Supporting Information

Chemical and Electronic Investigation of Buried $NiO_{1-\delta}$, PCBM, PTAA/$MAPbI_{3-x}Cl_x$ Interfaces using Hard X-ray Photoelectron Spectroscopy and Transmission Electron Microscopy

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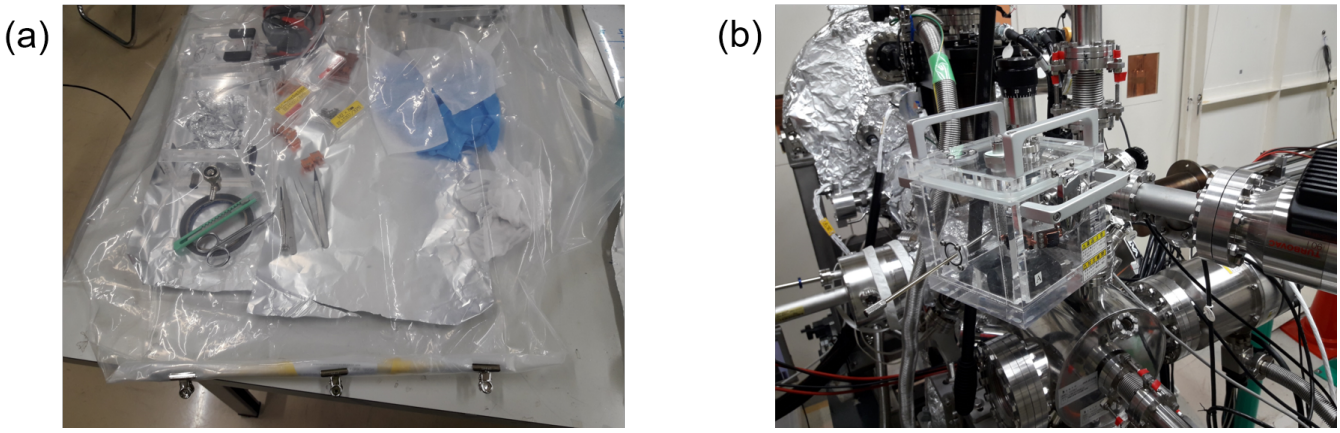

Figure S1: Transport samples for HAXPES analysis without subsequent contact with the ambient atmosphere: (a) unloading and sticking of samples on the sample holders under controlled environment and (b) prepared in the glove box (under argon) that fits to the introduction chamber at BL15XU of SPring-8.

Table S1: Summary of the peak fitting parameters from Pb 4f, I 3d, C 1s and N 1s elements: colors, components, binding energy (BE) in eV, Lorentzian Gaussian (L:G) ratio) and full width at half maximum (FWHM) are respectively listed.

Elements	Colors	Components	BE(eV)	GL(%)	FWHM (eV)
Pb 4f	Cyan	Pb reduced	136.9	30	0.60
	Wine	HaP	137.8	30	0.66 - 0.68
	Green	V'_{MA}/I'_I (HaP)	138.1	30	0.70 - 1
	Orange	PbI_2	138.7	30	0.70 - 1
I 3d	Wine	HaP	618.7	30	0.98 - 1
	Orange	PbI_2	619.4	30	1.2
	Yellow	HI/I_2	619.9	30	1.5
	Olive	CH_3I	620.7	30	1.3
C 1s	Magenta	C sp^2	284.4-284.6	30	0.9 - 1.0
	Cyan	C sp^3	284.9-285.1	30	0.9 - 1.2
	Wine	HAP/C-O/C-N	285.7-286.0	30	1.2 - 1.8
	Olive	MAI/C=O	286.8-287.0	30	1.2 - 1.8
	Orange	$COO-/CO_3$	288.6	30	2.3 - 2.5
	Green	$\pi \rightarrow \pi^\star$	291.0-293.1	30	2.5
N 1s	Violet	NH_3 ($NiO_{1-\delta}$)	398.4	30	1.2
	Blue	NH_3 (HaP)	398.9	30	1.2
	Light Gray	$CH-NH_2$	399.5	30	1.2
	Light Magenta	CH_3-NH_2	400.1	30	1.2
	Light Cyan	Dissociation MAI	401.0	30	1.2
	Wine	HaP	401.7	30	1.2
	Pink	MAI	402.5	30	1.2

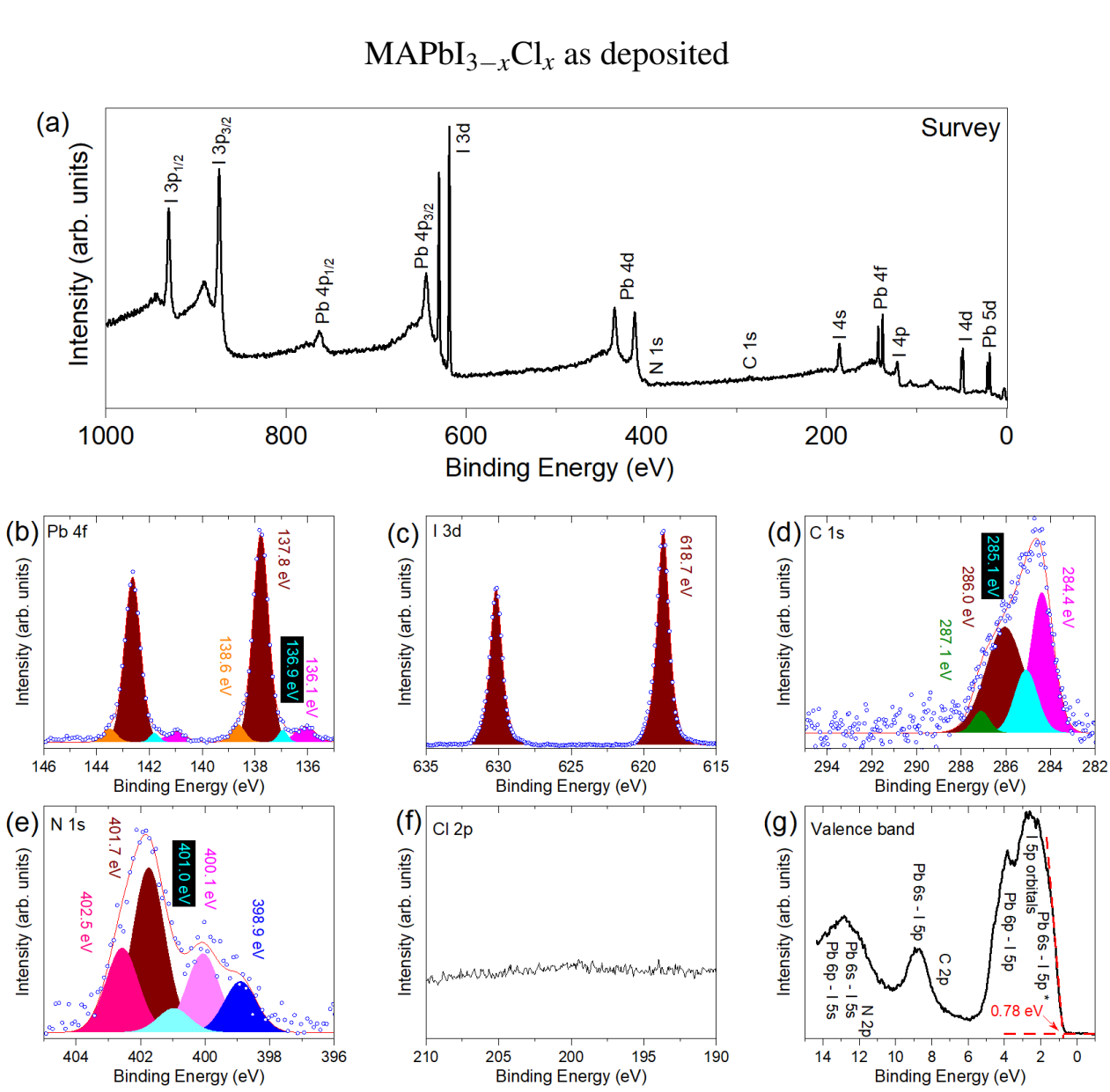

Figure S2: Bulk sensitivity of HAXPES measurements on the $MAPbI_{3-x}Cl_x$ (HaP: x < 1% and thickness around 300 nm) perovskite layer: (a) Survey, (b) Pb 4f, (c) I 3d, (d) C 1s, (e) N 1s, (f) Cl 2p and (g) valence band spectra. Open circles are the experimental points, red lines the best fit, colored peaks the different components. Descriptions of Pb 4f, I 3d, C 1s and N 1s components are reported in the Table S2.

Table S2: Experimental core level binding energy and components of Pb 4f, I 3d, C 1s and N 1s from HaP ($MAPbI_{3-x}Cl_x$) thin film in Fig. S2.

Pb 4f		I 3d		C 1s		N 1s	
Peaks (eV)	Components	Peaks (eV)	Components (eV)	Peaks (eV)	Components	Peaks (eV)	Components)
136.1	Pd^0	618.7	HaP/MAI	284.4	C sp^2	398.9	NH_3
136.9	Pb reduced	-	-	285.1	C sp^3	400.1	CH_3NH_2
137.8	HaP/MAI	-	-	286.0	HaP	401.0	Dissociation MAI
138.6	PbI_2	-	-	287.1	MAI	401.7	HaP
-	-	-	-	-	-	402.5	MAI

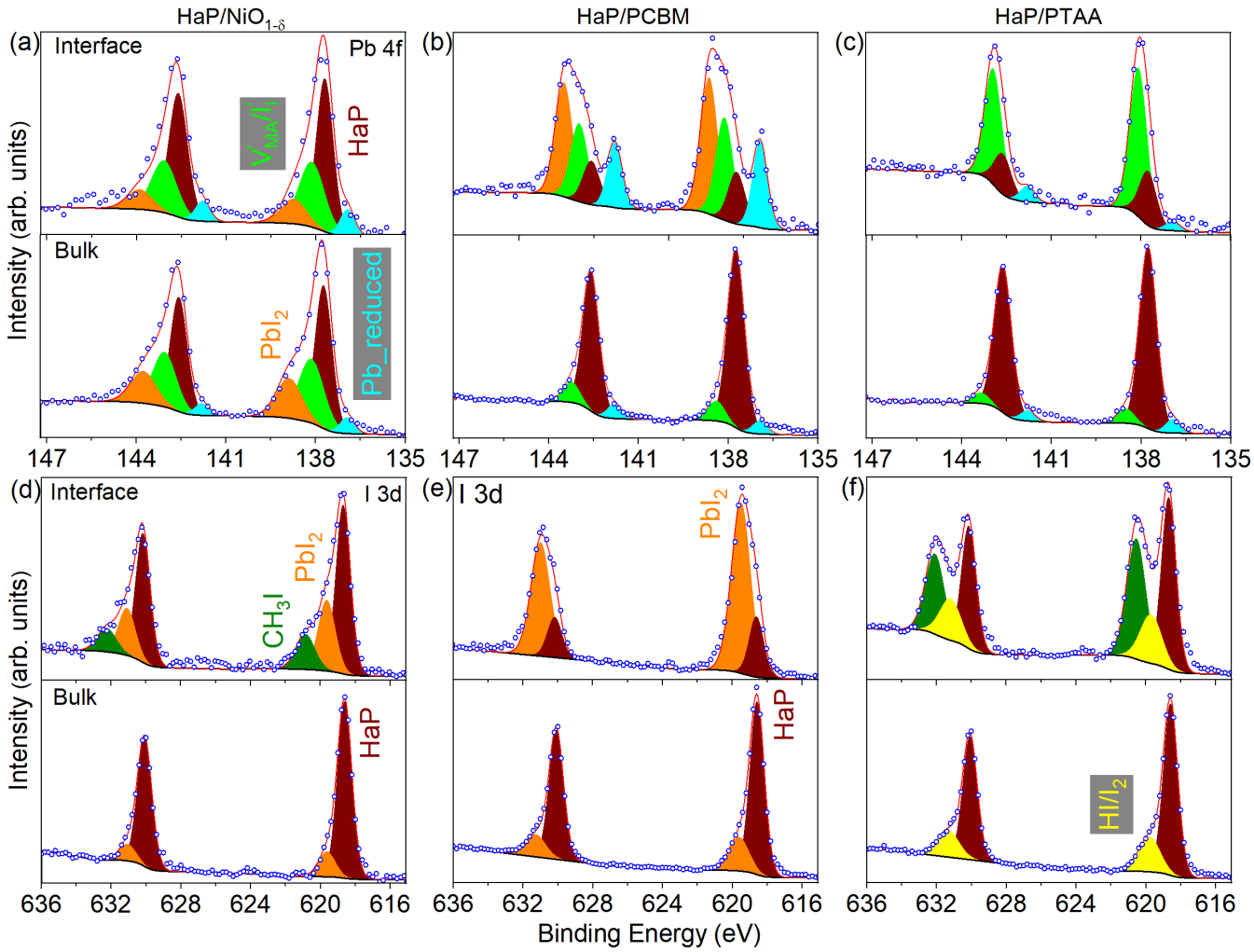

Figure S3: Core level Pb 4f (a–c) and I 3d (d–f) spectra from glass/ITO/HaP/TLM. TLM stands for transport layer material ($NiO_{1-\delta}$, PCBM and PTAA). From aging samples, bulk (θ = 87°) and interface (θ = 30°) enhanced sensitive probing are reported respectively.

Table S3: I/Pb ratio obtained from relative elemental concentrations of I 3d and Pb 4f core levels reported on Fig. S3

	HaP-bare	HaP/$NiO_{1-\delta}$	HaP/PCBM	HaP/PTAA
Bulk	2.8	0.2	1.9	0.7
Interface	-	1.8	0.9	4.2

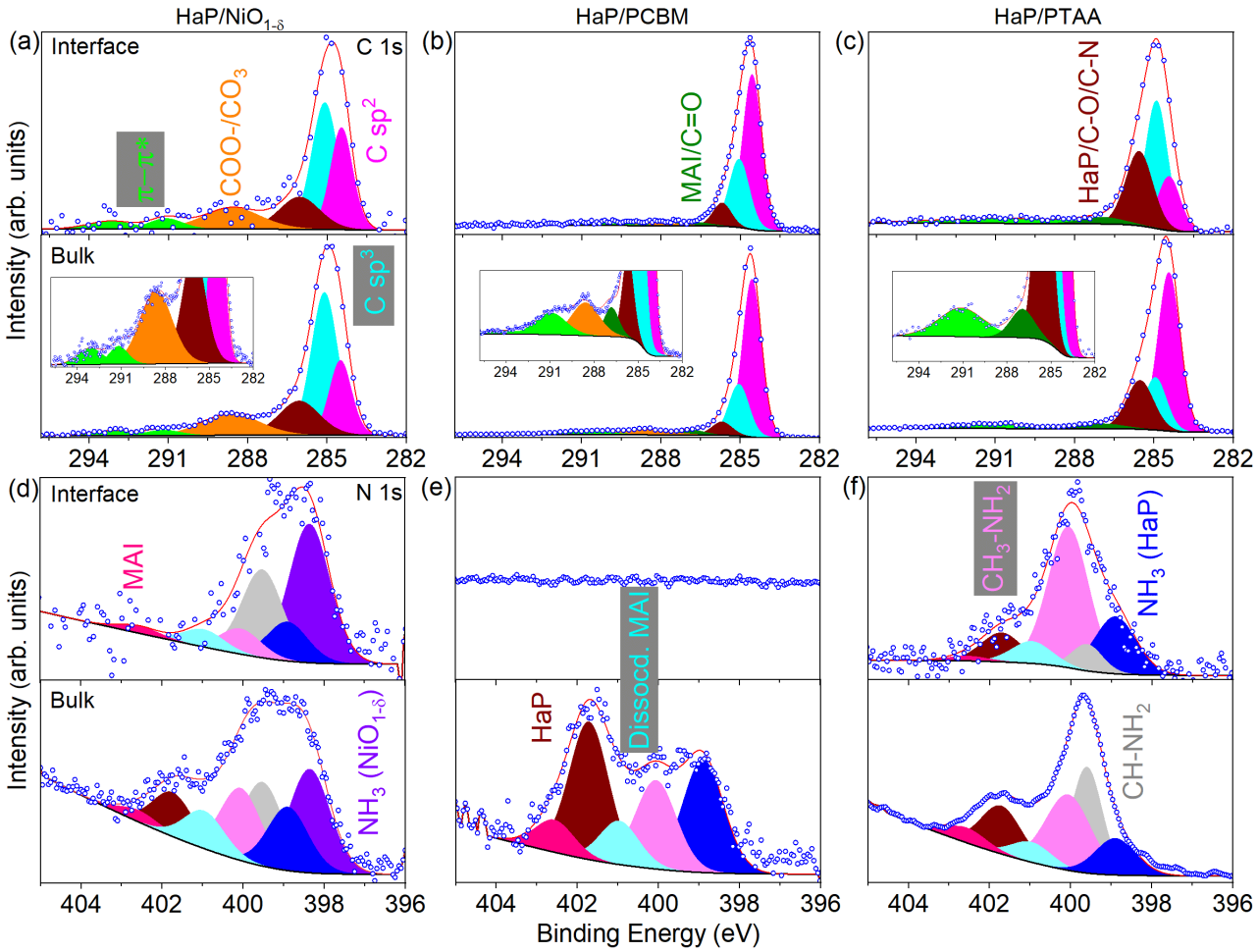

Figure S4: Core level C 1s (a–c) and N 1s (d–f) spectra from glass/ITO/HaP/TLM. TLM stands for transport layer material ($NiO_{1-\delta}$, PCBM and PTAA). From aging samples, bulk (θ = 87°) and interface (θ = 30°) enhanced sensitive probing are reported respectively.

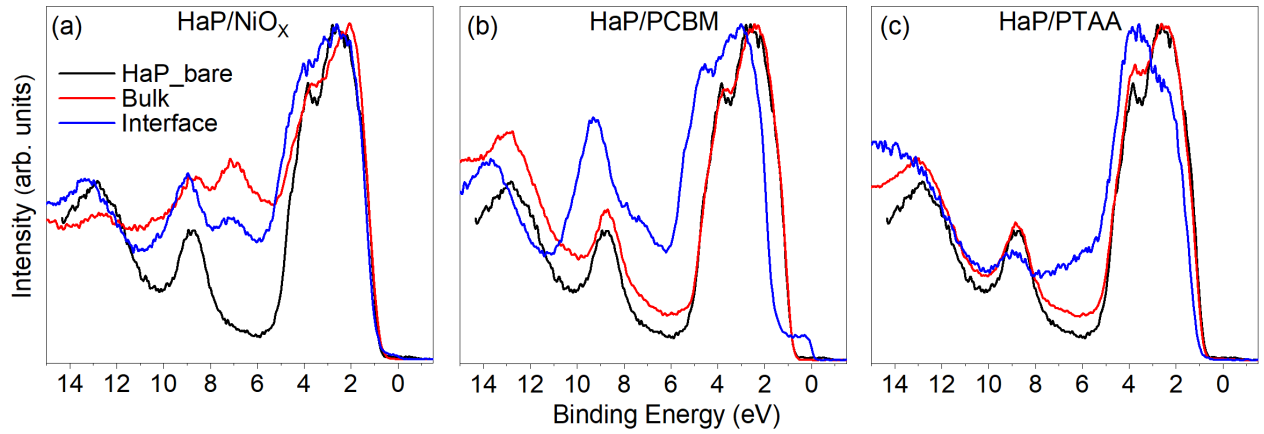

Figure S5: Valence band spectra from aging junctions: (a) HaP/$NiO_{1-\delta}$, (b) HaP/PCBM and (c) HaP/PTAA). Bulk and interface stand for bulk (θ = 87°) and interface (θ = 30°) sensitive probing, respectively. The valence state from the HaP as deposited (HaP-bare) is highlighted in the black curve.

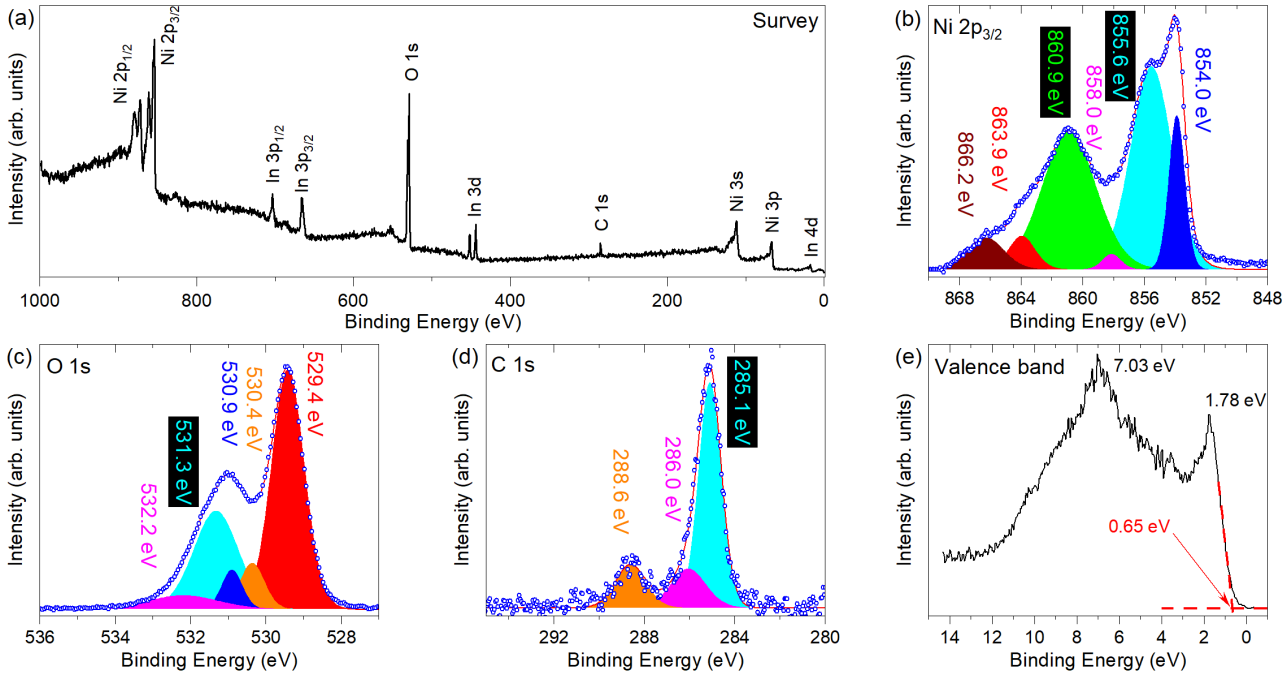

Figure S6: Bulk sensitivity of HAXPES measurements on the Glass/ITO/$NiO_{1-\delta}$ structures: (a) Survey, (b) Ni $2p_{3/2}$, (c) O 1s, (d) C 1s and (e) valence band spectra. Open circles are the experimental points, red lines the best fit, colored peaks the different components. Descriptions of Ni $2p_{3/2}$, O 1s and C 1s components are reported in the Table S4.

Table S4: Experimental core level binding energy and components of Ni $2p_{3/2}$, O 1s and adventitious C 1s from $NiO_{1-\delta}$ deposited on Glass/ITO substrate in Fig. S6 and Fig. S7.

Ni $2p_{3/2}$		O 1s		C 1s (adventitious)	
Peaks (eV)	Components	Peaks (eV)	Components (eV)	Peaks (eV)	Components
854.0	Ni^{2+}	529.4	NiO	285.1	C-C/C-H
855.6	Ni^{3+}	530.4	NiO*OH	286.0	C-O/C-N
858.0	Intersite	530.9	$Ni(OH)_2$	288.6	O-C=O
860.9	Sat I	531.3	Ni_2O_3	-	-
863.8.	Sat II	532.2	NiOO*H	-	-
866.6	Sat III	-	-	-	-

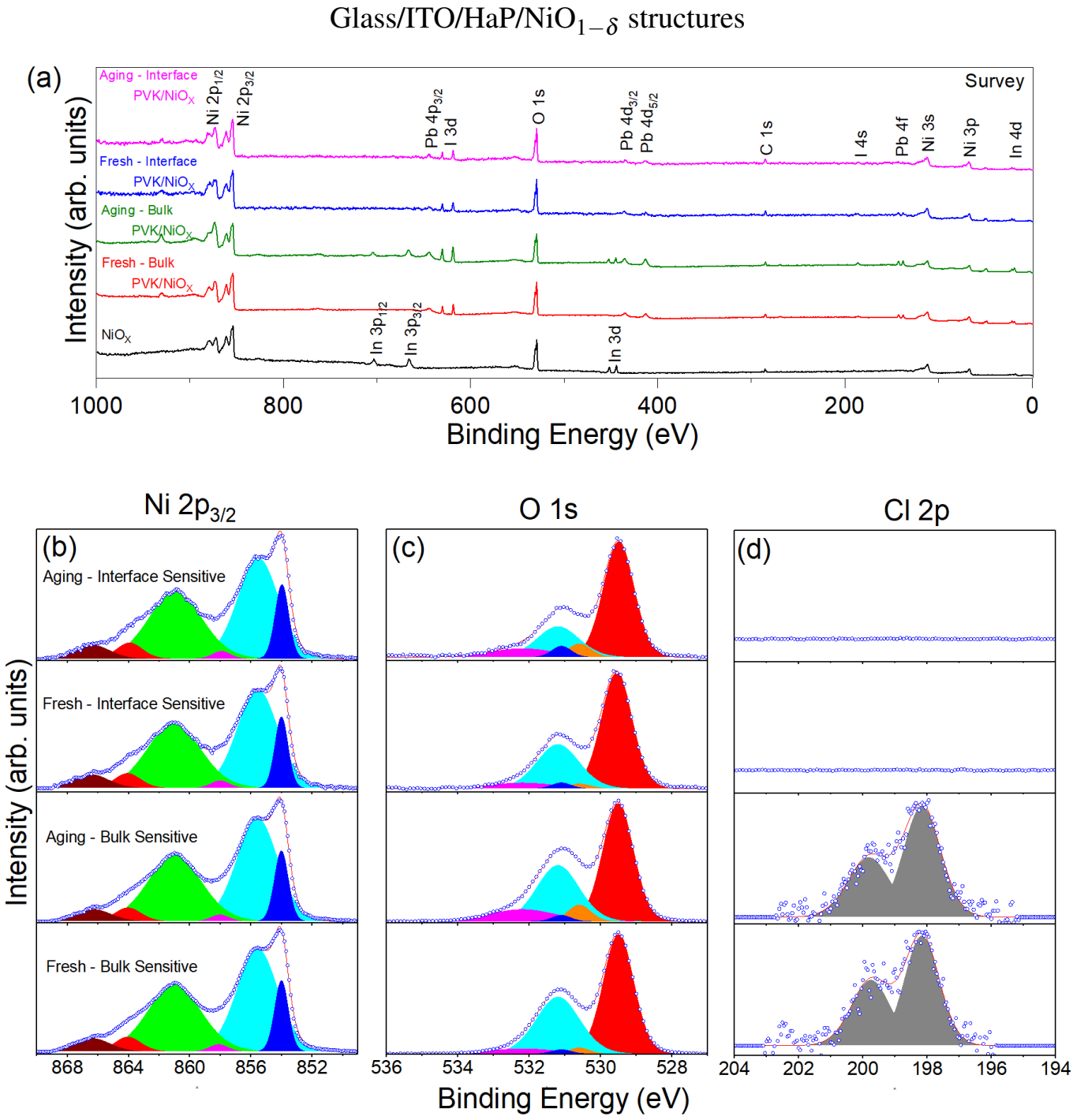

Figure S7: Probing depth HAXPES measurements for fresh and aging Glass/ITO/HaP/$NiO_{1-\delta}$ structures: (a) Survey, (b) Ni $2p_{3/2}$, (c) O 1s and (d) Cl 2p spectra. Cl is from the HaP. Open circles are the experimental points, red lines the best fit, colored peaks the different components. Descriptions of Ni $2p_{3/2}$ and O 1s components are reported above in the Table S3.

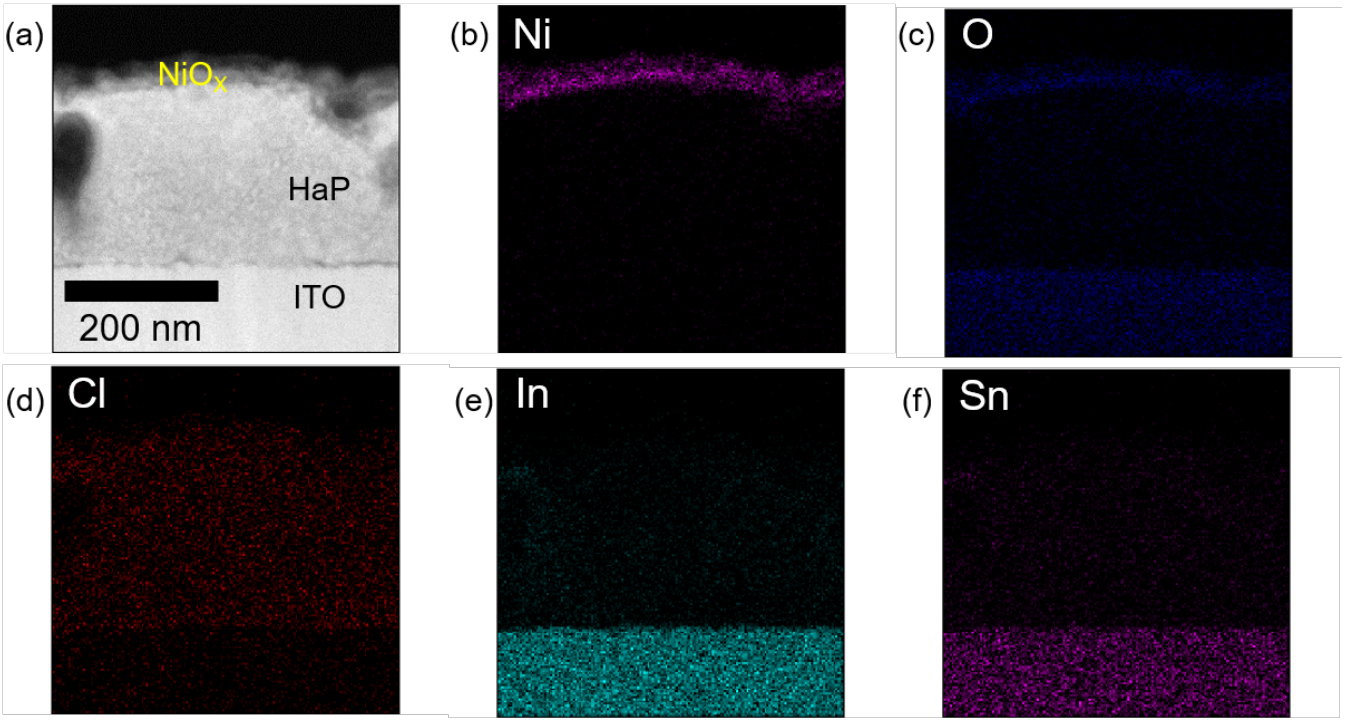

Figure S8: Cross-sectional STEM-ADF images and corresponding EDX maps of glass/ITO/HaP/$NiO_{1-\delta}$ structures. Glass/ITO/HaP/$NiO_{1-\delta}$ stacking (a) ADF image and individual chemical EDX maps of elemental (b) Ni, (c) O, (d) Cl, (e) In and (f) Sn.

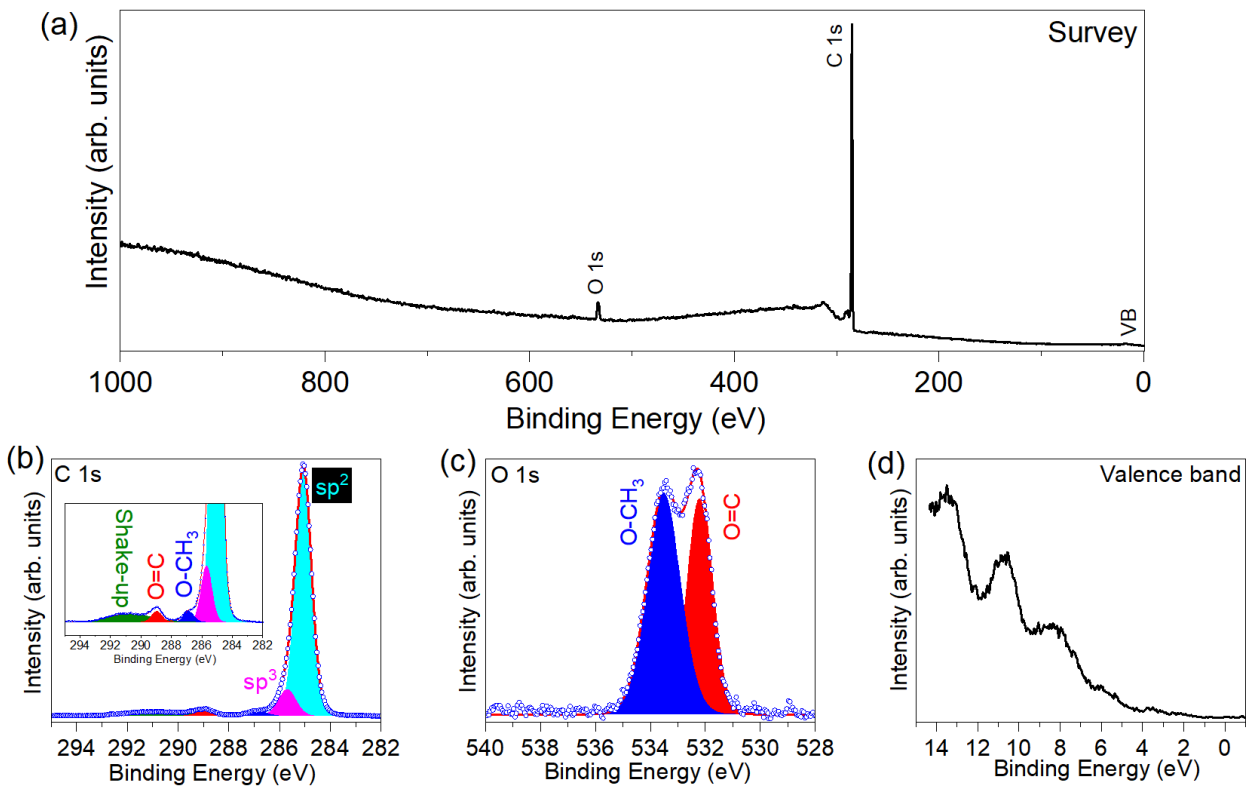

Figure S9: Bulk sensitivity of HAXPES measurements on the Glass/ITO/PCBM structures: (a) Survey, (b) C 1s, (c) O 1s and (d) valence band spectra. Open circles are the experimental points, red lines the best fit, colored peaks the different components. Descriptions of O 1s and C 1s components are reported in the Table S5.

Table S5: Experimental core level binding energy and components of C 1s and O 1s from PCBM deposited on Glass/ITO substrate in Fig. S9 and Fig. S10.

C 1s		O 1s	
Peaks (eV)	Components	Peaks (eV)	Components (eV)
285.0	C sp^2	530.7	-OH
285.7	C sp^3	531.7	-COO/CO_3
286.9	O-CH_3	532.2	O=C
289.0	O=C	533.0	C-O-C
290.7	Shake-up	533.5	O-CH_3

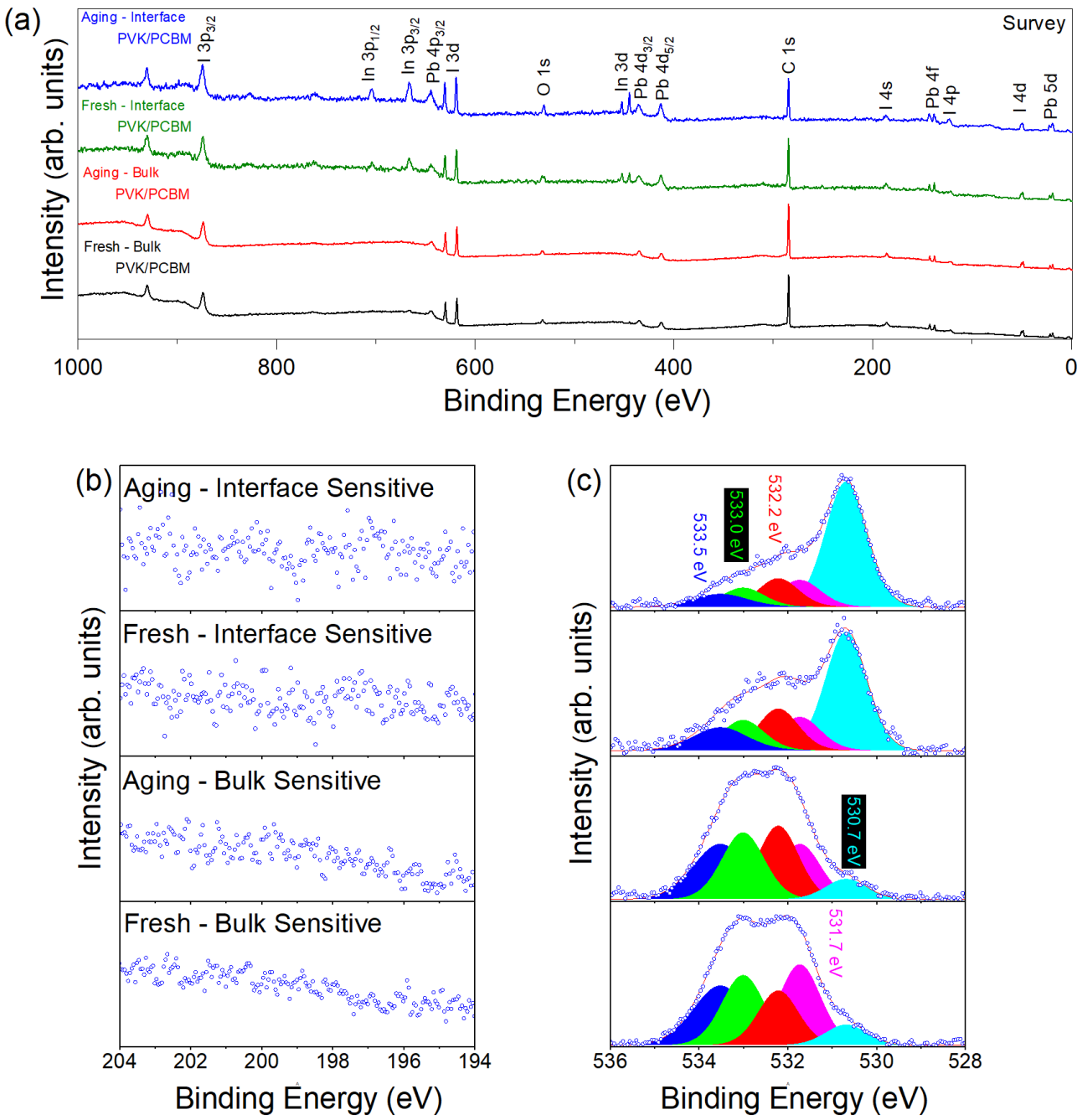

Figure S10: Probing depth HAXPES measurements for fresh and aging Glass/ITO/HaP/PCBM structures: (a) Survey, (b) Cl 2p and (c) O 1s spectra. Open circles are the experimental points, red lines the best fit, colored peaks the different components. Descriptions of O 1s components are reported above in the Table S4.

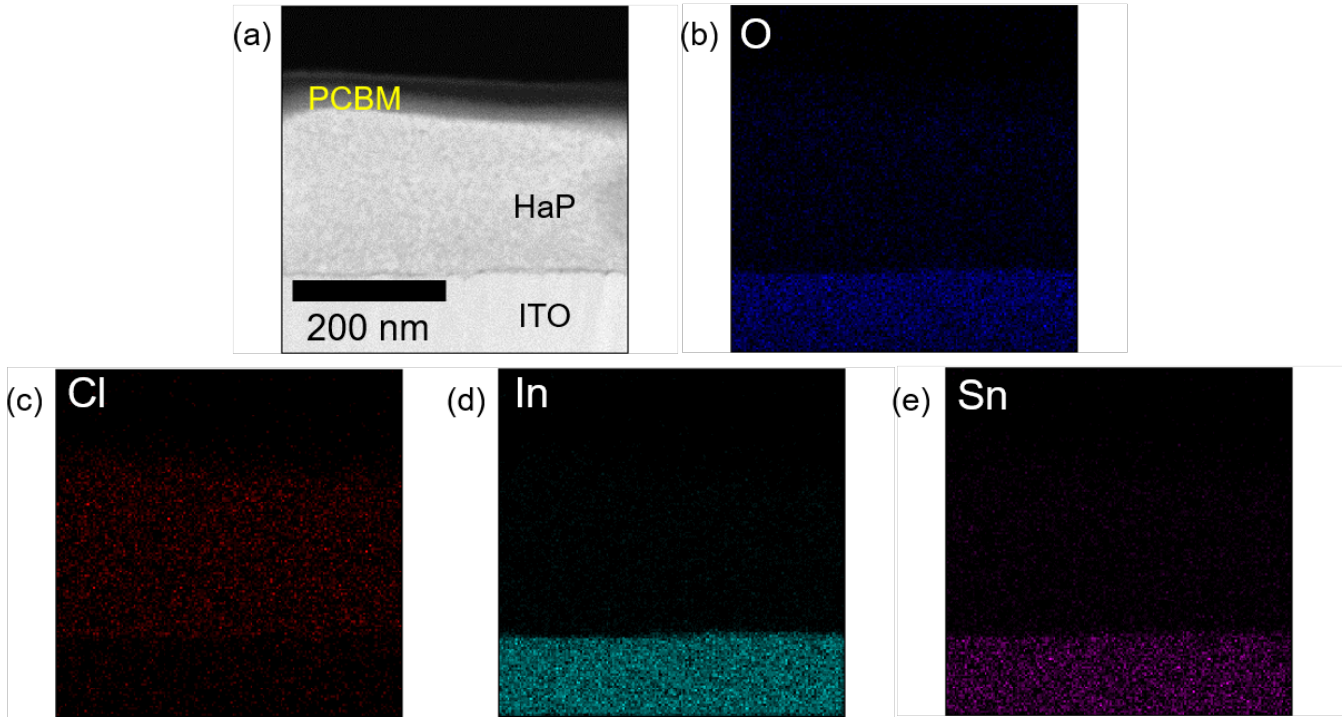

Figure S11: Cross-sectional STEM-ADF images and corresponding EDX maps of glass/ITO/HaP/PCBM structures. Glass/ITO/HaP/PCBM stacking (a) ADF image and individual chemical EDX maps of elemental (b) O, (c) Cl, (d) In and (e) Sn.

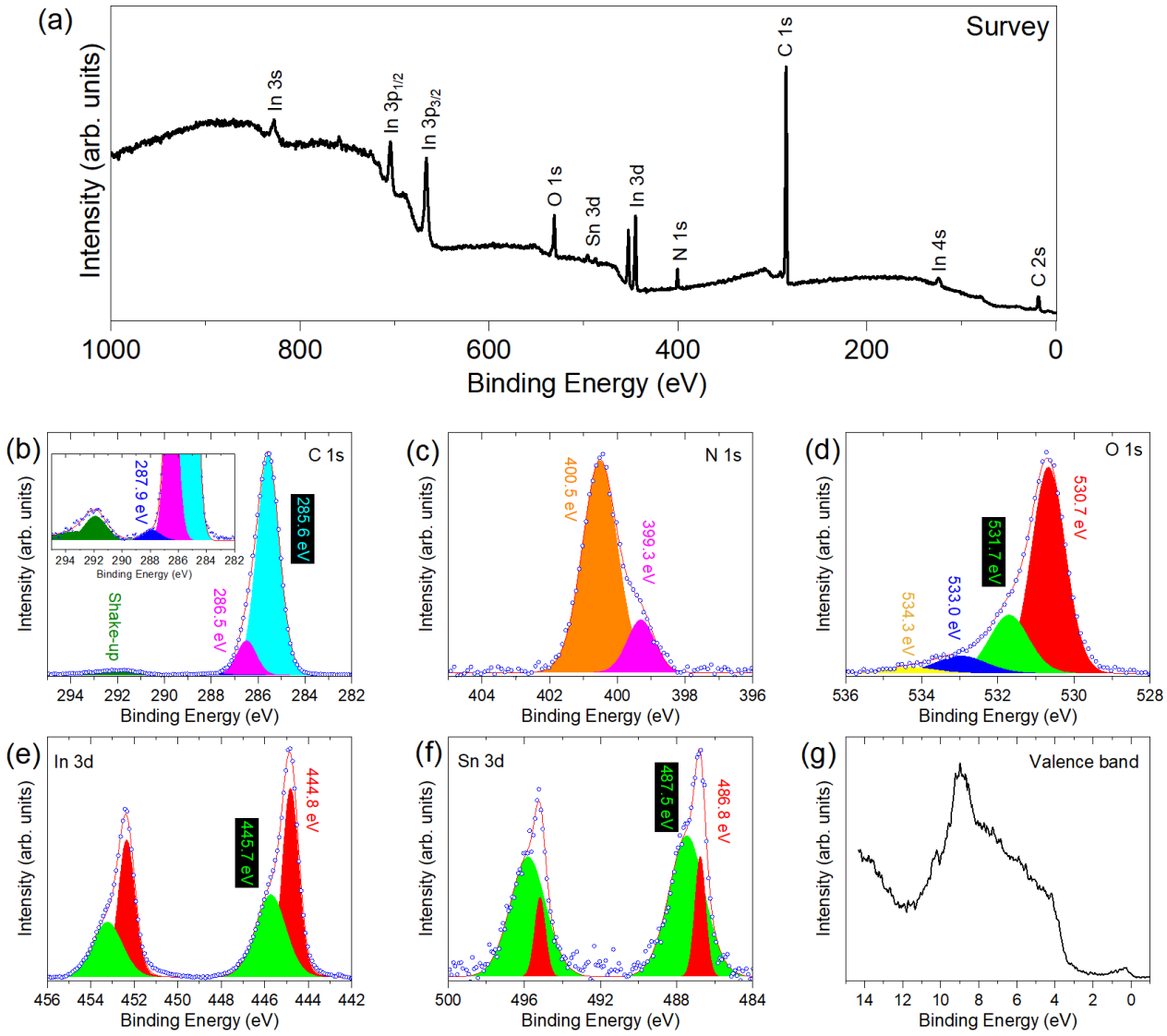

Figure S12: Bulk sensitivity of HAXPES measurements on the Glass/ITO/PTAA structures: (a) Survey, (b) C 1s, (c) N 1s, (d) O 1s, (e) In 3d, (f) Sn 3d and (g) valence band (PTAA + ITO). Open circles are the experimental points, red lines the best fit, colored peaks the different components. Descriptions of C 1s, N 1s, O 1s, In 3d and Sn 3d components are reported in the Table S6.

Table S6: Experimental core level binding energy and components of C 1s, N 1s, O 1s, In 3d and Sn 3d from PTAA deposited on Glass/ITO substrate in Fig. S12.

C 1s		N 1s		O 1s		In 3d		Sn 3d	
Peaks (eV)	Components	Peaks (eV)	Components (eV)	Peaks (eV)	Components	Peaks (eV)	Components	Peaks (eV)	Components
285.6	C sp^2/sp^3	399.3	-N$\cdots$ITO	530.7	-OH	444.8	ITO	486.8	ITO
286.5	C-N	400.5	PTAA	531.7	ITO	445.7	$In_2O_{3-x}(OH)_y$	487.5	Sn_xO_y/Sn-OH
287.9	C=O	-	-	533.0	C-O-C/H^+OH	-	-	-	-
291.9	Shaku-up	-	-	534.3	H-bonded (-OH$\cdots$O(ITO))	-	-	-	-
293.2	Shaku-up	-	-	-	-	-	-	-	-

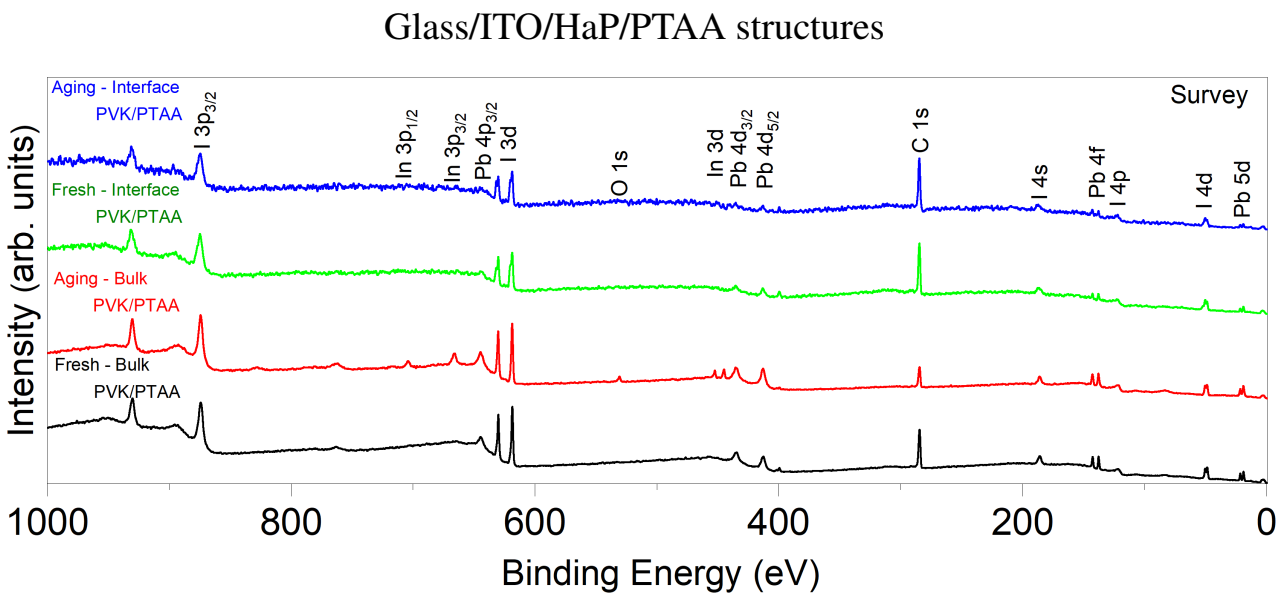

Figure S13: Surveys from Probing depth HAXPES measurements for fresh and aging Glass/ITO/HaP/PTAA structures

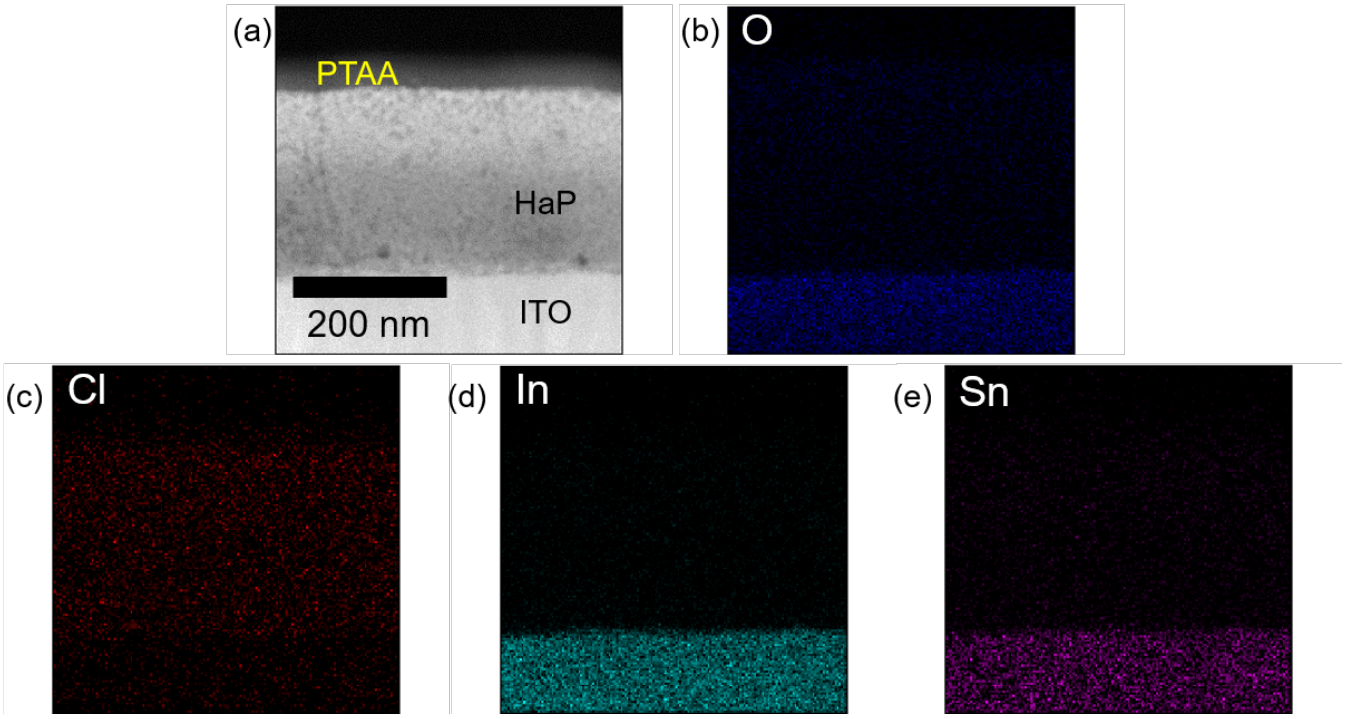

Figure S14: Cross-sectional STEM-ADF images and corresponding EDX maps of glass/ITO/HaP/PTAA structures. Glass/ITO/HaP/PTAA stacking (a) ADF image and individual chemical EDX maps of elemental (b) O, (c) Cl, (d) In and (e) Sn.

Glass/ITO/PTAA structures

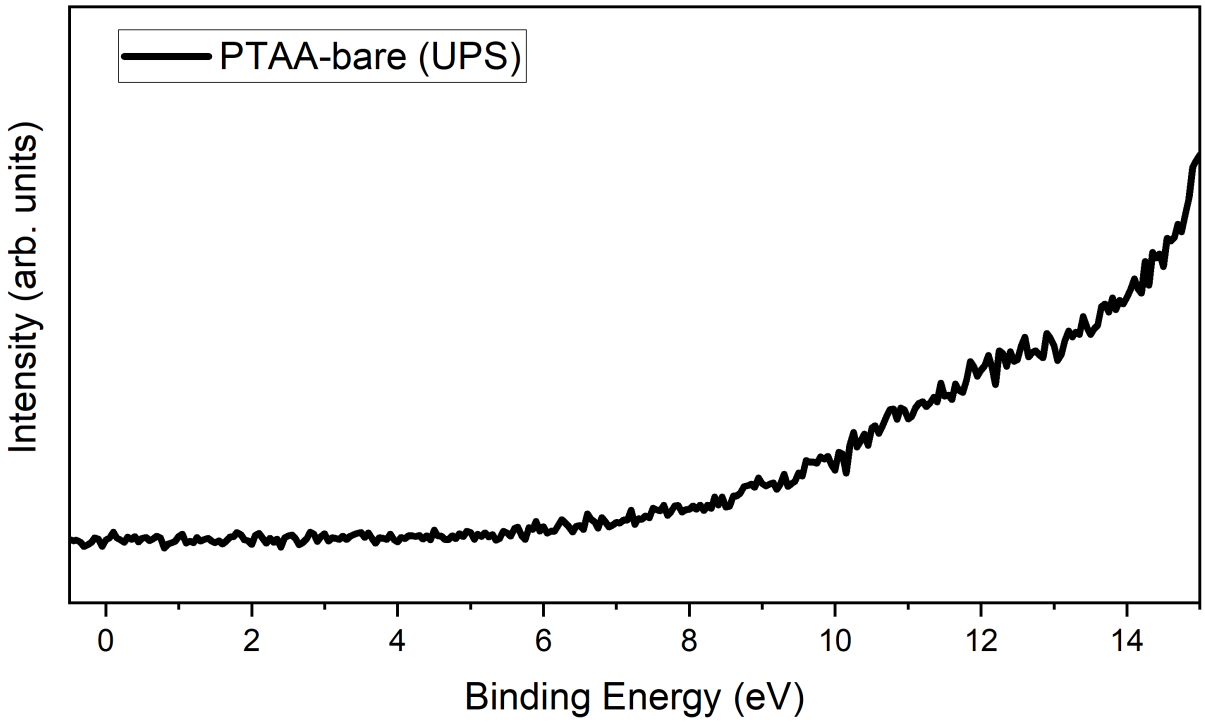

Figure S15: PTAA-bare valence band structure obtained from ultraviolet photoelectron spectroscopy (UPS).