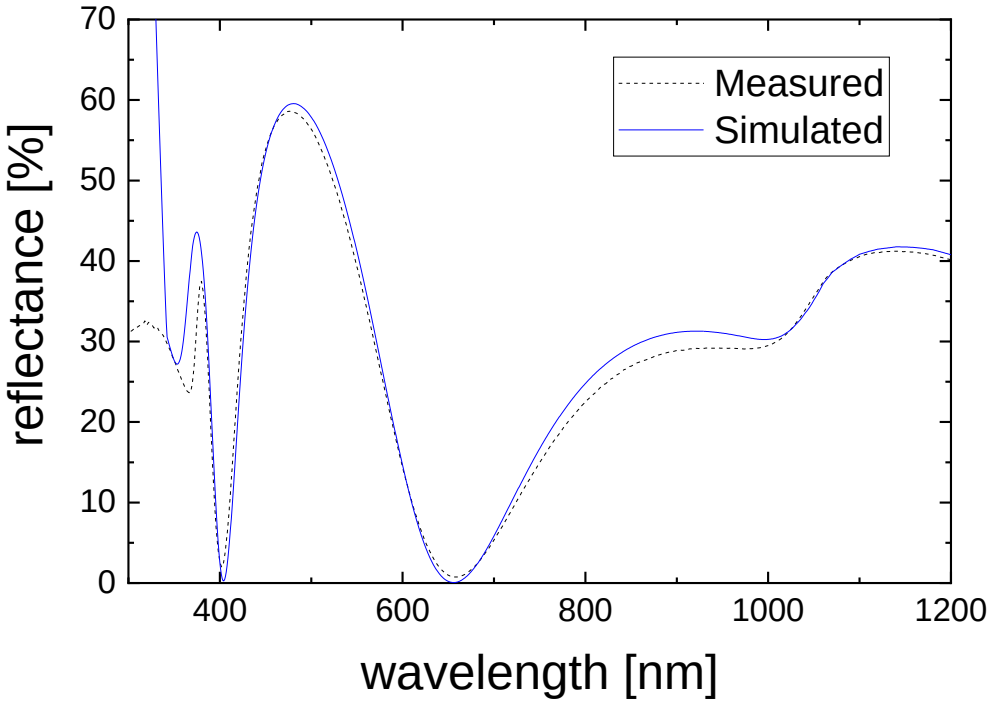
Photograph of solar modules featuring front glass panes sputtered with different MorphoColor® layers[1]

[1]B. Bläsi et al., "Morpho Butterfly Inspired Coloured BIPV Modules," in 33rd EU PVSEC, Amsterdam, The Netherlands, 2017, pp. 2630–2634.

Materials and Applications

Spraying of Thin Dielectric Layers – TiO_x / ZnO Layer Stacks for MorphoColor®

- Advantages of spray pyrolysis:
  - Spray coating of glass already established
  - Hard coat (chemically stable)
  - Energy from float process can be used
  - Cheaper process
- Needs alternating thin layer with high and moderate refractive index
  - 400°C sprayed TiOx (n~2.4)
  - Sprayed ZnO (n~1.8-2)



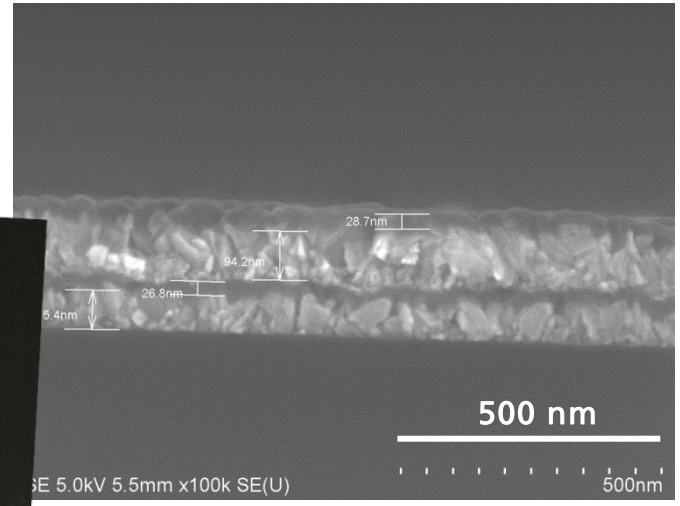
Simulated / measured reflectance of a four layer sprayed MorphoColor® stack

Materials and Applications

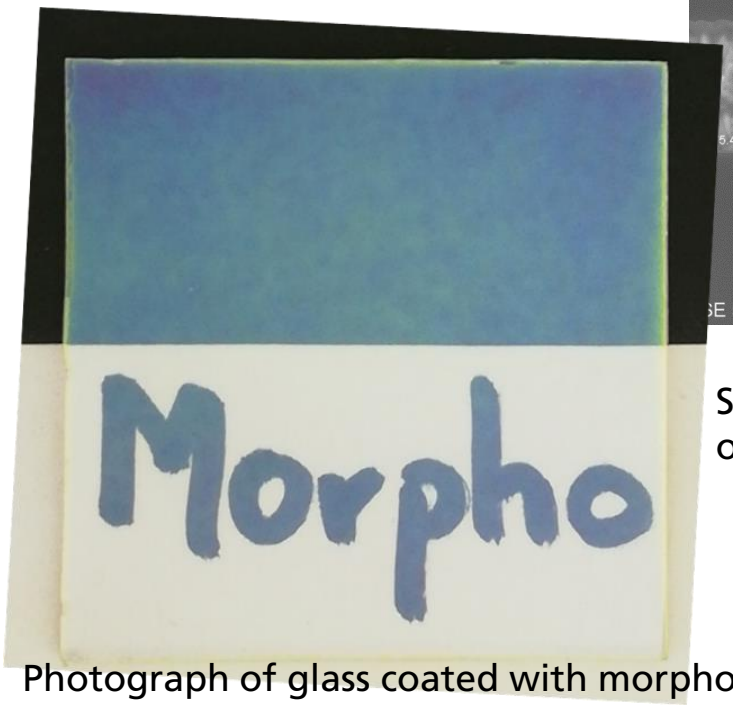
Spraying of Thin Dielectric Layers – TiO_x / ZnO Layer Stacks for MorphoColor®

- First demo with sprayed stack of TiO_x / ZnO successful
- So far, only four layer stack, not fully optimized

→ More layers will make colour impression more intense and reduce reflection



SEM of sprayed morpho layer stack of ZnO / TiO_x (≈ 70 nm / ≈ 30 nm)

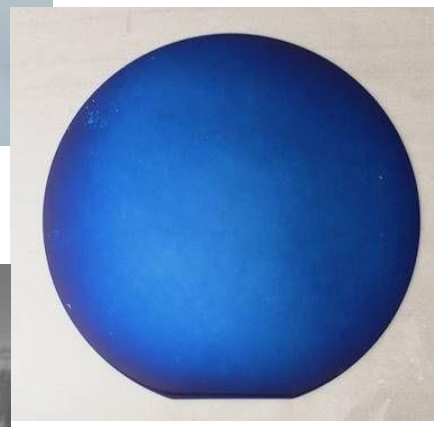


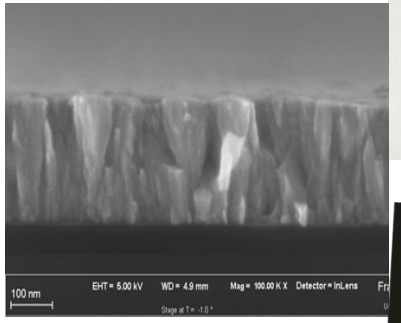
Photograph of glass coated with morpho layer stack before black background / white background with black writing „Morpho“

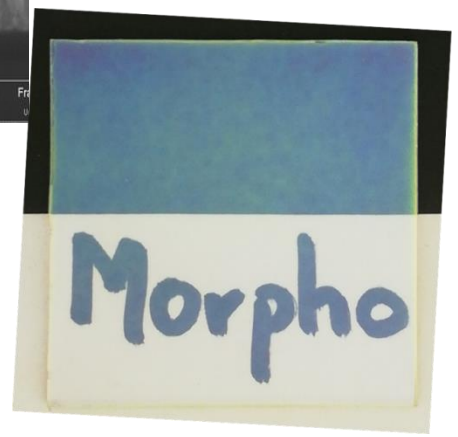
Summary and Conclusion

- Spray coating / pyrolysis deposits many different materials
- Simple process, very high throughput **(>20.000 Wafers/h)**
- **Cheap** chemical precursor solutions
- Overview – thin layer technology with many potential applications
- In detail: Optical layer applications (SHJ, MorphoColor®)
- More applications / ideas for the future (e.g., TiOx as barrier for PERC rear side, …)

- **High potential of spray processes in PV**







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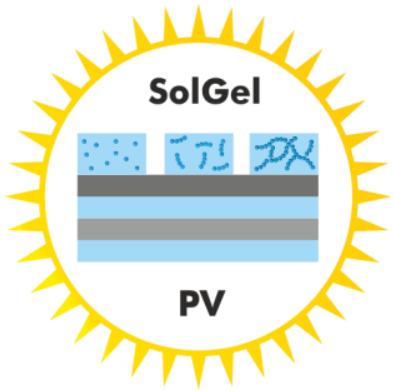

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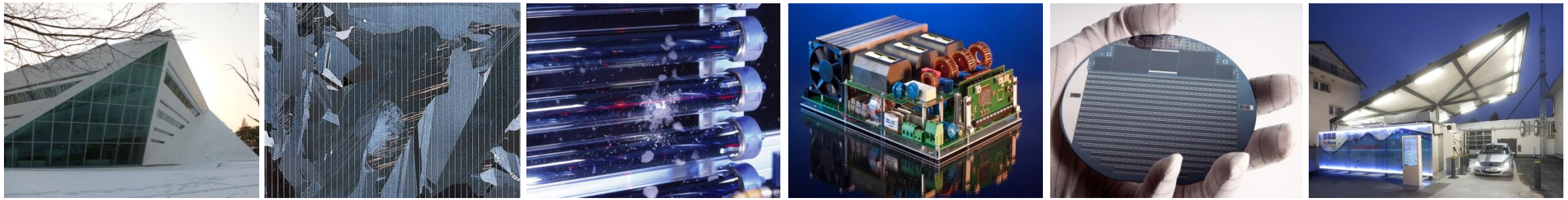

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