Thermal Stability and Degradation Mechanisms of sputtered ZTO and $AlSiO_xN_y$ Permeation Barrier Layers on PET Substrates under High Humidity

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Motivation: Encapsulation Challenge

Critical Requirement:
Long-term stability of flexible electronics relies heavily on high-performance thin-film permeation barriers.
Environmental Degradation:
Moisture ingress under harsh environmental conditions
(elevated temperature & high humidity / Damp-Heat stress) degrades device functionality.
Material Candidates:
Comparison of Zinc Tin Oxide (ZTO) and Aluminum Silicon Oxynitride $AlSiO_xN_y$ for robust encapsulation.

Scientific Gap

Degradation Mechanisms:
Lack of comparative microstructural analysis regarding defect formation, localized corrosion, and phase stability under hygrothermal stress.

Liner Interaction & Interface Stability:
The synergistic degradation between protective polymer liners and inorganic barrier layers under combined thermal and humidity loads remains insufficiently understood.

Dynamic Barrier Behavior:
Limited understanding of reversible vs. irreversible permeation kinetics (WVTR relaxation vs. thermally driven densification) during damp-heat cycling

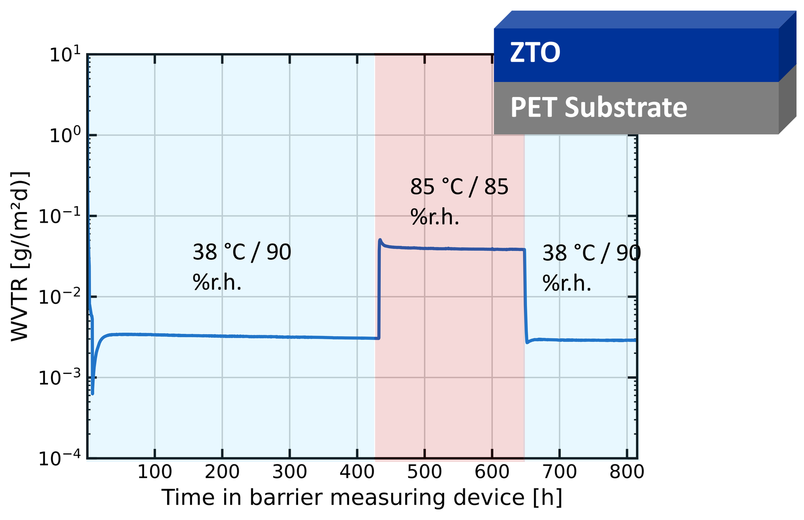
Experimental Workflow

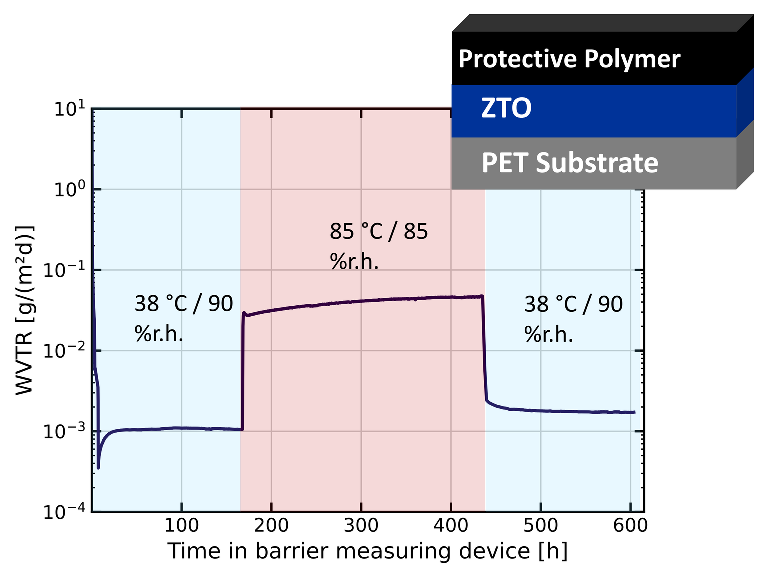
Thin-Film Deposition:
Reactive magnetron sputtering with systematic variation of chemical composition.

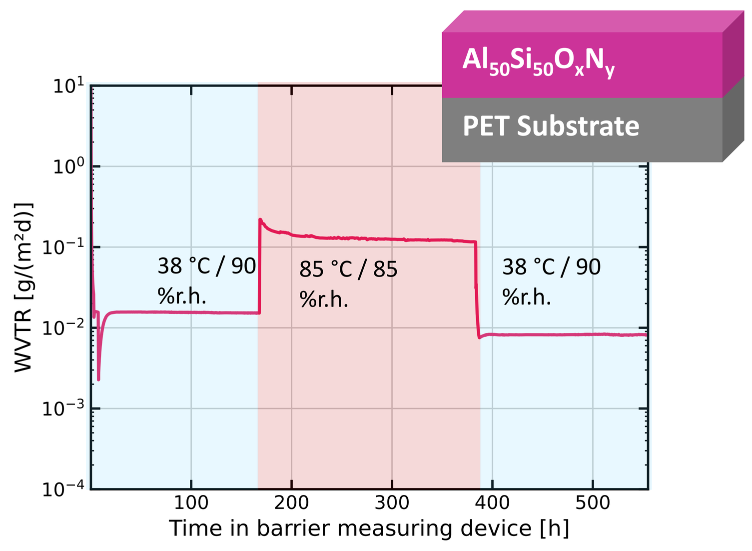
Accelerated Aging:
Damp-Heat testing (elevated temperature & relative humidity).

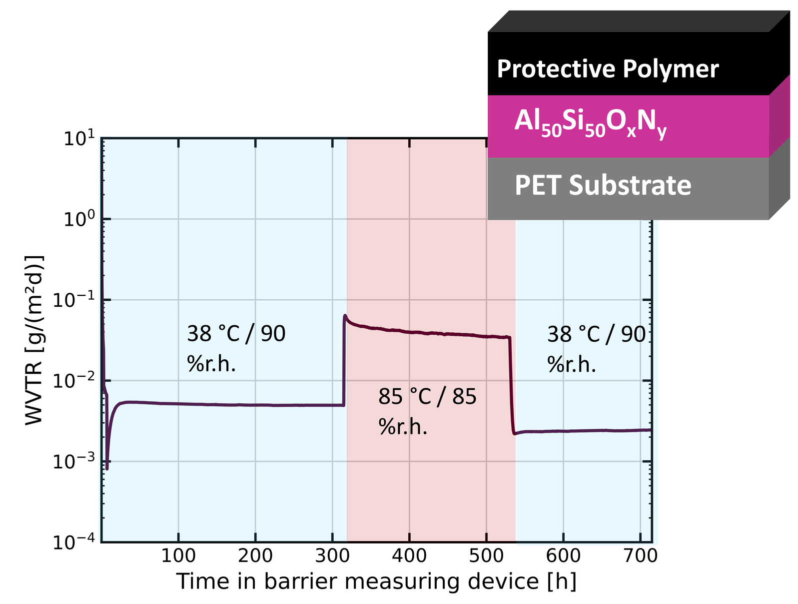
Microstructural Characterization:
SEM → Surface morphology, defect evolution, and critical failure mode analysis.

Barrier under Damp Heat Conditions









Reversible Stability (ZTO):
Pure ZTO exhibits high chemical resilience under damp heat
(85 °C / 85% r.h.); post-stress reconditioning fully restores the original baseline WVTR (approx. 0.003 g/(m²d)).

Liner-Induced Degradation (ZTO):
The introduction of a protective polymer film causes continuous, irreversible WVTR deterioration during thermal stress, elevating final permeability by nearly half an order of magnitude due to harmful ZTO-liner interactions.

Matrix Optimization ($AlSiO_xN_y$):
In contrast to ZTO, $AlSiO_xN_y$ barriers show continuous performance improvement (decreasing WVTR) throughout exposure to 85 °C heat.

Post-Stress Integrity ($AlSiO_xN_y$):
Returning to baseline conditions (38 °C / 90% r.h.) yields a final permeability significantly lower than initial pre-test values.

Protective Film Compatibility:
Unlike the ZTO system, the protective polymer has no adverse effects on $AlSiO_xN_y$, so that improvements are maintained after hygrothermal exposure.

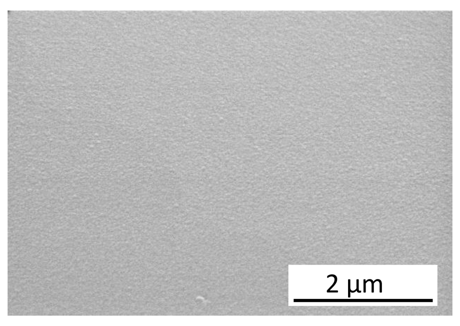
Morphology after Damp Heat

As-Deposited Morphology:
Both pristine ZTO (top-left) and $AlSiO_xN_y$ (bottom-left) thin films exhibit a highly homogeneous, smooth, and defect-free surface finish prior to climatic exposure.

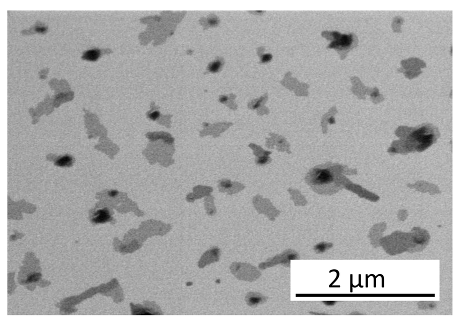
Localized Degradation (ZTO):
After 85 °C/85 %r.h damp-heat testing, ZTO (top-right) develops pronounced localized defect zones, flake-like structural alterations, and pinhole precursors across the surface.

Morphological Integrity ($AlSiO_xN_y$):
In contrast, the $AlSiO_xN_y$ layer (bottom-right) retains full structural and morphological stability after 85 °C/85 %r.h. exposure without any observable defect formation or micro-cracking.

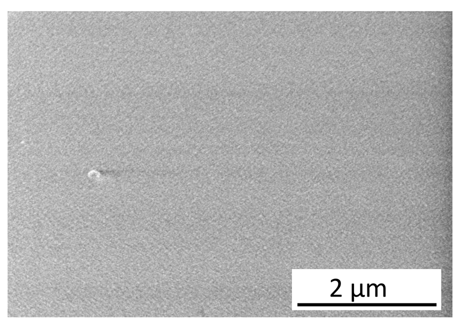
Microstructural Correlation:
SEM surface analysis confirms that while ZTO suffers localized surface corrosion under hygrothermal stress, chemically tuned $AlSiO_xN_y$ provides superior barrier resilience and moisture resistance.



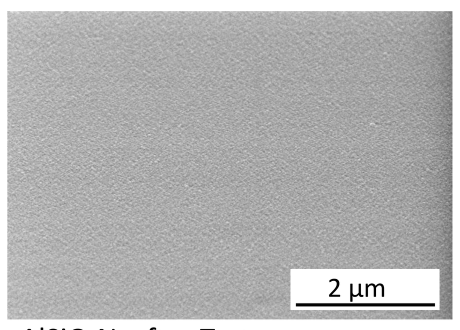
ZTO before Test



ZTO after Test



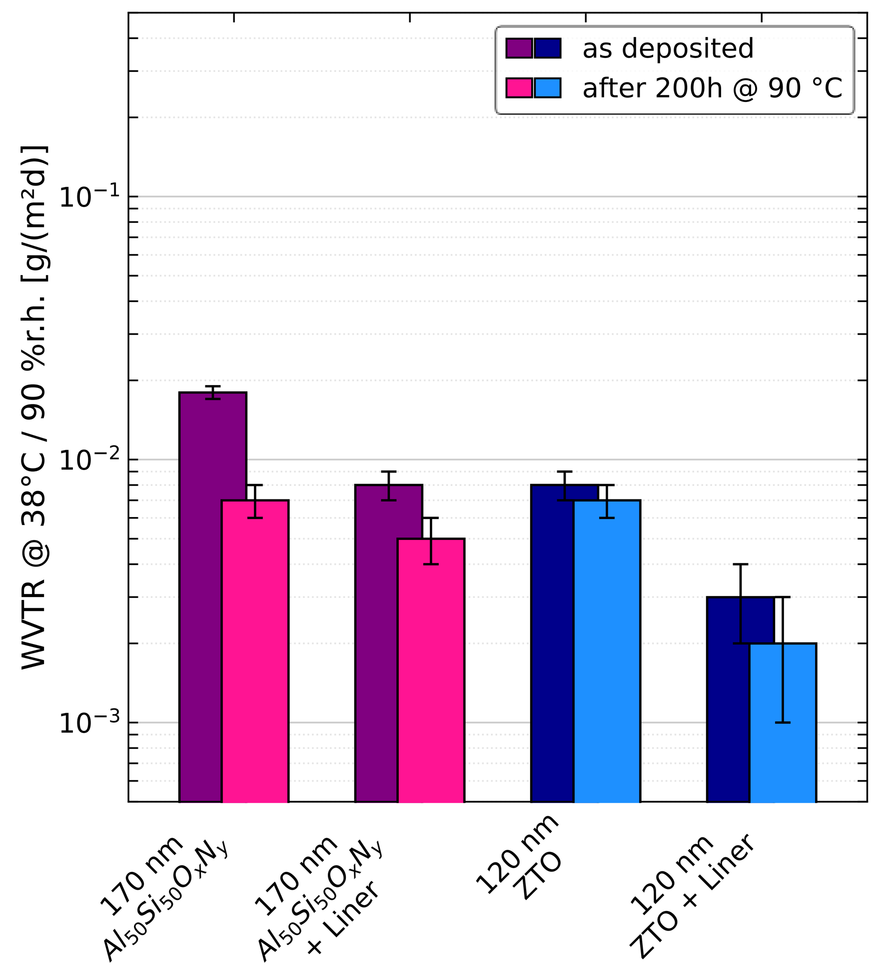
$AlSiO_xN_y$ before Test



$AlSiO_xN_y$ after Test

SEM-micrographs of barrier layer without protective polymer film, damp heat test performed with climate acting on substrate side.

Heat Treatment



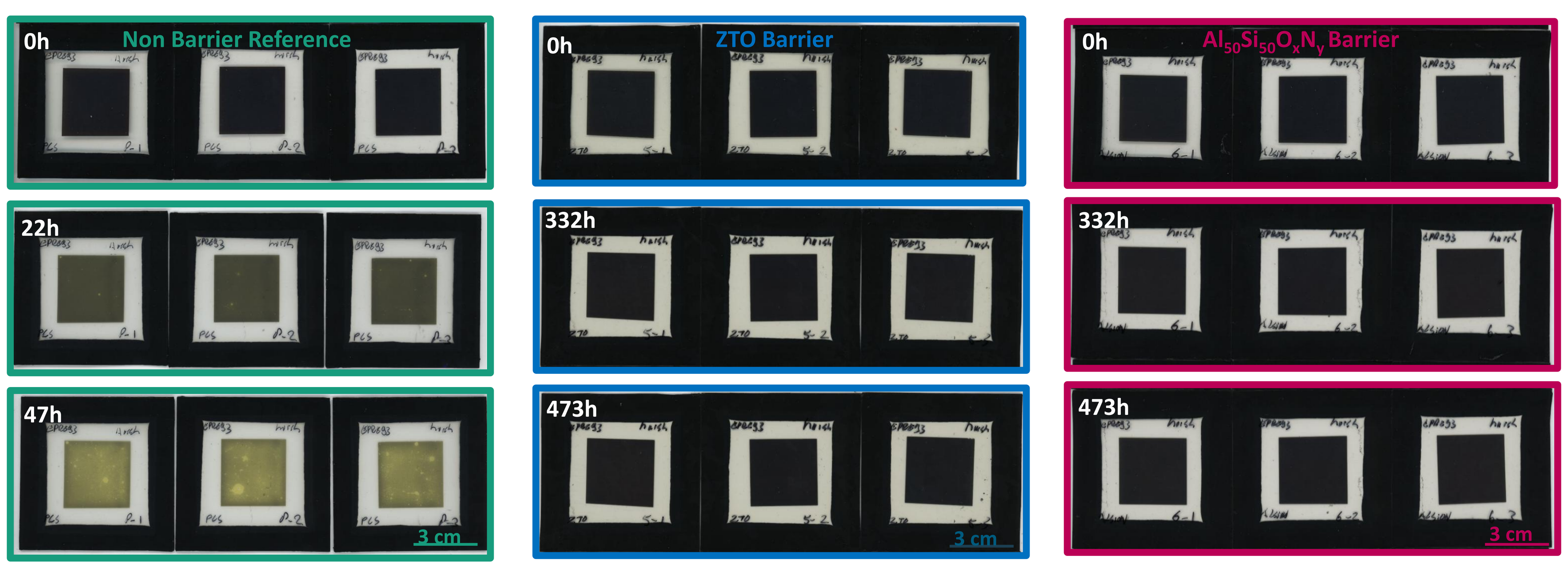
Matrix Densification ($AlSiO_xN_y$):
Structural compaction and defect closure occur independently of humidity, proving matrix densification is a temperature-driven process.

Dry Heat Stability (ZTO):
ZTO exhibits excellent resilience under dry thermal stress, maintaining nearly constant WVTR values both with (0.003 → 0.002 g/(m²d)) and without a liner (0.008 → 0.007 g/(m²d)).

Synergistic Degradation:
The severe degradation of ZTO liner systems at 85 °C/ 85 % r.h. is not driven by heat alone, but requires the combined presence of moisture and the protective polymer layer.

Core Implication:
Thermal stress enhances $AlSiO_xN_y$ barrier performance, whereas ZTO degradation is specifically triggered by hygrothermal (humidity-driven) interactions.

Proof of Concept: Encapsulated Perovskite Modules

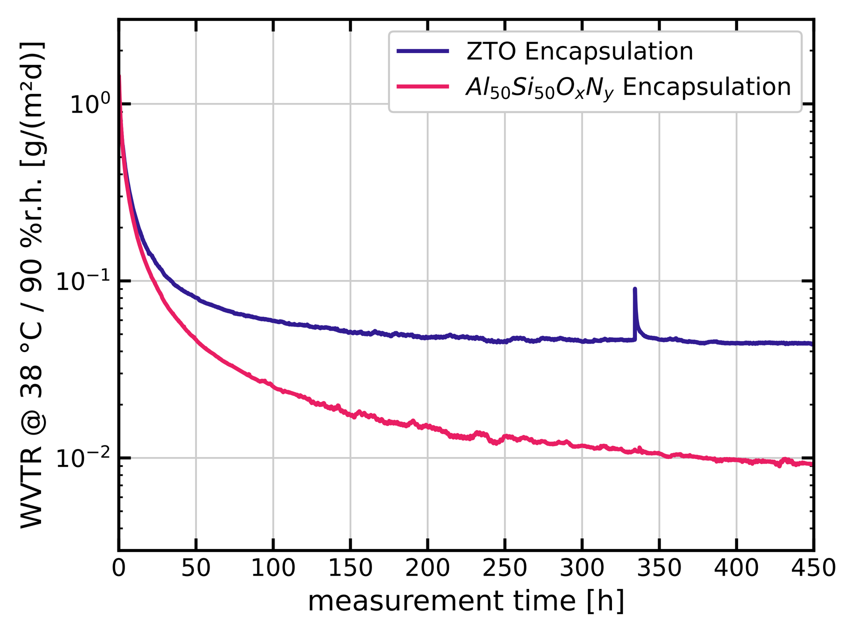


Visual test to evaluate the barrier film on perovskite samples under damp heat (85 °C / 85% r.h.) conditions
(7x7 cm² perovskite solar cell modules without contact stripes)

Samples without a barrier degrade rapidly (removed from the test after 47 hours)

The test is still ongoing.

After 473 hours, both encapsulations are stable and show no differences.

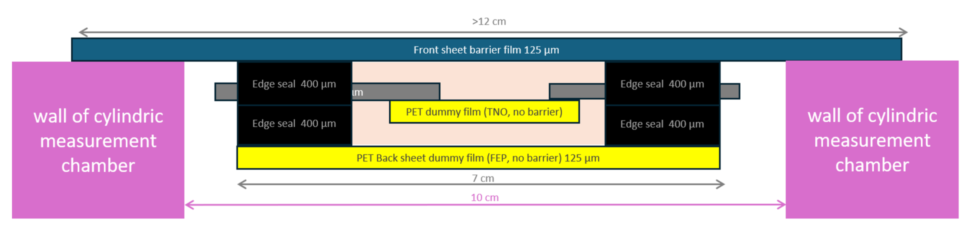


Barrier after encapsulation
(Integral WVTR-measurement of 7x7 cm² dummy solar cell modules without active layers but including all polymer films, contact stripes and front sheet encapsulation with barrier film).

The measurement takes a long time to stabilize.

ZTO appears to be damaged during encapsulation
(WVTR of 0.04 g/(m²d) compared to 0.001 g/(m²d) for initial ZTO-barrier foil).

$AlSiO_xN_y$ appears to be less damaged.



Next Steps

Compositional Mapping:
Systematically vary the N/O and Si/Al ratios during reactive sputtering to find the absolute minimum WVTR and optimal optical transparency.

Thickness Variation & Deposition Rates:
Optimize layer thickness down to minimum viable barrier levels to maximize Roll-to-Roll (R2R) throughput while maintaining defect-free morphology.

Interfacial Characterization:
Perform high-resolution cross-sectional analysis at the ZTO/polymer interface to clarify the chemical and mechanical reaction mechanism driving moisture-induced degradation.

Pre-Annealing Protocols:
Test systematic post-deposition thermal annealing of $AlSiO_xN_y$ prior to encapsulation to exploit the matrix densification effect before applying the protective polymer.

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