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Decoupling the Effects of Interfacial Chemistry and Grain Size in Perovskite Stability

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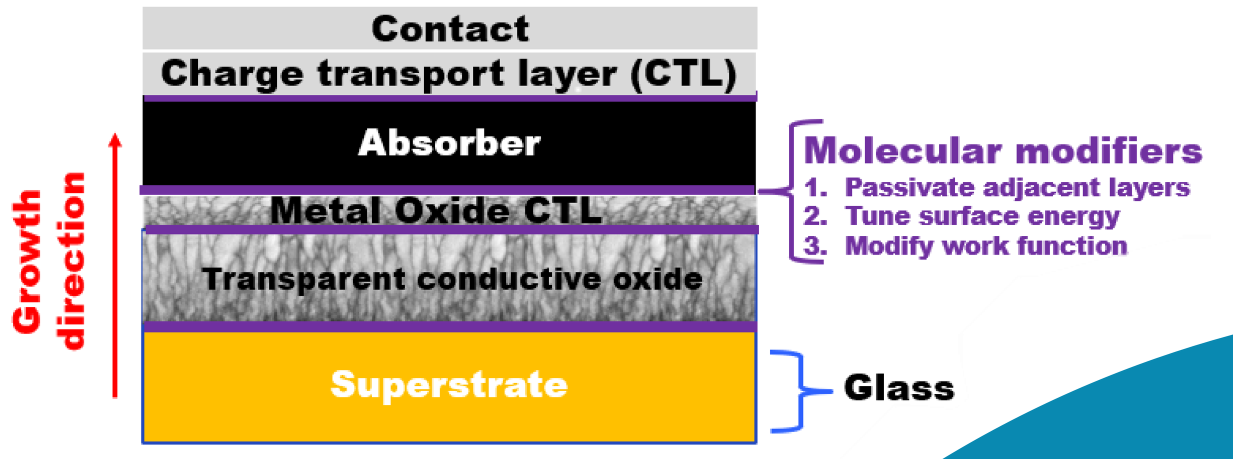
Introduction & Background

Interlayers, Film Properties, and Device Characteristics

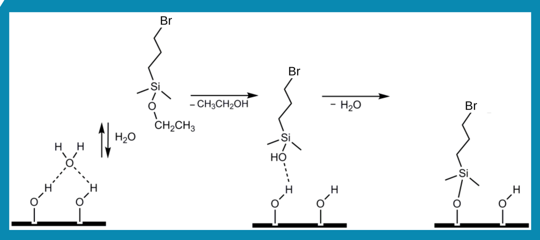
Interfacial modification affects:
- Film uniformity
- Crystallinity
- Grain size
- Defect density



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 organofunctional silane modification of metal oxide (MO) charge transport layer.



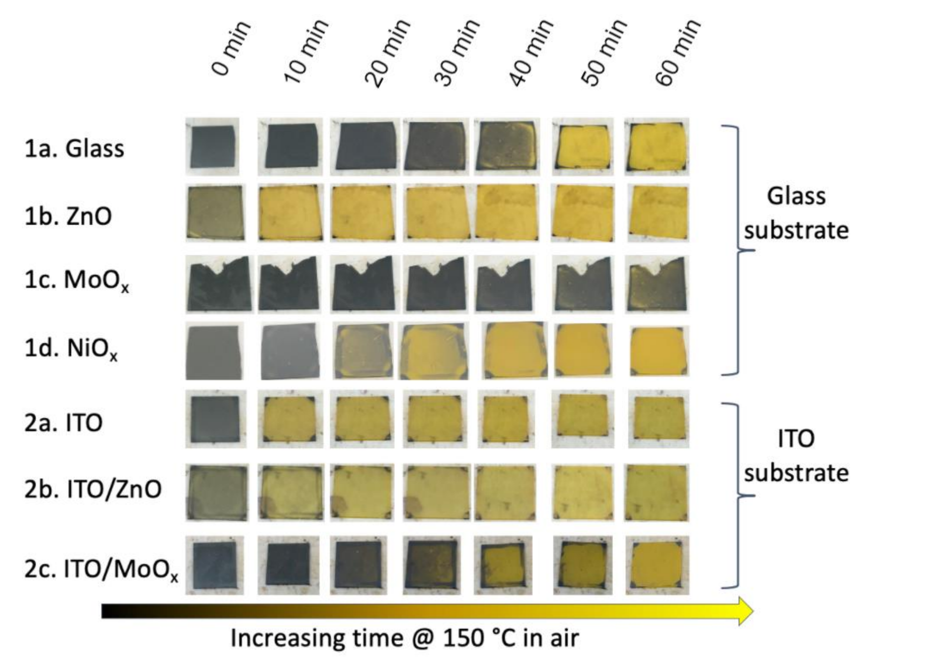
Chemical process of small molecule modification of a metal oxide.

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

Surface Modification and Stability

Degradation Profile with Varying MOs

- Order from least to most stable is generally ZnO < NiO_x < MoO_x
- Effect of MO is compounded with addition of ITO layer (seen with MoO_x), indicating diffusion/reaction of stack species during heating

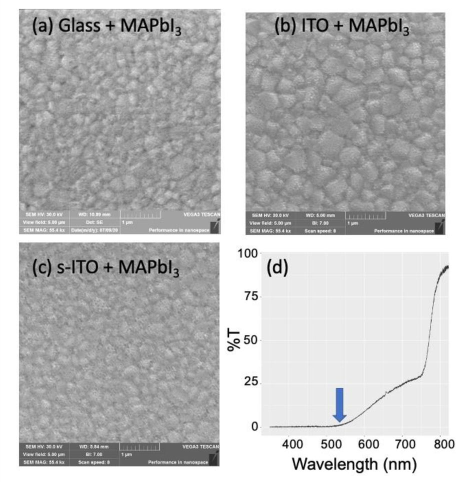


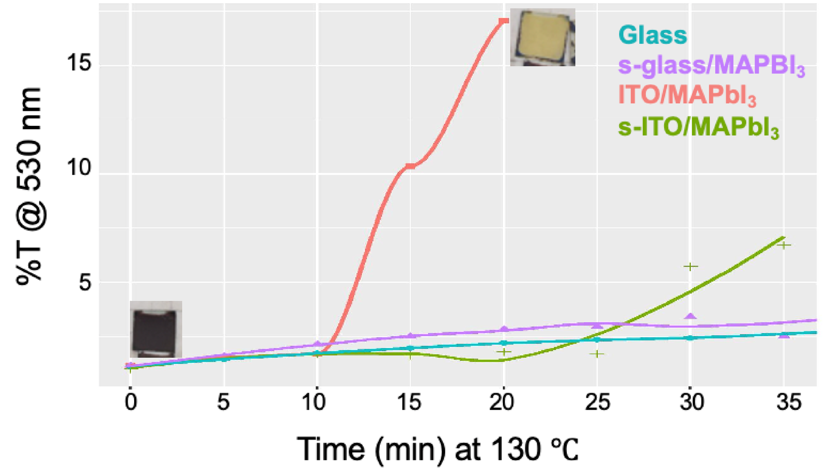
Results: MOs affect $MAPbI_3$ film degradation profile. BPTMS passivates interface and affects both film morphology and degradation.

Degradation Profile with BPTMS Modifier

- BPTMS results in smaller $MAPbI_3$ grains on ITO
- Despite decreased grain size, BPTMS improved $MAPbI_3$ stability
- Decouples effects of grain size from interfacial chemistry

- "s-" denotes inclusion of BPTMS interlayer



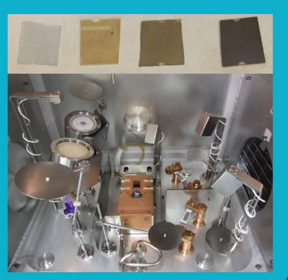


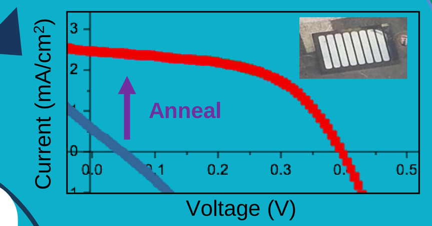
Materials Design for Reliability

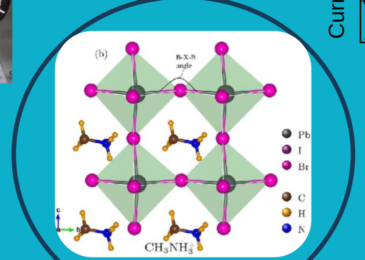
Materials Synthesis & Characterization

Device Fabrication & Optimization

Lifetime Enhancement







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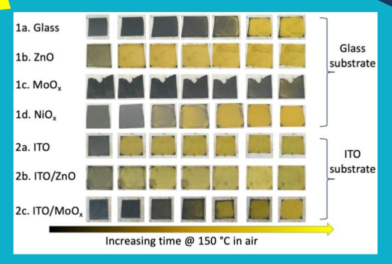


Modifier and Perovskite Deposition

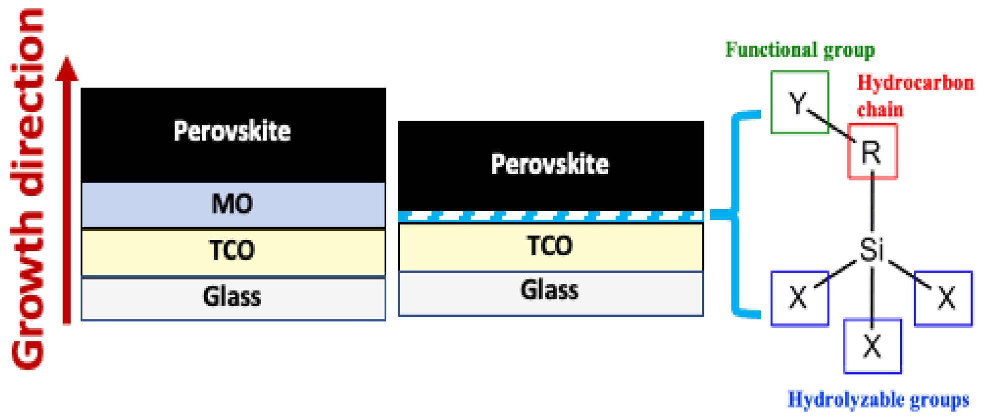
Experimental Flow

1. Clean substrates
2. Deposit organofunctional silane [7,8] or metal oxide [9]
3. Spin coat $MAPbI_3$ and anneal [6]
4. Characterization and degradation

Approach: Creation of stacks with varying MOs or molecular modifiers to investigate their effects on $MAPbI_3$ degradation.

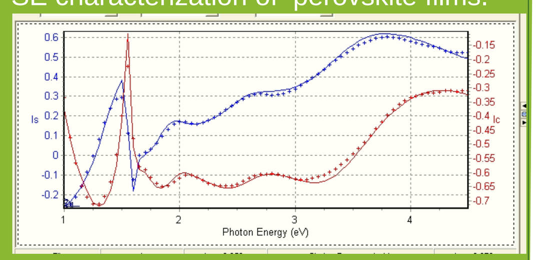
Materials	
Organofunctional Silanes	Metal Oxides
(3-bromo-propyl) trimethoxysilane [BPTMS]	ZnO, MoO_x, NiO_x

Schematic overview of film stacks



Metal oxide modified stack (left) and organofunctional silane modified stack] with general silane molecular structure (right).

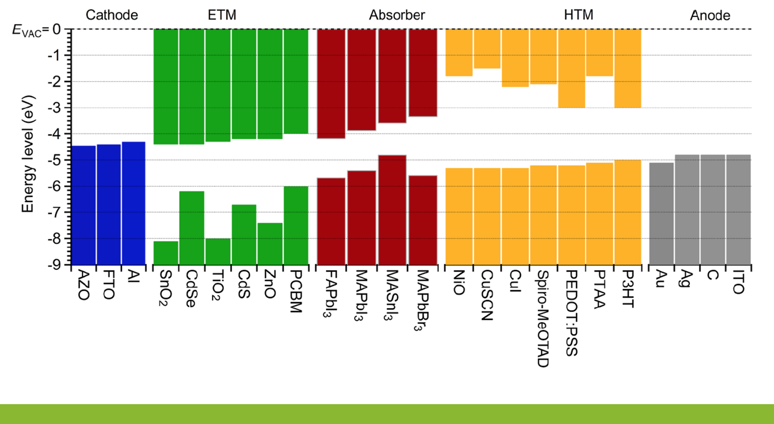
SE characterization of perovskite films.



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

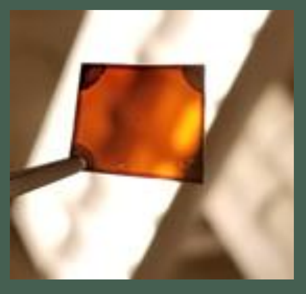
Left: Characteristics of BPTMS modified ITO and silicon. Silane thickness is modelled from spectroscopic ellipsometry measurements.

Right: Energy levels of different absorbers and charge transport materials [3].



Conclusions and Future Directions

Future Directions:
- Investigate systematically varied TCO/MO/silane combinations in half-stack degradation studies
- Select well-performing stacks for device studies



- Explore other organofunctional silanes (similar to work shown here with BPTMS)
- 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:
  - Different MOs clearly affect the degradation profile of the perovskite layer
  - Organofunctional silanes used as molecular modifiers can passivate a TCO/perovskite interface
- ❖ Interfacial modifiers have multifaceted effects on perovskite film morphology and lifetime

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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] *ChemPhysChem*, vol. 20, no. 20, pp. 2580–2586, 2019.
[6] *ACS Appl. Energy Mater*. 2020, 3, 3, 2386–2393 DOI:10.1021/acsaem.9b02052
[7] *Langmuir* 29 (2013), 4057-67. DOI:10.1021/la304719y
[8] *ACS Appl. Mater. Interfaces* 9 (2017), 17620-17628. DOI: 10.1021/acsami.7b02638
[9] *J. Mater. Chem*. C 6 (2018), 3990-3998. DOI: 10.1039/c7tc05820a
[10] *AIP Advances,* vol. 9, no. 8, p. 085123, 2019.