

# Vacuum-Deposited Halide Perovskites And Broadband Transparent Conducting Oxides For Photovoltaics

Pierre-Alexis  
Repecaud



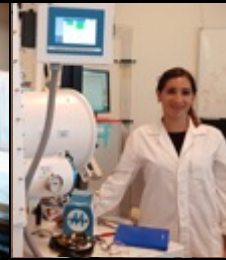
Yury  
Smirnov



Nathan  
Rodkey



Tatiana Soto-  
Montero



Dr. Monica Morales-Masis  
Associate Professor  
M<sup>3</sup> Optoelectronic Materials Group @ IMS



Dominic  
Post



Adem  
Mirza



Yorick  
Birkhölzer



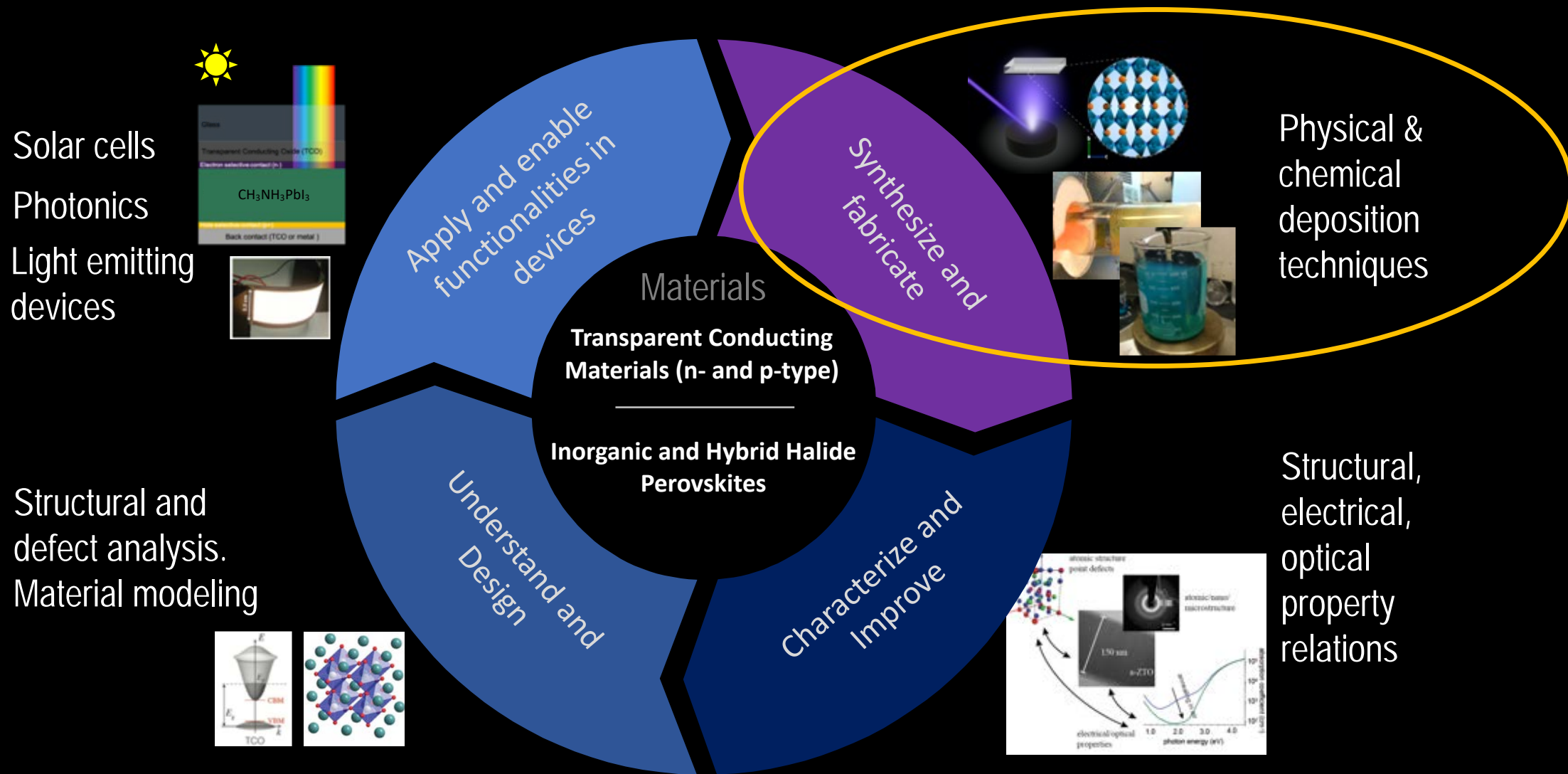
Wiria  
Soltanpoor



Monica  
Morales-Masis



# Optoelectronic Thin Film Materials



Reviews

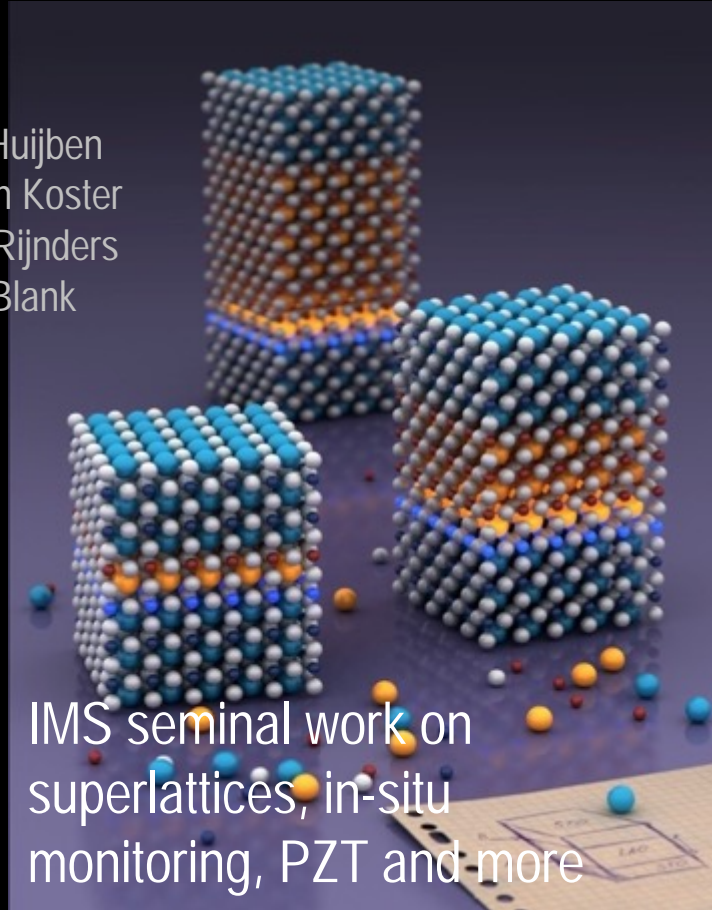
Morales-Masis M., et al. *Adv. Electron Mat.* Vol.3 (2017)  
 Fioretti A., Morales-Masis M. *J. Phot. Energy* (2020)  
 Soto-Montero T., Soltanpoor W., M.MM. *Invited APL Mat* (under review)



# Pulsed Laser Deposition (PLD)

Known for playing LEGO on atomic scale with complex oxides ...

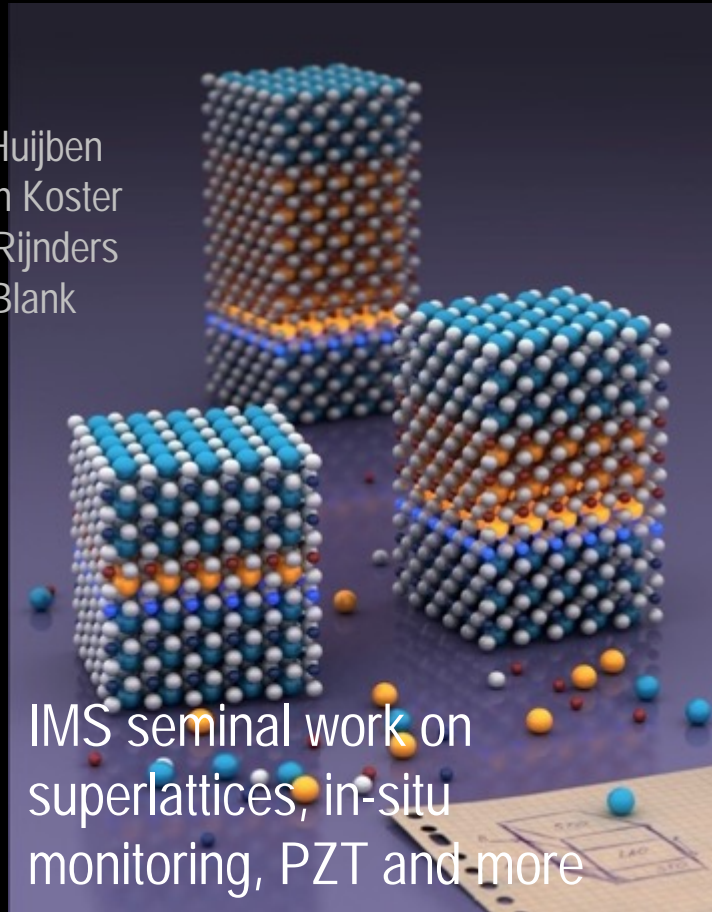
Prof. Mark Huijben  
Prof. Gertjan Koster  
Prof. Guus Rijnders  
Prof. Dave Blank



# Pulsed Laser Deposition (PLD)

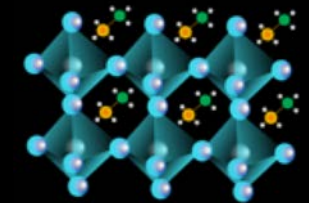
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Prof. Guus Rijnders  
Prof. Dave Blank



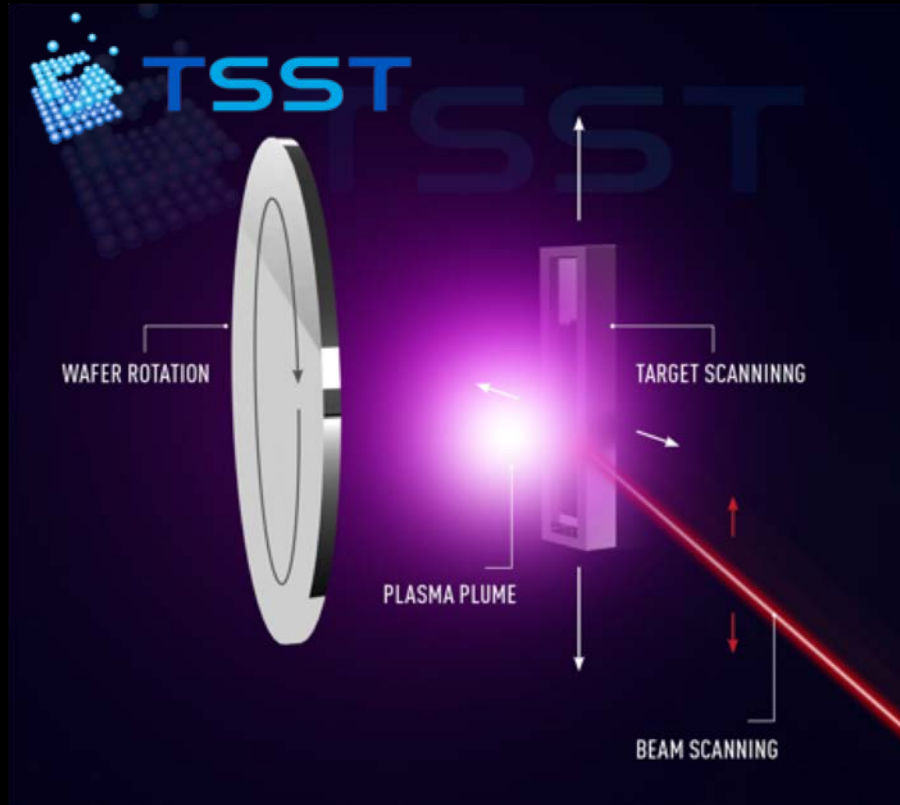
Complex optoelectronic materials for solar cells with PLD?

PLD properties	Interesting for ..
Near stoichiometric transfer of multi-compounds.	Halide Perovskites $ABX_3$ , $X = I, Br, Cl$
Volatility insensitive.	
Low-damage deposition of thin films on sensitive substrates.	Transparent Conducting Oxides (TCOs)
But absolute requirement for PV ...	
Scalability (deposition on wafer-size substrates)	





# Scalable (wafer-based) Pulsed Laser Deposition



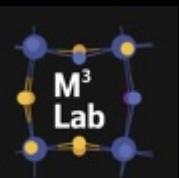
4 inch wafers



4 – 12 inch wafers

Scalable Pulsed Laser Deposition for TCOs in Solar Cells  
*Smirnov, Kuik, Schmengler, Repecaud, ... Morales-Masis M.*  
Adv. Mat. Technologies, 2020

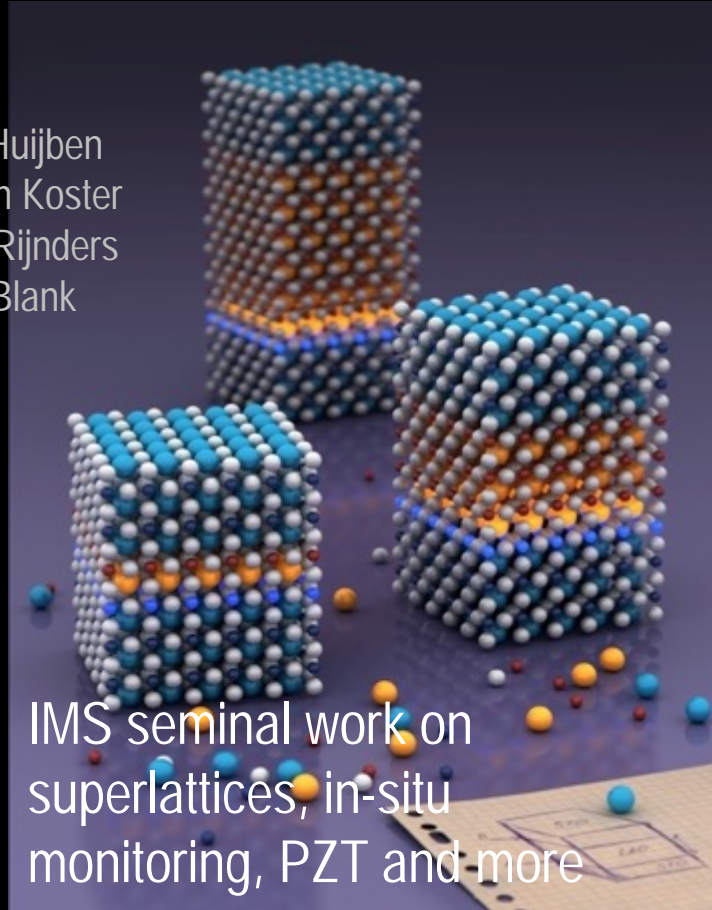
TCOs for passivated contacts  
Featured in PV Magazine



# Pulsed Laser Deposition (PLD)

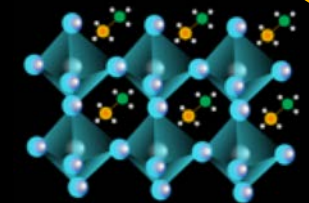
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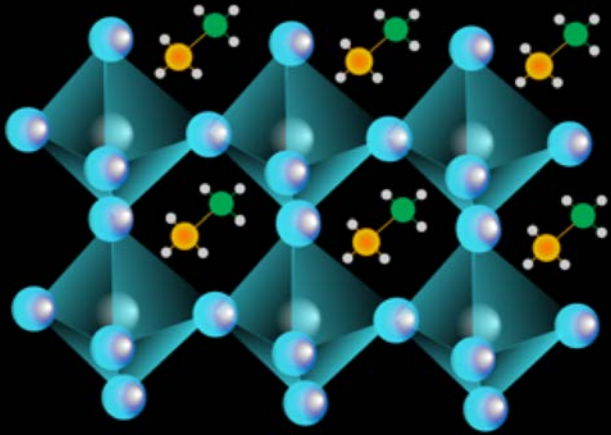
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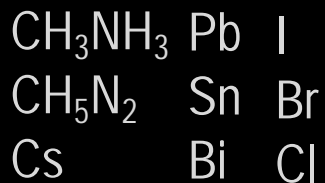
# PLD for halide perovskite growth?

## Hybrid and Inorganic Halide Perovskites



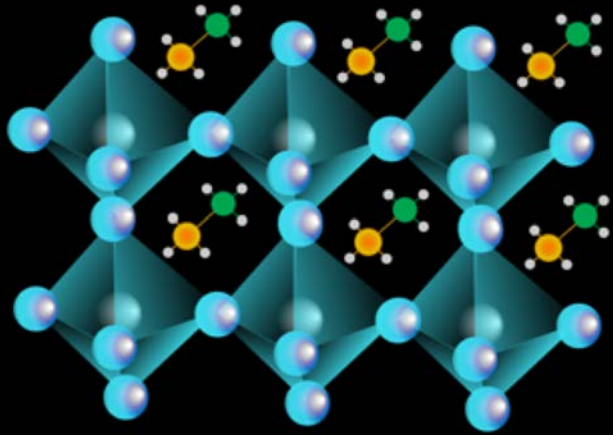
Record solar cell efficiencies  
High and tunable luminescence  
Defect tolerance  
Simple fabrication

But  
Unstable (thermal, environmental)  
Pb-based  
Lack of controlled growth



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Record solar cell efficiencies  
High and tunable luminescence  
Defect tolerance  
Simple fabrication



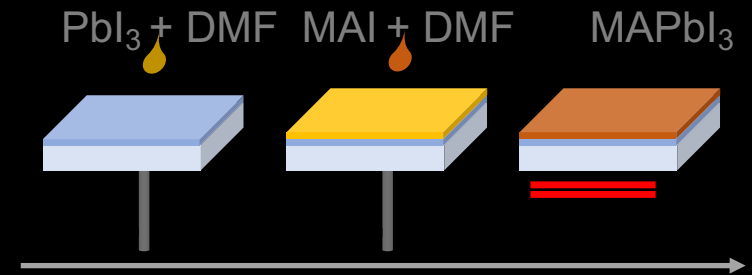
$\text{CH}_3\text{NH}_3$	Pb	I
$\text{CH}_5\text{N}_2$	Sn	Br
Cs	Bi	Cl

But  
Unstable (thermal, environmental)  
Pb-based  
Lack of controlled growth

## Current deposition methods

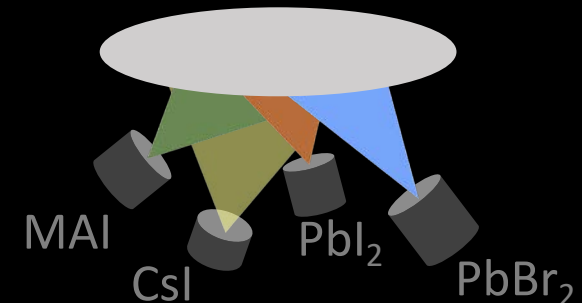
### Solution Process

Solubility dependent



### Thermal Co-Evaporation

Volatility dependent





# PLD for halide perovskite growth?

## New Laser-Based Methods

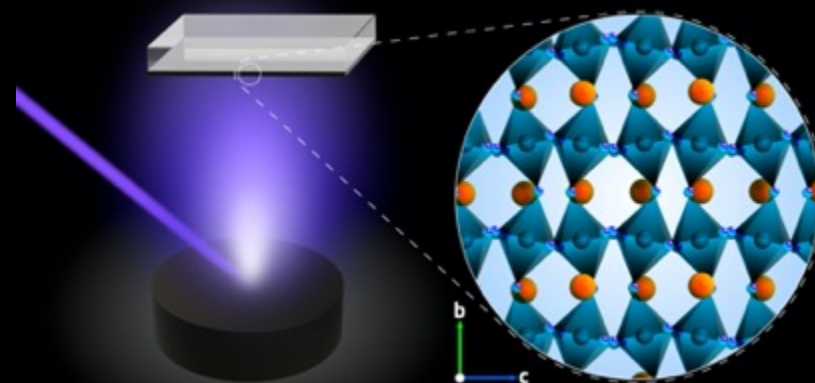
## Current deposition methods



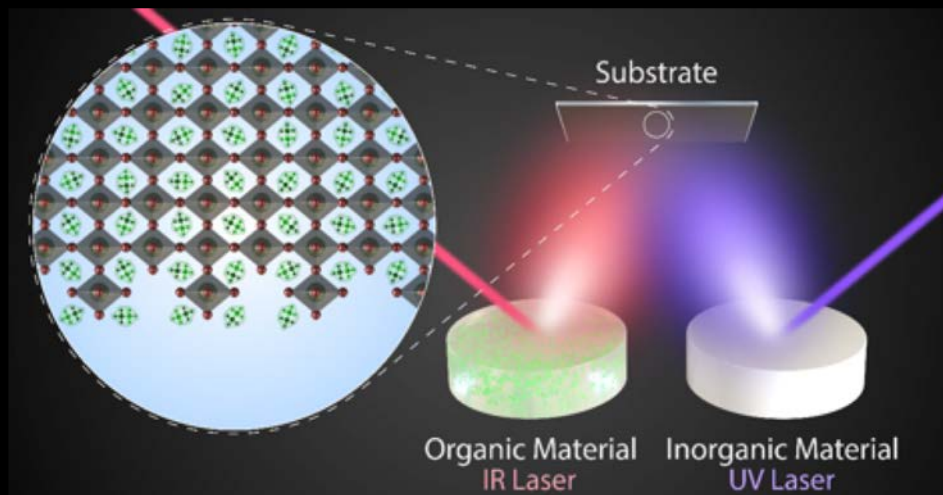
European Research Council  
Established by the European Commission

CREATE

Single-source

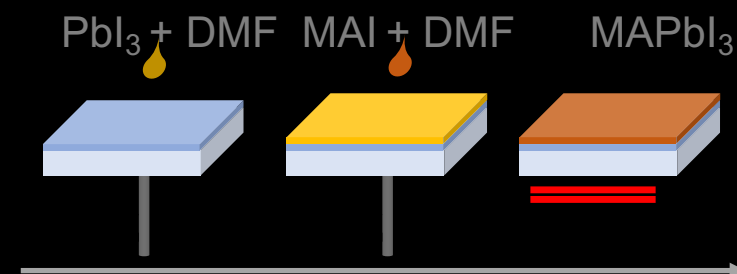


Dual-laser deposition



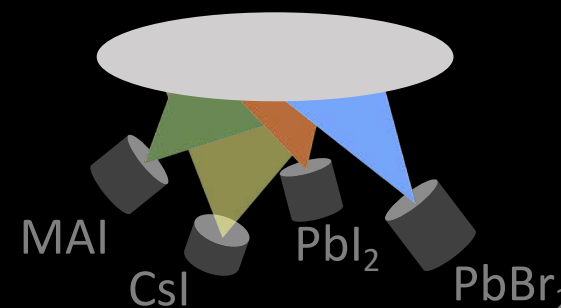
### Solution Process

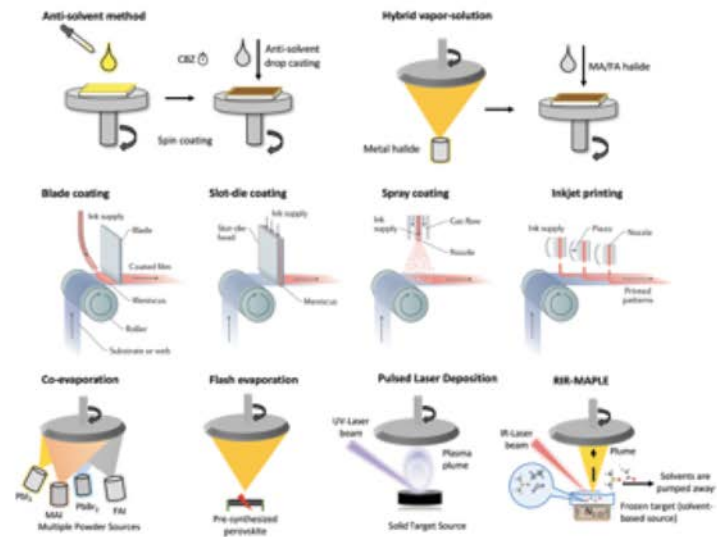
Solubility dependent



### Thermal Co-Evaporation

Volatility dependent





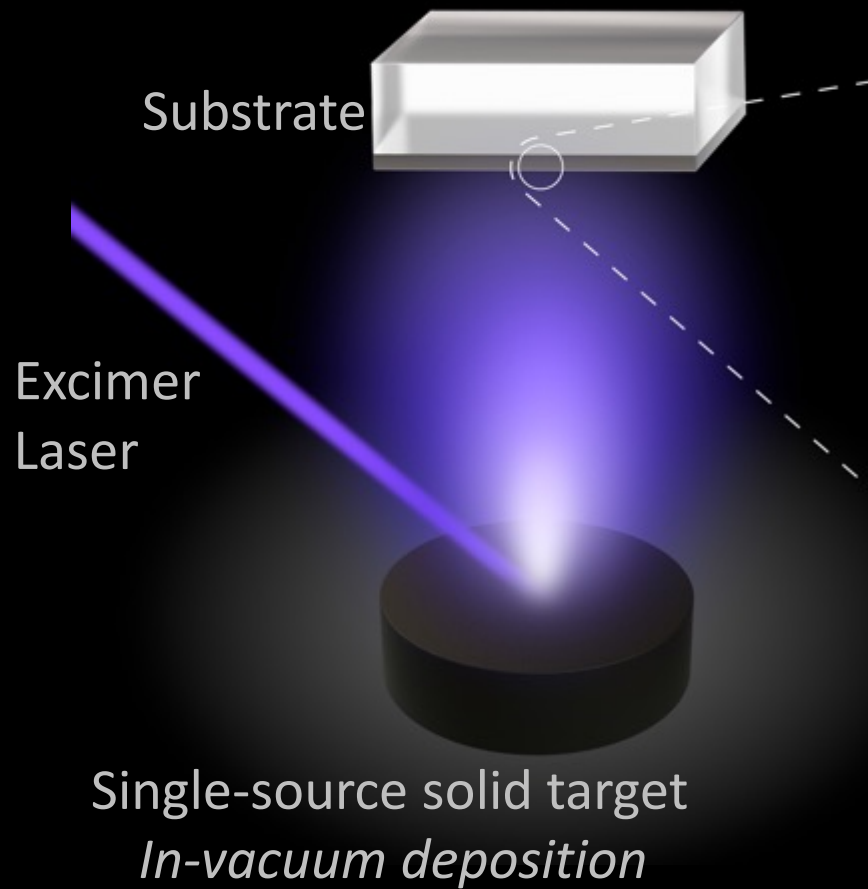
Volume 8, Issue 11, Nov. 2020

## Pressing challenges of halide perovskite thin film growth

APL Mater. 8, 110903 (2020); doi.org/10.1063/5.0027573

Tatiana Soto-Montero, Wiria Soltanpoor, and Monica Morales-Masis

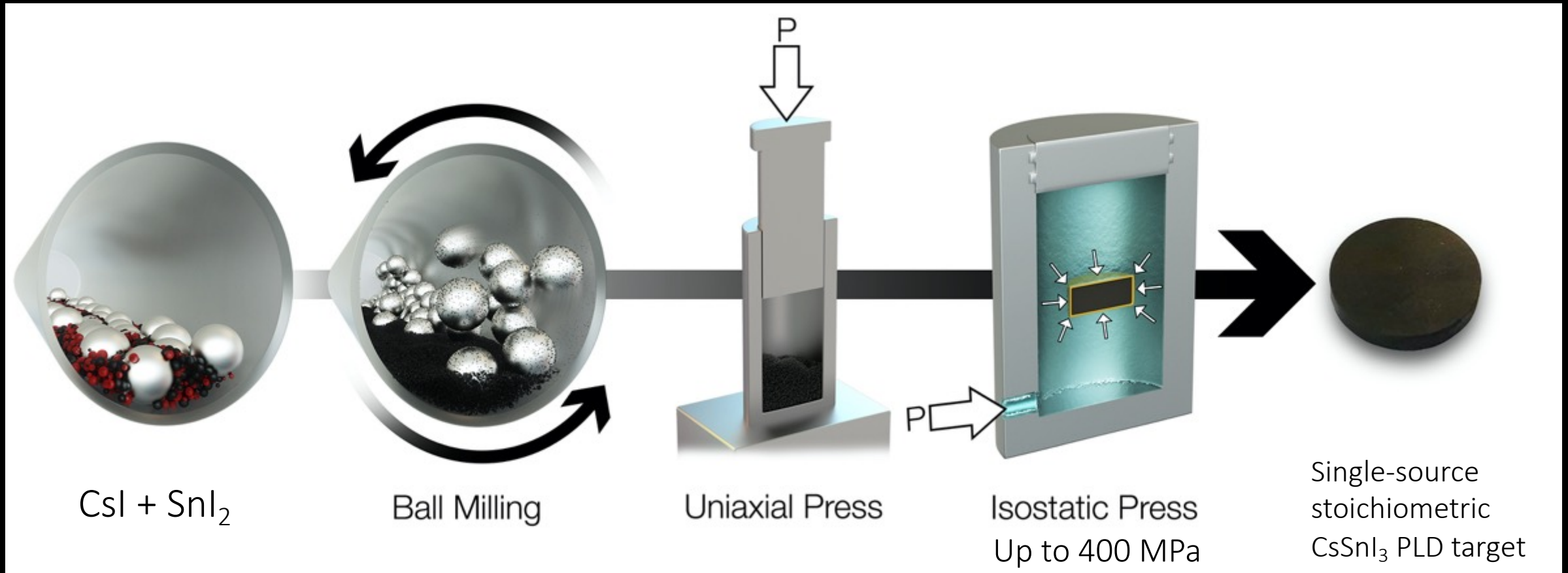
# Single Source PLD of Inorganic Halide Perovskites



Challenging material:

- Oxidation of Sn ( $\text{Sn}^{2+} - 2e^- \rightarrow \text{Sn}^{4+}$ )
- Two independent stable polymorphs at RT :
  - Optically active black-phase (orthorhombic B- $\gamma$ )
  - Non-optically active yellow-phase

# Single Source Halide PLD Target Fabrication





# Single Source PLD of Inorganic Halide Perovskites

Vacuum

Deposition under  
inert Ar atmosphere

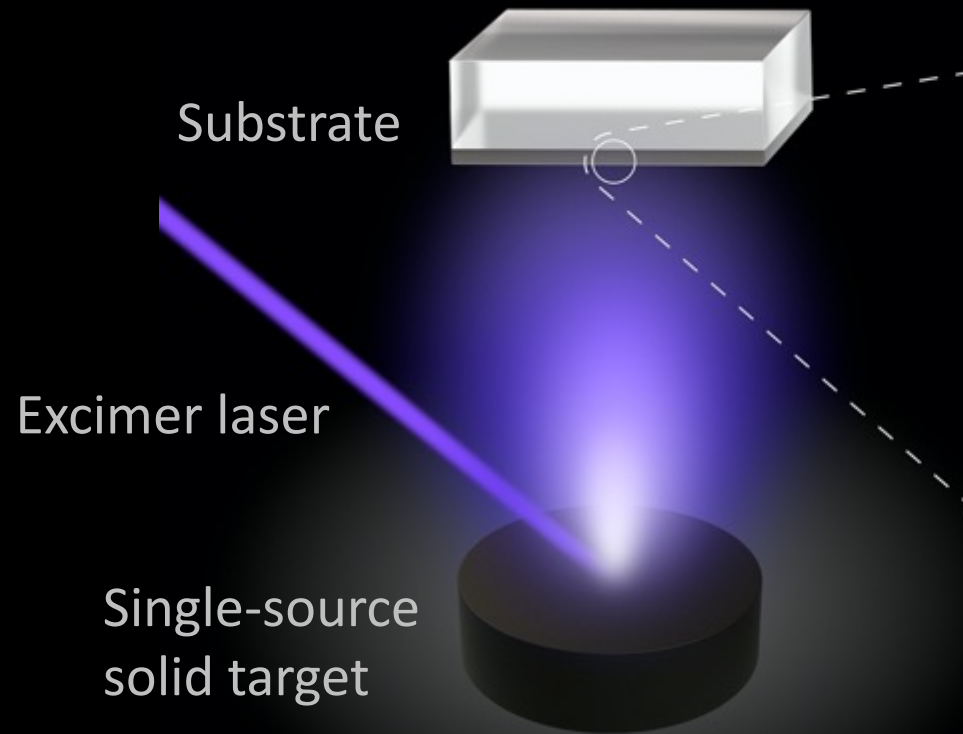
Substrate at RT:

Si/native SiO<sub>x</sub>

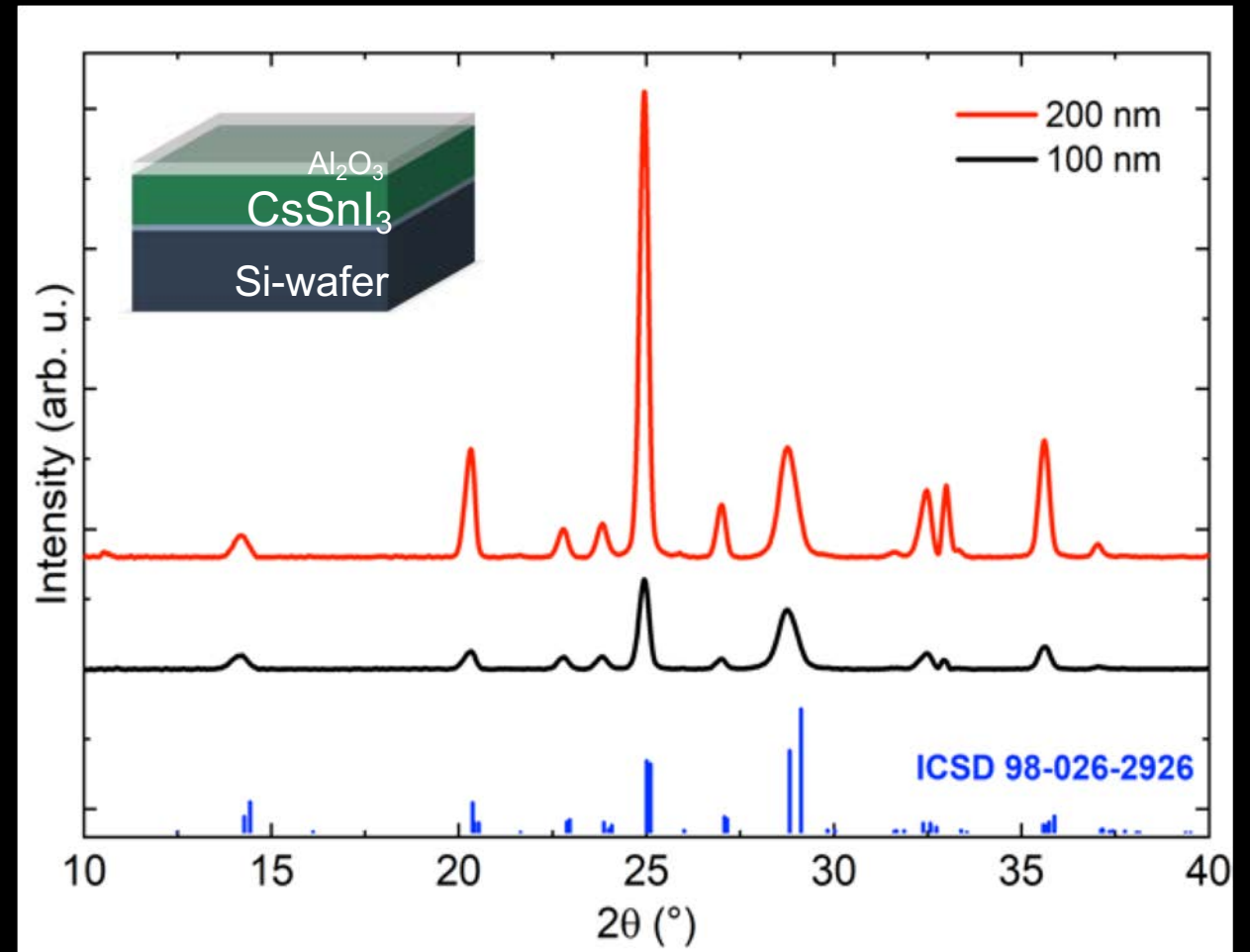
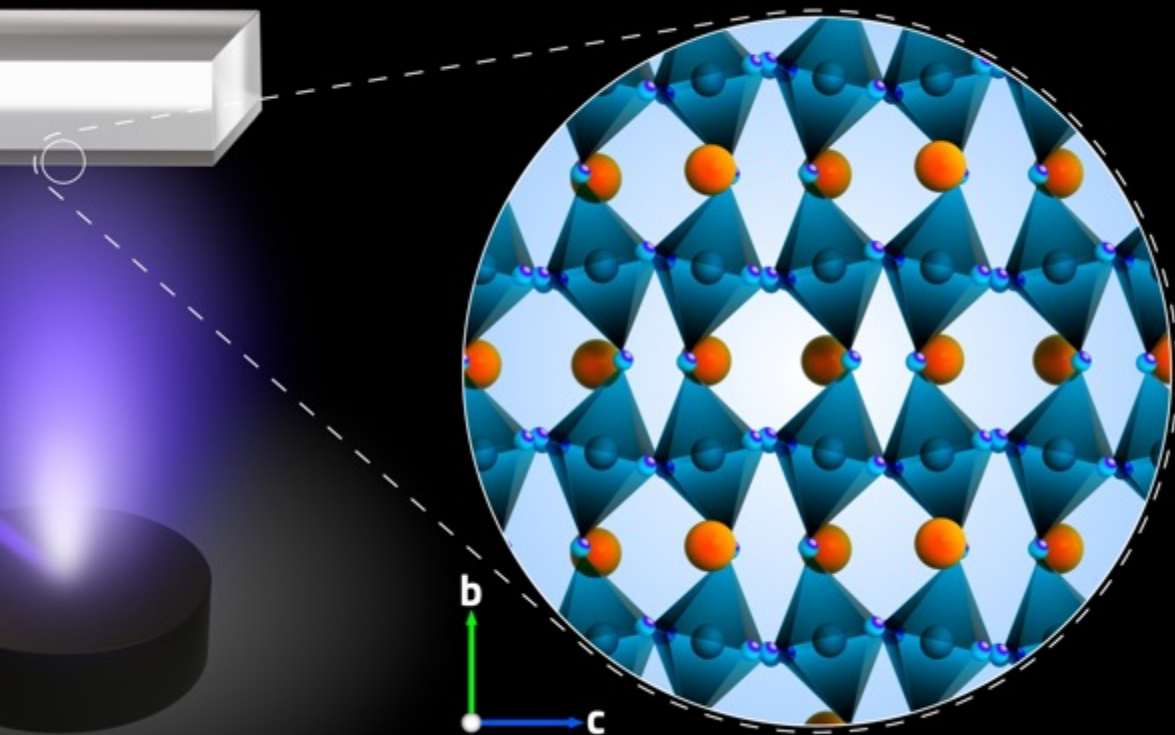
Fused silica

Glass

Al<sub>2</sub>O<sub>3</sub> capping layer

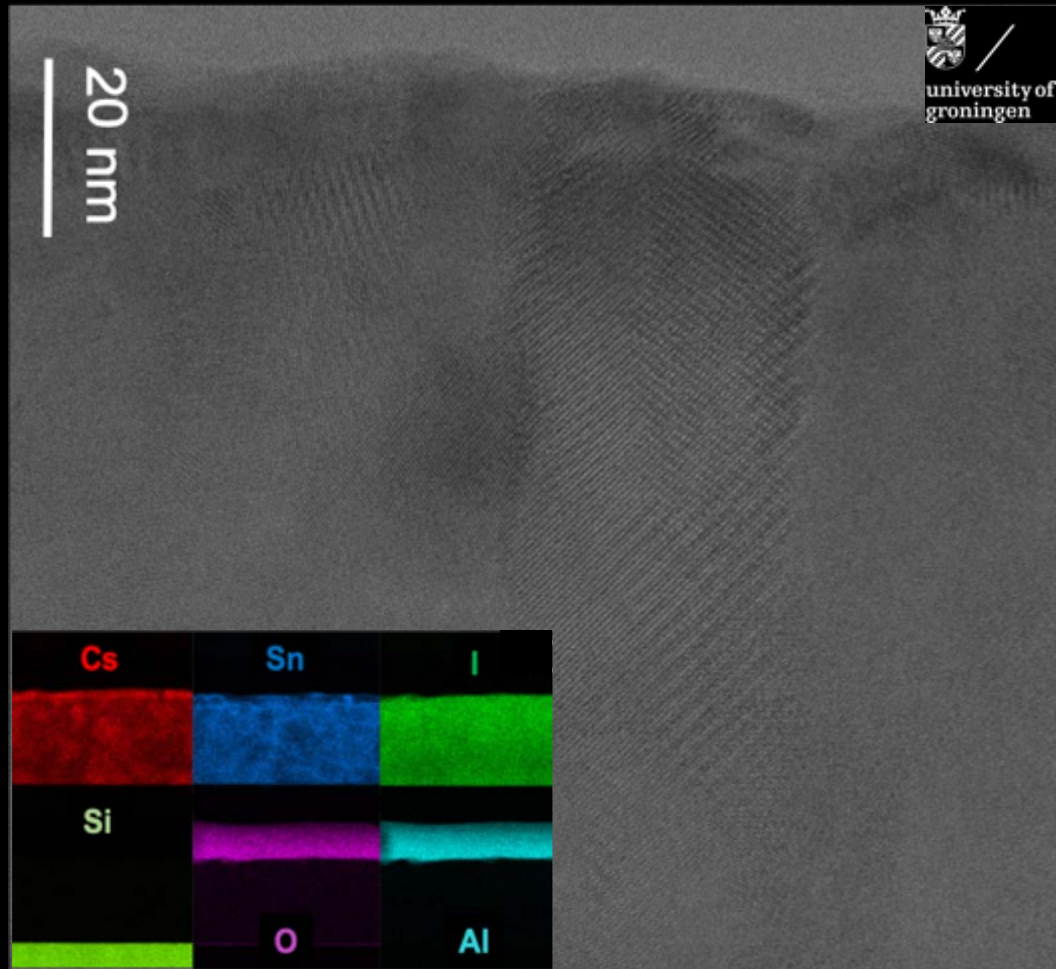


# Confirmation of Black- $\gamma$ -phase $\text{CsSnI}_3$ films

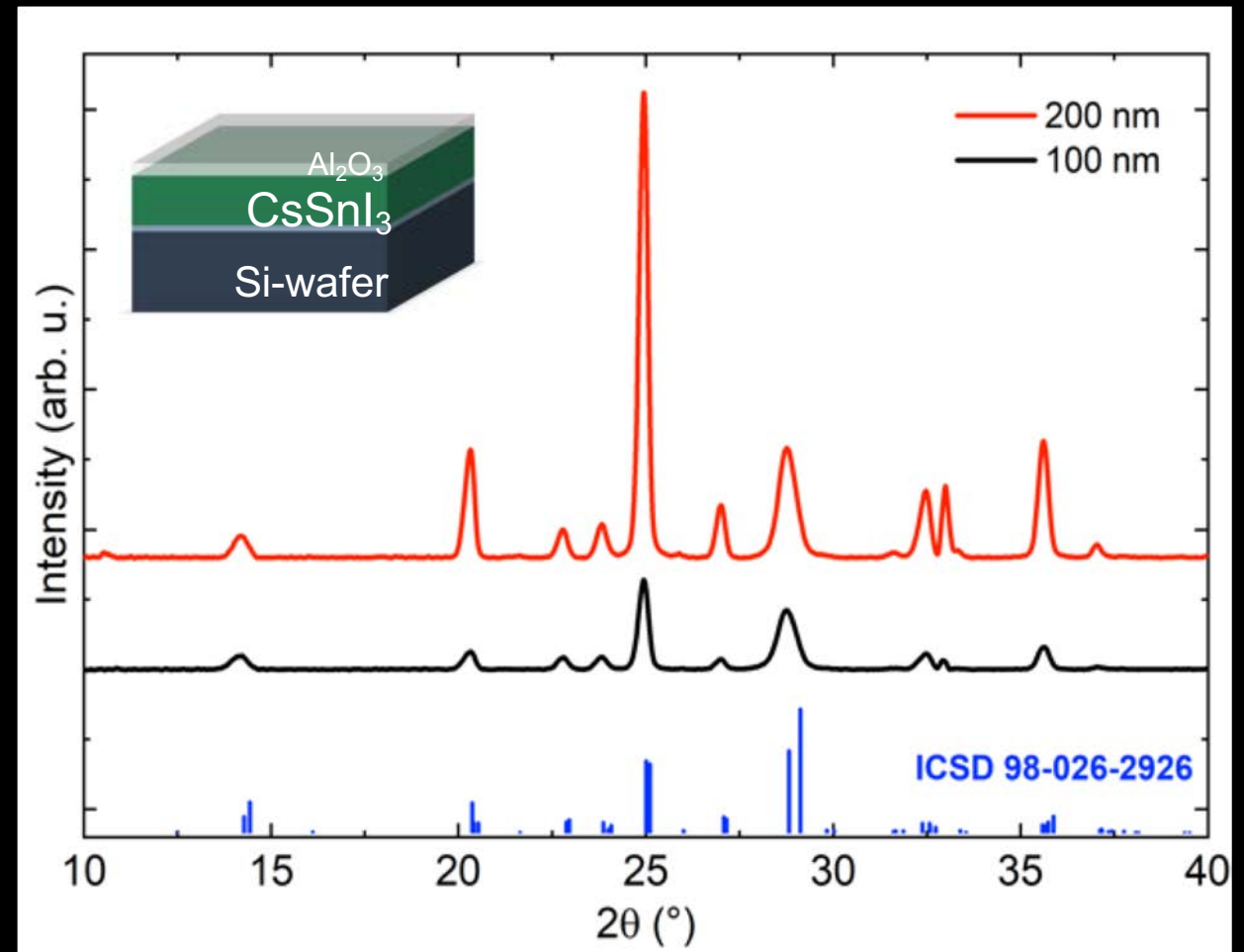


X-ray diffraction

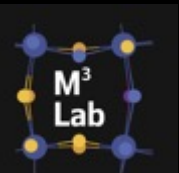
# Confirmation of Black- $\gamma$ -phase $\text{CsSnI}_3$ films



TEM - EDX



X-ray diffraction



# PLD $\text{CsSnI}_3$ : high absorption coefficient and optimum band gap for PV

Band Gap of 1.32 eV

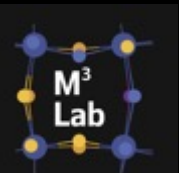
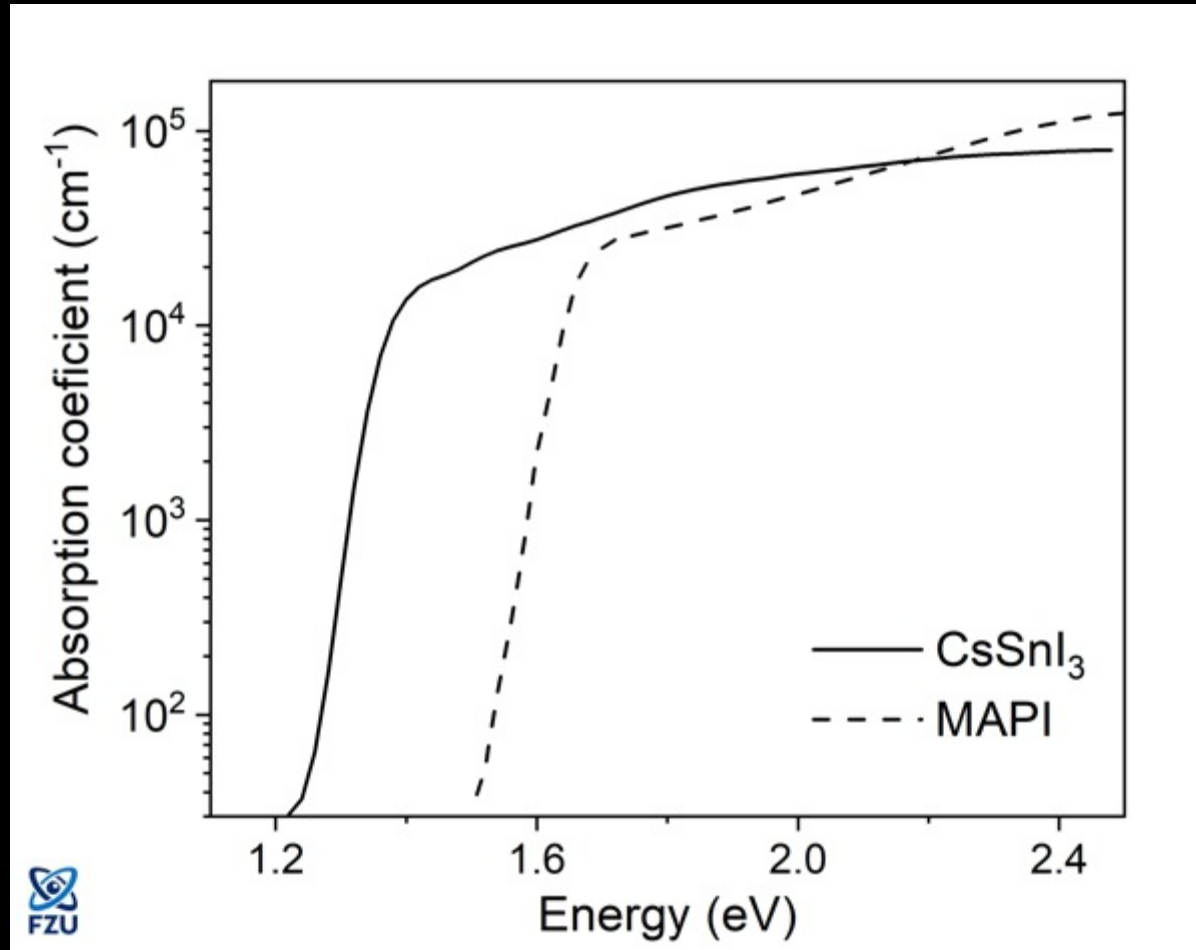
Sharp Absorption Edge

High quality film quantified by  
Urbach energy ( $E_U$ )

$$\alpha \propto \exp(-h\nu/E_U)$$

$E_U$  -  $\text{CsSnI}_3$ : 12.9 meV

$E_U$  -  $\text{MAPbI}_3$ : 12.5 meV





# PLD CsSnI<sub>3</sub>: Higher absorption coefficient than c-Si

Band Gap of 1.32 eV

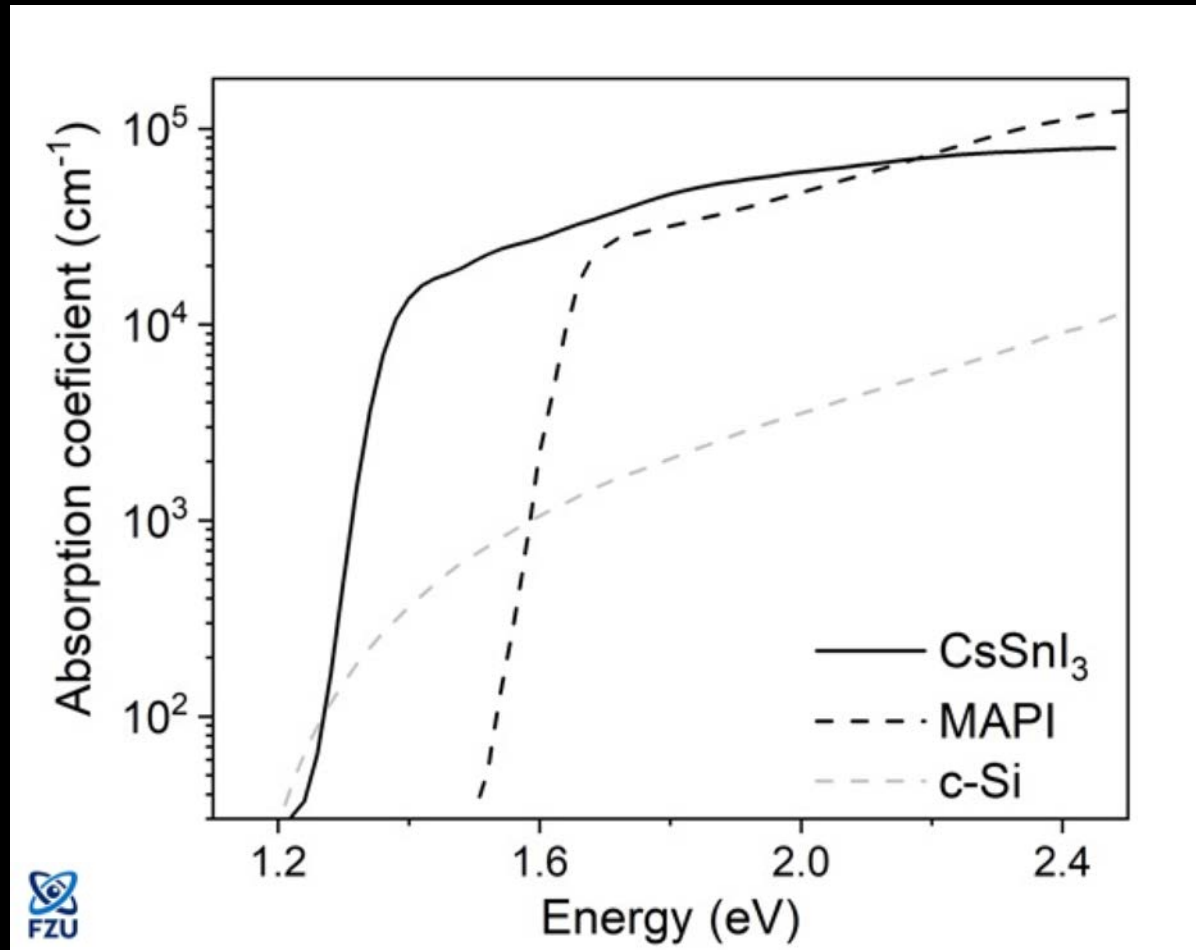
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# PLD CsSnI<sub>3</sub>: NIR Photoluminescence

Band Gap of 1.32 eV

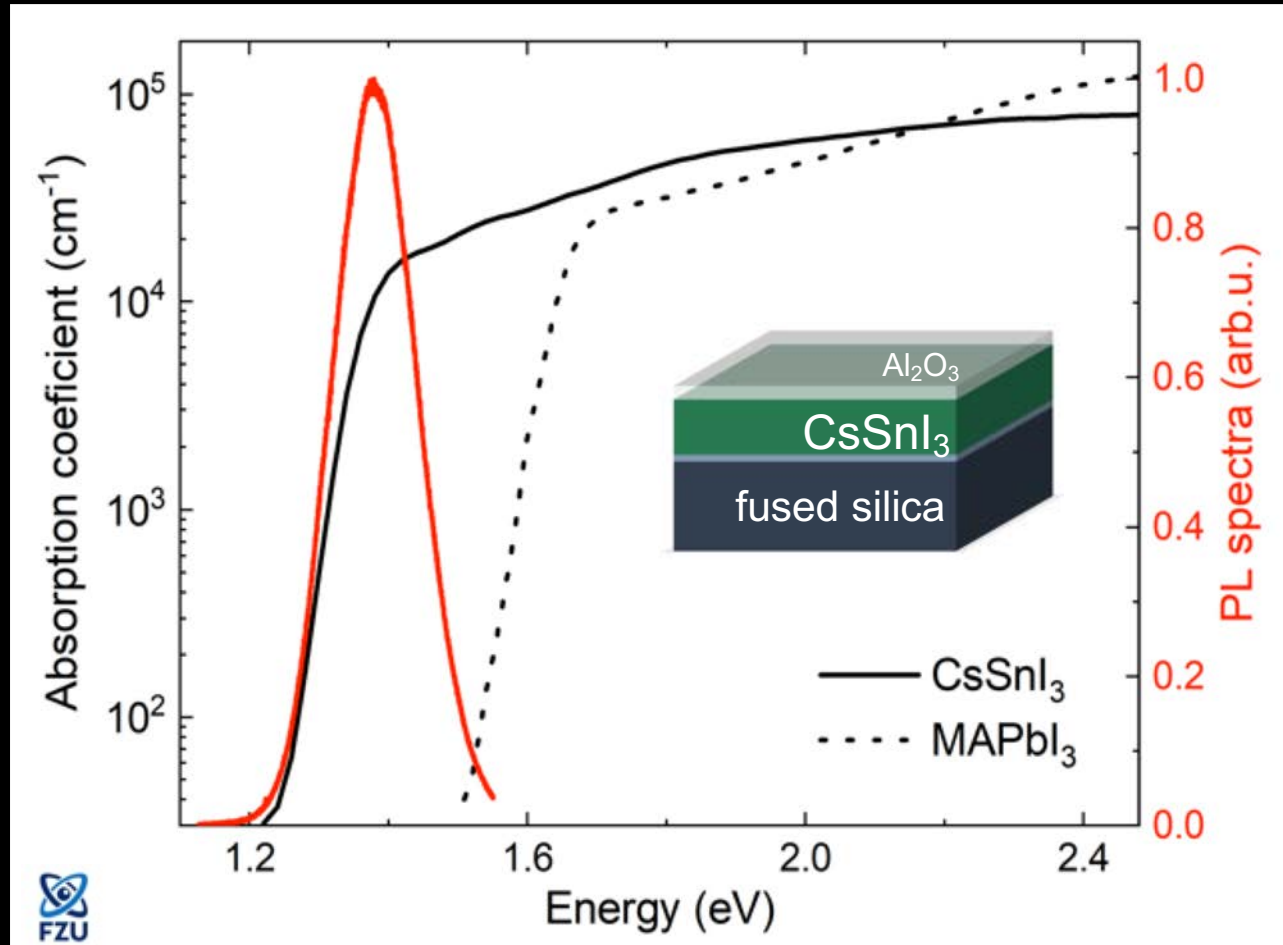
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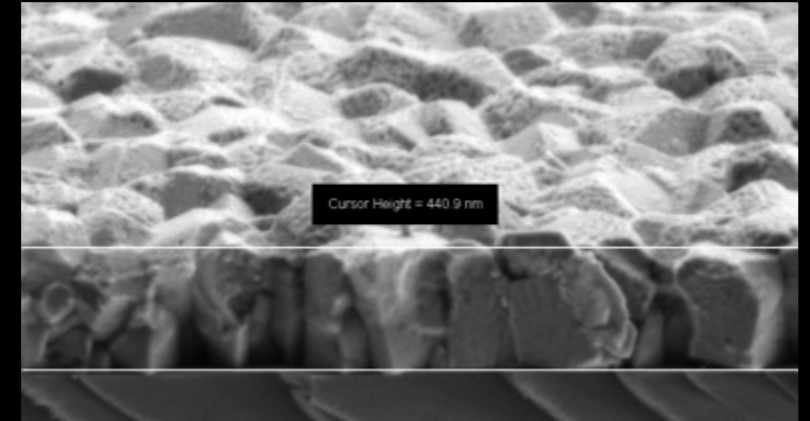
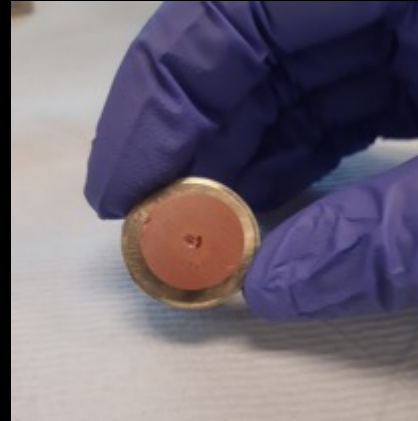
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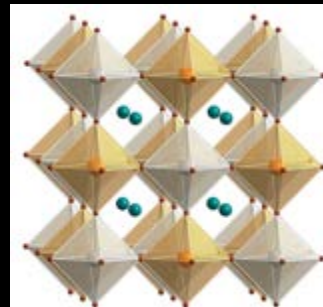
Direct Band Gap  
High PL



# Other halide perovskite compositions?



Mechanochemical synthesis



*Nathan Rodkey, Stan Kaal, et al unpublished results*

# Solar Cells?

Collaboration with solar cell groups:



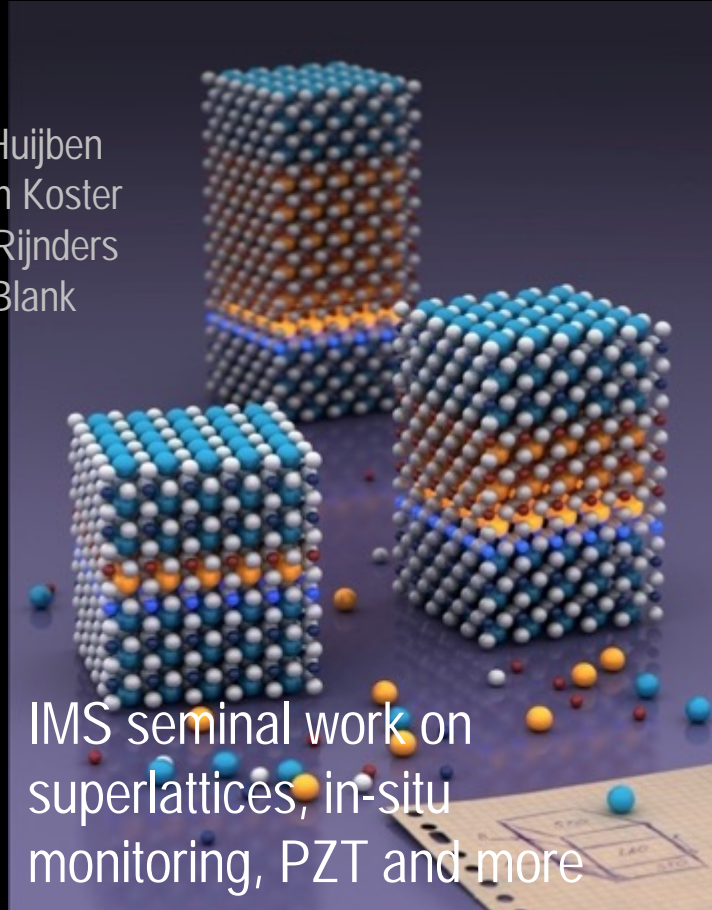


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Complex optoelectronic materials for solar cells with PLD?

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Prof. Dave Blank



IMS seminal work on superlattices, in-situ monitoring, PZT and more

## PLD properties

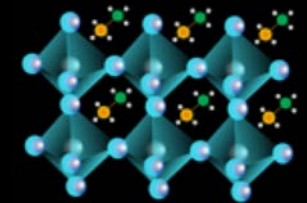
Near stoichiometric transfer of multi-compounds.

Volatility insensitive.

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## Interesting for ..

Halide Perovskites  
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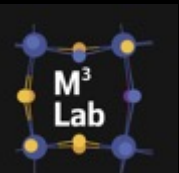


Transparent Conducting Oxides (TCOs)



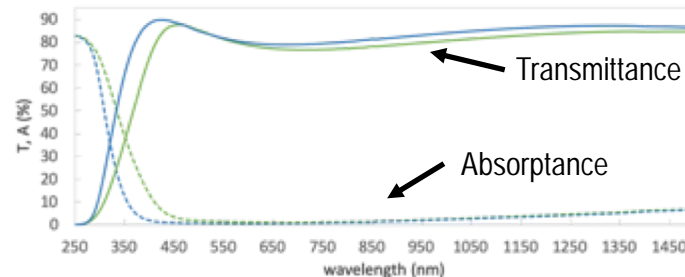
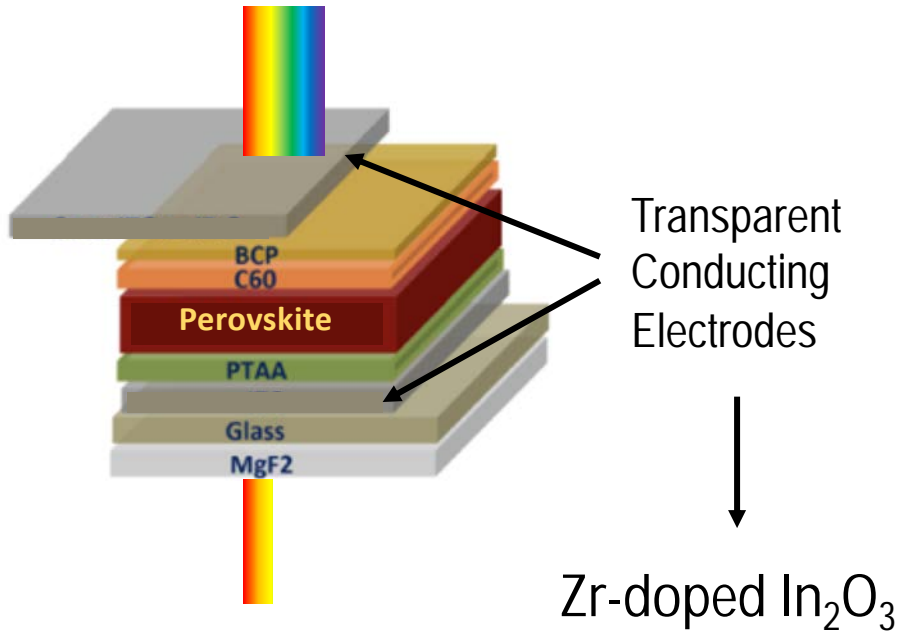
But absolute requirement for PV ...

Scalability (deposition on wafer-size substrates)



# Scalable PLD of Transparent Conducting Oxides for Solar Cells

Zr-doped  $\text{In}_2\text{O}_3$  (IZrO) as Vis-NIR transparent and conductive material



$\sigma = 1500 \, \Omega^{-1}\text{cm}^{-1}$  (amorphous)

$\sigma = 4200 \, \Omega^{-1}\text{cm}^{-1}$  (polycrystalline)



M. Morales-Masis, et al. IEEE JPV, Vol.8, 2018

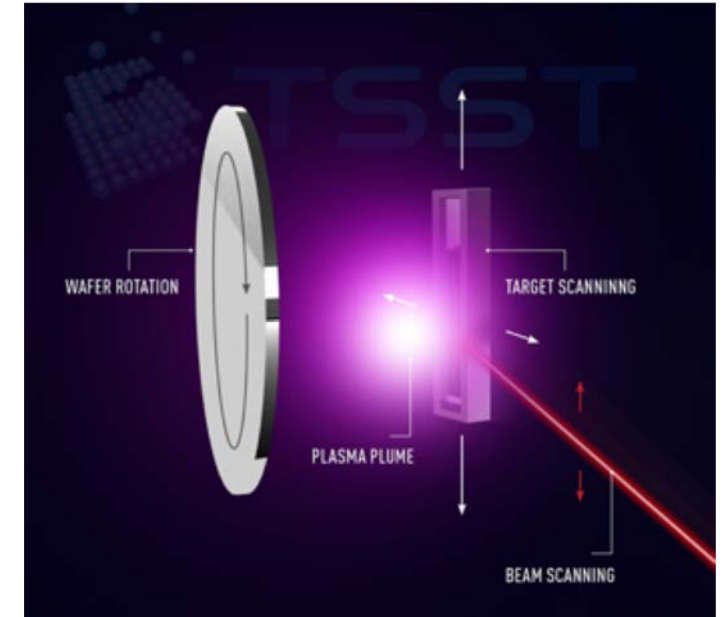
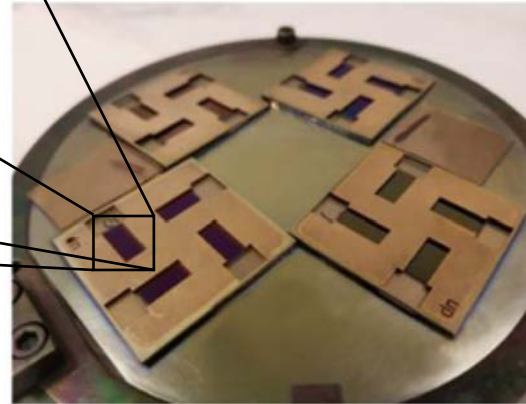
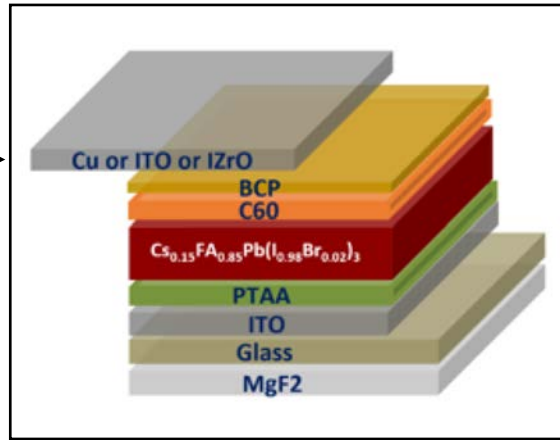
E. Aydin, ...Y. Smirnov, M. Morales-Masis, ...S. De Wolf et al. Adv. Funct. Mater. 2019

MESA+  
INSTITUTE FOR NANOTECHNOLOGY

UNIVERSITY  
OF TWENTE.

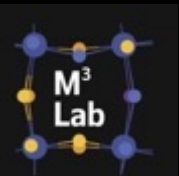
# PLD of IZrO as Rear Electrode for Semitransparent Perovskite Solar Cells

Transparent  
Conducting  
Rear Electrode



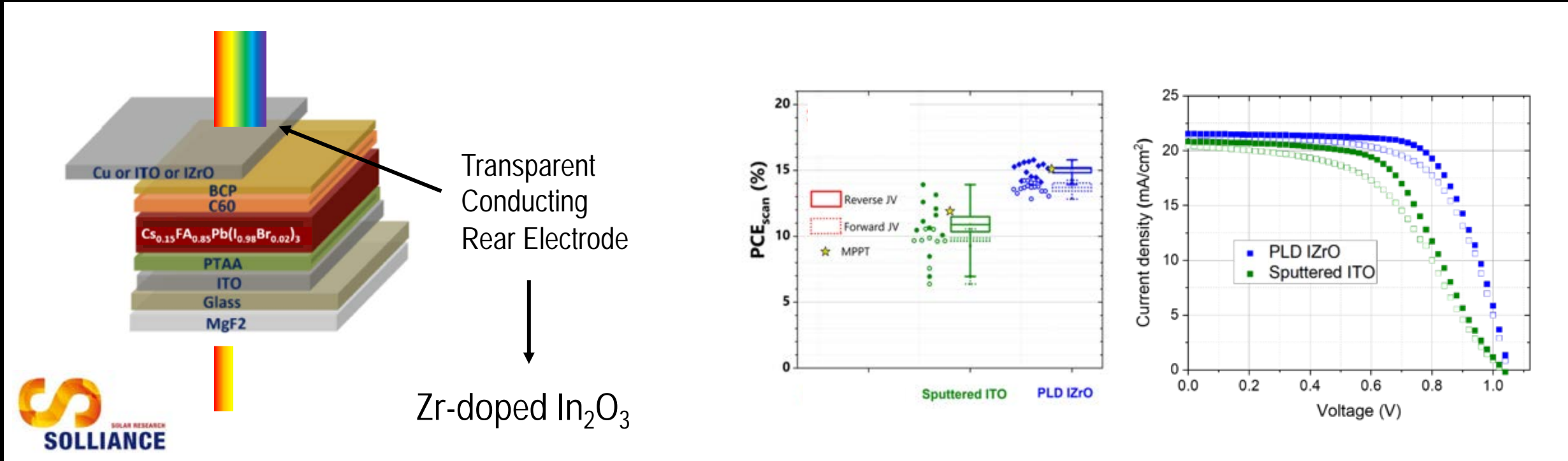
Wafer scale PLD of IZrO:

- 4 substrates (30 x 30 mm) with 4 cells (0.09 cm<sup>2</sup>) per deposition;
- RT deposition (50 Ohm/sq)



Ref.  
Smirnov, Schmengler, Kuik,... Morales-Masis – In-Press, Adv. Mater. Technol. 2020

# PLD of IZrO as Rear Electrode for Semitransparent Perovskite Solar Cells

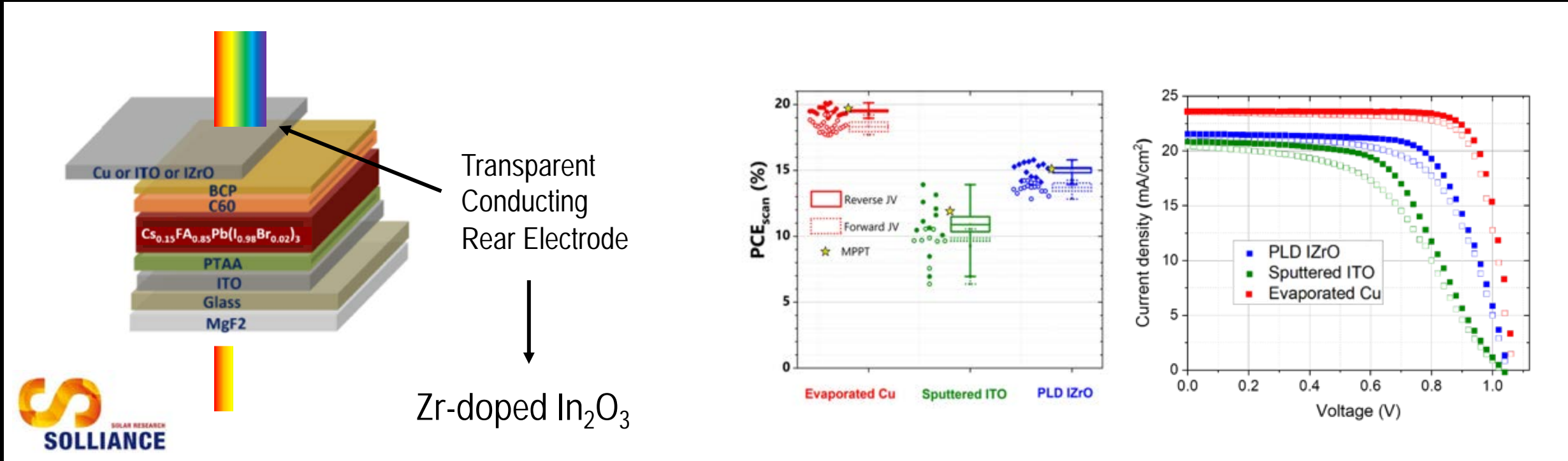


Cells with PLD IZrO:

- No S-shape IV ( $R_{\text{sh}}$  of ITO and IZrO  $\sim 50 \text{ Ohm}/\text{sq}$ )
- Improved FF and  $V_{\text{oc}}$  compared to sputtered ITO



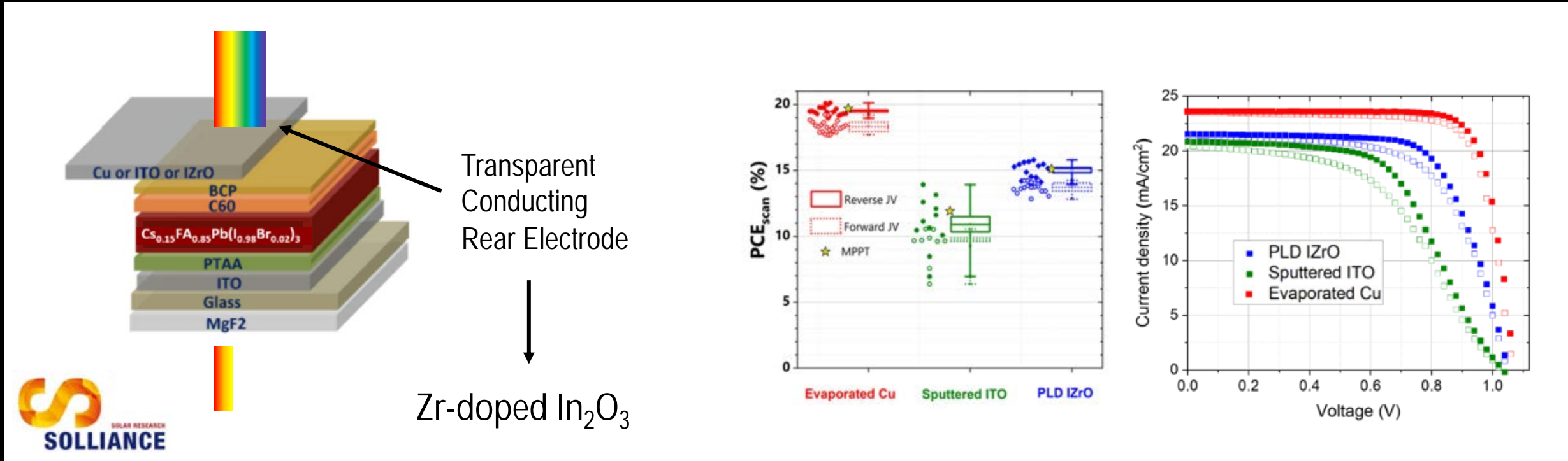
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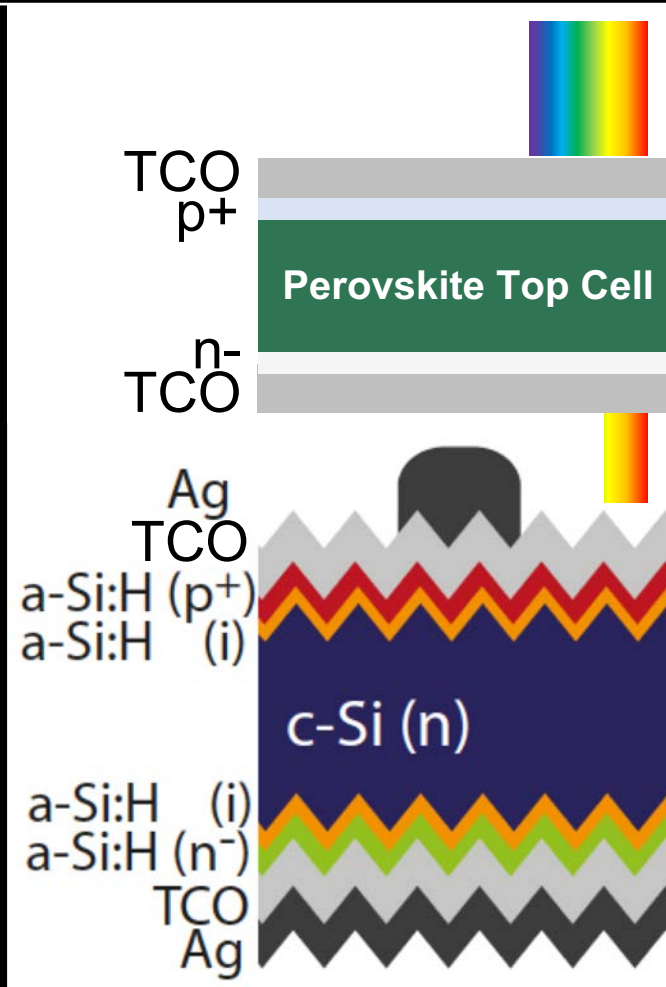
- Cu baseline = 20% (high quality absorber)
- Improved FF and  $V_{\text{oc}}$  compared to sputtered ITO

# Outlook

Tandems: potential for >30% efficiency

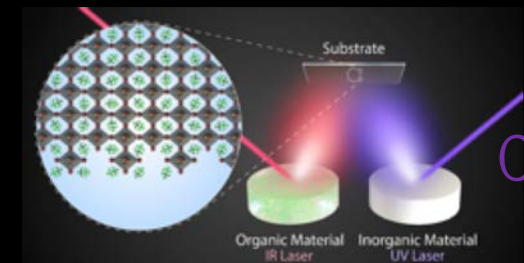
Hybrid perovskite top cell  
Excellent blue-Vis response  
Low subgap absorption

SHJ solar cell  
Excellent red response  
Excellent surface passivation  
( $V_{oc}$  up to 750 mV)

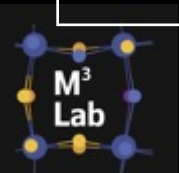


PLD

1. Monolithic integration of halide perovskites on textured silicon bottom cells
2. Soft deposition of the contacts on top of sensitive device layers.
3. Exploration of new stable and Pb-free perovskite compositions



CREATE



# Thank you

Team members, IMS group, NEM cluster and MESA+

## Collaborators



## Funding

