The influence of the buried interface on the orientational crystallization and thermal stability of halide perovskite thin films

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Fig S1. Diffractograms of perovskite thin films grown on NiO_x , MeO-2PACz, and $NiO_x/MeO-2PACz$ (b) Orientation degree of crystallographic planes relative to the (100) plane of the cubic perovskite.



Figure S2. Crystal structure of PbI_2 and diffractograms of perovskite thin films grown on FTO, SnO_2 , and $NiO_x/MeO-2PACz$ highlighting the PbI_2 001 peak.



Figure S3. Diffractograms of perovskite thin films grown on FTO (purple), SnO_2 (blue), and $NiO_x/MeO-2PACz$ (green) after thermal stress at 85 °C for 500h.



Figure S4. Relative intensity ratio of PbI_2 (001) and perovskite (100) diffraction peaks of perovskite thin films grown on FTO (purple), SnO_2 (blue), and $NiO_x/MeO-2PACz$ (green) after thermal stress at 85 °C for 500h.



Figure S5. Steady-state photoluminescence measurements of perovskite films grown on FTO, SnO_2 , and $NiO_x/MeO-2PACz$, before and after thermal stress at 85 °C for 500 h.



Figure S6. Time-resolved photoluminescence measurements of perovskite thin films grown on FTO, SnO_2 , and $NiO_x/MeO-2PACz$, before and after thermal stress at 85 °C for 500 h.



Figure S7. Diffractograms of perovskite thin films grown on FTO (purple), SnO_2 (blue), and $NiO_x/MeO-2PACz$ (green) after 1 week of ambient exposure, along with the respective film pictures.



Figure S8. SEM images of fresh perovskite films grown on FTO, SnO₂, and NiO_x/MeO-2PACz.



Figure S9. SEM images of perovskite films grown on FTO, SnO_2 , and $NiO_x/MeO-2PACz$ after thermal stress at 85 °C for 500 h.



Figure S10. Cathodoluminescence (CL) mapping of the perovskite films grown on FTO, SnO₂, and NiOx/MeO-2PACz (a-c) without thermal stress and (d-f) submitted to thermal stress at 85 °C for 500 h, respectively.



Figure S11. Scanning electron microscopy and elemental mappings of cesium (Cs), lead (Pb), and iodine (I) obtained by energy-dispersive X-ray spectroscopy (EDS) of (a) FTO, (b) SnO₂, and (c) NiOx/MeO-2PACz thin films submitted to thermal stress at 85 °C for 500 h.



Figure S12. (a) SEM images and Cathodoluminescence (CL) mapping of the perovskite films grown on FTO using a bandpass filter of (b) 600 to 650, (c) 650 to 700, and (d) 700 to 750nm.

The Tauc plot method is widely used to estimate the optical band gap energy (Eg) of semiconductors and insulators from UV-Vis absorption spectra. It is based on the Tauc relation, which describes how the absorption coefficient depends on the photon energy near the absorption edge.

$$(\alpha h\nu)^n = A(h\nu - E_g)$$
 Equation 1

Where, α is the Absorption coefficient, *h* is Planck's constant, *v* is the Photon frequency, *hv* is the Photon energy, E_g is the Optical band gap energy, and *n* is the exponent depending on th type of electronic transition. Throughout the UV-Vis absorption spectra and equation 1, the graph $(\alpha hv)^n vs hv$ can be constructed, and the linear region of the curve can be extrapolated to intersect the x-axis. The intercept gives the optical band gap energy E_g .



Figure S13. UV-Vis and Tauc plot of a FA_{0.90}Cs_{0.10}PbI₃ thin film.

The UPS was performed to build the energy level diagram between the perovskite and the transport layers used in different architectures. Work function (WF) is calculated from the cutoff energy (Ecutoff) through WF= 21.22 eV – Ecutoff as shown in Figure S14. To determine the valence band maximum (VBM), use the energy difference between the WF and the onset energy (Eonset), which is determined from the logarithmic scale UPS data extracted from Figure S14.



Figure S14. The UPS data. a-d) the cut-off edge for SnO_2 , NiO_x , MeO 2PACz, and Perovskite. eh) Valence band for SnO_2 , NiO_x , MeO 2PACz, and Perovskite. i-l) Energy level scheme for the perovskite and the electron transport layer (SnO_2) and hole transport layer (NiO_x , MeO 2PACz, and NiO_x/MeO 2PACz).



Figure S15. Photovoltaic parameters of the fabricated perovskite solar cells with different charge transport underlayers. (a) open-circuit voltage (V_{OC}), (b) short-circuit current (J_{SC}), (c) fill factor (FF), and (d) power conversion efficiency (PCE).



Figure S16. Backward (solid lines) and forward (dashed lines) current density (*J*) versus voltage curves of the best-performing perovskite solar cells based on NiO_x, MeO-2PACz, NiO_x/MeO-2PACz, and SnO₂ as the underlayer.



Figure S17. Normalized PCE of the perovskite solar cells based on SnO_2 , NiO_x , MeO-2PACz, and NiO_x/MeO -2PACz underlayers.

Table S1. TRPL decay parameters for perovskite growth on FTO, SnO_2 , and $NiO_x/MeO-2PACz$ films. T₁ and T₂ represent the fast and slow decay time constants, respectively, while A₁ and A₂ are their corresponding relative amplitudes.

	FTO	SnO ₂			NiO _x /MeO-2PACz		
	Fresh	500 h 85 °C	Fresh	500 h 85 °C	Fresh	500 h 85 °C	
A 1	0.37	8.31	6.37	18274.60	9.60	1396.36	
t ₁	36.00	17.80	20.00	6.18	21.50	8.75	
A ₂	1.00	1.04	1.19	2.16	0.52	0.22	
t ₂	722.00	205.60	130.99	47.82	392.06	297.91	

Table S2. Average photovoltaic parameters of the perovskite solar cells based on SnO_2 , NiO_x , MeO-2PACz, and NiO_x/MeO -2PACz underlayers: open-circuit voltage (V_{OC}), short-circuit current (J_{SC}), fill factor (FF), and power conversion efficiency (PCE).

	Direction	V _{oc} (V)	J _{sc} (mA cm ⁻²)	FF (%)	PCE (%)
SnO₂	Backward	1.03 ± 0.01	23.69 ± 0.38	75.08 ± 1.03	18.39 ± 0.33
	Forward	0.99 ± 0.02	23.78 ± 0.26	70.12 ± 1.10	16.45 ± 0.51
NiO _x	Backward	1.03 ± 0.01	23.47 ± 0.56	73.18 ± 1.37	17.72 ± 0.37
	Forward	1.01 ± 0.02	23.76 ± 0.40	66.38 ± 0.03	15.89 ± 2.59
MeO-2PACz	Backward	1.04 ± 0.02	23.03 ± 0.70	76.34 ± 1.16	18.32 ± 0.40
	Forward	1.03 ± 0.02	23.03 ± 0.67	71.58 ± 3.85	16.93 ± 1.07
NiO _x /MeO-2PACz	Backward	1.06 ± 0.02	23.75 ± 0.63	75.93 ± 0.65	19.18 ± 0.62
	Forward	1.04 ± 0.01	23.72 ± 0.64	72.73 ± 0.97	17.92 ± 0.50

Effect of Focused Ion Beam (FIB) damage.

Focused Ion Beam (FIB) processing, while essential for the preparation of thin lamellae suitable for transmission electron microscopy (TEM) analysis, can induce significant damage to perovskite films. The high-energy Ga⁺ ion beam can lead to physical destruction of the delicate perovskite structure, including partial grain collapse, amorphization, and the creation of defects such as vacancies and interstitials [1,2]. Moreover, perovskite materials, due to their soft ionic nature and low formation energy, are particularly susceptible to beam-induced degradation compared to more robust inorganic crystals [3]. During the deposition of protective layers (commonly platinum) and the subsequent welding processes, FIB can also introduce metallic nanoparticle contamination onto the sample surface, which can obscure or modify the intrinsic microstructural features [4]. To mitigate these effects, regions where the perovskite grains remained intact and free from deposition-induced contamination were carefully selected for high-resolution TEM and Selected Area Electron Diffraction (SAED) analyses, ensuring the structural characterization remained representative of the original material.



Figure S18 (a-b) Example of a region where FIB-induced damage is evident, showing partial destruction of grains and the presence of platinum nanoparticles deposited during the protection and welding steps. (c-d) Example of an intact perovskite grain, free from deposition contamination, used for high-resolution TEM and SAED analyses to ensure accurate structural characterization.

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