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

Adrienne D. Stiff-Roberts
Jeffrey N. Vinik Professor
Department of Electrical and Computer Engineering
University Program in Materials Science and Engineering

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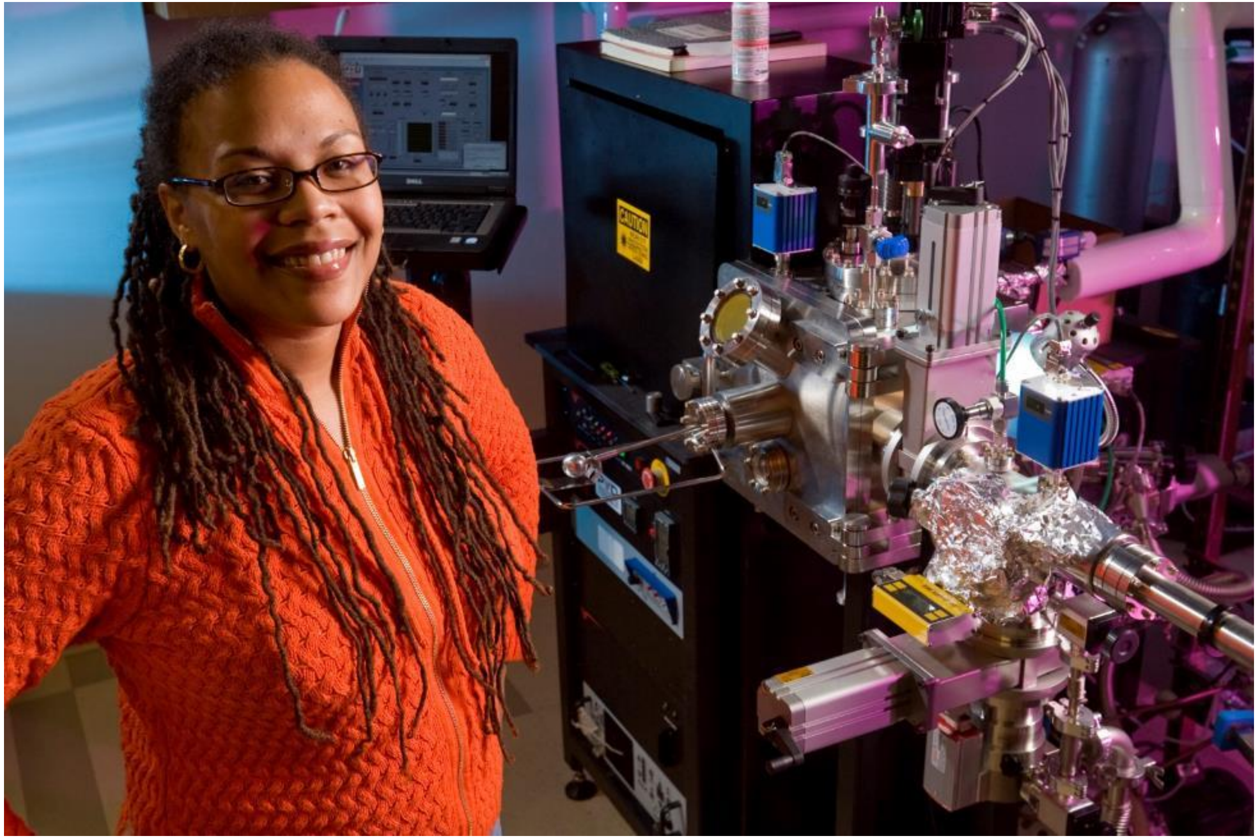
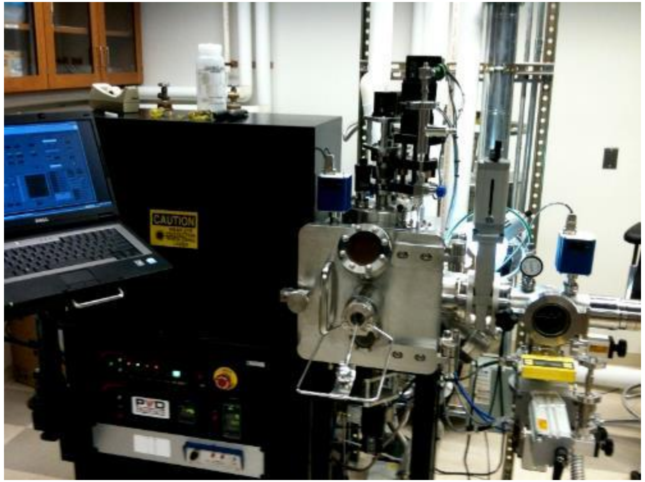
PVD PRODUCTS

Dr. James A. Greer
President
PVD Products, Inc

PVD Products 17,000 Sq. Foot Facility Located in Wilmington, MA USA

History with PVD Products, Inc





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Outline

- 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

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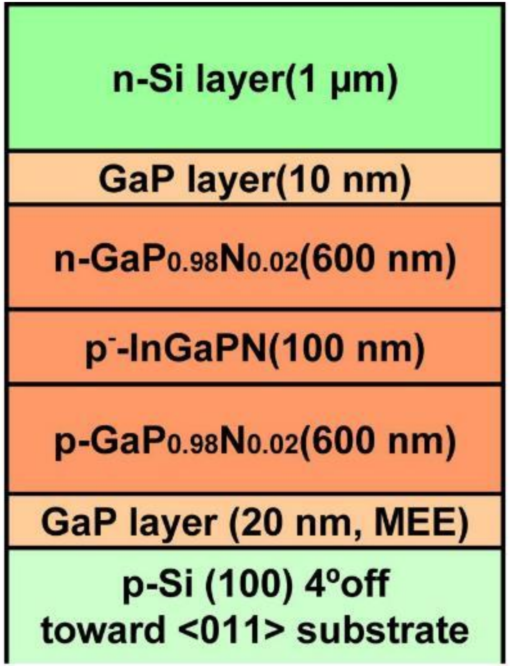
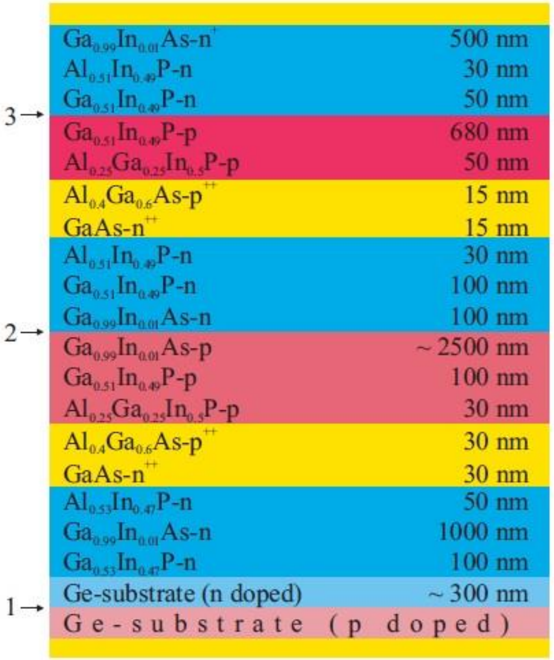
Light Emitting Diode



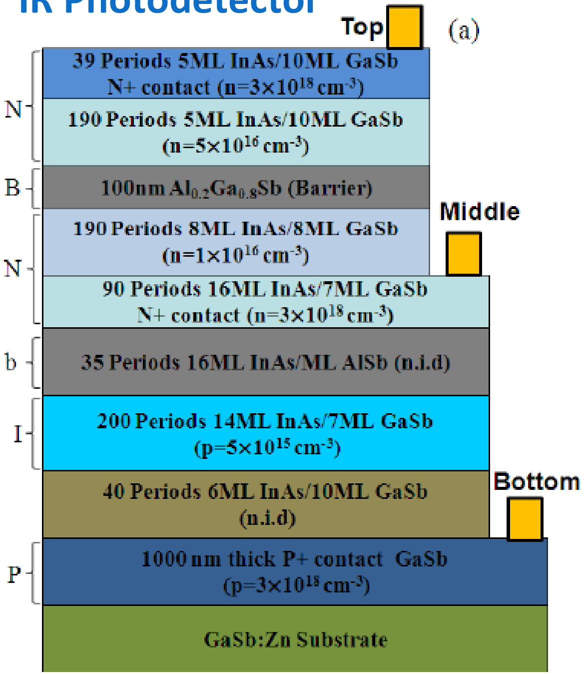
https://spie.org/news/0914-monolithic-integration-of-light-emitting-devices-and-silicon-transistors?SSO=1

Multi-junction Solar Cell



https://www.azonano.com/article.aspx?ArticleID=3052

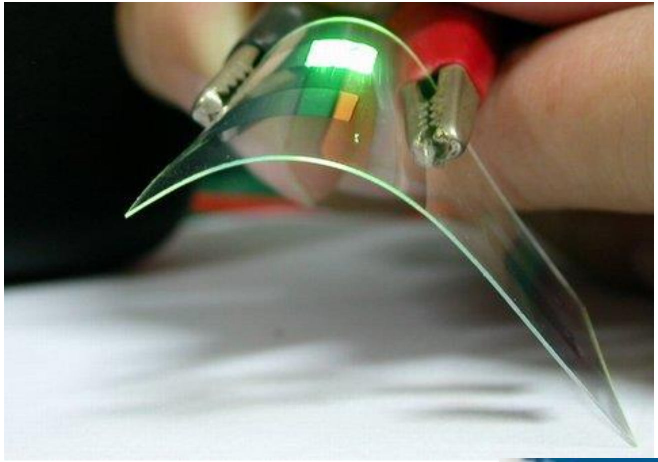
Strained-Layer Superlattice IR Photodetector



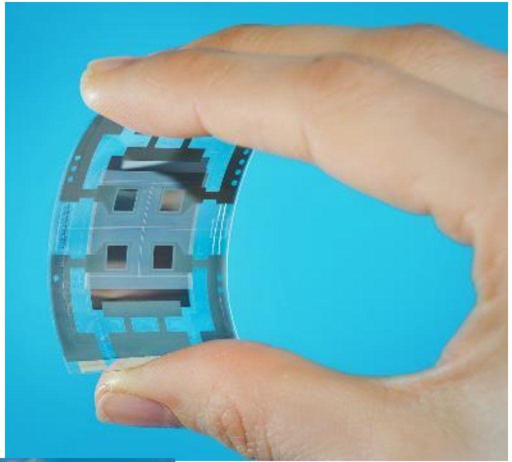
https://www.researchgate.net/publication/241425946_Performance_of_longwave_infrared_InAsGaSb_strained_layer_superlattice_detectors_for_the_space_applications

Inorganic optoelectronic devices benefit from well-established deposition techniques that enable heterostructure design.

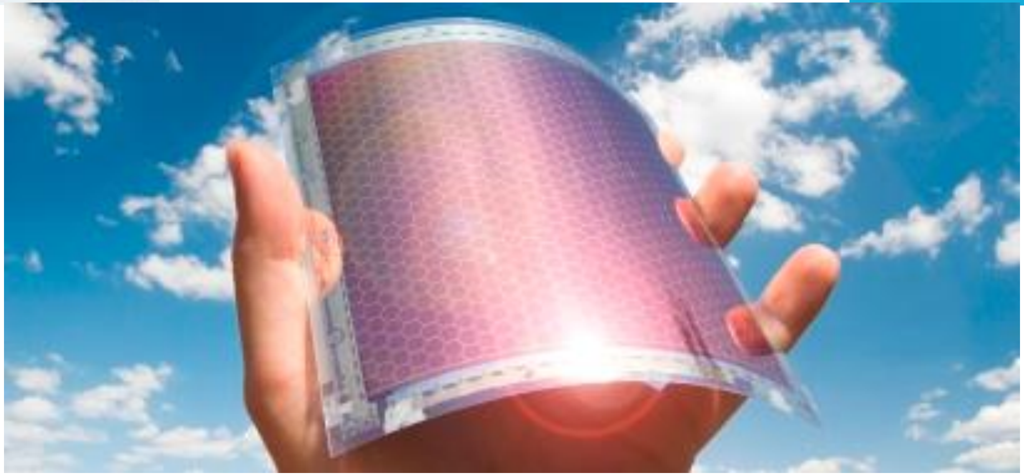
Light Emitting Diodes (LEDs)



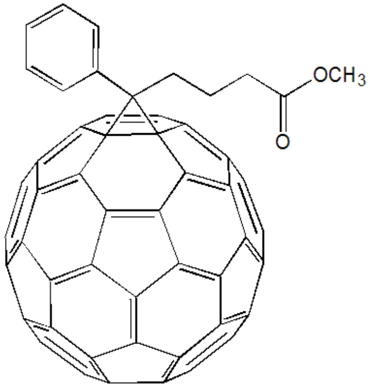
Photodiodes (or Photodetectors)



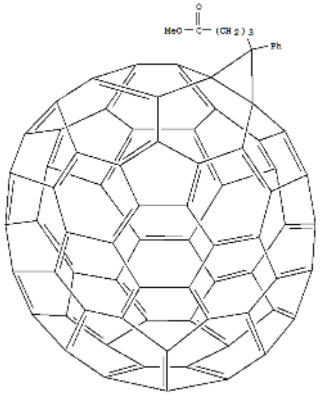
Photovoltaic Diodes (or Solar Cells)



Organic Semiconductors



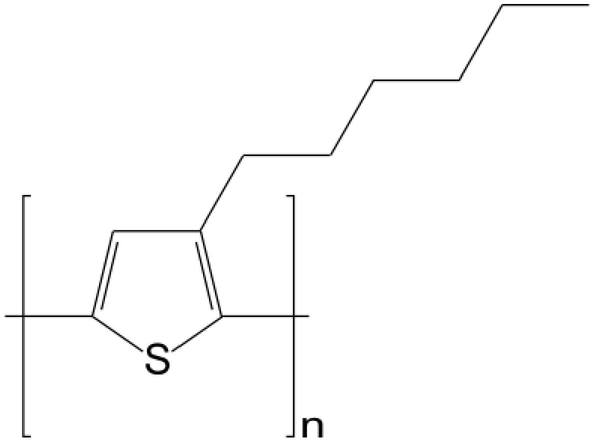
$PC_{61}BM$



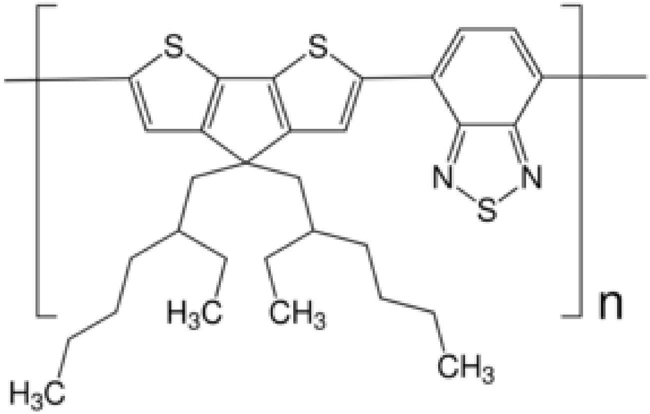
$PC_{71}BM$

Small Molecules

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



P3HT (Wide band gap polymer)



PCPDTBT (Narrow band gap polymer)

Conjugated Polymers

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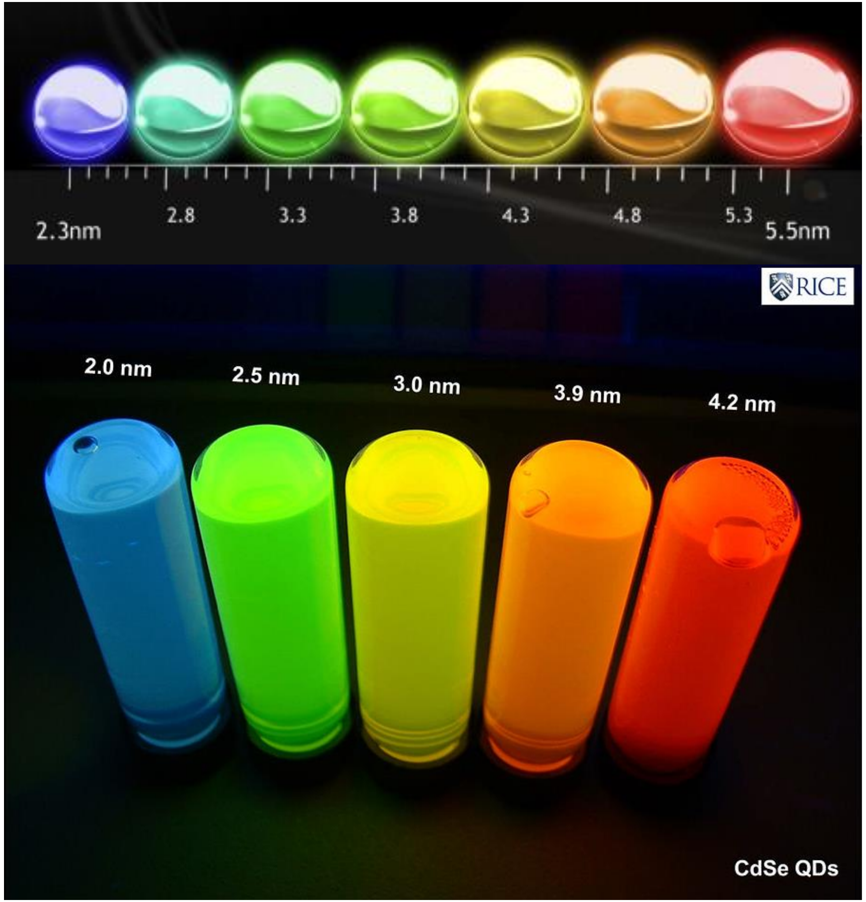
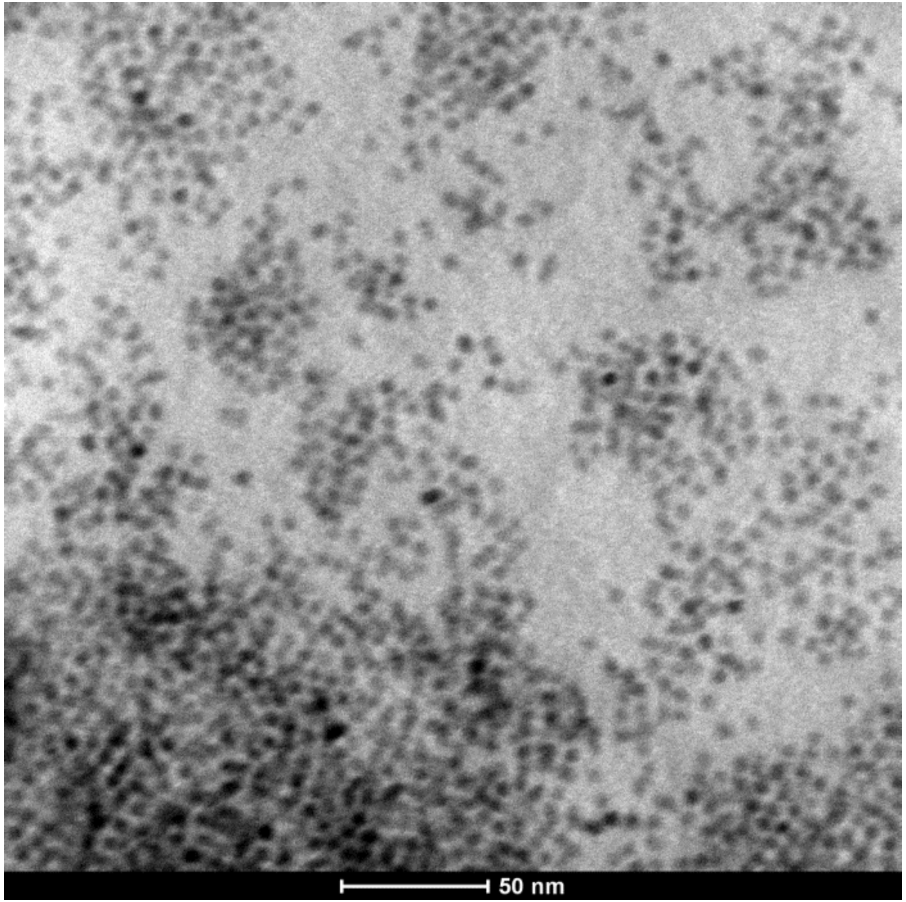
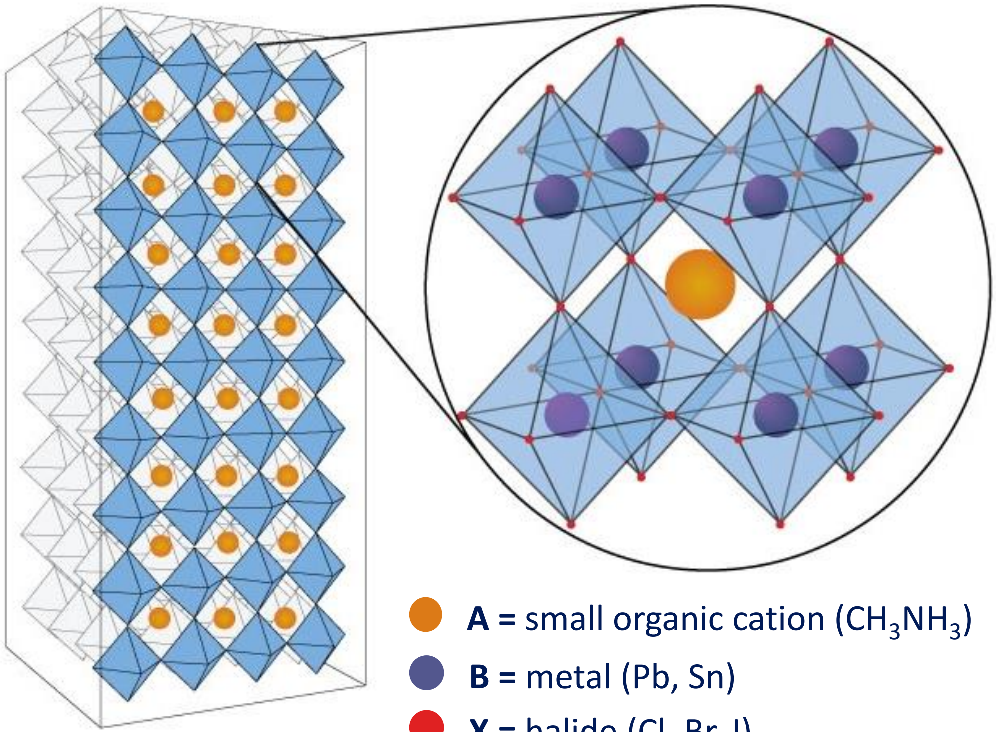

2.3nm
2.8
3.3
3.8
4.3
4.8
5.3
5.5nm
RICE
2.0 nm
2.5 nm
3.0 nm
3.9 nm
4.2 nm
CdSe QDs

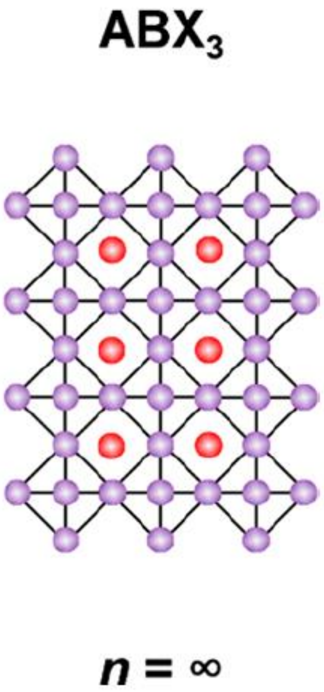

50 nm

Hybrid Organic-Inorganic Perovskites



www.sciencenews.org

- **A** = small organic cation (CH_3NH_3)
- **B** = metal (Pb, Sn)
- **X** = halide (Cl, Br, I)

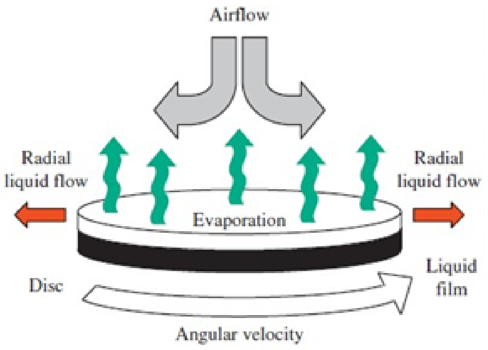


W. A. Dunlap-Shohl, et. al., *Chem. Rev.*, **119**, 3193 (2019).

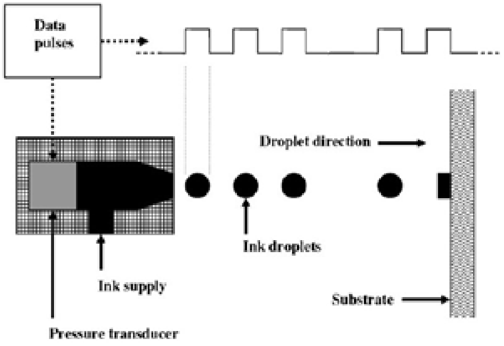
Materials described by ABX_3 formula

Most hybrid organic-inorganic perovskite demonstrations use simple, small organic cations that are optically and electrically inert.

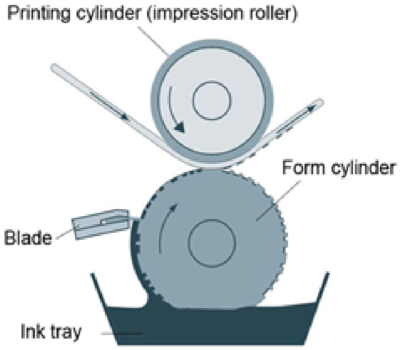
Most organic materials are soluble in organic solvents and can be deposited by solution-processed deposition techniques, which are simple methods to deposit organic thin films with low cost and on a large scale.



Spin-casting



Ink jet printing



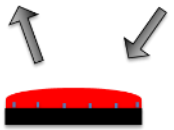
Gravure printing

Krebs, F.C., *Solar Energy Materials and Solar Cells*, **93**, 394 (2009).

Solution-processed depositions involve three steps:

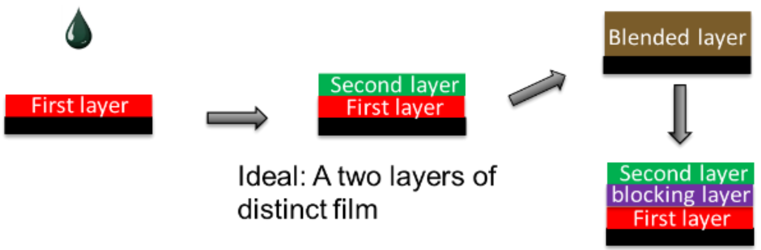
a) Preparation of target materials solution.
b) Spread the solution onto the substrate.
c) Evaporation of the solvent and film formation.

1. Film coverage and uniformity depends on wettability.



Solution: functionalize the substrate surface

2. Multilayer films deposition:



Reality: A smeared film without distinct interface

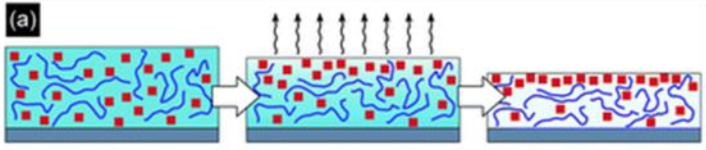
Ideal: A two layers of distinct film

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.



Smith, J., et al., Journal of Materials Chemistry, 2010. 20(13): p. 2562-2574.

Depositing films in a "dry" state could potentially address these challenges.

RIR-MAPLE Deposition Process

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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

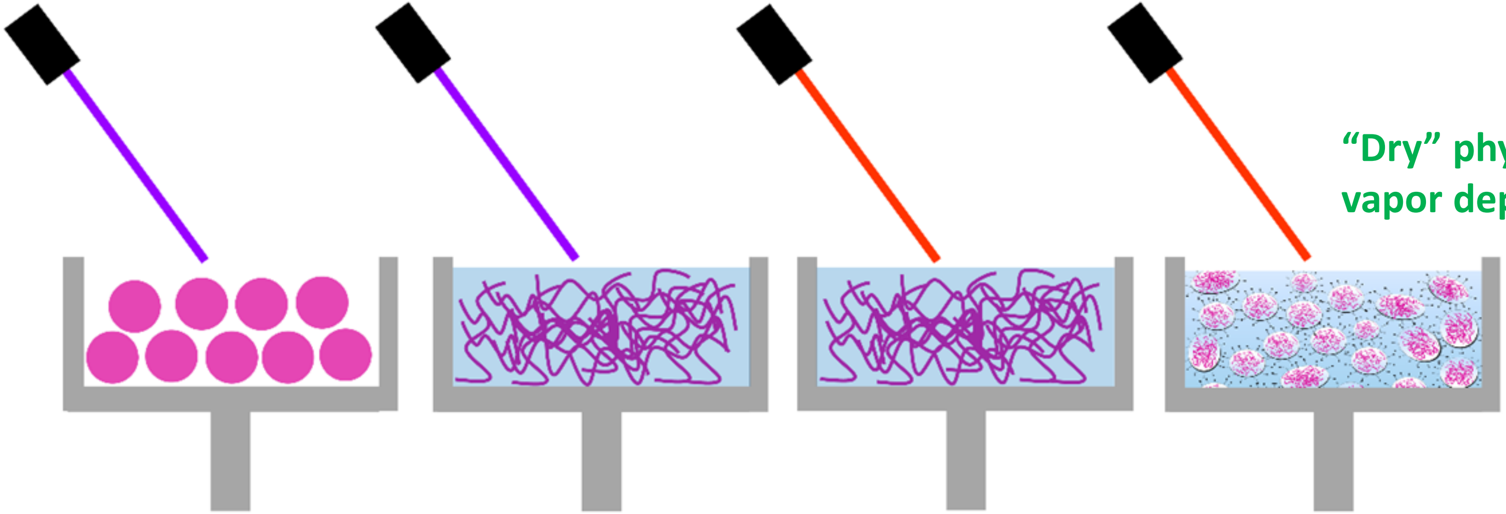
Deposition Species:
Less degraded molecular polymer chains

Emulsion-based RIR-MAPLE

Target:
Frozen polymer emulsion

Laser:
IR-laser

Deposition Species:
molecular polymer chains

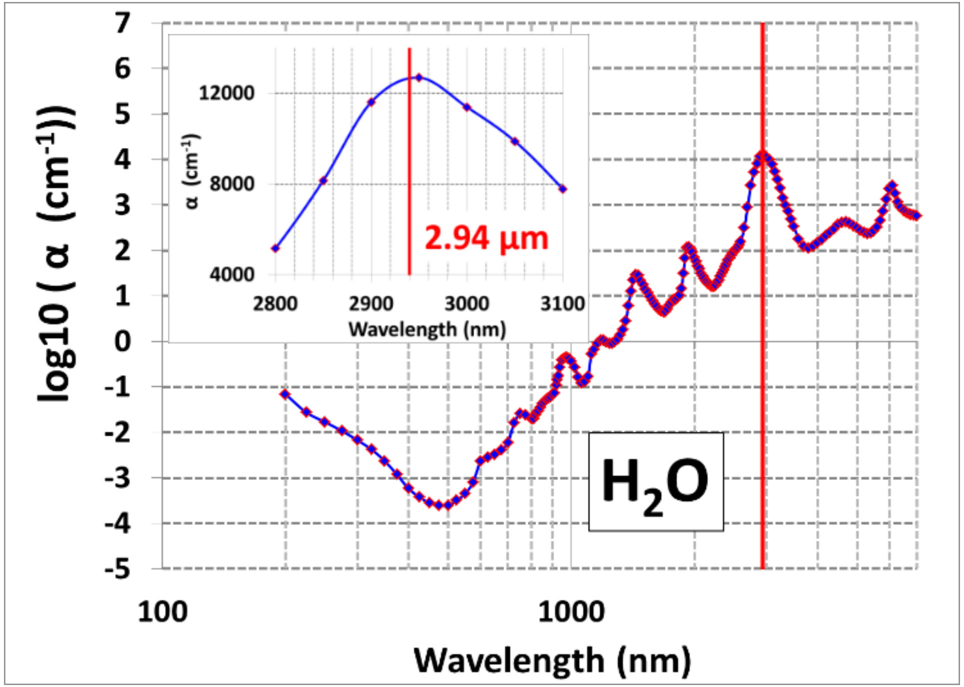


"Dry" physical vapor deposition

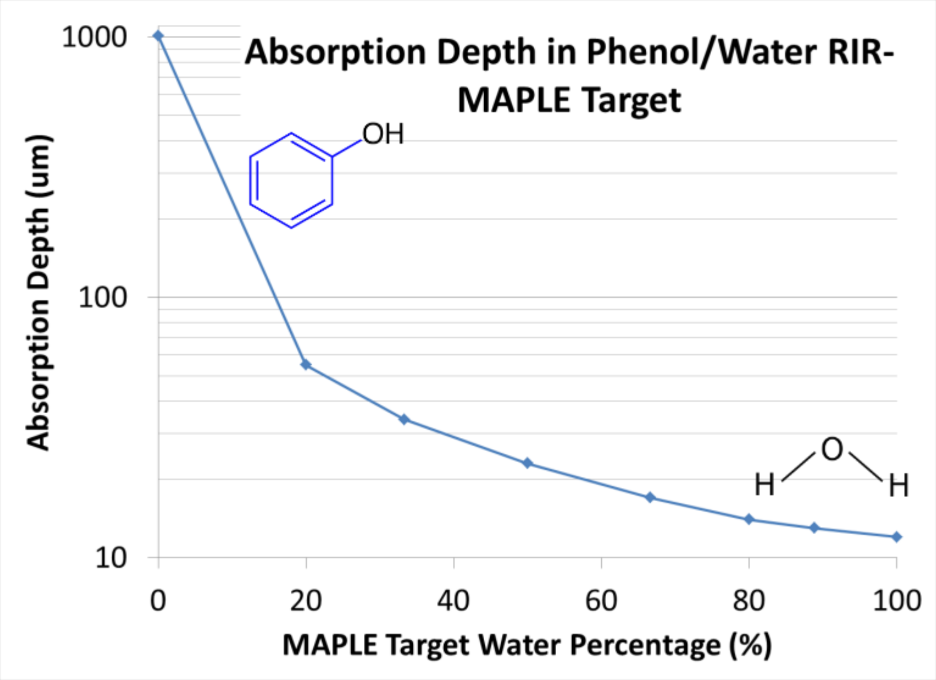
A. D. Stiff-Roberts and W. Ge, *Appl. Phys. Rev.*, **4**, 041303 (2017).

Resonant Absorption of Infrared Laser

- 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.



G. M. Hale and M. R. Querry, *Appl. Opt.*, **12**, 555 (1973).



R. Pate and A. D. Stiff-Roberts, *Chem. Phys. Lett.*, **477**, 406 (2009).

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RIR-MAPLE Emulsion Targets

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

Polymer target composed of multi-phase emulsions:

- Polymer
- Primary Solvent
- Phenol
- Water
- Surfactant

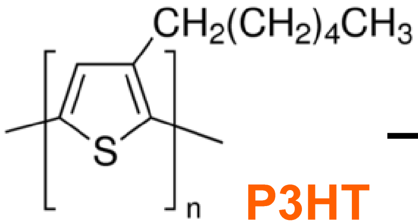
P3HT dissolved in TCB

Adding phenol

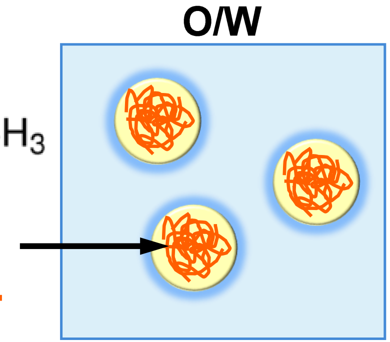
P3HT dissolved in TCB, phenol

Adding DI water (w/ surfactant)

Emulsion target



P3HT (hydrophobic)



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

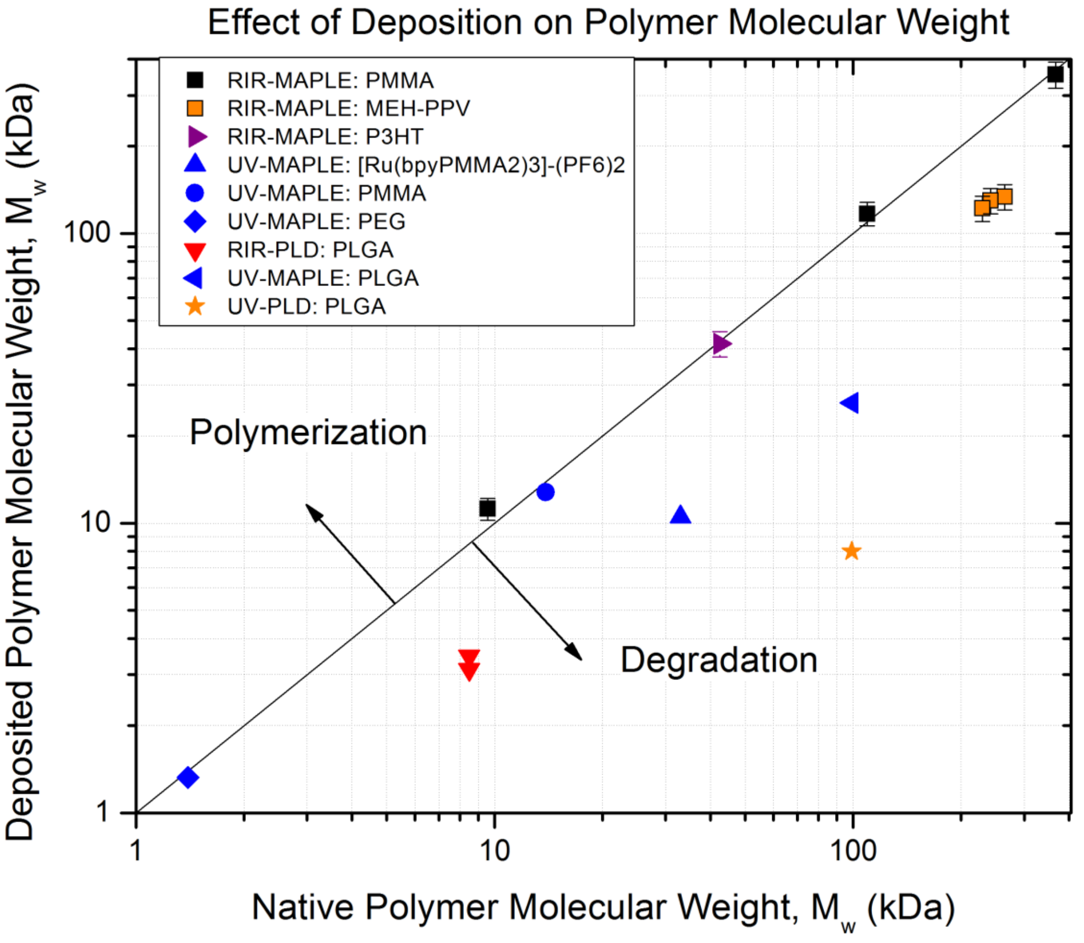
The emulsion approach decouples the organic-based target material from the laser energy.

R. Pate and A. D. Stiff-Roberts, *Chemical Physics Letters*, **477**, 406 (2009).

Emulsion-Based RIR-MAPLE

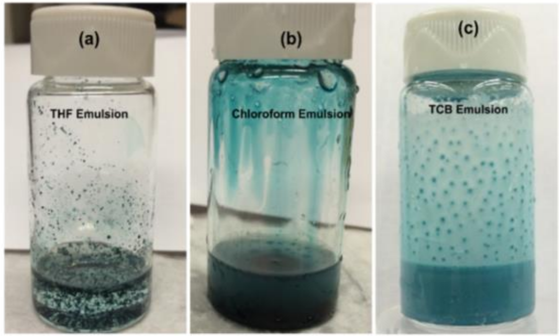
- ▲ Fitz-Gerald et al., Appl. Phys. A, 80, 1109-1113 (2005)
- ● Sellinger et al., Thin Solid Films, 516, 6033-6040 (2008)
- ◆ Bubb et al., J. Appl. Phys., 91, 2055-2058 (2002)
- ▼ Bubb et al., Appl. Phys. A, 123-125 (2002)
- ◀ and ★ Mercado et al., Appl. Phys. A, 81, 591-599 (2004)

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



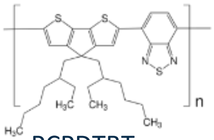
R. McCormick, J. Lenhardt, and A. D. Stiff-Roberts, *Polymers*, **4**, 341 (2012).

Emulsion-Based RIR-MAPLE



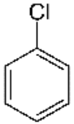
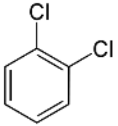
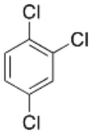
(a)	(b)	(c)
Solubility-in-water: 30 g/100g RED: 0.77	Solubility-in-water: 0.792g/100g RED:0.61	Solubility-in-water: 0.00488 g/100g RED:0.74

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).



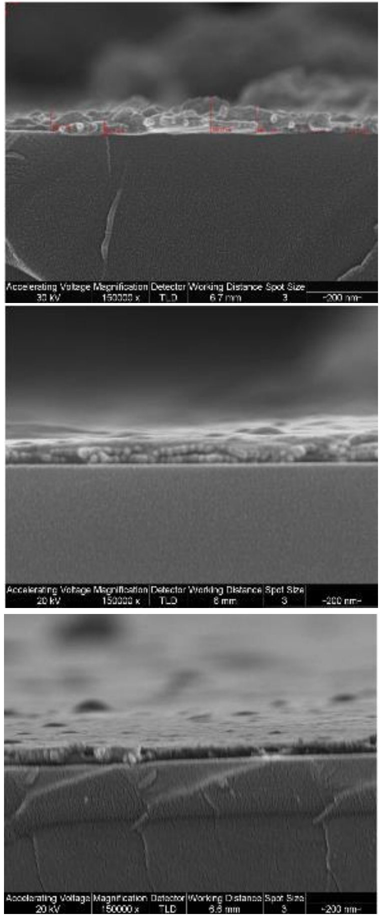
PCPDTBT

Chlorinated aromatic solvents

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

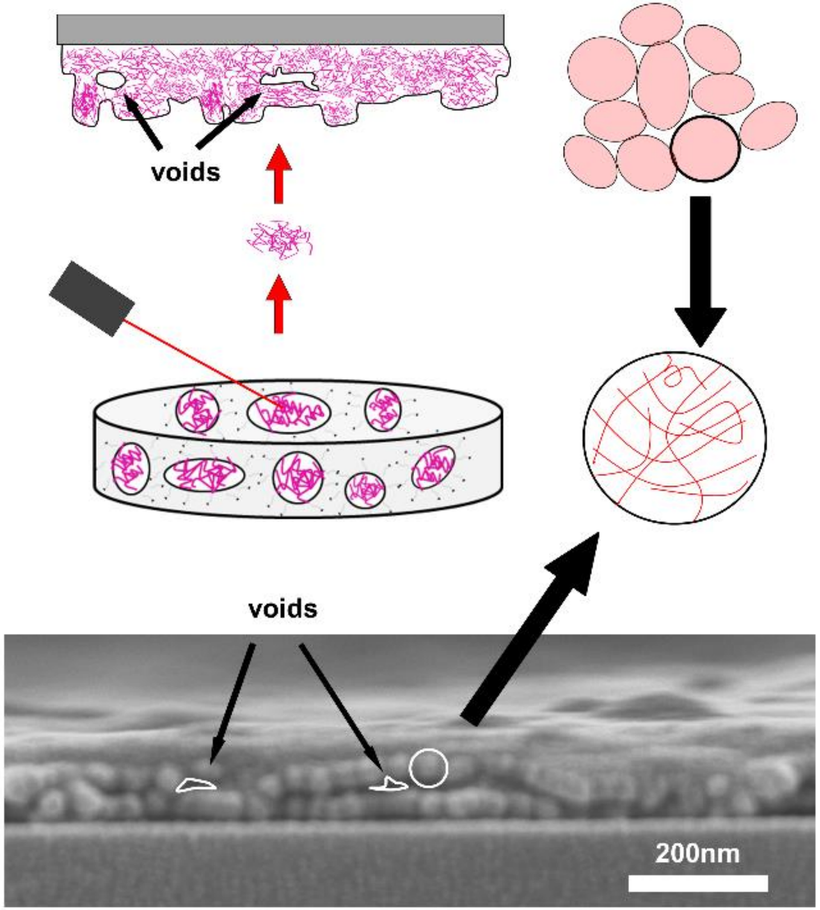
Decreasing vapor pressure and solubility-in-water



Decreasing vapor pressure and solubility-in-water

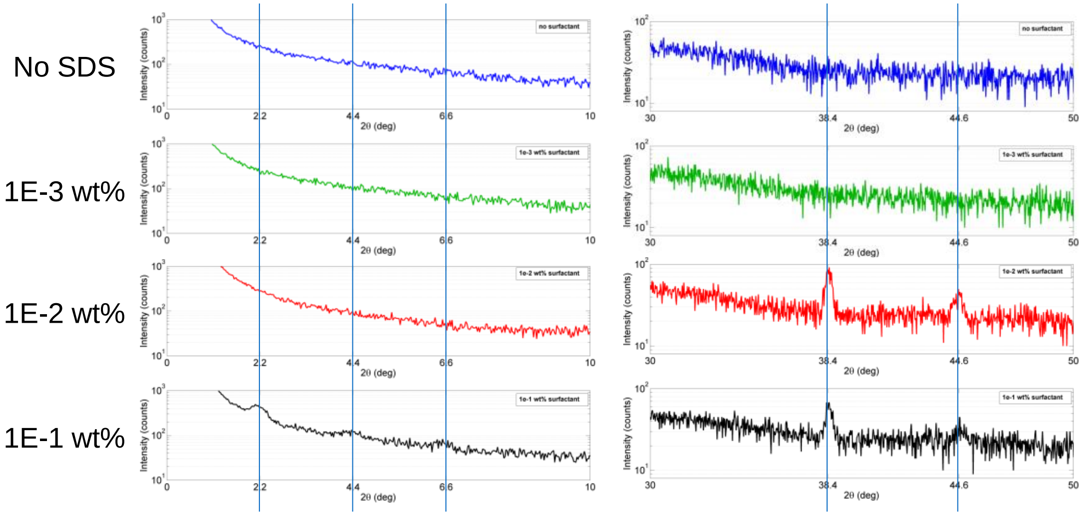
W Ge, NK Li, RD McCormick, E Lichtenberg, YG Yingling, AD Stiff-Roberts, *ACS Appl Mat & Interfaces* **8**, 19494 (2016).

Emulsion-Based RIR-MAPLE



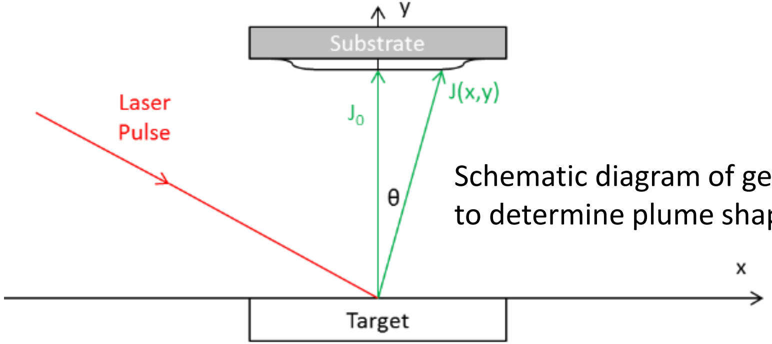
Polymer films are formed by direct transfer of emulsified particles by laser irradiation of the target.

- 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.



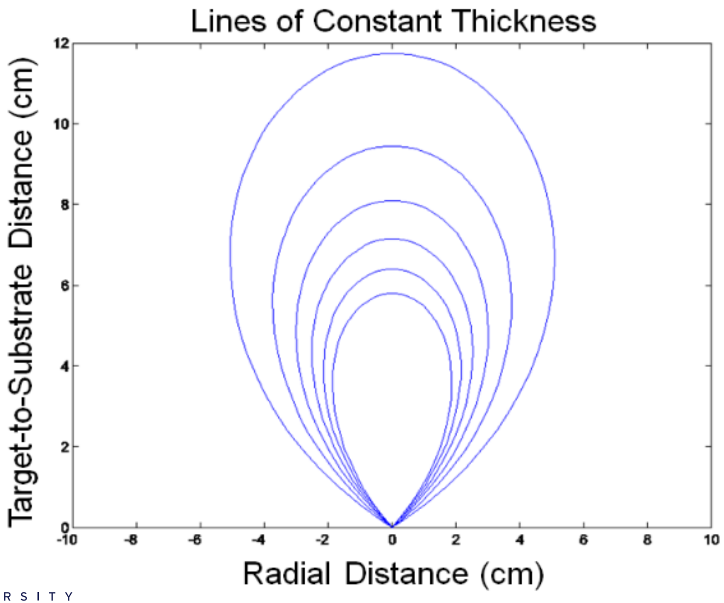
A. D. Stiff-Roberts, R. D. McCormick, and W. Y. Ge, *Proceedings of SPIE*, **9350**, 935007 (2015).
W Ge, NK Li, RD McCormick, E Lichtenberg, YG Yingling, AD Stiff-Roberts, *ACS Appl Mat & Interfaces* **8**, 19494 (2016).

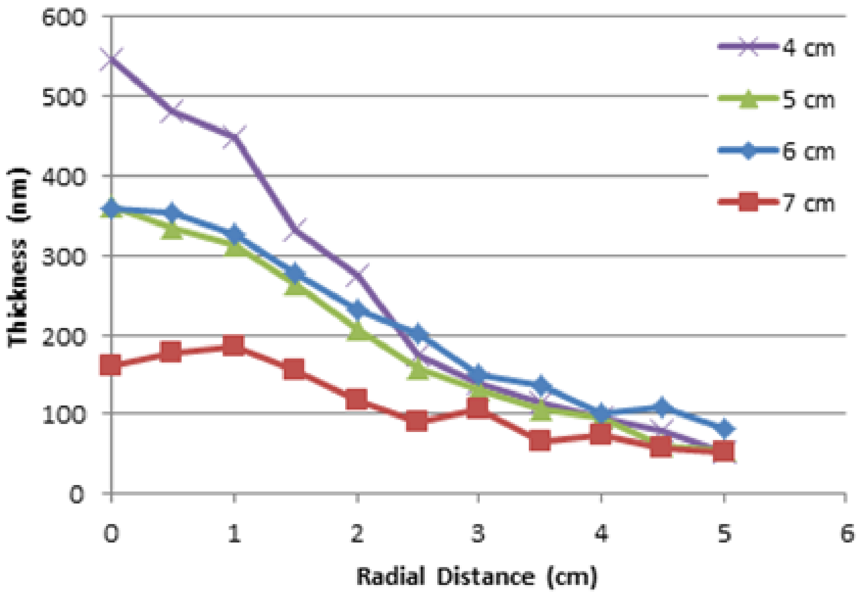
Emulsion-Based RIR-MAPLE



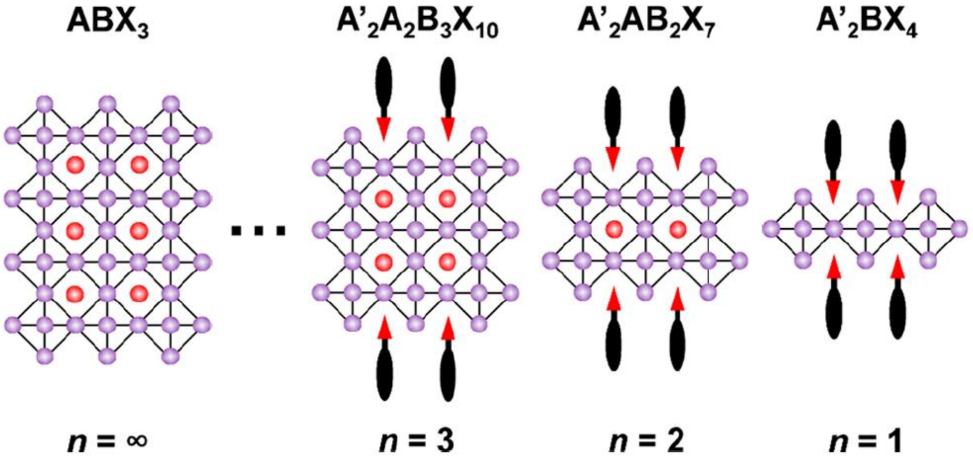
Schematic diagram of geometry to determine plume shape.

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).





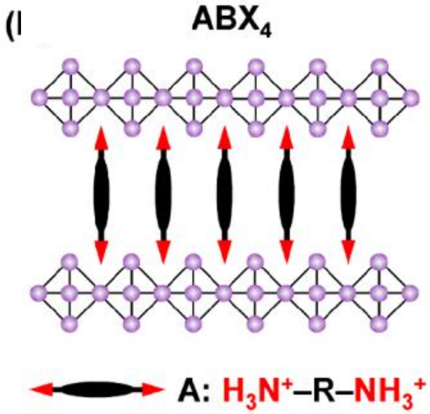
RIR-MAPLE Growth of Hybrid Perovskites



Complex organic cations can be difficult to incorporate into hybrid perovskite thin films.

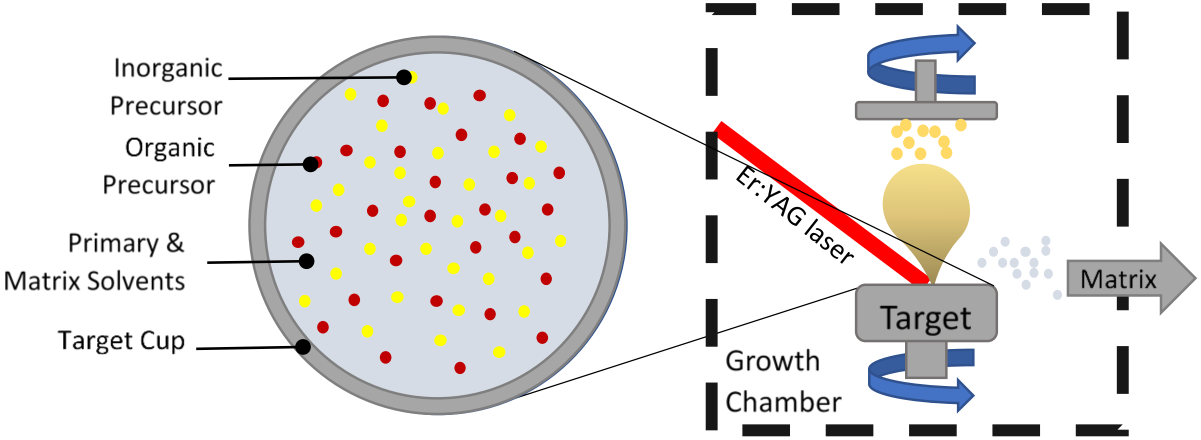
Benefits of RIR-MAPLE for Hybrid Perovskites:

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.



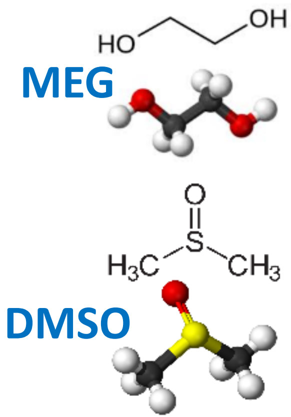
W. A. Dunlap-Shohl, et. al., *Chem. Rev.*, **119**, 3193 (2019).

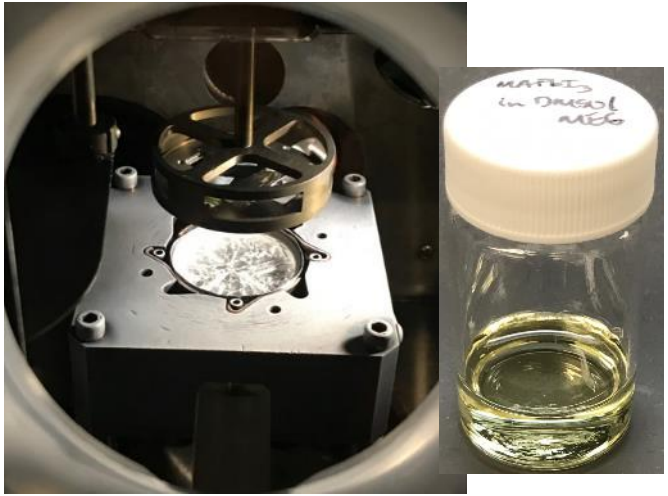
RIR-MAPLE Growth of Hybrid Perovskites



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

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

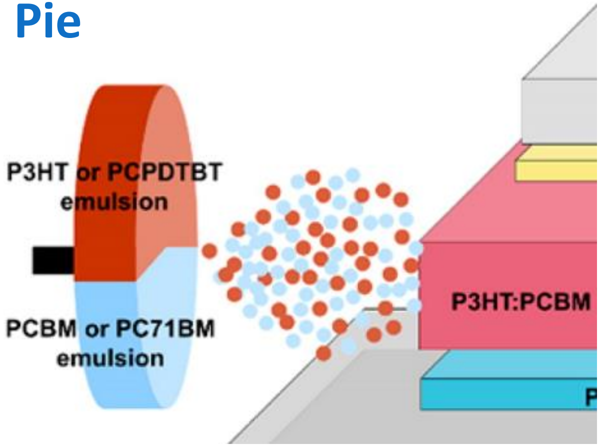




E.T. Barraza, et. al., *J. Electron. Mater.*, **47**, 917 (2018).
W. A. Dunlap-Shohl, et. al., *ACS Ener. Lett.*, **3**, 270 (2018).

RIR-MAPLE Deposition of Multi-component Films

Pie



Donut

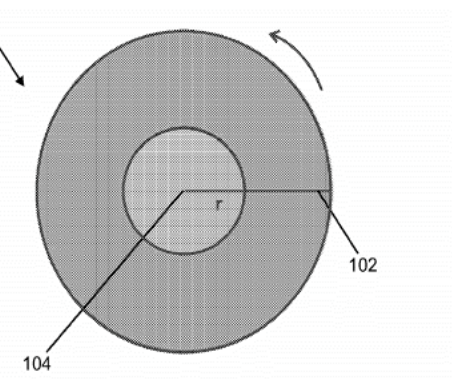
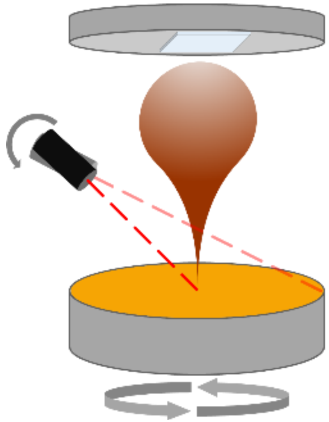
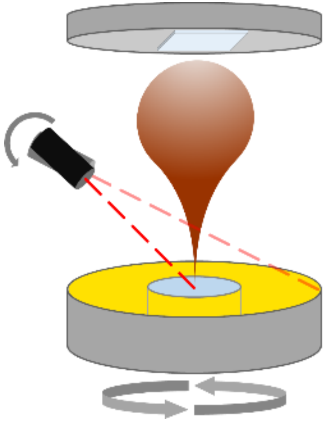


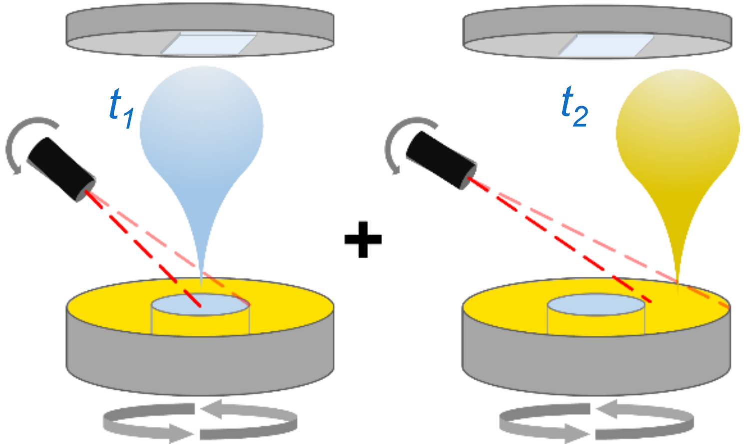
FIG. 1



Simultaneous Deposition



Sequential Deposition



Layered Deposition

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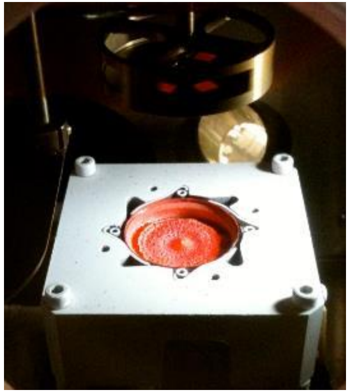
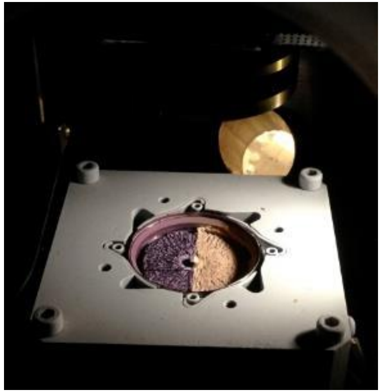
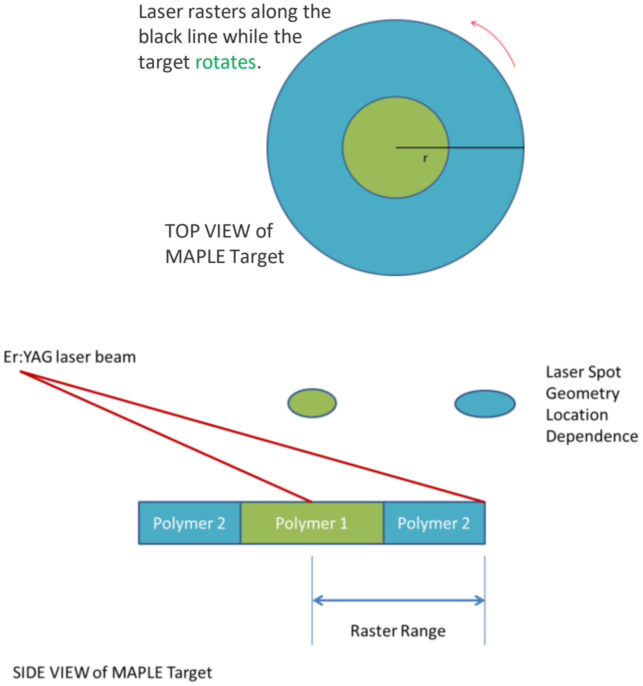
RIR-MAPLE Deposition of Multi-component Films



Simultaneous Deposition

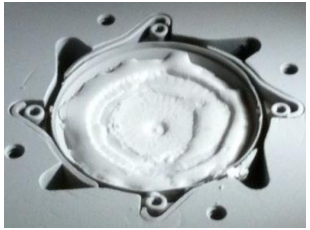


Sequential Deposition



New Target

After center calibration



After annulus calibration

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

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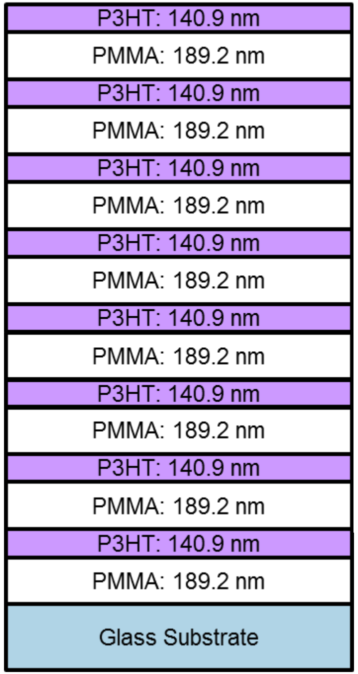
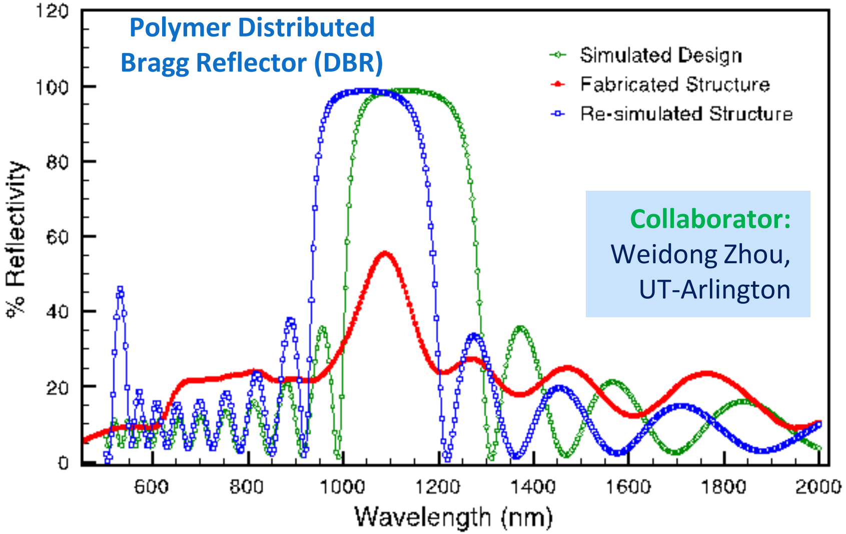
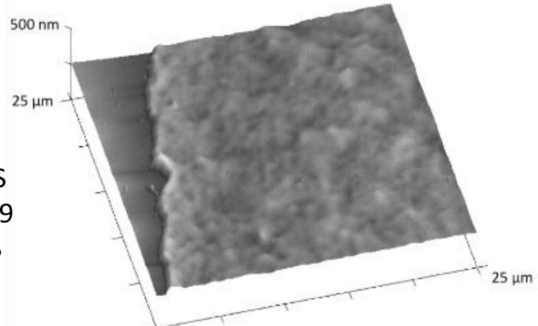




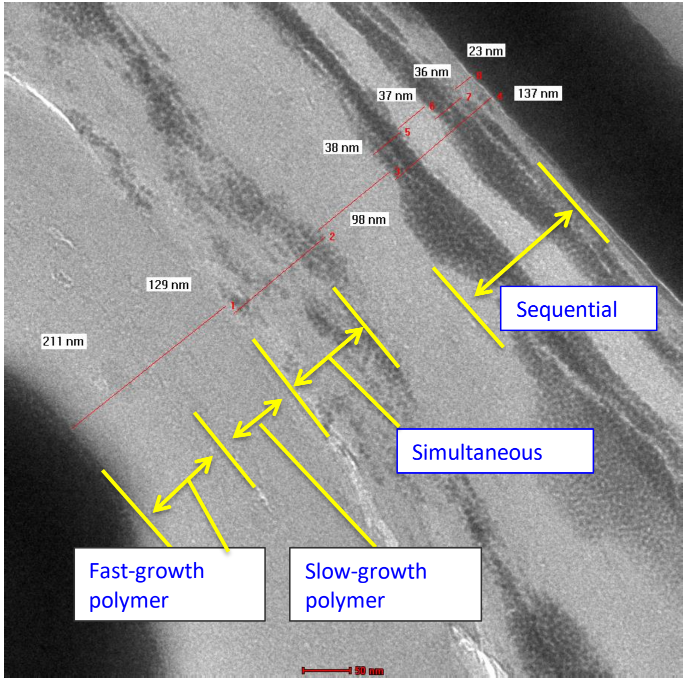
16-layer polymer DBR demonstrated!

PMMA: 8nm RMS roughness, n=1.49
P3HT: 13nm RMS roughness, n=2.0



0

PMMA



- RIR-MAPLE can create layered heterostructures of similar-solubility materials.
- Interfaces between layers are well-defined.

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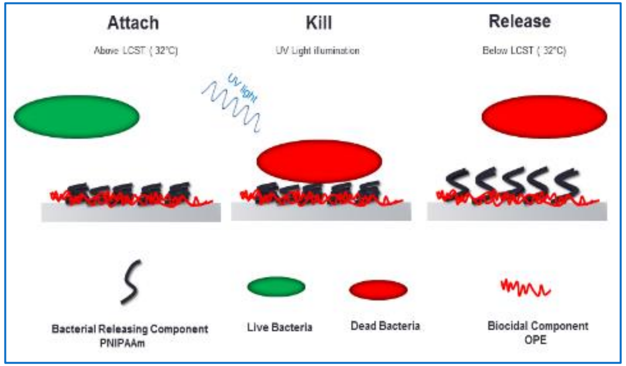
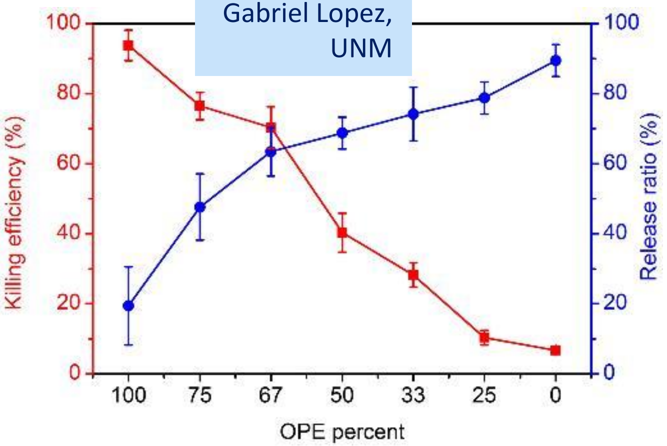
R. Pate, R. McCormick, L. Chen, W. Zhou, and A. D. Stiff-Roberts, *Appl. Phys. A: Materials Science and Processing*, **105**, 555 (2011).

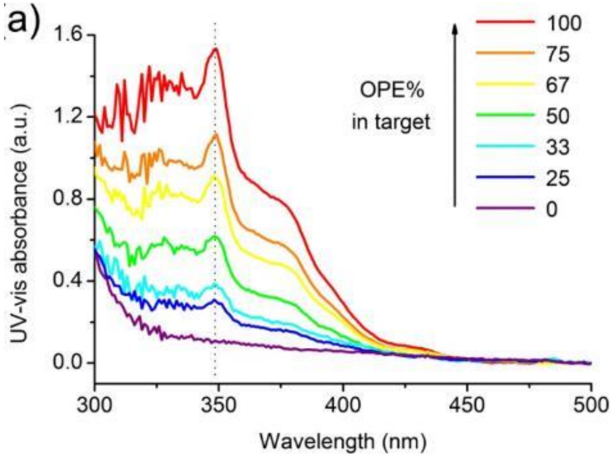
Nanoscale Blending of Multiple Components

Antimicrobial and Fouling-Release Films

Collaborator: Gabriel Lopez, UNM

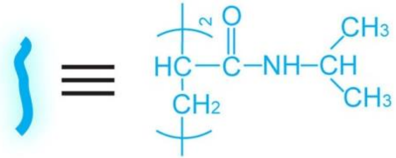




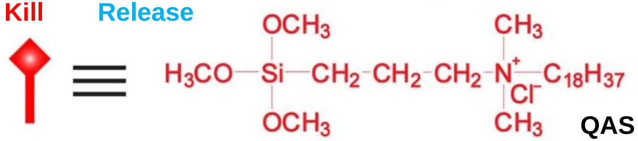


PPE [poly(2,5-dioctylphenylene-1,4-ethynylene)]:
1(CB):0.5(Phenol):3(0.001wt% SDS DI water)

Silane Terminated PNIPAAm [poly(N-isopropylacrylamide)]:
30% methanol/70% water



PNIPAAm



QAS

or

PPE

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.

QAS: 3-(trimethoxysilyl)-propyldimethyloctadecyl ammonium chloride

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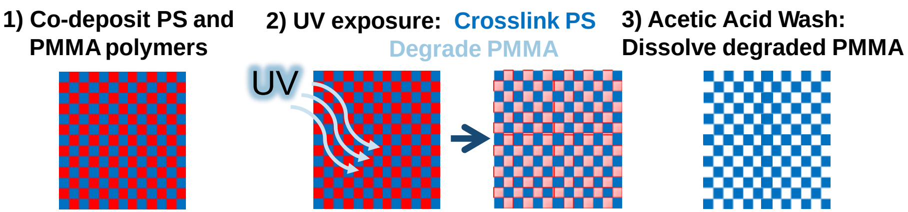
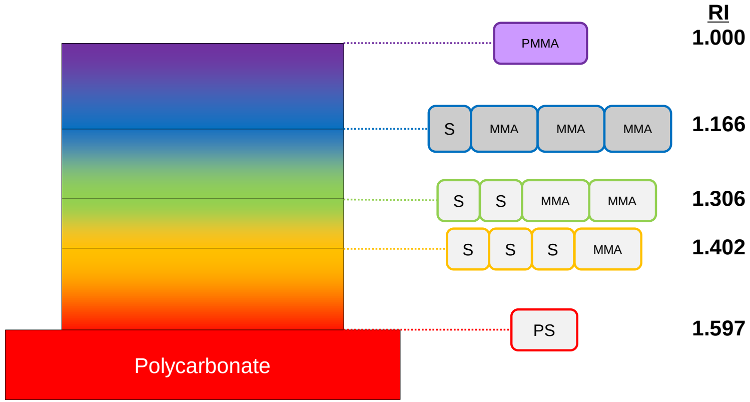
W. Y. Ge, Q. Yu, G. P. López, and A. D. Stiff-Roberts, *Colloids and Surfaces B: Biointerfaces*, **116**, 786 (2014).
Q. Yu, W. Ge, A. Atewologun, A. D. Stiff-Roberts, and G. P. López, *Colloids and Surfaces B: Biointerfaces*, **126**, 328 (2015).

Gradient Composition Films

GRIN Anti-Reflection Coating



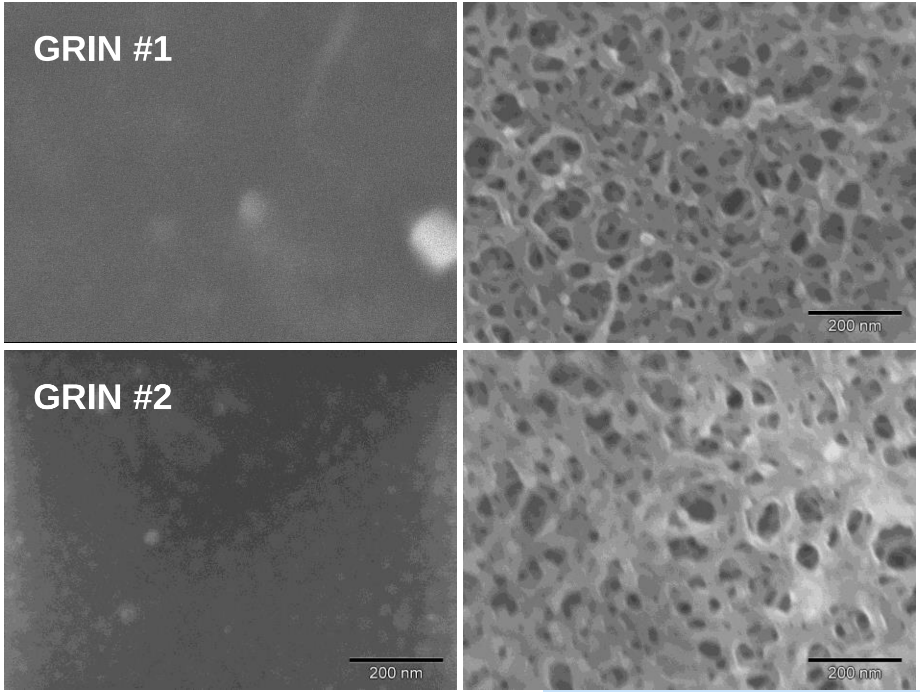


2 prototype structures with linear gradient RI profile.
Total thickness: 1 µm

- GRIN #1: 10 nm constant-ratio slices: 100 slices
- GRIN #2: 20 nm constant-ratio slices: 50 slices

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

SEM: GRIN Films Before and After UV & Acid Wash



R. D. McCormick, E. D. Cline, A. S. Chadha, W. D. Zhou, and A. D. Stiff-Roberts, *Macromolecular Chemistry and Physics*, **214**, 2643 (2013).

Collaborator:
Weidong Zhou, UT-Arlington

Hybrid Nanocomposite Thin Films

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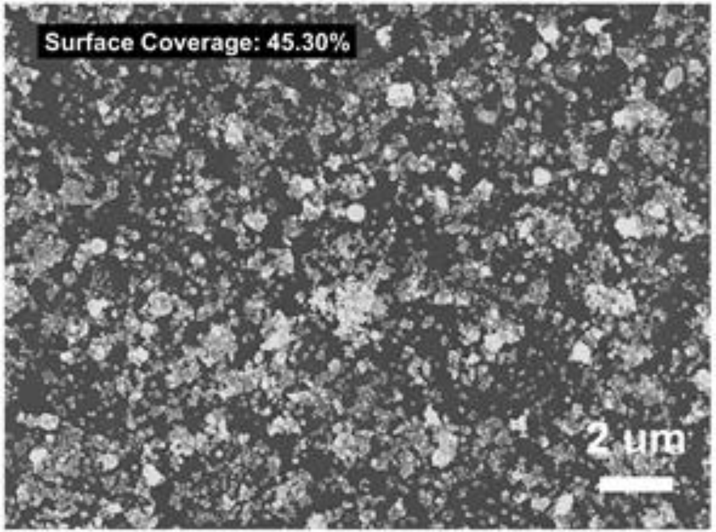
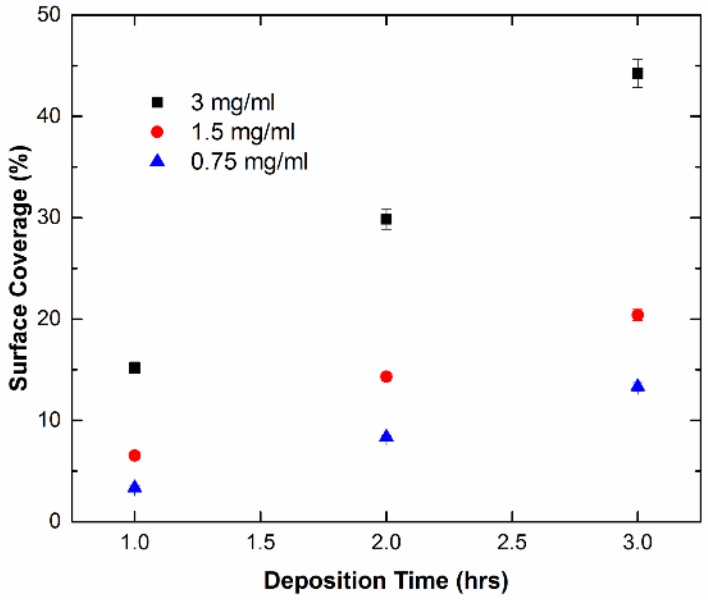
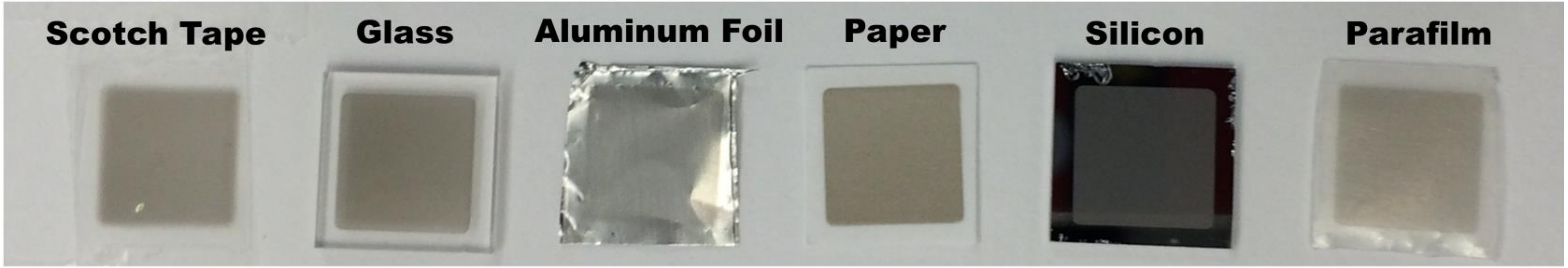
Minimal Influence of Solvent







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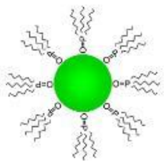
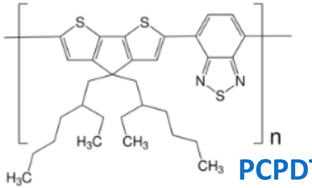
W. Ge, T. B. Hoang, M. H. Mikkelsen, A. D. Stiff-Roberts, *Appl Phys A*, **122**, 824 (2016).

Minimal Influence of Solvent

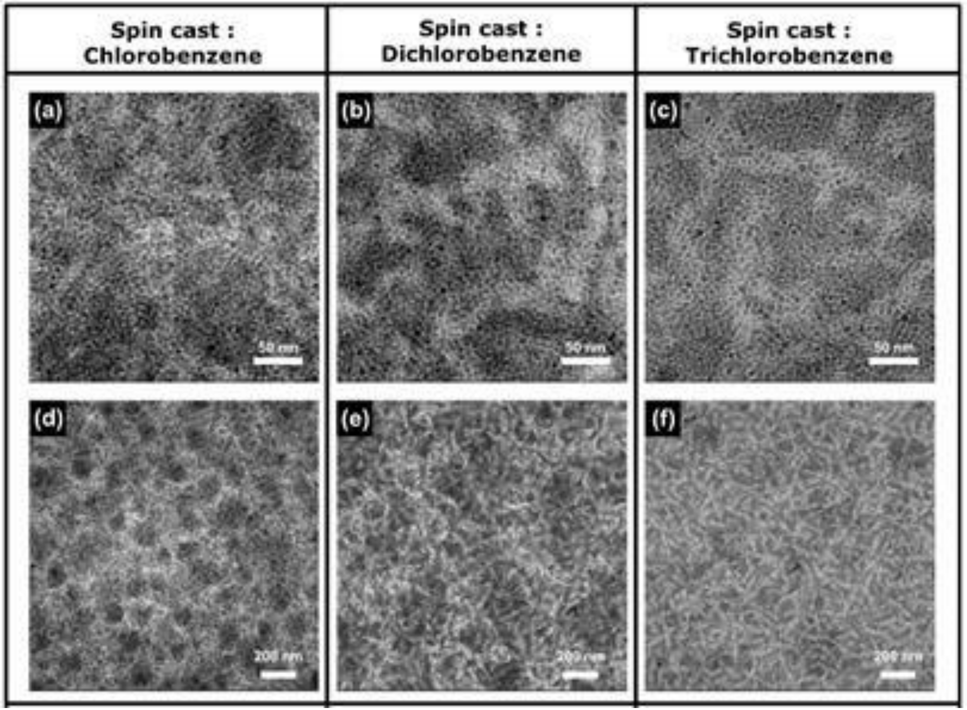


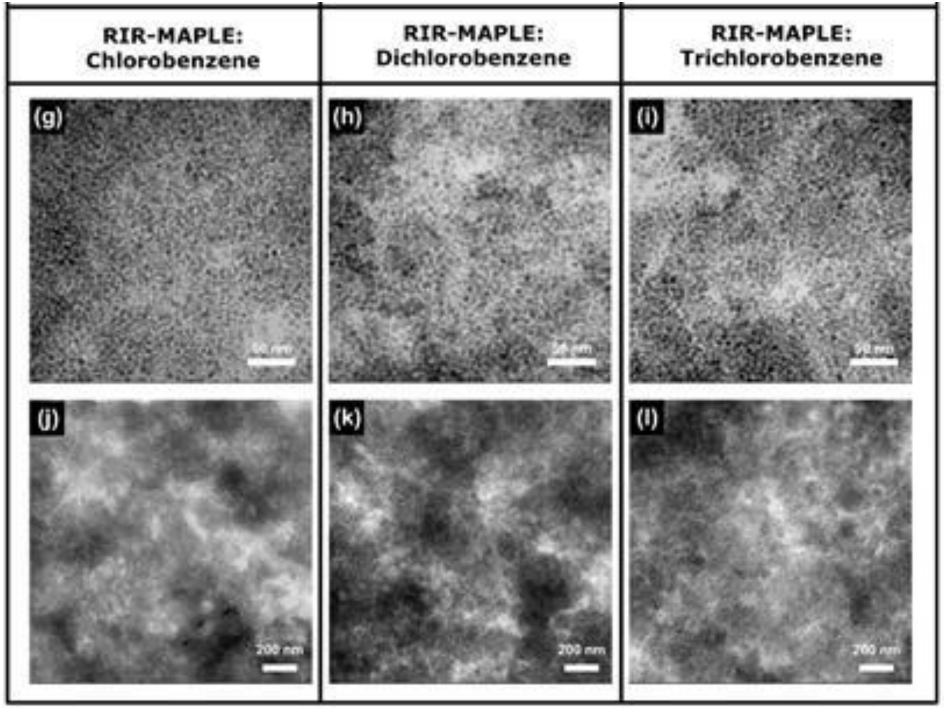
TOPO-capped CdSe



PCPDTBT

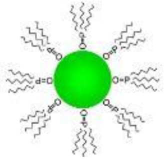
The morphology of RIR-MAPLE blended films is independent of the primary solvent used.



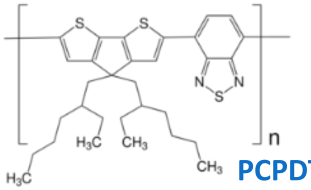


W. Y. Ge, A. Atewologun and A. D. Stiff-Roberts, *Organic Electronics*, **22**, 98 (2015).

Minimal Influence of Solvent

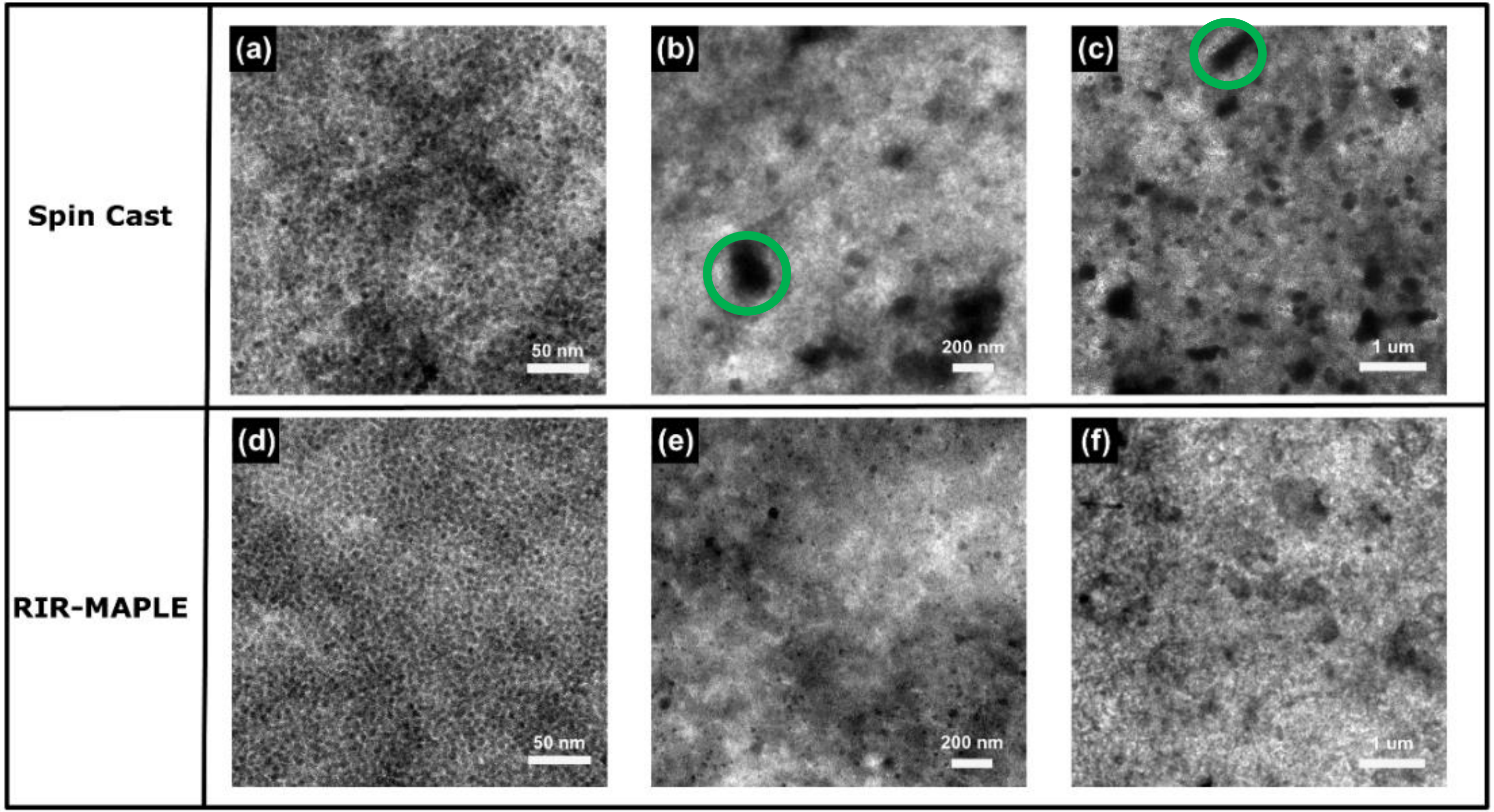


TOPO-capped CdSe



PCPDTBT

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



W. Y. Ge, A. Atewologun and A. D. Stiff-Roberts, *Organic Electronics*, **22**, 98 (2015).

Hybrid Organic-Inorganic Perovskite Thin Films

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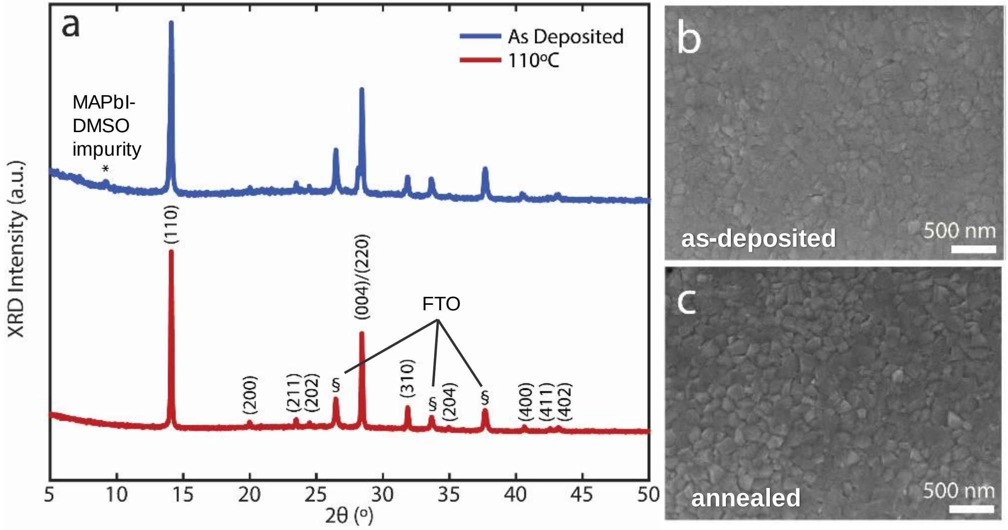
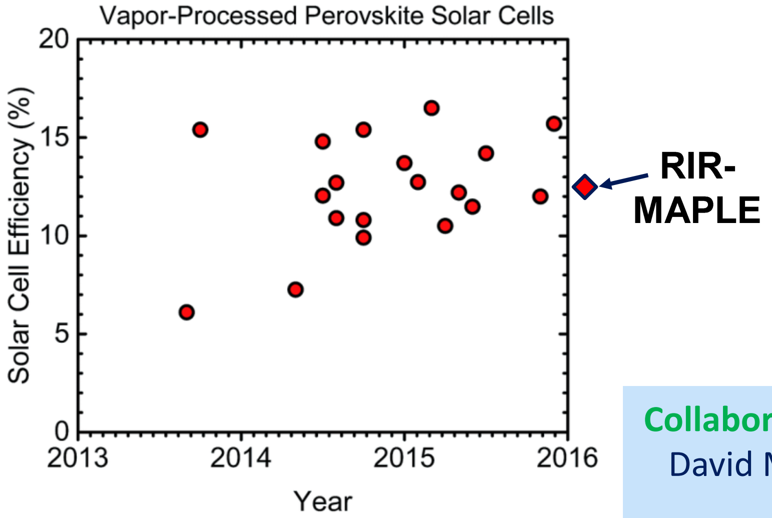
Hybrid Perovskite Solar Cell Deposited by RIR-MAPLE

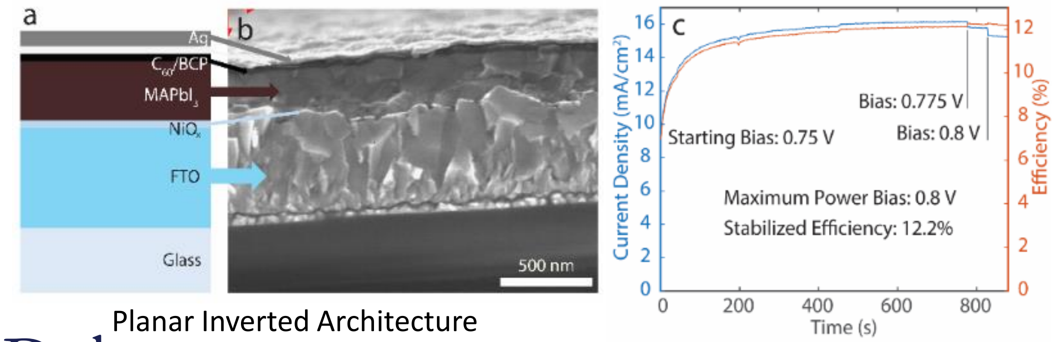




Ono, Leyden, et al., *J. Mater. Chem. A.* **4** (2016)

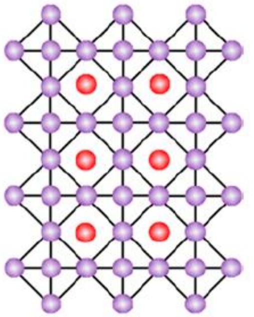
Collaborator: David Mitzi, Duke

RIR-MAPLE-deposited $MAPbI_3$ films on FTO/NiO_x substrates



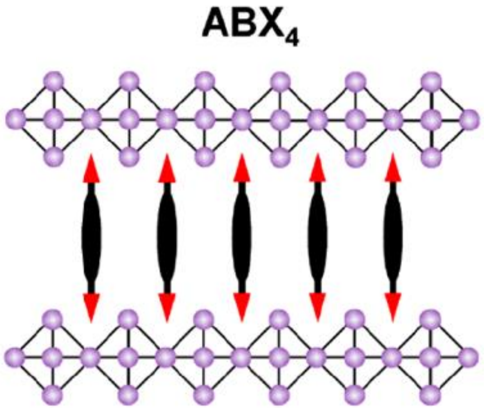
Planar Inverted Architecture

Obtained 12.2% PCE (stabilized)

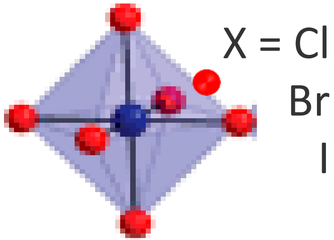


W. A. Dunlap-Shohl, et. al., *ACS Energy Letters*, **3**, 270 (2018).

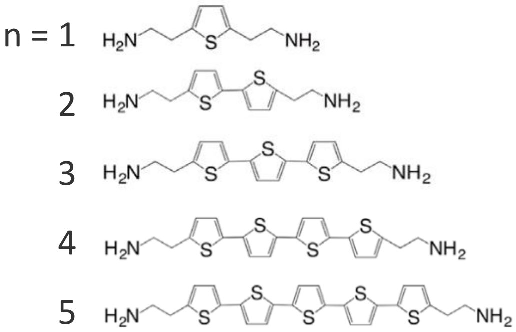
Collaborators:
Volker Blum &
David Mitzi, Duke

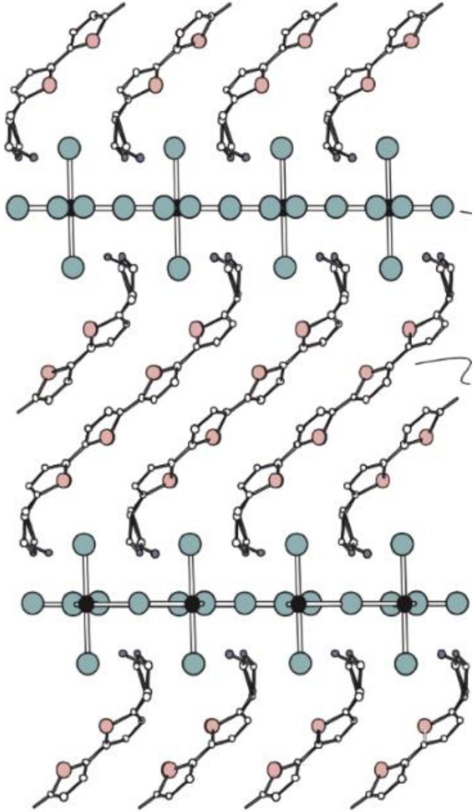


Halide selection for bandgap control

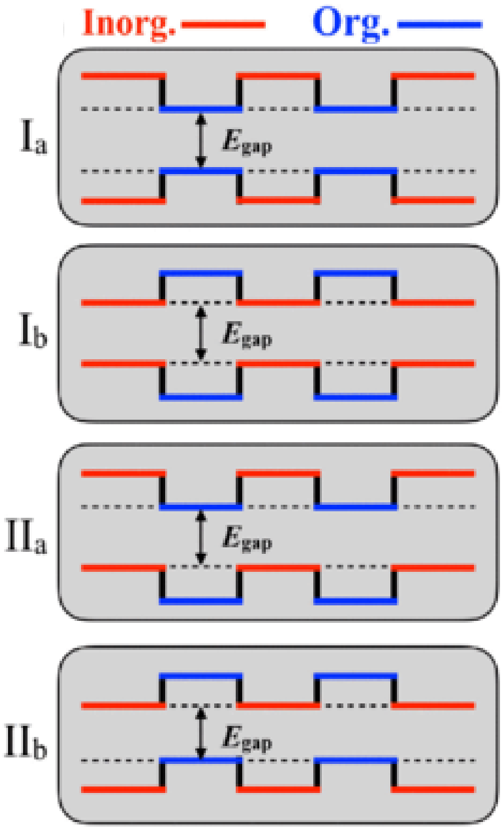


Organic cation selection for targeted functionality





W. Huhn, Energy Research Collaboration Workshop, Duke University, May 2016.



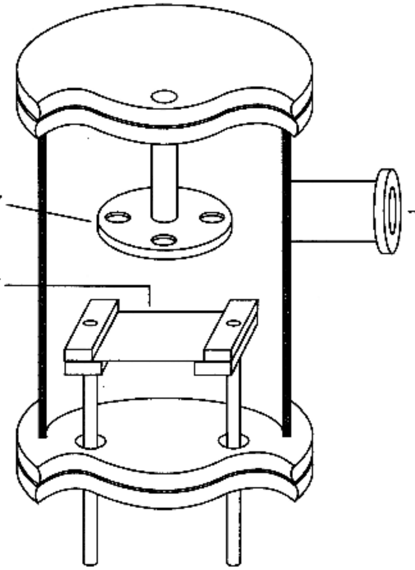
C. Liu, et. al., *Phys. Rev. Lett.* **121**, 146401 (2018).

RIR-MAPLE Growth of Hybrid Perovskites with Complex Organic Molecules

	AE2T	AE3T	AE4T
Cl	Type IIB	Type IIB	Quasi-Type IA*
Br	Quasi-Type IB	Type IIB	Type IIB*
I	Type IB	Quasi-Type IB	Type IIB*

Collaborators:
Volker Blum &
David Mitzi, Duke

*Single Source Thermal Ablation (SSTA)



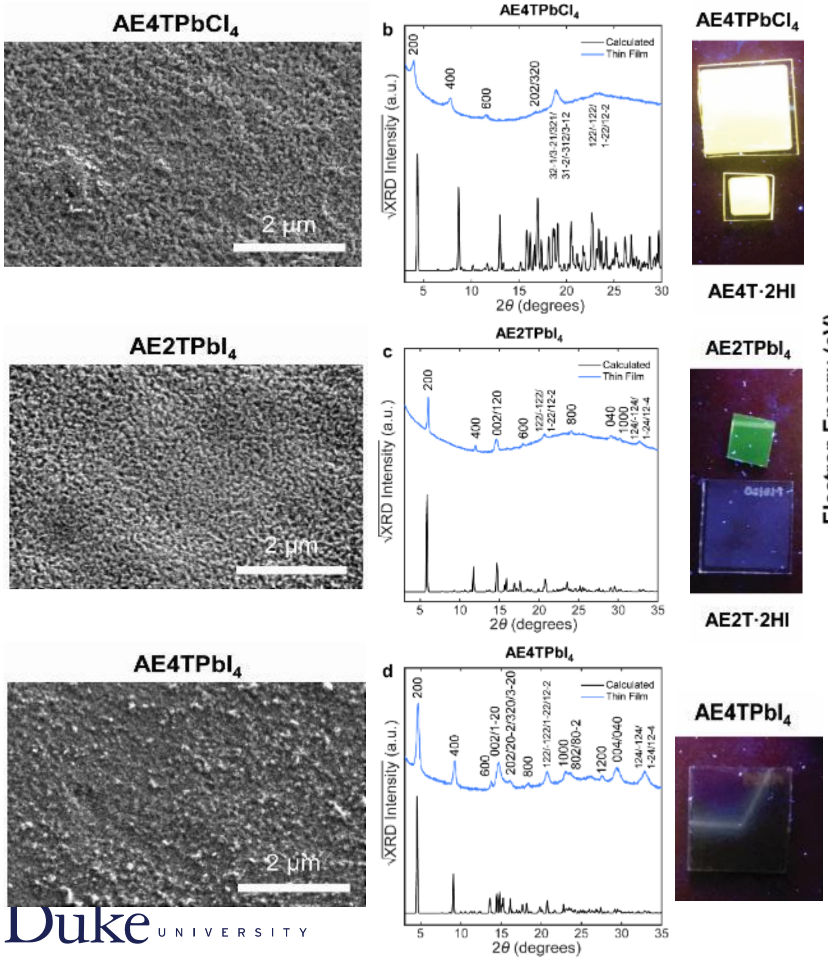
D.B. Mitzi, et. al., *Chem. Mater.*, **11**, 542 (1999).

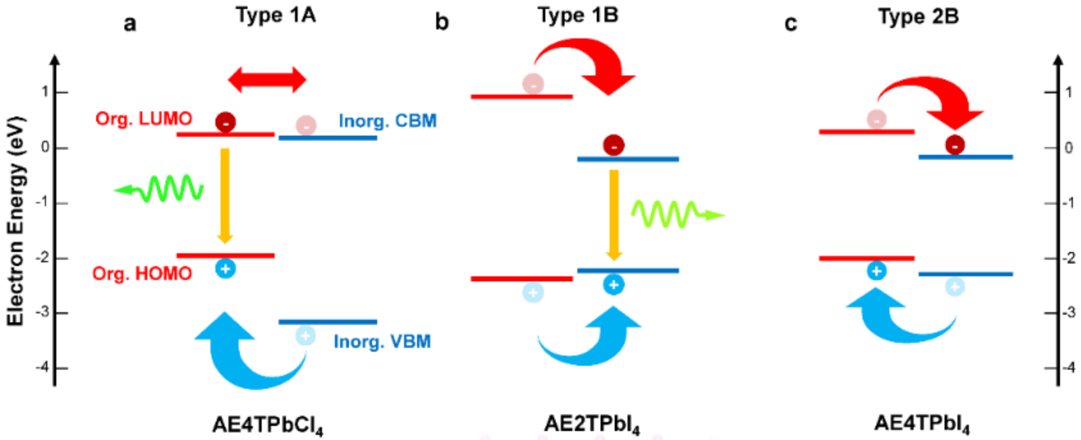
Challenges of Oligothiophene-based Perovskite Synthesis:

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 $(AE4T)PbI_4$ have only recently been reported [C. Liu, et. al., *Phys. Rev. Lett.* **121**, 146401 (2018)]; Single crystals of $(AE4T)PbCl_4$ have not been reported.
4. SSTA used to synthesize oligothiophene-based perovskite thin films, $(AE4T)PbX_4$; in general, it can be difficult to control film thickness and composition using vapor-phase growth of hybrid organic-inorganic perovskites.

RIR-MAPLE Growth of Hybrid Perovskites with Complex Organic Molecules

Collaborators:
Volker Blum &
David Mitzi, Duke





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

W. A. Dunlap-Shohl, et. al., *Mat. Horizons*, **6**, 1707 (2019).

Future Outlook

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

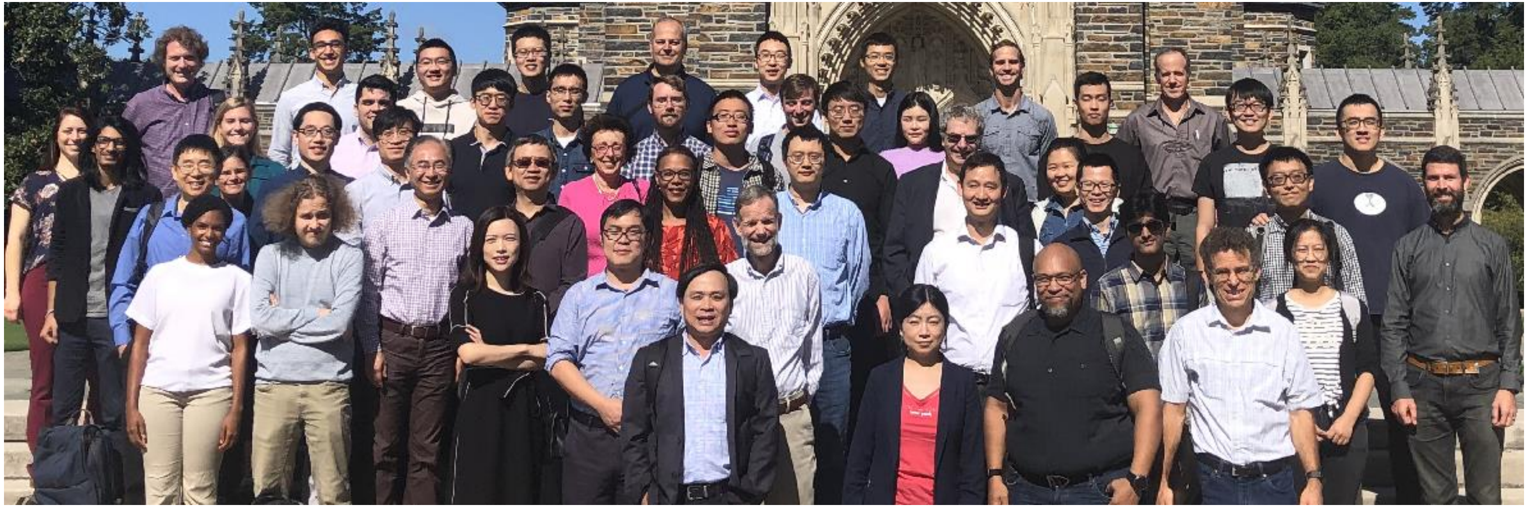
Scale-up Fabrication

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

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

PVD Products PLD-4000/5000

Acknowledgements



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Center for Hybrid Organic Inorganic Semiconductors for Energy

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www.choise-efrc.org
Choise.efrc@nrel.gov

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

Q&A

For questions or advice:

James Greer, Ph.D.
jgreer@pvdproducts.com
pvdproducts.com

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

Thank you!

For questions or advice:

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