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

**M3 Optoelectronic Materials Group @ IMS**

<table>
<thead>
<tr>
<th>Pierre-Alexis Repecaud</th>
<th>Yury Smirnov</th>
<th>Nathan Rodkey</th>
<th>Tatiana Soto-Montero</th>
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<tr>
<td>Dominic Post</td>
<td>Adem Mirza</td>
<td>Yorick Birkholzer</td>
<td>Wiria Soltanpoor</td>
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<td>Monica Morales-Masis</td>
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Dr. Monica Morales-Masis  
Associate Professor  
M3 Optoelectronic Materials Group @ IMS

4TU Meeting Materials—December 2020
Optoelectronic Thin Film Materials

- Inorganic and Hybrid Halide Perovskites
- Transparent Conducting Materials (n- and p-type)
- Synthesize and fabricate
- Characterize and improve
- Understand and design
- Apply and enable functionalities in devices

Materials

- Physical & chemical deposition techniques
- Solar cells
- Photonics
- Light emitting devices
- Structural and defect analysis
- Material modeling

Structural, electrical, optical property relations

Solar cell image

Material: CH$_3$NH$_3$PbI$_3$

Applications:
- Solar cells
- Light emitting devices

Reviews:
- Soto-Montero T., Soltanpoor W., M.M. 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

IMS seminal work on superlattices, in-situ monitoring, PZT and more
**Pulsed Laser Deposition (PLD)**

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**PLD properties**

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But absolute requirement for PV …

Scalability (deposition on wafer-size substrates)

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**Complex optoelectronic materials for solar cells with PLD?**

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**IMS Lab**
Scalable (wafer-based) Pulsed Laser Deposition

4 inch wafers

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

4 – 12 inch wafers

TCOs for passivated contacts
Featured in PV Magazine
Pulsed Laser Deposition (PLD)

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PLD properties
- Near stoichiometric transfer of multi-compounds.
- Volatility insensitive.
- Low-damage deposition of thin films on sensitive substrates.

Interesting for..
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Complex optoelectronic materials for solar cells with PLD?

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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

$\text{ABX}_3$

$\text{CH}_3\text{NH}_3$, Pb, I
$\text{CH}_5\text{N}_2$, Sn, Br
Cs, Bi, Cl
PLD for halide perovskite growth?

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New Laser-Based Methods

- Single-source
- Dual-laser deposition

Current deposition methods

- **Solution Process**
  - Solubility dependent
  - \( \text{PbI}_3 + \text{DMF} \)
  - \( \text{MAI} + \text{DMF} \)
  - \( \text{MAPbI}_3 \)

- **Thermal Co-Evaporation**
  - Volatility dependent
  - \( \text{MAI} \)
  - \( \text{CsI} \)
  - \( \text{PbI}_2 \)
  - \( \text{PbBr}_2 \)
Pressing challenges of halide perovskite thin film growth

Tatiana Soto-Montoro, Wina Soltanpour, and Monica Morales-Maxia

Single Source PLD of Inorganic Halide Perovskites

Challenging material:
- Oxidation of Sn ($Sn^{2+} - 2e^- \rightarrow Sn^{4+}$)
- Two independent stable polymorphs at RT:
  - Optically active black-phase (orthorhombic B-γ)
  - 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 SiOx
Fused silica
Glass

Al$_2$O$_3$ capping layer

Confirmation of Black-γ-phase CsSnI$_3$ films

Confirmation of Black-$$\gamma$$-phase CsSnI$_3$ films

PLD 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 ($E_U$)

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

$E_U$ - CsSnI$_3$: 12.9 meV
$E_U$ - MAPbI$_3$: 12.5 meV

PLD CsSnI$_3$: Higher absorption coefficient than c-Si

Band Gap of 1.32 eV

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PLD CsSnI$_3$: NIR Photoluminescence

Band Gap of 1.32 eV

Sharp Absorption Edge
High quality film quantified by Urbach energy ($E_U$)

$$\alpha \propto \exp(-\frac{\hbar v}{E_U})$$

- $E_U$ - CsSnI$_3$: 12.9 meV
- $E_U$ – MAPbI$_3$: 12.5 meV

Direct Band Gap
High PL

Other halide perovskite compositions?

$\text{Cs}_2\text{AgBiBr}_6$

CsBr + AgBr + Bi(III)Br -> CsAgBiBr$_6$

Mechanochemical synthesis

Nathan Rodkey, Stan Kaal, et al unpublished results
Solar Cells?

Collaboration with solar cell groups:
**Pulsed Laser Deposition (PLD)**

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Scalable PLD of Transparent Conducting Oxides for Solar Cells

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

σ = 1500 Ω$^{-1}$cm$^{-1}$ (amorphous)
σ = 4200 Ω$^{-1}$cm$^{-1}$ (polycrystalline)

M. Morales-Masis, et al. IEEE JPV, Vol.8, 2018
PLD of IZrO as Rear Electrode for Semitransparent Perovskite Solar Cells

Wafer scale PLD of IZrO:
- 4 substrates (30 x 30 mm) with 4 cells (0.09 cm2) per deposition;
- RT deposition (50 Ohm/sq)

PLD of IZrO as Rear Electrode for Semitransparent Perovskite Solar Cells

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

PLD of IZrO as Rear Electrode for Semitransparent Perovskite Solar Cells

Cells with PLD IZrO:
- No S-shape IV ($R_{sh}$ of ITO and IZrO ~ 50 Ohm/sq)
- Improved FF and $V_{oc}$ compared to sputtered ITO

PLD of IZrO as Rear Electrode for Semitransparent Perovskite Solar Cells

Cells with PLD IZrO:
- Cu baseline = 20% (high quality absorber)
- Improved FF and $V_{oc}$ 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)

**Planned development (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
Thank you

Team members, IMS group, NEM cluster and MESA+

Collaborators

Funding