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Perovskite Film Formation for Solar Cell Absorbers: Effects of Substrate Modification

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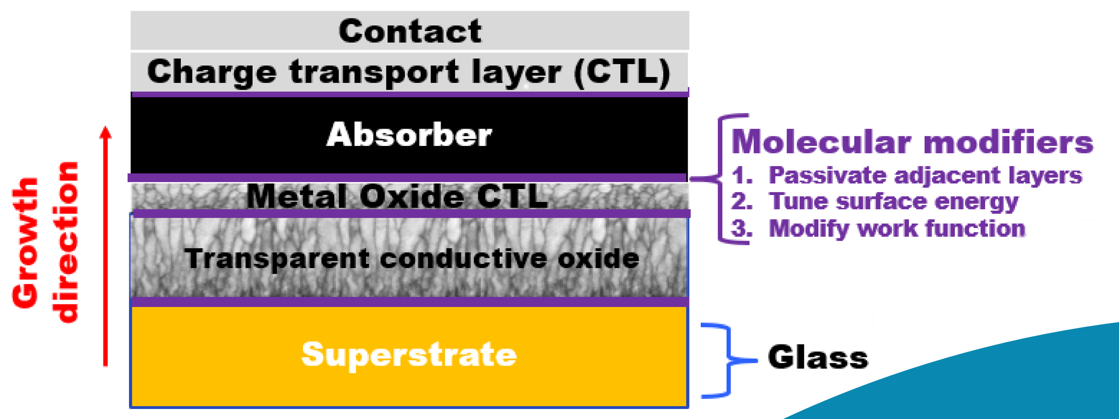
Introduction & Background

Pb-Based Perovskite Films as an Emerging PV Absorber

Record devices are over 20% efficient but there are materials problems that need to be solved [1].

Interfacial modification affects:

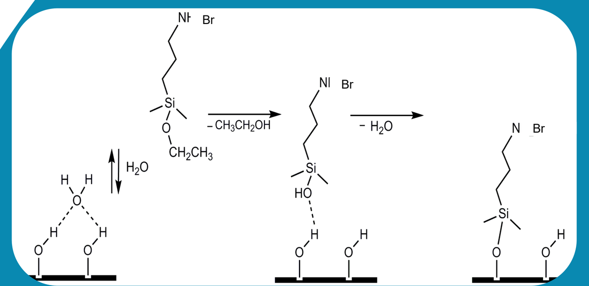
- Film uniformity
- Crystallinity
- Grain size
- Defect density



Small molecule modifiers and their positive effects on device performance. Data from references [2] and [4].

Modifier	Stack Structure	V_{oc} [V]	J_{sc} [mA cm^{-2}]	PCE [%]
Bromobenzoic Acid *(Br-BA)* [2]	ITO/NiO_x/ $MAPbI_3$/PCBM /bis-C_{60}/Ag	1.07	19.1	15.3
	ITO/NiO_x/ **Br-BA**/ $MAPbI_3$/PCBM /bis-C_{60}/Ag	1.11	21.7	18.4
(3-Aminopropyl) triethoxysilane *(APTES)* [4]	FTO/SnO_2/ $MAPbI_3$/ Spiro-OMeTAD/Au	1.065	20.84	14.69
	FTO/SnO_2/ **APTES**/ $MAPbI_3$/ Spiro-OMeTAD/Au	1.16	21.23	17.03

Goal: Improve stability of perovskite absorbers through small molecule modification of perovskite-TCO interface.



Chemical process of small molecule modification of a metal oxide.

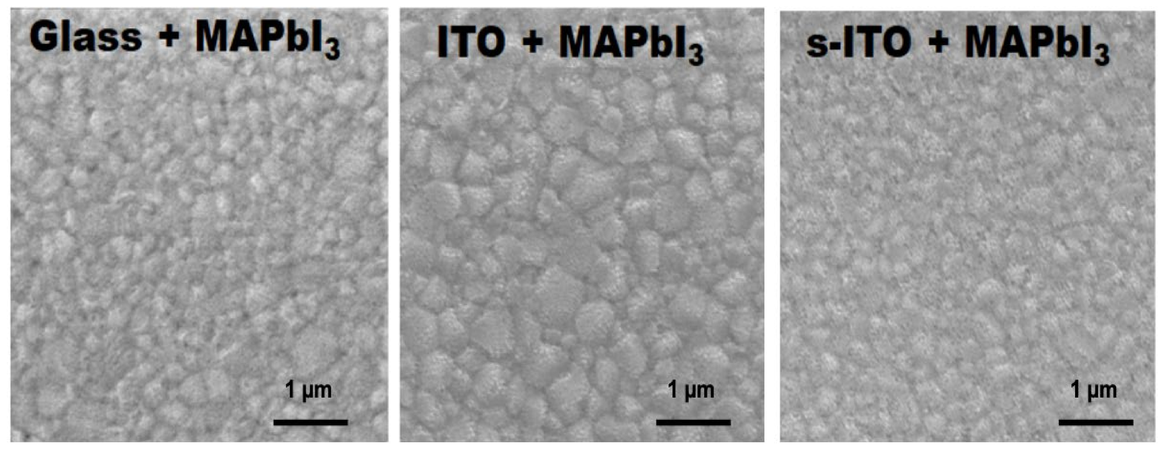
Device properties and performance are directly tied to perovskite film properties [3].

Interfacial Modification and Stability

BPTMS and $MAPbI_3$ Grain Growth

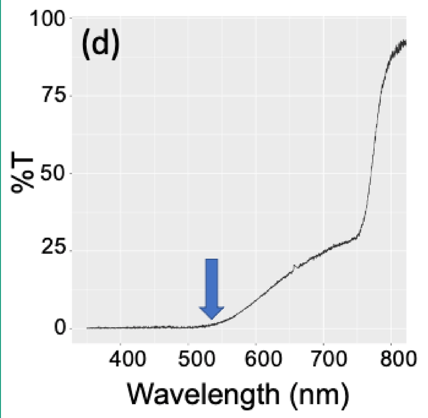
- BPTMS leads to growth of smaller grains on ITO
- $MAPbI_3$ grains on s-ITO comparable in size to those grown on glass

"s-" denotes inclusion of BPTMS interlayer



(a) (b) (c)

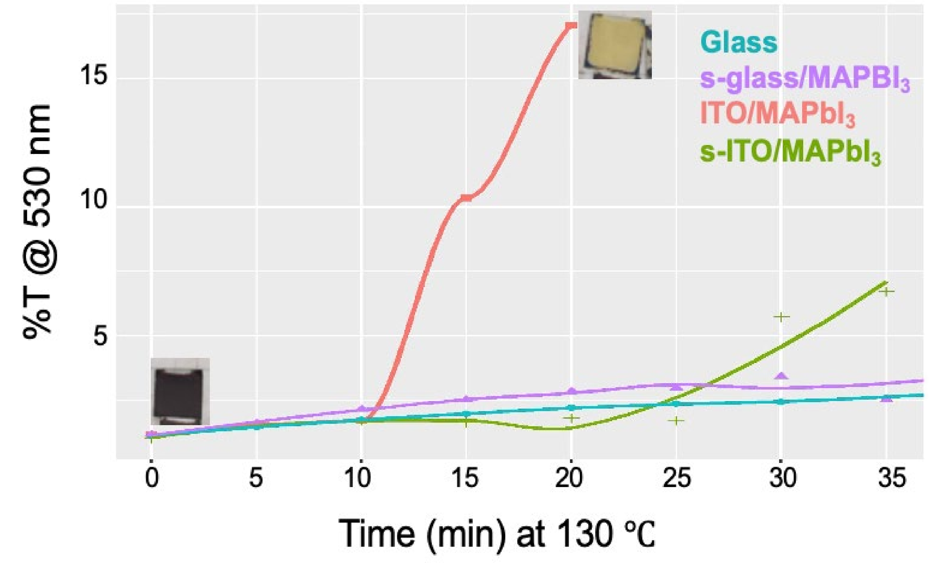
Results: BPTMS passivates the perovskite-TCO interface, affecting both the film morphology and degradation profile of the perovskite.

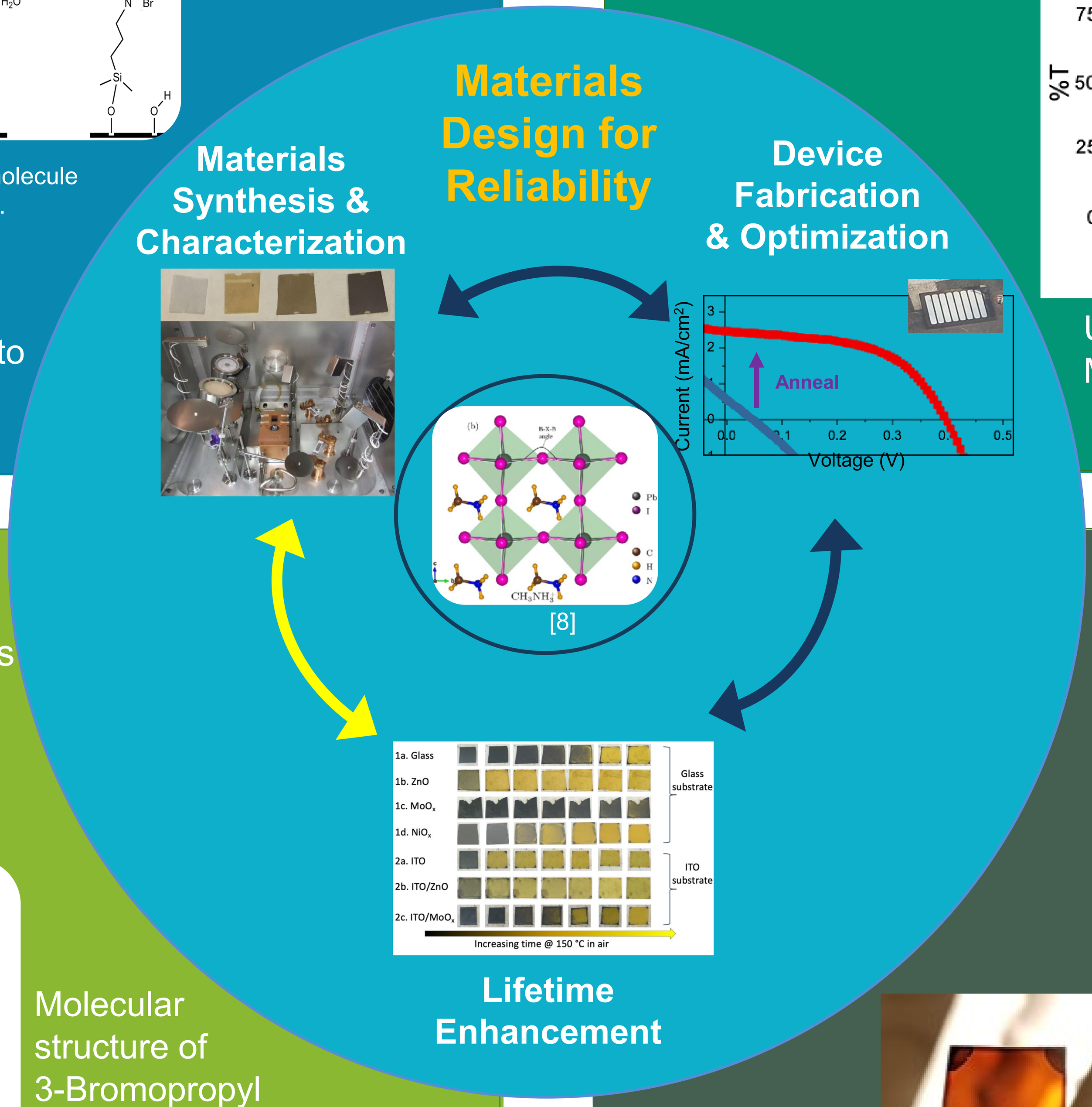


UV-Vis spectrum of $MAPbI_3$ on s-ITO.

BPTMS and $MAPbI_3$ Degradation

- BPTMS mitigates $MAPbI_3$ degradation on ITO (in green) compared to the unmodified control (in red)
- Decouples effects of grain size from interfacial chemistry in terms of stability

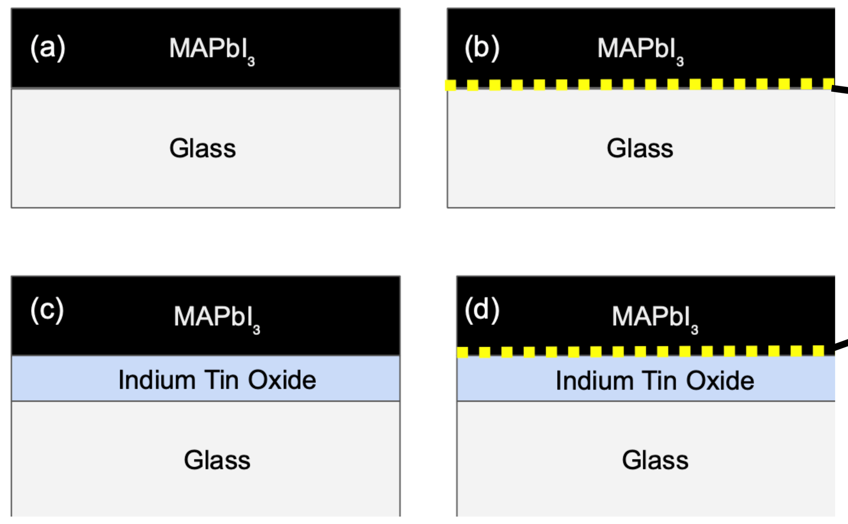




Experimental Flow

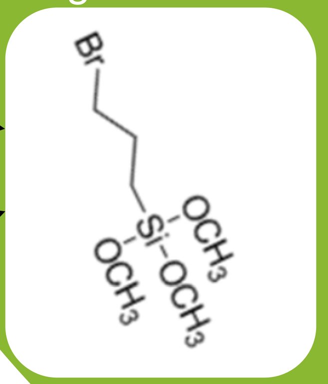
1. Clean substrates
2. Deposit organofunctional silane [6,7]
3. Spin coat $MAPbI_3$ and anneal [5]
4. Characterization and degradation

Schematic overview of film stacks



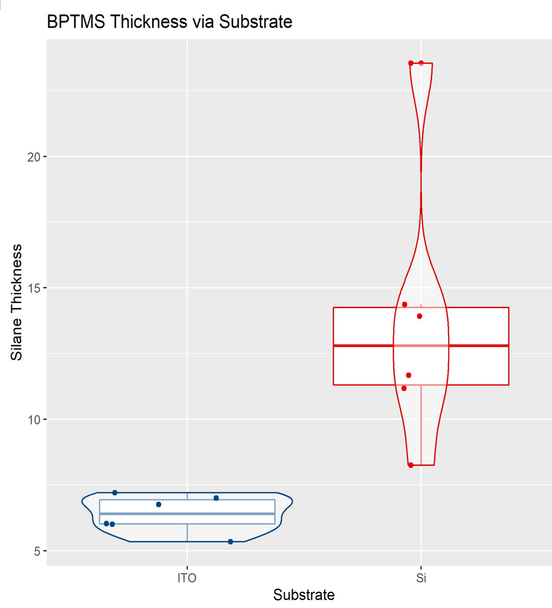
Dashed line indicates organofunctional silane layer

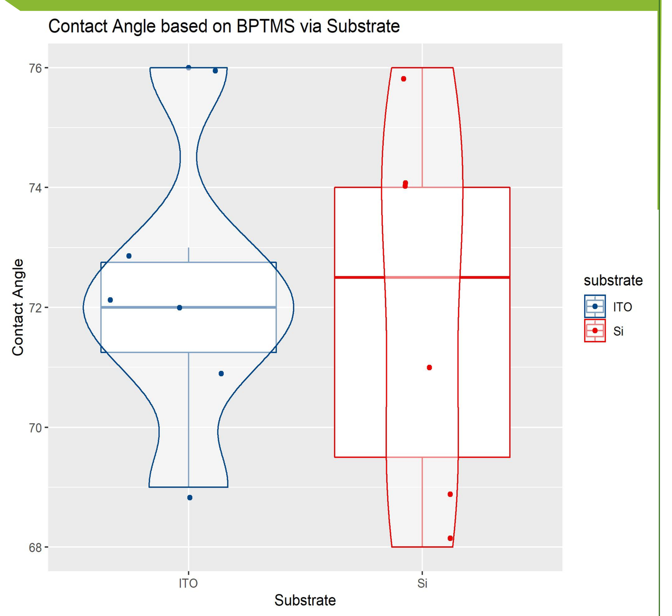
Approach: Deposition of $MAPbI_3$ on bare and silane-modified substrates to systematically investigate effects of a BPTMS interlayer on perovskite degradation.



Molecular structure of 3-Bromopropyl trimethoxysilane [BPTMS]

Substrate	Thickness, Å	Contact Angle, degrees
Silicon	11 ± 1	62 ± 3
	24 ± 1	81 ± 2
	34 ± 2	84 ± 1
ITO	6 ± 1	72 ± 2

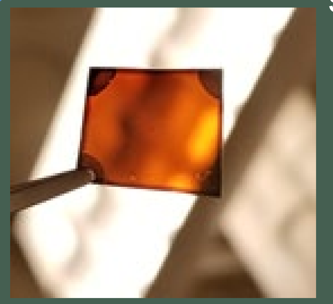




Silane and Perovskite Deposition

Future Directions:

- Apply silanes to MOs (Metal Oxides), commonly used as PV charge transport layers
- Investigate systematically varied TCO/MO/silane combinations in half-stack degradation studies



- Further investigate silane-MO interface and its effects on the perovskite film with SE and XPS

Conclusions

- Results highlight importance of film studies under device-relevant conditions
- Organofunctional silanes used as molecular modifiers can passivate a TCO/perovskite interface
- Interfacial modifiers have multifaceted effects on perovskite film morphology and lifetime
- BPTMS forms mono- to multilayers on SiO_2 and a monolayer on ITO.
- As silanes bond to surface hydroxyl groups, this is likely due to differences in properties of the oxide surface, specifically the availability and/or spacing of the hydroxyl groups

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References

[1] *Nature Energy*, vol. 4, pp. 1, Jan. 2019.
[2] *ChemSusChem,* 10 (2017), 3794-3803. DOI: 10.1002/cssc.201701262.
[3] *J. Photon. Energy* 6(2), 022001 (2016), DOI: 10.1117/1.JPE.6.022001.
[4] *Journal of Materials Chemistry A*, vol. 5, no. 4, pp. 1658–1666, 2017.
[5] *ACS Appl. Energy Mater*. 2020, 3, 3, 2386–2393 DOI:10.1021/acsaem.9b02052
[6] *Langmuir* 29 (2013), 4057-67. DOI:10.1021/la304719y
[7] *ACS Appl. Mater. Interfaces* 9 (2017), 17620-17628. DOI: 10.1021/acsami.7b02638
[8] *AIP Advances,* vol. 9, no. 8, p. 085123, 2019.

Conclusions and Future Directions