Organic and Hybrid Thin Film Deposition by Resonant Infrared, Matrix-Assisted Pulsed Laser Evaporation (RIR-MAPLE)

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History with PVD Products, Inc

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PVD Products 17,000 Sq. Foot Facility Located in Wilmington, MA USA
History with PVD Products, Inc
• Motivation for PVD of Organic/Hybrid Thin Films
• RIR-MAPLE Deposition Process
• Multi-component Organic Thin Films
• Hybrid Nanocomposite Thin Films
• Hybrid Organic-Inorganic Perovskite Thin Films
• Future Outlook
Motivation for PVD of Organic/Hybrid Thin Films
Inorganic semiconductors for optoelectronic devices benefit from well-established deposition techniques that enable heterostructure design.
Organic/Hybrid Semiconductors for Optoelectronic Devices

Light Emitting Diodes (LEDs)

Photovoltaic Diodes (or Solar Cells)

Photodiodes (or Photodetectors)
Conjugated Polymers

- P3HT (Wide band gap polymer)
- PCPDTBT (Narrow band gap polymer)

Small Molecules

- PC$_{61}$BM
- PC$_{71}$BM

Thermal evaporation is appropriate for organic small molecules that are thermally robust, but not for macromolecules and polymers that can decompose at elevated temperatures.
Hybrid Nanocomposites

CdSe QDs

2.0 nm  2.5 nm  3.0 nm  3.9 nm  4.2 nm

2.3 nm  2.8 nm  3.3 nm  3.8 nm  4.3 nm  4.8 nm  5.3 nm  5.5 nm
Materials described by ABX$_3$ formula

Most hybrid organic-inorganic perovskite demonstrations use simple, small organic cations that are optically and electrically inert.
Most organic materials are soluble in organic solvents and can be deposited by solution-processed deposition techniques, which are simple methods to deposit organic thin films with low cost and on a large scale.

Solution-processing depositions involve three steps:

a) Preparation of target materials solution.
b) Spread the solution onto the substrate.
c) Evaporation of the solvent and film formation.

Challenges Facing Solution-based Processing

1. Film coverage and uniformity depends on wettability.
   - Good wetting: uniform film
   - Poor wetting: non-uniform film
   Solution: functionalize the substrate surface

2. Multilayer films deposition:
   - Ideal: A two layers of distinct film
   - Reality: A smeared film without distinct interface
   Solution: use a blocking layer in between

3. Blended film deposition:
   a. If components have different solubility characteristics:
      They cannot co-dissolve into a common solvent for deposition.
   b. Even if they can co-dissolve into a common solvent:
      Phase segregation could happen driven by solvent evaporation.


Depositing films in a “dry” state could potentially address these challenges.
Matrix-Assisted Pulsed Laser Evaporation

**PLD**
- **Target:** Solid polymer pellets or powder
- **Laser:** UV-laser
- **Deposition Species:** Atomic, diatomic, molecular, ionic and other low-mass material species

**UV-MAPLE**
- **Target:** Frozen polymer solution
- **Laser:** UV-laser
- **Deposition Species:** Mostly degraded molecular polymer chains, possible atomic species

**RIR-MAPLE**
- **Target:** Frozen polymer solution
- **Laser:** IR-laser
- **Deposition Species:** Less degraded molecular polymer chains

**Emulsion-based RIR-MAPLE**
- **Target:** Frozen polymer emulsion
- **Laser:** IR-laser
- **Deposition Species:** Molecular polymer chains

“Dry” physical vapor deposition

- The laser energy is resonant with hydroxyl bond (O-H) vibrational modes.
- The concentration of hydroxyl bonds in the target can be tuned by using oil-in-water emulsions.


The emulsion target contains:

- **Primary solvent**: dissolves the target organic materials.
- **Secondary solvent**: prevents frozen target sublimation under the vacuum, also increases the hydroxyl bond concentration in the target
- **DI water (containing surfactant)**: provides resonant absorption of laser energy

Oil-in-Water Emulsion
1 : 0.25 : 3 (% vol.)
Solvent : phenol : water
5/10/20 mg/ml polymer

P3HT dissolved in TCB
Adding phenol

P3HT dissolved in TCB, phenol
Adding DI water (w/ surfactant)

Emulsion target

P3HT (hydrophobic)

The emulsion approach decouples the organic-based target material from the laser energy.

Photochemical and structural degradation are minimal in polymer films deposited by RIR-MAPLE.
Emulsion-Based RIR-MAPLE

For lower solubility-in-water, the solvent reduces its surface energy at the water interface by forming smaller emulsified particles (with the help of surfactant).

Chlorinated aromatic solvents

<table>
<thead>
<tr>
<th>Primary Solvent Properties</th>
<th>Chlorobenzene (CB)</th>
<th>1,2 Dichlorobenzene (ODCB)</th>
<th>1,2,4 Trichlorobenzene (TCB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RED</td>
<td>0.89</td>
<td>0.79</td>
<td>0.74</td>
</tr>
<tr>
<td>Vapor Pressure (Kpa), 25°C</td>
<td>1.2</td>
<td>0.16</td>
<td>0.038</td>
</tr>
<tr>
<td>Solubility in water (g/100g)</td>
<td>0.0472</td>
<td>0.0156</td>
<td>0.00488</td>
</tr>
</tbody>
</table>

W Ge, NK Li, RD McCormick, E Lichtenberg, YG Yingling, AD Stiff-Roberts, ACS Appl Mat & Interfaces 8, 19494 (2016).
Polymer films are formed by direct transfer of emulsified particles by laser irradiation of the target.

- While solvent contamination of the substrate is significantly reduced, some solvent is incorporated into the film.
- The surfactant concentration used in the emulsion results in minimal incorporation into the film.
A natural parameter to use as a representation of the plume is the mass flux, $J(x,y)$, as a function of the axis normal to the target surface ($y$-axis) and the axis parallel to the target surface ($x$-axis).
Complex organic cations can be difficult to incorporate into hybrid perovskite thin films.

Benefits of RIR-MAPLE for Hybrid Perovskites:

1. Technique offers control of film composition and thickness.
2. Gentle deposition is less likely to induce degradation of organic components.
3. Solubility problems can be mitigated by using low concentration precursor solutions (~ 10 mM or less).
4. Enables perovskite heterostructures of films featuring similar solubility.

RIR-MAPLE Growth of Hybrid Perovskites

Target Recipe
1:1 DMSO to MEG
22 mM Concentration
Equimolar
Organic:Inorganic

Solvent Function

<table>
<thead>
<tr>
<th>Solvent Function</th>
<th>Emulsion-Based RIR-MAPLE</th>
<th>Hybrid Perovskite RIR-MAPLE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrix solvent</td>
<td>Water (with surfactant, SDS)</td>
<td>Monoethylene glycol (MEG)</td>
</tr>
<tr>
<td>Primary solvent</td>
<td>Non-polar solvent</td>
<td>Dimethyl sulfoxide (DMSO)</td>
</tr>
<tr>
<td>Low vapor pressure solvent</td>
<td>Phenol</td>
<td>MEG / DMSO</td>
</tr>
</tbody>
</table>

RIR-MAPLE Deposition of Multi-component Films

**Pie**

- P3HT or PCPDTBT emulsion
- PCBM or PC71BM emulsion

**Donut**

- Top View of MAPLE Target

**Simultaneous Deposition**

**Sequential Deposition**

**Layered Deposition**

**FIG. 1**
Advantages of sequential deposition:
- Provides co-deposition, but different solvents chosen to optimize solubility and film morphology of each component
- Sequential deposition reduces the impact of solubility characteristics of one component on the deposition of another component.
Multi-component Organic Thin Films
Multi-layer Deposition

<table>
<thead>
<tr>
<th>Material</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT</td>
<td>140.9</td>
</tr>
<tr>
<td>PMMA</td>
<td>189.2</td>
</tr>
<tr>
<td>P3HT</td>
<td>140.9</td>
</tr>
<tr>
<td>PMMA</td>
<td>189.2</td>
</tr>
<tr>
<td>P3HT</td>
<td>140.9</td>
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<tr>
<td>PMMA</td>
<td>189.2</td>
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<tr>
<td>P3HT</td>
<td>140.9</td>
</tr>
<tr>
<td>PMMA</td>
<td>189.2</td>
</tr>
<tr>
<td>Glass Substrate</td>
<td></td>
</tr>
</tbody>
</table>

**16-layer polymer DBR demonstrated!**

PMMA: 8nm RMS roughness, $n=1.49$

P3HT: 13nm RMS roughness, $n=2.0$

Polymer Distributed Bragg Reflector (DBR)

- **Simulated Design**
- **Fabricated Structure**
- **Re-simulated Structure**

Collaborator:
Weidong Zhou,
UT-Arlington

**RIR-MAPLE** can create layered heterostructures of similar-solubility materials.

- Interfaces between layers are well-defined.

Nanoscale Blending of Multiple Components

The deposition of a bulk, multi-functional film that combines two or more disparate properties depends on the ability to deposit the film components with nanoscale domain sizes.

**Antimicrobial and Fouling-Release Films**

- **PPE** [poly(2,5-dioctylphenylene-1,4-ethynylene)]:
  1(CB):0.5(Phenol):3(0.001wt% SDS DI water)
- **Silane Terminated PNIPAAm** [poly(N-isopropylacrylamide)]:
  30% methanol/70% water

**QAS**:
3-(trimethoxysilyl)-propyldimethyloctadecyl ammonium chloride

**PNIPAAm**

Create porous PS film that performs as an effective medium to visible light (400-750 nm). Requires nanoscale pores < 0.1\(\lambda\).

SEM: GRIN Films Before and After UV & Acid Wash

2 prototype structures with linear gradient RI profile. Total thickness: 1 \(\mu\)m
- GRIN #1: 10 nm constant-ratio slices: 100 slices
- GRIN #2: 20 nm constant-ratio slices: 50 slices


Collaborator: Weidong Zhou, UT-Arlington
Hybrid Nanocomposite Thin Films
Minimal Influence of Solvent

Surface Coverage: 45.30%

![Graph showing surface coverage vs. deposition time for different concentrations of 3 mg/ml, 1.5 mg/ml, and 0.75 mg/ml.]

Scotch Tape  Glass  Aluminum Foil  Paper  Silicon  Parafilm

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The morphology of RIR-MAPLE blended films is independent of the primary solvent used.
The morphology of RIR-MAPLE blended films is independent of the primary solvent used.

Hybrid Organic-Inorganic Perovskite Thin Films
Hybrid Perovskite Solar Cell Deposited by RIR-MAPLE

RIR-MAPLE-deposited MAPbI₃ films on FTO/NiOₓ substrates

Obtained 12.2% PCE (stabilized)

Collaborator: David Mitzi, Duke

Halide selection for bandgap control

Organic cation selection for targeted functionality

$X = \text{Cl, Br, I}$

$n = 1, 2, 3, 4, 5$


Challenges of Oligothiophene-based Perovskite Synthesis:

1. Difficult to dissolve oligothiophenes in solvents commonly used for lead halides.
2. Solvents appropriate for both oligothiophenes and lead halides often lead to problematic substrate wetting.
3. Single crystals of \((\text{AE4T})\text{PbI}_4\) have only recently been reported \([\text{C. Liu, et. al., Phys. Rev. Lett. 121, 146401 (2018)}]\); Single crystals of \((\text{AE4T})\text{PbCl}_4\) have not been reported.
4. SSTA used to synthesize oligothiophene-based perovskite thin films, \((\text{AE4T})\text{PbX}_4\); in general, it can be difficult to control film thickness and composition using vapor-phase growth of hybrid organic-inorganic perovskites.

*Single Source Thermal Ablation (SSTA)*

<table>
<thead>
<tr>
<th></th>
<th>AE2T</th>
<th>AE3T</th>
<th>AE4T</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>Type IIB</td>
<td>Type IIB</td>
<td><strong>Quasi-Type IA</strong> *</td>
</tr>
<tr>
<td>Br</td>
<td>Quasi-Type IB</td>
<td>Type IIB</td>
<td>Type IIB *</td>
</tr>
<tr>
<td>I</td>
<td>Type IB</td>
<td>Quasi-Type IB</td>
<td>Type IIB *</td>
</tr>
</tbody>
</table>

**Collaborators:**
Volker Blum & David Mitzi, Duke
RIR-MAPLE Growth of Hybrid Perovskites with Complex Organic Molecules

Able to confirm predictions of tunable quantum well band offset and alignment


Collaborators:
Volker Blum & David Mitzi, Duke
RIR-MAPLE can serve as an enabling, platform growth technology!

1. provides **nanoscale blending** to enable bulk effective media, regardless of miscibility

2. deposits **multi-layer films** regardless of solubility

3. controls **film morphology** (at the surface and within the film bulk)

4. applicable to a **wide range of organic and hybrid thin-film materials**

5. compatible with a **variety of substrates**
Enabling Technology for Multi-component Organic/Hybrid Thin Films

**Scale-up Fabrication**

- **Materials synthesis**  
  (high volume, sustainable)
- **Thin-film processing**  
  (high throughput, large area, high yield)
- **Life-cycle assessment**  
  (from raw materials to waste products)

**PVD Products PLD-4000/5000**

- In-situ monitoring and feedback
- Standardized preparation of frozen emulsion targets
- Custom raster patterns
- Multiple laser beams for large area, uniform deposition
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Q&A

For questions or advice:

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Thank you!

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