

THE RELATIONSHIP BETWEEN SURFACES,
INTERFACES, AND BULK PROPERTIES IN
ORGANOMETALLIC HALIDE MATERIALS

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Abstract

In this work, organometallic halides as a photovoltaic material are investigated. In particular, photovoltaic devices based on the widely used composition MAPbI_3 were subjected to a range of degradation stress tests in which the relationship between electrode layers and interfacial phenomena (e.g. metal diffusion, metal-halide formation) were studied to a greater extent with surface characterisation techniques: Time-of-flight secondary ion mass spectrometry (ToF-SIMS), low-energy ion scattering (LEIS), and X-ray photoelectron spectroscopy (XPS).

Additionally, given the lack of empirically determined surface stoichiometry and discrepancies in reported quantification from XPS, surface stoichiometry of MAPbI_3 and compositional analogues are investigated using LEIS and ToF-SIMS. Results suggest that a Cs-deficient surface (at the first atomic layer) exists for Cs-substituted compositions and extrapolating to pure MAPbI_3 composition, suggests an MA-deficient surface; consequently a Pb-I rich surface.

A significant effort in determining the effect of organic (processing) additives on surface defect passivation was also undertaken. In particular, surface mass spectra show mass fragments derived from corresponding organic additives. Surface stoichiometry of I and Pb was deduced from LEIS and showed a deviation from pristine MAPbI_3 . These results support the hypothesised surface bonding mechanism(s) as well as the applicability of these techniques in characterising these materials.

The interactions of such ion beams and X-ray irradiation are also discussed and show that certain restrictions exist in using these techniques which are laid out in the following work.

Declaration of Originality

I hereby declare that the entirety of the work presented in this thesis was undertaken by myself; unless otherwise stated where specific contributions were appropriately credited. All figures and data are my own, unless stated otherwise with appropriate references and permission.

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Contents

List of Abbreviations	20
1 Introduction	24
1.1 Motivation	25
1.2 Thesis Outline	27
2 Literature Review	28
2.1 Photovoltaic Devices: A Brief Overview	28
2.2 MAPbI ₃ as a Photoactive Material	31
2.3 Stability of Organometallic Halides as a Photoactive Layer	33
2.3.1 Moisture Stability	34
2.3.2 Interaction of Light and Oxygen	35
2.3.3 Structural Stability	38
2.4 Photocurrent Hysteresis	41
2.4.1 Energy Level Alignment	42
2.4.2 Effects of Precursor Ratio	45
2.4.3 PbI ₂ Secondary Phase	45
2.5 Surface & Bulk Composition	46

2.5.1	Effects on Electronic Properties	48
2.5.2	Effect of X-ray Irradiation	50
2.6	Defect Passivation	53
2.7	Interlayer Reactions in a Perovskite Solar Cell	55
2.7.1	Transport Layer/MAPbI ₃ Interface	57
2.7.2	Electrode-Dependent Degradation	59
2.8	Concluding Remarks	64
3	Materials & Methods	66
3.1	Sample Fabrication & Device Testing	66
3.1.1	Thin Film Preparation and Deposition	66
3.1.2	Device Fabrication	68
3.1.3	J-V Characterisation	68
3.2	Stability Testing	68
3.3	Time-of-Flight Secondary Ion Mass Spectrometry	69
3.3.1	Theory	69
3.3.2	Ionisation and Molecular Mass Fragmentation	71
3.3.3	Dynamic SIMS	72
3.3.4	Instrumentation	74
3.3.5	Measurement Parameters	75
3.3.6	Data Analysis	76
3.4	Low-Energy Ion Scattering	77
3.4.1	Theory	77
3.4.2	Instrumentation	79

3.4.3	Measurement Parameters	80
3.4.4	Data Analysis	81
3.5	X-ray Photoelectron Spectroscopy	83
3.5.1	Theory	83
3.5.2	Instrumentation	86
3.5.3	Measurement Parameters	86
3.5.4	Data Analysis	86
3.6	X-ray Diffraction	88
3.6.1	Theory	88
3.6.2	Measurement Parameters	89
3.7	Scanning Electron Microscopy	90
3.7.1	Instrumentation & Measurement Parameters	91
4	Instrument Material Interactions	92
4.1	Motivation	92
4.1.1	Scope of Work	93
4.2	X-ray Photoelectron Spectroscopy	93
4.2.1	Irradiation Effects	95
4.2.2	Ultra-High Vacuum Effects	100
4.2.3	Cumulative vs. Iterative	101
4.3	Low Energy Ion Scattering	102
4.3.1	Morphological Effects	103
4.3.2	Chemical Effects	104
4.3.3	Static Limit	107

4.4	Time-of-Flight Mass Spectrometry	108
4.4.1	MAPbI ₃ Mass Fragment Analysis	109
4.4.2	Ag/C ₆₀ Interface	116
4.4.3	C ₆₀ /MAPbI ₃ Interface	119
4.5	Conclusions	120
5	Surface Composition of MAPbI₃ & Analogues	122
5.1	Motivation	122
5.1.1	Scope of Work	124
5.2	Stabilising Effects of Organic Additives	126
5.2.1	Iodine Diffusion	127
5.2.2	Thermal Stability	130
5.3	Mass Spectra Analysis	131
5.4	Organic Molecules Additives	137
5.4.1	Peak Integral Ratio $R_{I/Pb}$	137
5.4.2	I/Pb Stoichiometry	138
5.4.3	Peak Integral Variations	142
5.5	Surface Composition of MAPbI ₃ and Analogues	143
5.5.1	‘A’-Site Identification	146
5.6	Conclusions	149
6	Degradation and Diffusion in Organometallic Halide Devices	150
6.1	Motivation	150
6.1.1	Scope of Work	152

6.2	Electrode Dependent Degradation	152
6.2.1	Single Electrode Configuration	154
6.2.2	Bilayer Electrode Configuration	159
6.2.3	Diffusion of Metal-Electrodes	163
6.2.4	Errors	164
6.2.5	Conclusions	166
6.3	Thermally Induced Degradation	168
6.3.1	Instability of Cu and Au-based Devices	168
6.3.2	Extended Thermal Ageing	172
6.3.3	Cr Blocking Layer	176
6.3.4	Inter-electrode Degradation	185
6.3.5	Errors	187
6.3.6	Conclusions	188
7	Conclusions & Future Work	190
7.1	Instrument-Material Interactions	190
7.2	Surface Composition Analysis	191
7.2.1	Organic Molecules Additives	192
7.2.2	Surface Composition	193
7.3	Electrode Dependent Degradation	193
7.3.1	Electrode-Induced Degradation	193
7.3.2	Other Factors	194
7.4	Thermal Degradation	195

Appendices	223
A Rights and Permissions	224
B Supplementary Figures	225

List of Figures

2.1	Energy alignment within a typical photovoltaic device	28
2.2	Current density vs. voltage (J-V) and power vs. voltage (P-V) plots (Example)	30
2.3	Device architectures of organometallic halide based photovoltaic devices.	32
2.4	ToF-SIMS mass fragment intensities showing hydration-induced degradation	35
2.5	Evidence for increased superoxide yield with higher number of grain boundaries.	36
2.6	Interfacial energetics of various HTL and ETL that are independently obtained.	42
2.7	Illustration of band alignment	43
2.8	Time-resolved XPS showing defect tolerance of MAPbI ₃	52
2.9	Illustration of possible (interfacial) reactions and diffusion pathways within a photovoltaic device	56
2.10	Illustration of I ⁻ (green) from MAPbI ₃ and S ⁻ (blue) from PEDOT:PSS accumulating at the Ag/PCBM interface	58
2.11	Evidence for metal diffusion from various references.	61
2.12	Evidence for metal diffusion from various references.	62
2.13	XPS: Pb 4 <i>f</i> core-level spectra for various metal/organometallic halide composition interfaces	64
3.1	Mass separation based on time-of-flight.	69

3.2	An illustrated example of distinct regions expected in a concentration profile of a multi-layer sample.	74
3.3	Illustration of crater edge effects, underlining the need for a sufficiently small analysis area.	76
3.4	LEIS: Illustration of first atomic layer surface sensitivity.	78
3.5	Illustration of LEIS instrumentation.	80
3.6	LEIS: Data acquisition methodology.	82
3.7	LEIS: Peak fitting procedures	83
3.8	A typical survey spectra with photoemission peaks corresponding to the core-levels of the detected elements within the information depth.	84
3.9	XPS: Inelastic mean free path	88
3.10	SEM: Illustration of generated information from incident electrons.	90
4.1	XPS: Measurement protocol and timescales of iteration	94
4.2	Illustration of XPS experiment on a single MAPbI ₃ sample on five different areas: Area A ($t_{rad} = 0.5$ h, $t_{vac} = 0.5$ h), Area B ($t_{rad} = 1.0$ h, $t_{vac} = 1.5$ h), Area C ($t_{rad} = 1.5$ h, $t_{vac} = 3.0$ h), Area D ($t_{rad} = 2.0$ h, $t_{vac} = 5.0$ h), and Area E ($t_{rad} = 3.0$ h, $t_{vac} = 8.0$ h) . . .	95
4.3	XPS: Intensity plots of time-resolved core-level spectra	96
4.4	XPS: Core-level spectra of Area E ($t_{rad} = 3.0$ h)	97
4.5	XPS	100
4.6	Effects of UHV exposure on XPS spectra.	101
4.7	XPS: Cumulative core-level spectra.	102
4.8	SEM SE-Imaging: Top down images of MAPbI ₃ films bombard with ions within XPS analysis area.	103
4.9	SEM SE-Imaging: Top down images of MAPbI ₃ films bombard with ions.	104
4.10	XPS: Core-level spectra of areas bombarded with ⁴ He ⁺ (1 kV), ²⁰ Ne ⁺ (5 kV), ⁴⁰ Ar ⁺ (8 kV).	105

4.11	XPS: Core-level spectra of areas bombarded with $^{20}\text{Ne}^+$	107
4.12	XPS: Peak quantification post $^{20}\text{Ne}^+$ bombardment.	107
4.13	Dynamic ToF-SIMS: Surface mass spectrum of MAPbI_3 in negative polarity.	111
4.14	Dynamic ToF-SIMS: Surface mass spectrum of MAPbI_3 in negative polarity.	112
4.15	Static ToF-SIMS: Surface mass spectrum of MAPbI_3 in negative polarity.	113
4.16	Static ToF-SIMS: Surface mass spectrum of MAPbI_3 in negative polarity.	114
4.17	ToF-SIMS: Isotope Distribution of Pb_xI_y^-	115
4.18	Dynamic ToF-SIMS: Depth profiles of the Ag/C_{60} interface of $\text{ITO}/\text{MAPbI}_3/\text{C}_{60}/\text{Ag}$ device using Cs^+ , O_2^+ , Ar_x cluster ion beams.	117
4.19	Dynamic ToF-SIMS: Depth profiles of the $\text{C}_{60}/\text{MAPbI}_3$ interface of $\text{ITO}/\text{MAPbI}_3/\text{C}_{60}/\text{Ag}$ device using Cs^+ , O_2^+ , Ar_x cluster ion beams.	119
5.1	Optical stability of MAPbI_3 -AVA.	123
5.2	Illustration of chemical structure of organic additives, XRD data, and visual evolution of photostability.	124
5.3	SEM (SE-Imaging): Top-down images of MAPbI_3 made from precursor solutions with different additives.	126
5.4	PCE of MAPbI_3 and MAPbI_3 -Gly from MPP-tracking measurements.	127
5.5	Dynamic ToF-SIMS: Depth profiles of Au_x^- mass fragments	128
5.6	Dynamic ToF-SIMS: Depth profiles of I_x^- mass fragments	129
5.7	Dynamic ToF-SIMS: Depth profiles of Pb_xI_y^- mass fragments	130
5.8	Dynamic ToF-SIMS: Depth profiles showing thermal stability of MAPbI_3 and MAPbI_3 -Gly.	131
5.9	Chemical structures of organic additives used for mass spectra analysis.	132
5.10	Static ToF-SIMS: Mass spectra of fragments from NMA, glycine, and AVA.	135
5.11	Static ToF-SIMS: Mass spectra of fragments from NMA, glycine, and AVA.	136

5.12 LEIS: I and Pb peak integrals obtained from various precursor solutions with organic additives.	139
5.13 LEIS: Illustration of organic molecule bonding.	141
5.14 LEIS: Peak integral ratio variations between MAPbI ₃ samples and measurement runs. . .	142
5.15 LEIS: Scattering data from MAPbI ₃ and PbI ₂	144
5.16 LEIS: Low mass element identification.	145
5.17 LEIS: Scattering information from MAPbI ₃ , Cs _{0.05} (MA) _{0.95} PbI ₃ , and (FA) _{0.85} Cs _{0.15} PbI ₃ samples.	146
5.18 LEIS: Scattering data from post-oxygen treatment of MAPbI ₃ , Cs-substituted MAPbI ₃ , and (FA) _{0.85} Cs _{0.15} PbI ₃ samples.	147
5.19 LEIS: Scattering data from MAPbI ₃ and (MA) _{0.8} Cs _{0.2} PbI ₃	148
6.1 PCE reduction over time with Al, Cu, Ag, and CuAg based devices.	153
6.2 Dynamic ToF-SIMS: Depth profiles of pristine and degraded Al-based devices.	155
6.3 Dynamic ToF-SIMS: Depth profiles of pristine and degraded Cu-based devices.	156
6.4 Dynamic ToF-SIMS: Depth profiles of pristine and degraded Ag-based devices.	157
6.5 ToF-SIMS Ion Images: (x,y) spatially resolved inhomogeneities from degraded Ag-based devices.	158
6.6 ToF-SIMS Ion Images: (y,z-depth) spatially resolved inhomogeneities from degraded Ag-based devices.	159
6.7 Dynamic ToF-SIMS: Depth profiles of pristine and degraded CuAg-based devices.	160
6.8 XRD: Diffraction data showing suspected metal-halide diffraction peaks.	162
6.9 Dynamic ToF-SIMS: Depth profiles of pristine and thermally aged Ag-based devices. . . .	164
6.10 ToF-SIMS errors.	165
6.11 Dynamic ToF-SIMS: Depth profiles of pristine and thermally aged Cu-based devices. . . .	170

6.12 ToF-SIMS Depth Profile: Reference and thermally aged Au-based devices.	171
6.13 Dynamic ToF-SIMS: Depth profiles of pristine and thermally aged Cu-based devices for 24 h to 72 h	174
6.14 Dynamic ToF-SIMS: Depth profiles of pristine and thermally aged Au-based devices for 24 h to 72 h.	176
6.15 Device metric plots and J-V curves of CrAu, CrCu, Au, Cu based devices.	178
6.16 Dynamic ToF-SIMS: Depth profiles of pristine and thermally aged CrCu and CrAu-based devices for 24 h to 72 h.	179
6.17 Dynamic ToF-SIMS: Depth profiles of Au_x from monoatomic Ar sputter beam.	180
6.18 SEM SE-Imaging: Cross-section images of thermally aged CrCu and CrAu based devices.	181
6.19 XPS: Core-level spectra of peeled off electrodes.	182
6.20 XPS: I 3d, Au 4f, Cu 2p core-level spectra of peeled off electrodes for Cu, Au, CrAu.	184
6.21 Dynamic ToF-SIMS: Depth profiles of area between electrodes.	185
6.22 Illustration of mass fragment distribution and possible mass interferences.	186
6.23 Dynamic ToF-SIMS: Depth profiles of $m/z = 316.77$	187
 B.1 Chapter 4 , XPS: ore-level spectra of C 1s core-level from all analysis areas (A, B, C, D, E). Each spectrum is obtained from a single iteration loop ($t_{acq} = 57.3$ s).	225
B.2 Chapter 4 , XPS: Core-level spectra of N 1s core-level from all analysis areas (A, B, C, D, E). Each spectrum is obtained from a single iteration loop ($t_{acq} = 54.3$ s).	226
B.3 Chapter 4 , XPS: Core-level spectra of I 3d core-level from all analysis areas (A, B, C, D, E). Each spectrum is obtained from a single iteration loop ($t_{acq} = 45.2$ s).	227
B.4 Chapter 4 , XPS: Core-level spectra of Pb 4f core-level from all analysis areas (A, B, C, D, E). Each spectrum is obtained from a single iteration loop ($t_{acq} = 30.2$ s).	228
B.5 Chapter 5 , Static ToF-SIMS: Mean peak intensities of MAPbI ₃ -pristine (-).	229
B.6 Chapter 5 , Static ToF-SIMS: Mean peak intensities of MAPbI ₃ -pristine (+).	229

B.7	Chapter 5 , Static ToF-SIMS: Mean peak intensities of MAPbI ₃ -NMA-pristine (-).	230
B.8	Chapter 5 , Static ToF-SIMS: Mean peak intensities of MAPbI ₃ -NMA-pristine (+).	230
B.9	Chapter 5 , Static ToF-SIMS: Mean peak intensities of MAPbI ₃ -Gly-pristine (-).	231
B.10	Chapter 5 , Static ToF-SIMS: Mean peak intensities of MAPbI ₃ -Gly-pristine (+).	231
B.11	Chapter 5 , Static ToF-SIMS: Mean peak intensities of MAPbI ₃ -AVA-pristine (-).	232
B.12	Chapter 5 , Static ToF-SIMS: Mean peak intensities of MAPbI ₃ -AVA-pristine (+).	232
B.13	Chapter 6 , XPS: Survey spectra of peeled Cu electrodes for pristine and thermally aged devices.	233
B.14	Chapter 6 , XPS: Survey spectra of peeled Au electrodes for pristine and thermally aged devices.	233
B.15	Chapter 6 , XRD: Diffraction data of aged (by MPP-tracking and LED illumination) and pristine samples of Cu, Ag, CuAg-based devices.	234
B.16	Chapter 6 , XPS: C 1s core-level spectra of of pristine and thermally aged Au and Cu-based devices.	234

List of Tables

1.1	List of photovoltaic device data from various absorber layers.	25
2.1	Phase transition temperatures of various organometallic halide compositions.	39
2.2	Organometallic halide core-level binding energies from XPS and related stoichiometry. . .	47
2.3	Electronic structure of organometallic halides as obtained from references.	50
3.1	ToF-SIMS: Secondary ions used for mass calibration.	77
3.2	LEIS: Theoretical scattering energies for C, N, Cs, I, and Pb.	81
4.1	ToF-SIMS: Secondary ions used for layer identification.	109
5.1	Device data of thermal resistance of MAPbI ₃ - <i>Gly</i> compared to MAPbI ₃	131
5.2	Static ToF-SIMS: Mass fragment analysis of organic additives	133
6.1	ToF-SIMS: Secondary ions used for layer identification.	154
6.2	Interface widths (in seconds) calculated from the width between 16% and 84% of the maximum intensity.	155
6.3	Device data of pristine and thermally aged Cu-based devices.	168
6.4	Device data for thermally aged Au and Cu-based devices for 24 h to 72 h.	173
6.5	Device data for pristine and thermally aged CrAu and CrCu based devices.	177

6.6	XPS: Peak fitting data	183
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List of Abbreviations

MAPbI₃-AVA	MAPbI ₃ -5-aminovaleric acid.
MAPbI₃-NMA	MAPbI ₃ -1-naphthyl methylamine.
MAPbI₃-β	MAPbI ₃ -β-alanine.
MAPbI₃-γ	MAPbI ₃ -γ-butyric acid.
MAPbI₃-Gly	MAPbI ₃ -Glycine.
I_{MA}[×]	Iodide–methylammonium antisite.
I_{Pb}[•]	Iodide–Lead (II) antisite.
MA_I[×]	Methylammonium–Iodide antisite.
Pb_I[•]	Lead (II)–Iodide antisite.
I_i'	Iodide interstitial.
J_{sc}	Short-circuit current.
MA_i[•]	Methylammonium interstitial.
Pb_i^{••}	Lead (II) interstitial.
V_I[•]	Iodide vacancy.
V_{MA}'	Methylammonium vacancy.
V_{oc}	Open-circuit voltage.
V_{Pb}''	Lead (II) vacancy.
AFM	Atomic force microscopy.
BCP	Bathocuprine.
c-AFM	Conductive atomic force microscopy.
c-TiO₂	Compact titanium dioxide.
CB	Conduction band.
CB_{min}	Conduction band minimum.

CuPc	Copper phthalocyanine.
CVD	Chemical vapour deposition.
DMF	Dimethyl formamide.
DMSO	Dimethyl sulfoxide.
DOS	Density of states.
DSC	Dual-ion source column.
E_F	Fermi level.
E_v	Valence band onset.
EA	Electron affinity.
EDX	Energy dispersive X-ray.
ETL	Electron transport layer.
ETM	Electron transport material.
FA⁺	Formamidinium.
FAI	Formamidinium iodide.
FF	Fill factor.
FIB	Focussed ion beam.
FTO	Fluorine tin-doped oxide.
HAXPES	Hard X-ray photoelectron spectroscopy.
HOMO	Highest occupied molecular orbital.
HTL	Hole transport layer.
HTM	Hole transport material.
IP	Ionisation potential.
IPES	Inverse photoelectron spectroscopy.
J-V	Current density-voltage.
KPFM	Kelvin probe force microscopy.
LEIS	Low energy ion scattering.

LMIG	Liquid metal ion gun.
LUMO	Lowest unoccupied molecular orbital.
m-TiO₂	Mesoporous titanium dioxide.
MA⁺	Methylammonium.
MAI	Methylammonium iodide.
MCP	Multi-channel plate.
MPP	Maximum power point.
NMR	Nuclear magnetic resonance.
P-V	Power-voltage.
P3HT	Poly(3-hexylthiophene).
P3TAA	Poly(3-thiophenyl acetic acid).
Pb⁰	Metallic lead.
PCBM	[6,6]-phenyl-C61-butyric acid methyl ester.
PCE	Power conversion efficiency.
PEDOT:PSS	Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate).
PES	Photoemission Spectroscopy.
PFN	Poly[(9,9-bis(3'-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)].
PL	Photoluminescence.
PMMA	Poly(methyl methacrylate).
PTAA	Poly(triarylamine).
SE	Secondary electron.
SEM	Scanning electron microscopy.
sNiO_x	Sol-gel nickel oxide.
Spiro-OMeTAD	2,2',7,7'-tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene.
SRH	Shockley-Read-Hall.
STEM	Scanning transmission electron microscopy.
STEM-HAADF	Scanning transmission electron microscopy-High angle annular dark field.
ToF-SIMS	Time-of-flight secondary ion mass spectrometry.

UHV	Ultra high vacuum.
UPS	Ultraviolet-ray photoelectron spectroscopy.
VB	Valence band.
VB_{max}	Valence band maximum.
WF	Work-function.
XPS	X-ray photoelectron spectroscopy.
XRD	X-ray diffraction.

Chapter 1

Introduction

In light of the increasing need for renewable energy sources, there has been a spate of research in photovoltaics, more so organic photovoltaics (OPV)—owing to their low production costs. There has been an exponential rise in interest in organometallic halide materials, with the perovskite crystal structure ABX_3 with a range of possible applications in photovoltaic devices, water-splitting, and light-emitting devices. Perhaps the most widely studied and *de facto* composition is $CH_3NH_3PbI_3$ (where A-site: CH_3NH_3 , B-site: Pb, X-site: I and given the designation $MAPbI_3$). A range of possible cationic and anionic substitutions to improve performance and stability exist but are not the focus in this thesis. Instead, only $MAPbI_3$ and A-site and X-site substitutions are discussed in greater lengths where appropriate. The popularity can be attributed to an extremely simple deposition method where material fabrication can be completed in minutes. This allowed for high volume production in a laboratory setting with minimal capital costs. However, that in itself poses several problems such as reproducibility of data.

At present, the highest performance conversion efficiency (PCE)¹ national renewable energy laboratory (NREL)-certified single-junction device for an analogue of $MAPbI_3$ is at 25.2% compared to 22.8% for a polycrystalline Si device, beaten only by inorganic devices such as copper indium gallium selenide (CIGS), single-crystal Si, and multijunction devices [1]. Other independent bodies for photovoltaic cell certification also exist. An up-to-date compilation of these data can be found in [2]. **Table 1.1** shows the highest performing devices from various materials.

Despite their advantages, organometallic halides (specifically $MAPbI_3$) are known to be unstable in the presence of oxygen, light, water, and excessively high temperatures. Research in these areas have shown that water creates hydrated complexes, destabilising the crystal structure which allows other

¹Describing the device's efficiency in converting light to energy.

Table 1.1 Photovoltaic cell device data of different materials. Data obtained from [2] and cited references within. OMH: organometallic halide

Device	PCE(%)	V_{oc}	V_{oc}/E_g
<i>poly</i> -Si	22.3 ± 0.4	0.6742	0.61
<i>amorphous</i> -Si	10.2 ± 0.3	0.89	0.81
<i>poly</i> -GaAs	18.4 ± 0.5	0.99	0.70
Mixed OMH	20.9 ± 0.7	1.125	0.76
Organic	11.2 ± 0.3	0.780	

degradation mechanisms to initiate at accelerated rates. Under short exposures to water, the hydration process is reversible. The combined action of light and oxygen results in the formation in what is known as superoxide species (O_2^-) that initiates degradation of the material through acid-base reactions [3, 4], forming degradation products such as I_2 , CH_3NH_3I , CH_3I , NH_3 , $HI(g)$, $Pb(s)$, $PbI_2(s)$, though the dominant degradation by-products still need to be reconciled as certain discrepancies still exist. Indeed, because of the ease of fabrication at relatively low temperatures ($\sim 100^\circ C$), its low energy requirements for formation also mean an equivalence for decomposition to its constituents/degradation by-products [5] and may play a part in the degradation process.

1.1 Motivation

At present, the research field has several focal points and are subcategorised into fundamental material research and device research in this thesis. Materials research include (1) Compositional variations through substitution of the 'A'-site cation with larger organic cations (e.g. $CH(NH_2)_2^+$) or inorganic ones (e.g. Cs^+) to stabilise the perovskite crystal structure. (2) Compositional variations through substitution of X^- halogen anion to tune its intrinsic bandgap and for stability improvements. (3) Hysteresis phenomenon observed in the current-voltage sweep which is inherently tied to inherently high ion mobilities. (4) Defect control/mitigation to inhibit degradation from extrinsic factors.

Device research include (1) effects of various interlayers on device stability against extrinsic factors such as oxygen and light and against interlayer diffusion such as metal diffusion. (2) Ion diffusion (originating from $MAPbI_3$) throughout a device and related interfacial phenomena.

Given the thickness of such thin-film devices ($< 700\text{ nm}$), interfaces have a major role and have been shown to significantly influence device properties such as hysteresis and stability. For instance, certain interlayers can either behave as sources of, or barriers to, degradation. Interlayer chemical reactions could result in the formation of interfacial species that degrade device performance. Furthermore, at

present there have been little to no *empirical* data describing surface terminations of these materials. This can pose a problem as surface defects have been shown to be detrimental to device stability, resulting in extensive use of defect passivation/management strategies.

Thus, the focus of this thesis is on how various factors affect surface/interfacial phenomena in solid-state planar heterojunction device architectures; in particular, the relationship between surface/interfaces and stability of MAPbI₃ film and related devices. Stability in this case refers to thermal stability, photostability (stability against light and oxygen), and device performance stability.

Data obtained and discussed in this thesis are from surface sensitive characterisation techniques: X-ray photoelectron spectroscopy (XPS), low-energy ion scattering (LEIS), and time-of-flight secondary ion mass spectrometry (ToF-SIMS). Main consideration is given to significant changes in properties that are arguably attributed to a fundamental change in the physical or chemical characteristics at the interfaces and surfaces.

XPS relies on an excitation source to induce emission of photoelectrons within the sample. When said photoelectrons originate from certain core-levels of elemental species on the sample surface, the intensity of the detected photoelectrons are plotted against their recorded binding energies resulting in characteristic photoemission peaks. The peak position and any shifts observed can provide chemical information (such as oxidation states and chemical bonding information) from a depth of up to 10 nm from the surface while the intensity of such photoemission peaks can aid in relative atomic quantification of chemical species. As such, chemical and compositional changes to the material can be deduced.

LEIS provides ion scattering information from the first atomic layer of the sample, though capability for depth-resolved data also exists, allowing for the surface composition of the material to be characterised.

ToF-SIMS provides chemical information from the first atomic layer of the sample, though through a different process from LEIS. While obtained mass spectra cannot be used to quantify the surface composition, with prior knowledge of the sample(s), surface chemical species can be deduced, supporting scattering data from LEIS. ToF-SIMS can also be used to obtain depth-resolved chemical information which forms the core of this thesis where interfacial species are identified.

1.2 Thesis Outline

The following chapters aim to address certain aspects of the current research landscape. In particular:

Chapter 2 aims to review fundamental material and stability related issues, comprising the following topics: MAPbI₃ surface composition, defect passivation, and the intrinsic stability of organometallic halides. Finally, interlayer reactions are discussed to greater lengths with a focus on electrode and transport layer induced degradation phenomena.

Chapter 3 provides a description of the materials and fabrication processes. A brief introduction into physical processes underpinning main characterisation methods and their data analysis methods are also provided.

Chapter 4 supplements current understanding of the effects of x-ray irradiation and ultra-high vacuum conditions on obtained photoemission data. Given that there has yet to be any published work investigating these issues further analysis on interactions of low-energy ion beams (⁴He⁺, ²⁰Ne⁺, ⁴⁰Ar⁺) on the surface of MAPbI₃ is provided. Finally, the effects of different sputter beams (O₂⁺, Ar_x, Cs⁺) on chemical depth profiles for planar devices obtained with ToF-SIMS. The data reported and discussed in this chapter also serves to validate data discussed in the following chapters.

Chapter 5 investigates scattering information using LEIS as a function of various organic molecule additives and therefore by extension the effects of such organic molecules on MAPbI₃ surface stoichiometry. Surface stoichiometry of pristine MAPbI₃ and Cs-substituted MAPbI₃ are also investigated to characterise surface terminations.

Chapter 6 explores chemical depth profiles, using ToF-SIMS, of electrode-dependent degradation, specifically thermally deposited Ag and Cu electrodes and the stabilising effects of a Cu/Ag bilayer electrode. Additionally, thermal stabilities of Cu and Au electrodes are investigated, with the efficacy of a Cr blocking layer between the electron-transport material and the electrode further discussed. In particular, interfacial phenomena at the electrode/transport layer interface are analysed.

Chapter 7 provides a summary of conclusions to the work discussed in this thesis. Various experimental continuations are also discussed.

Chapter 2

Literature Review

2.1 Photovoltaic Devices: A Brief Overview

Photovoltaic devices exploit the ability of semiconductors, with a sufficiently low bandgap (E_g), to form electron-hole pairs from the excitation of ground state electrons in the valence band (VB) to the conduction band (CB) by incident photons ($h\nu$), where $h\nu > E_g$. In a simplified picture, if contacts (or terminals) with appropriate energy levels are put on either side of the material, the separation of electrons and holes from the semiconductor (or ‘absorber layer’ in this case) in opposite directions will generate a current and therefore power can be extracted from the system. This is known as a *p-i-n* solar cell where one contact has a valence band maximum ($VB_{\max}$) higher (*p*) than the absorber layer (*i*) and one whose conduction band minimum ($CB_{\min}$) is lower than that of the absorber layer (*n*)—with reference to the vacuum level. A simplified illustration of this process is shown in **Figure 2.1**.

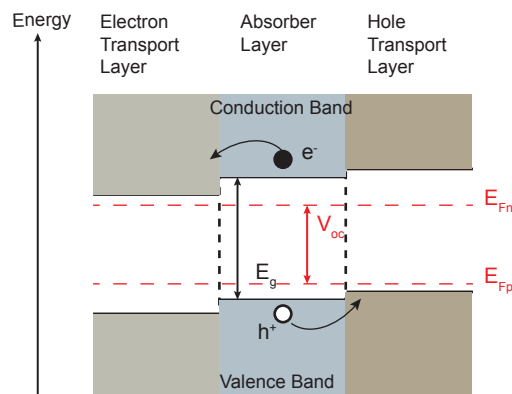


Figure 2.1 Typical energy level alignment of transport layers with respect to the absorber layer. E_{Fn} and E_{Fp} are the quasi-Fermi levels of the electron transport and hole transport layers, respectively.

A photovoltaic device has a few important parameters: its short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF), and power conversion efficiency. (PCE, η).

Mathematically, the current density vs. voltage (J-V) curve (**Figure 2.2**) is obtained through the superposition approximation [1]:

$$J = J_{SC} - J_0(e^{\frac{qV}{kT}} - 1) \quad (2.1)$$

where the right term is usually known as the dark current (J_{dark}) which is the current flowing through the device in opposite direction to the light (or photon) generated current under the presence of a potential difference between the selective contacts. Rearranging **Equation 2.1**, the V_{oc} of a device which is the highest voltage the device can obtain when current in a device is zero (*i.e.* when photogenerated current flowing through the device is balanced by the opposing diffusion current) and therefore sets the limit of a device is given by:

$$V_{oc} = \frac{k_B T}{q} \ln \left(\frac{J_{sc}}{J_0} + 1 \right) \quad (2.2)$$

The efficiency of a photovoltaic device can be found from the following:

$$\eta = \frac{V_{oc} J_{sc} FF}{P_{in}} \quad (2.3)$$

P_{in} = Incident power (W)

By applying a voltage across a device under illumination, the following J-V plot and power (output)-voltage (P-V) plots are obtained (**Figure 2.2**), showing the determination of V_{oc} and J_{sc} . When the P-V plot is at a maximum ($\frac{dP}{dV} = 0$), it corresponds to what is known as the maximum power point (MPP) and is obtained from the product of J_{max} and V_{max} . These values, in addition to V_{oc} and J_{sc} are used to calculate FF which describes the ideality of a device, where $FF = 1.0$ for an ideal device (**Equation 2.4**).

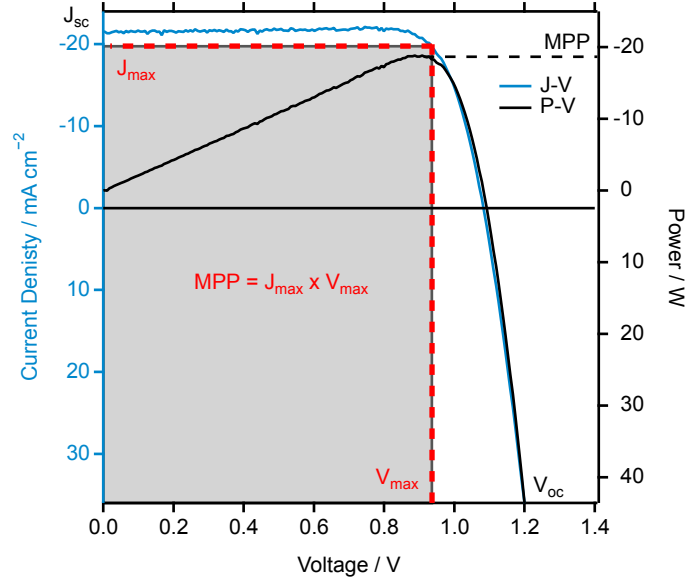


Figure 2.2 Example of current density vs. voltage (J-V) and power vs. voltage (P-V) plots of a photovoltaic device. The maximum point of the P-V plot gives J_{max} and V_{max} with J_{sc} and V_{oc} obtained from the J-V plot.

$$FF = \frac{J_{max} \times V_{max}}{J_{sc} \times V_{oc}} = \frac{P_{max}}{J_{sc} \times V_{oc}} \quad (2.4)$$

J_{max}, V_{max} = Values corresponding to the MPP shown in **Figure 2.2**

It is worthy to note that the above definitions of V_{oc} and J_{sc} (**Equation 2.2** and **Equation 2.1**) are based on ideal conditions and are lower in reality due to recombination processes of which there are two main types: radiative and non-radiative.

Radiative recombination processes are unavoidable and inherent to the material. It involves e-h pair annihilation in which the excited electron loses energy in the form of an emitted photon (hence, radiative) and recombines with a h^+ in the VB.

Whereas non-radiative recombination can be dependent on more extrinsic factors such as interfacial species introducing deep trap states. There are two types of non-radiative recombination: one involves transitions of excited electrons to lower energy states that do not result in photon emission, also known as Shockley-Read-Hall (SRH) recombination. The source of these lower energy states are usually defects in the crystal structure and microstructure that result in states within E_g . The other is known as Auger recombination and involves the same process as in radiative recombination with the energy released transferred to a ground-state electron in the VB. The excited Auger electron then relaxes to its ground state in the VB by releasing thermal energy to the crystal lattice.

In fact, device-specific V_{oc} determination takes the form [2, 3]:

$$V_{oc} = V_{oc,rad} + \frac{kT}{q} \ln(\eta_{ext}) \quad (2.5)$$

Where $V_{oc,rad}$ the radiative V_{oc} limit and η_{ext} is the external photoluminescence quantum efficiency (PLQE) in which non-radiative recombination processes are disregarded. Technologically speaking, the attainable V_{oc} of a device can also be thought to be the difference between the quasi-Fermi levels of the selective contacts ($V_{oc} = E_{Fn} - E_{Fp}$) and therefore depends on the workfunction of the selective contacts, as well as that of the the absorber layer (a review of the various interlayers used and their energetics, specific to organometallic halide absorber layers are given in **Section 2.4.1**).

2.2 MAPbI₃ as a Photoactive Material

An ideal photovoltaic material at its basis, with efficiency considerations, is a semiconducting material at room temperature, exhibiting a direct bandgap *i.e.* excitation of electrons results in direct transition from the valence band (VB) to conduction band (CB) without energy input or output (usually in the form of phonons). This organic-inorganic hybrid class of materials is known to possess such desirable qualities and its popularity amongst many researchers is further fortified in its ease of fabrication and ability to be compositionally fine-tuned [4–6].

Over the years, there have been progress in device structure employing MAPbI₃ and its analogues as the absorber layer. Initial devices started off as adaptations of solid-state dye-sensitised solar cells (ss-DSSC) [7] which progressed on to the adsorption of the photoactive material onto a mesoporous structure (e.g. TiO₂, Al₂O₃) [8–10]. The three main device architectures: *n-i-p* mesoporous-based device employing a mesoporous scaffold within the absorber layer, *n-i-p* planar device, and an inverted *p-i-n* planar device (shown in **Figure 2.3**). Because of the fundamental improvement in stability and ease of processing compared to an electrolyte based dye-sensitised solar cell, solid-state devices have since been the chief focus in the field, particularly planar heterojunction architectures [11, 12].

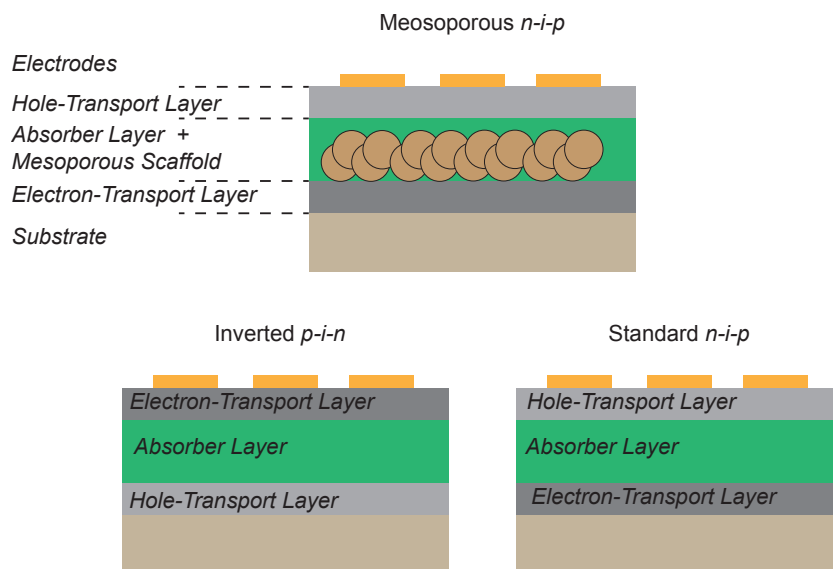


Figure 2.3 Device architectures of organometallic halide based photovoltaic devices.

In 2013, Ball *et al.* [12] reported the fabrication of a planar device; comprising a 350 nm thick organometallic halide absorber layer, TiO₂ compact layer as the electron transport layer, and 2,2',7,7'-tetrakis[*N,N*-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (Spiro-OMeTAD) as the hole transport layer (HTL). Concurrently, a HTL-free device was also reported [13] demonstrating the hole transporting capabilities of these materials. Thus, conclusively, the use of a mesoporous scaffold is unnecessary in electron extraction processes and in fact a relatively thick absorber film is of itself capable of ambipolar charge transport, and that TiO₂ can be replaced by Al₂O₃ without affecting device performance significantly. Initial work by Jeng *et al.* [14] and Malinkiewicz *et al.* [15] demonstrated that organic materials can replace TiO₂ for completely solution-processed devices. While there were initial issues with device performance, they were resolved by using thicker absorber layers.

As support for the empirical observations for the photovoltaic capabilities of scaffold-less devices, studies have shown that organometallic halides have long charge carrier diffusion lengths [16–19]. Thus, unlike mesoscopic devices, here the absorber thickness is a bigger factor as explored by Liu *et al.* [20]. They note an optimum thickness of 330 nm for their device architecture—observing an increase in device metrics from 100 nm thick films but recording an apparent drop when thickness increased to 600 nm. They suggested that thicker (> 330 nm) films extended beyond the diffusion length of electrons which was calculated to be 100 nm [18]. In contrast, Eperon *et al.* [21] defined an optimum film thickness of 400 nm to 700 nm.

Theoretical studies have been carried out to better reason empirical evidence for high diffusion lengths in these materials. It was posited by Yin *et al.* [22] that the formation energies of defects responsible for deep traps within the band-gap e.g. antisite substitutions, are large while defects responsible for

shallow traps have much lower formation energies (e.g. $V_I^\bullet$, V_{MA}') [23]. It was also shown by Kim *et al.* [24] that Schottky and Frenkel defects (e.g. PbI_2 , MAI vacancies and $I(V_I^\bullet)$, $Pb(V_{Pb}'')$, $CH_3NH_3(V_{MA}')$ vacancies respectively) do not form gap-states but rather “extended” states, in agreement with Yin *et al.* who showed that shallow trap states form beyond their energy band minimum/maximum. These explain low non-radiative recombination in these materials and therefore the empirically determined long diffusion lengths and a comparatively high V_{oc}/E_g ratio.

As a means of reconciling fundamental theory on device properties and material characteristics, one might need to consider the relationship of organometallic halide precursor ratios [25], processing conditions [26, 27], film morphology (grain size, continuity) and grain orientation [28]. Other factors such as the effects layer thickness on light absorption and device properties [20, 29, 30], surface composition (discussed in **Section 2.5**) and their effects on interfacial electronic structure are also crucial in device engineering.

Apart from the photoactive organometallic halide layer, one needs to consider transport layer properties such as energy-level alignment (**Section 2.4.1**), layer thickness [31, 32], interfacial chemistry between the organometallic halide material and transport layers can also dictate device stability by inducing interfacial degradation (**Section 2.7**).

Other areas of importance lie in composition tuning through substituting the ‘A’-site cation for a more stable crystal structure and defect passivation (**Section 2.6**) to improve material stability and ultimately device stability. As is reviewed in the later sections, there is an interdependence between stability, defects, and device performance; where degradation is accelerated with a higher density of surface defects (e.g. vacancies) and where deep trap states, leading to non-radiative recombination, originate from said defects. Thus, the following sections aim to review aspects of organometallic halide stability and properties with respect to its surface.

2.3 Stability of Organometallic Halides as a Photoactive Layer

In this section, compositional and chemical stabilities of organometallic halide materials are reviewed. Aspects such as structural stability and retention of photovoltaic properties are also discussed, as they are caused by chemical changes. A detailed review on changes in charge transport properties, while certainly relevant in the development of more stable devices, is not within the scope of this thesis. The stability of photovoltaic devices using these materials as photoactive layers and issues pertaining to other interlayers are also discussed as the interactions between them can influence the overall perfor-

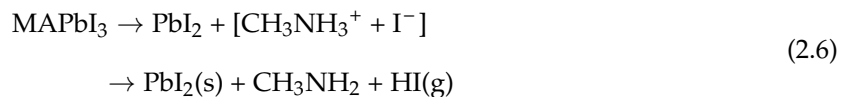
mance.

There are a number of environmental stressors that induce degradation of the active layer, namely: humidity, oxygen exposure, temperature, and irradiation. Even under storage, in the presence of these stressors, organometallic halides undergo degradation, limiting their storage lifetime stabilities.

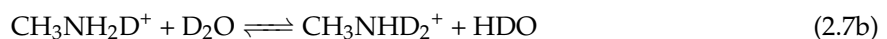
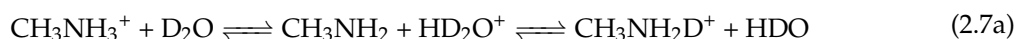
2.3.1 Moisture Stability

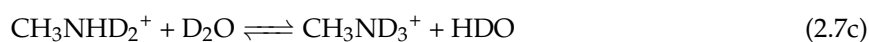
With atmospheric moisture, one can expect the hydration of the perovskite crystal structure to form intermediate monohydrate $\text{CH}_3\text{NH}_3\text{PbI}_3 \cdot \text{H}_2\text{O}$ and dihydrate phases $(\text{CH}_3\text{NH}_3)_4\text{PbI}_6 \cdot 2\text{H}_2\text{O}$ [33] that weaken the overall structure and increase their susceptibility to processes arising from other environmental stressors. The ease by which these hydrated complexes form is attributed to the strong hydrogen bonding between water and the CH_3NH_3^+ (MA) cation. The authors proposed that the deprotonation of the MA cation to the water results in the eventual decomposition of the material and liberation of $\text{CH}_3\text{NH}_2(\text{g})$ and with it, destabilising the $[\text{PbI}_6]^{4-}$ octahedron resulting in the formation of PbI_2 and HI . However, it was suggested that the hydration process can be partly reversed and does not always lead to irreversible degradation.

A generalised and simplified degradation process can be summarised by the following steps:



Compositional variations, as a result of moisture-assisted decomposition were elucidated by Lin *et al.* [34]. By using deuterated water (D_2O) and the high mass-resolution obtainable from time-of-flight secondary ion mass spectrometry (ToF-SIMS), they showed qualitative compositional changes with moisture exposure, over time. By discriminating deuterated mass fragments from others, they were able to deconvolute the evolution of mass spectra as a result of chemical reactions with water and show distinctly different mass spectra with increasing exposure time to moisture. They suggested the following reactions based on proton exchange with $[\text{CH}_3\text{NH}_3]^+$:





Based on **Figure 2.4**, the evolution of $[\text{CH}_3\text{NH}_3]^+$ and mass fragments $m/z = 33$ to $m/z = 35$ over time is certainly consistent with the well-regarded supposition that the hydrolysis of organometallic halides results in degradation and eventual liberation of volatile organic by-products. The reactions (**Equation 2.7a** to **Equation 2.7c**) described above are certainly plausible but caution should be made in using mass spectra obtained from ToF-SIMS to rationalise any chemical processes as the possibility of matrix effects influencing the ionisation process cannot be disregarded.

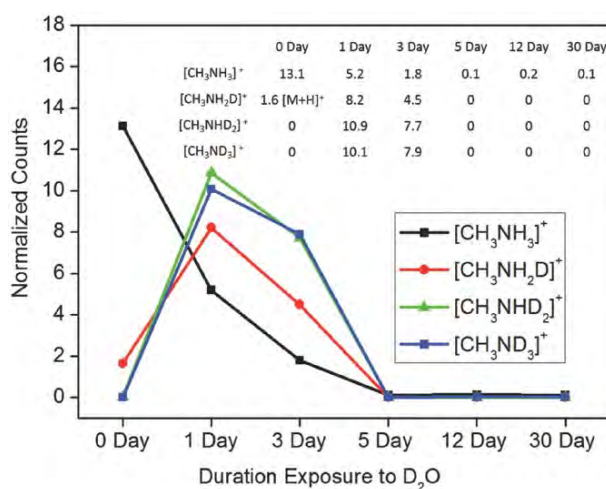


Figure 2.4 The evolution of intensities of mass fragments $[\text{CH}_3\text{NH}_3]^+$ ($m/z = 32$), $[\text{CH}_3\text{NH}_2\text{D}]^+$ ($m/z = 33$), $[\text{CH}_3\text{NHD}_2]^+$ ($m/z = 34$), $[\text{CH}_3\text{ND}_3]^+$ ($m/z = 35$) with counts normalised to the total counts. Image reproduced with permission from [34] Copyright © 2016 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

2.3.2 Interaction of Light and Oxygen

In the absence of other factors, oxygen is generally harmless to the absorber layer. Empirically, it has been shown that the combination of light and oxygen results in device degradation [35, 36]. This phenomenon is suggested to have arisen from the generation of superoxide that initiates degradation. There is direct evidence that diffusion of oxygen, through ^{18}O exchange and ToF-SIMS measurements, was kinetically enhanced with increasing illumination intensity [37].

Diffusion and incorporation of oxygen in these materials occur *via* two pathways: interstitially or through vacancies with considerations of size constraints. One would expect that (a) a pristine material, in the absence of external influence, would have some pre-defined defect density and (b) that diffusion kinetics is controlled by interfacial properties (e.g. chemistry and defect density). Following

that, it was observed that there was an inverse relationship between grain size and superoxide yield [38]. Three samples of different grain sizes: **Figure 2.5(a)** 100 nm, **(b)** 150 nm, **(c)** 250 nm were subjected to superoxide yield measurements in which the samples were submerged into a compatible solution whose PL intensity was measured. An intensity increase is the result of increased concentration of superoxide in solution **Figure 2.5(e)**. Coupled with optical absorption stability measurements **Figure 2.5(d)**, the authors found a direct relationship between smaller grain size, increased superoxide yield, and lower optical stability. This behaviour was rationalised to be due to the increased surface defect densities in samples with larger grain boundaries (100 nm: $6.0 \times 10^{17} \text{ cm}^{-3}$, 250 nm: $2.4 \times 10^{17} \text{ cm}^{-3}$) leading to increased number of sites for oxygen absorption [38]. A similar effect of suppressing superoxide yield was observed when using iodine salts as a means of passivating these defect sites.

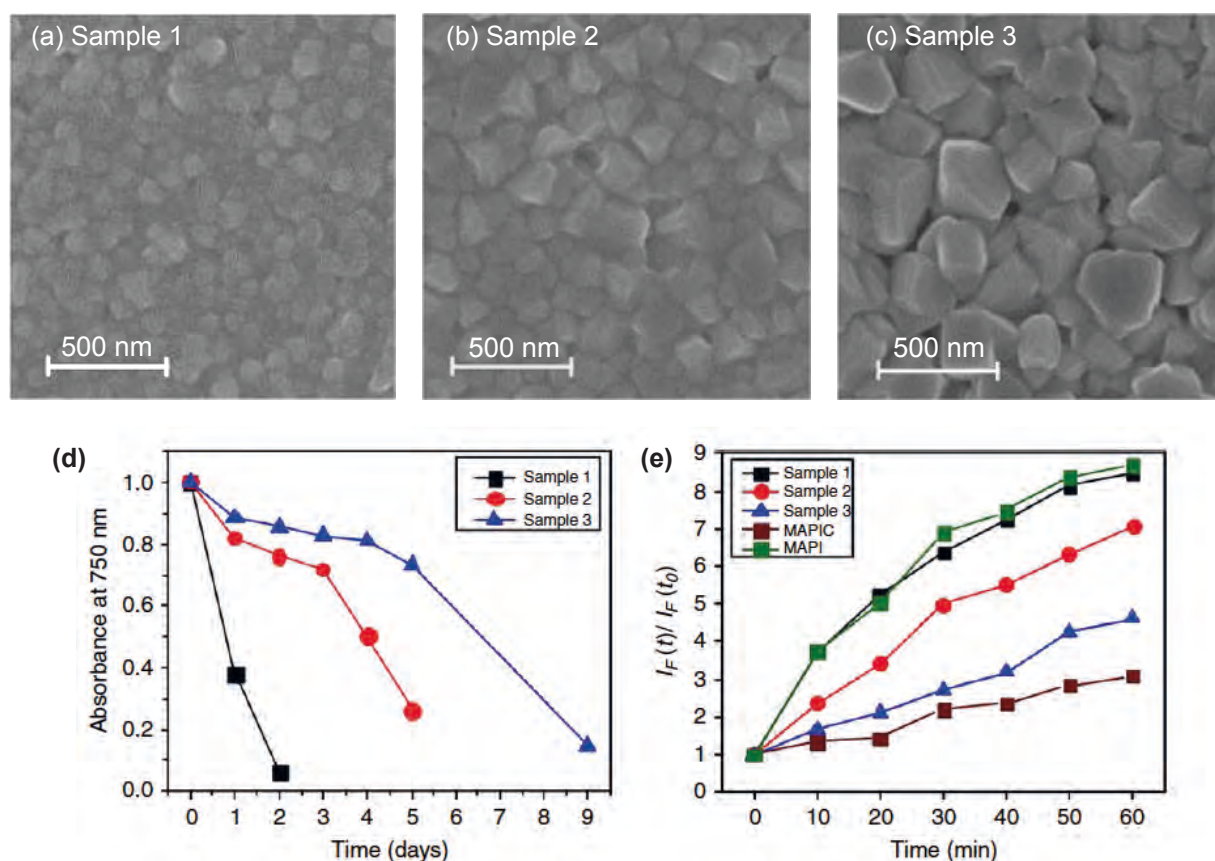


Figure 2.5 SEM images of MAPbI₃ prepared with different concentrations of MAI-treatment: **(a)** 0.063 M (Sample 1, avg. grain size: 100 nm), **(b)** 0.0050 M (Sample 2, avg. grain size: 150 nm), **(c)** 0.038 M (Sample 3, avg. grain size: 250 nm). **(d)**: time-resolved normalised absorption under 25 mW cm^{-2} illumination. **(e)**: superoxide yield of Sample 1, 2, 3, MAPI: untreated MAPbI₃, and MAPIC: MAPbI_{3-x}Cl_x. Left axis shows PL intensity of solution containing the samples whose values have a direct relationship with concentration of oxygen in samples. Image reproduced from [38] Copyright © 2017 Nat. Comm. Springer Nature

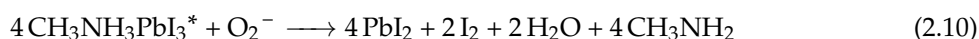
It was further shown that ionic conductivity (σ_{ion}) increases significantly when MAPbI₃ was illuminated [39], which seems to describe the increased diffusion rate of molecular oxygen upon illumination suffi-

ciently. Phenomenologically, the authors suggested the increased conductivity was brought about by an increase in iodide vacancies which is consistent with observed increased oxygen diffusion upon illumination [37]. This increase was attributed to the interaction of holes, from photogenerated electron-hole pairs, with the orbitals of I in the valence band which results in a site exchange between the I^- interstitial and lattice sites with the form [39]:



The implication being that with an increase in interstitial neutral I, at some point a saturation point will be reached and an apparent chemical potential gradient between the surroundings and the material will drive the removal of I from it. Furthermore, direct evidence for ion migration (namely, I^- and $CH_3NH_3^+$) has already been observed [40].

It is argued that oxygen diffusion is more pronounced under light because of the increased density of iodide vacancies ($V_I^\bullet$) in which O_2^- can occupy. Under illumination, the excited state of $MAPbI_3$ ($CH_3NH_3PbI_3^*$) reacts with O_2 through transfer of photoexcited electrons to form superoxide O_2^- that causes degradation by the process of an acid-base reaction with the MA^+ cation [38]. The resulting reaction is shown in **Equation 2.10**.



In agreement with these empirical observations, when using an electron-accepting mesoporous scaffold TiO_2 as opposed to Al_2O_3 , degradation was not as severe. They ascribed this observation to the diminished superoxide formation due to enhanced electron extraction suppressing superoxide formation.

2.3.3 Structural Stability

The crystal transition temperatures of organometallic halides are dependent on the exact composition, with a large influencing factor being the choice of the A-site cation, **Table 2.1** summarises experimentally obtained transition temperatures from various references. There are three defined crystal structures: Cubic (α); Tetragonal (β); Orthorhombic (γ). A study by Baikie *et al.* [41] using differential scanning calorimetry of MAPbI₃ showed a tetragonal $\leftrightarrow$ cubic transition temperature of 329 K to 330 K. Consistent behaviour was observed separately by Dualeh *et al.* [42] who reported transitions at 328.2 K and 330.3 K for heating and cooling, respectively—their reported reproducibility strongly suggests that the presence of an intermediate phase is a possible explanation for this asymmetric transition behaviour. But, the exact implication of an intermediate phase has not been well-studied on a theoretical basis; however, it might be sufficient to rely on ascertaining temperature-dependent properties which is discussed in the section below. The tetragonal $\leftrightarrow$ orthorhombic transition at 152 K was also observed by Baikie *et al.* [41] during single-crystal X-ray diffraction (XRD). These results are in agreement with studies done in 1980s to 1990s [43, 44].

Experimental characterisation of crystal structures so far only involved pristine MAPbI₃ films. Dittrich *et al.* [45] recorded a tetragonal $\leftrightarrow$ cubic transition temperature range at 305 K to 313 K which was significantly lower than other reported values (see **Table 2.1**). This discrepancy was attributed to increased pressure from the poly(methyl methacrylate) (PMMA) overlayer which reduced the transition temperature. Unfortunately, this area has yet to be studied in any depth and the stress-strain effect of overlayers on electronic structure adds further complications. There is a barrier to ascertaining this relationship as common methods such as X-ray photoelectron spectroscopy (XPS) has a depth-resolution of 5 nm to 10 nm (the exact value depends on the material) and UV-photoelectron spectroscopy (UPS) smaller than that. Therefore, it is important to realise that the crystal structure, electronic structure, and overlayers in the device are intertwined. This limiting factor must be taken into account when characterising interfaces and as discussed in subsequent sections the electronic structure at the interface/surface is highly dependent on a range of factors.

Table 2.1 Phase Transition Temperatures of organometallic halide compositions as obtained from literature.

MAPbX ₃	Cubic $\leftrightarrow$ Tetragonal (K)	Tetragonal $\leftrightarrow$ Orthorhombic (K)	Ref
MAPbI₃			
	330.4	161.4	[43]
	327.4	162.2	[44]
	329-330	152	[41]
	328-330	-	[42]
	305-313	-	[45]
MAPbBr₃			
	236.3	154.0 / 148.8	[43]
	236.9	155.1 / 145.0	[44]
MAPbCl₃			
	177.2	171.5	[43]
	178.8	172.9	[44]

More Stable Structures

Purely based on geometric stability, the Goldschmidt tolerance factor t takes into account the ionic radii of the A, B cations and X anion for a cubic perovskite crystal structure:

$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)} \quad (2.11)$$

where r_A, r_B, r_X are the effective ionic radii of the constituents A, B, and X respectively. The values of r_B and r_X can be obtained by using the Shannon radii [46], originally derived from metal oxides and fluorides. This gives values of 1.19 Å and 2.20 Å for r_{Pb} and r_I , respectively. Though the value for Pb has seen some revision by considering the covalency of Pb-I bonds as opposed to the metal-oxide and metal-fluoride bonds used in the previous determination [47], giving value a value of 1.03 Å. Additionally, the value of r_A is difficult to estimate as it is not spherical in nature as would be B and X. Nevertheless, ionic radii of the following A-site cations have been proposed: methylammonium, MA⁺ (2.16 Å), formamidinium, FA⁺ (2.53 Å) [47].

When $t = 1$, one would expect an ideal cubic perovskite crystal structure that is geometrically stable. With a value of $t < 0.8$, an orthorhombic phase is expected, and $t > 1.0$, a hexagonal phase [48]. The tolerance factor of MAPbI₃ is calculated to be 0.89 and therefore predominantly exists in the tetragonal

phase due to relaxation effects of the $[\text{PbI}_6]^{4-}$ octahedra in accommodating the size of MA^+ in relation to the octahedra volume [49].

Additionally, based on a statistical and data-driven approach, Bartel *et al.* devised a new tolerance factor [50]—

$$\tau = \frac{r_X}{r_B} - n_A \left(n_A - \frac{r_A/r_B}{\ln(r_A/r_B)} \right) \quad (2.12)$$

where n_A refers to the oxidation state of A and where $r_A > r_B$. The new tolerance factor is seen to excel at predicting structural stabilities which is useful for the design of more stable compositions [50]. Materials with the perovskite crystal structure have values of $\tau < 4.18$ with MAPbI_3 calculated to have a τ of 3.89 (using Shannon radii [46], I^- : 2.20 Å, Pb^{2+} : 1.19 Å, MA^+ : 2.16 Å [47]).

Apart from geometrical considerations, thermodynamic stability needs to be considered as well. A linear dependence between enthalpies of formation and the tolerance factor was found for a range of organometallic halide compositional analogues [51]. Their results show that MAPbI_3 is the most thermodynamically unstable, followed by MAPbBr_3 and MAPbCl_3 . The implication being that even without environmental stressors, decomposition of MAPbI_3 is thermodynamically favourable.

The structural transitions of each structure are crucial as well as the low-temperature phase is often not photoactive. The transition temperature of MAPbI_3 (tetragonal) to MAPbI_3 (cubic) was reported to be around 330 K or 55 °C which is well within the well-regarded operating temperature range of solar cells: −15 °C to 65 °C; while other analogues have transition temperatures that result in non-photoactive phases at room temperature.

Improving the stability of the perovskite crystal structure for organometallic halides is therefore crucial and can be achieved by partial substitution of MA^+ . Current ions that have shown great promise in increasing stability are: FA^+ and Cs^+ both of which increase the tolerance factor. To that end, stable and high performing triple cation compositions have been reported [52]. Halide substitution (Cl, Br) has been used not only to tune the bandgap of the organometallic halide but also in improving stability and is often implemented with the aforementioned cation substitution in order to further compensate the difference in ionic radii.

While the stability of the crystal structure is crucial in determining the temperature range in which the material can operate, there must also be thermodynamic and kinetic considerations of temperature on chemical processes. For instance, it has been shown that at 85 °C under ambient and atmospheric

conditions, degradation of MAPbI₃ occurs and PbI₂ is formed. A detailed review of independent observations of this feature is not given in this thesis instead, a more thorough review of the interrelationship between environmental stressors, different interlayers in the device and that of device stability is given in **Section 2.7**.

2.4 Photocurrent Hysteresis

Photocurrent hysteresis observed in MAPbI₃-based devices, draws into question reported device metric values and is fundamentally useful in understanding ion mobilities. It is characterised by different J-V curves depending on the direction of scanning *i.e.* forward bias $\leftrightarrow$ reverse bias. It is further exacerbated by different measurement parameters such as scan-rate and incident flux as investigated by Tress *et al.* [53].

One of the prevailing theories of its origin was thought to be charge trapping at interfaces. If one also considers the low formation energies, as stipulated in many studies, of shallow-trap states above/below the CB_{min}/VB_{max} it certainly lends more credence to this theory. Some have reported a reduction in hysteresis *via* passivation of the absorber-layer/transport-layer interface using fullerene-derivatives [54, 55]. Kim *et al.* argued that choosing the right transport layers was crucial in reducing hysteresis caused by ion-conduction [56]. However, as explained in succeeding sections, these materials often result in better energy band alignment. Thus, as to whether reduction in hysteresis is attributed to passivation of trap-states, energy-band alignment, or both still requires further investigation.

An *in situ* XPS study of MAPbI_{3-x}Cl_x with an applied bias shows the increasing in I/Pb ratio at different areas of the film, with highest concentrations near the positive electrode [57]. This points toward I⁻ migration (concomitantly, defect migration) as a possible contribution towards hysteresis. These results require further confirmation but I⁻/defect migration is an indication that energy band alignment is not static under operation. It was argued that when a positive bias was applied to Spiro-OMeTAD (HTM), there was favourable energy band alignment, whereas a negative bias caused misalignment which resulted in increased barriers for charge extraction/injection.

Certainly, more needs to be done to determine the exact mechanism(s) responsible for photocurrent hysteresis. In particular, providing instrumental barriers are overcome, it would be of great significance to determine the interfacial energetics under bias for non-stoichiometric films.

2.4.1 Energy Level Alignment

This section aims to bring together several reported energy levels of MAPbI₃ and transport layers where often transport layer selection is predicated on reported energy levels; though such values *can* be influenced by instrumental factors and can vary between different measurement techniques. In particular, only photoemission studies are used in this review. **Figure 2.6** shows illustrated energy level alignments for several HTL and ETL obtained from references where energy levels were obtained from photoemission spectroscopy (PES).

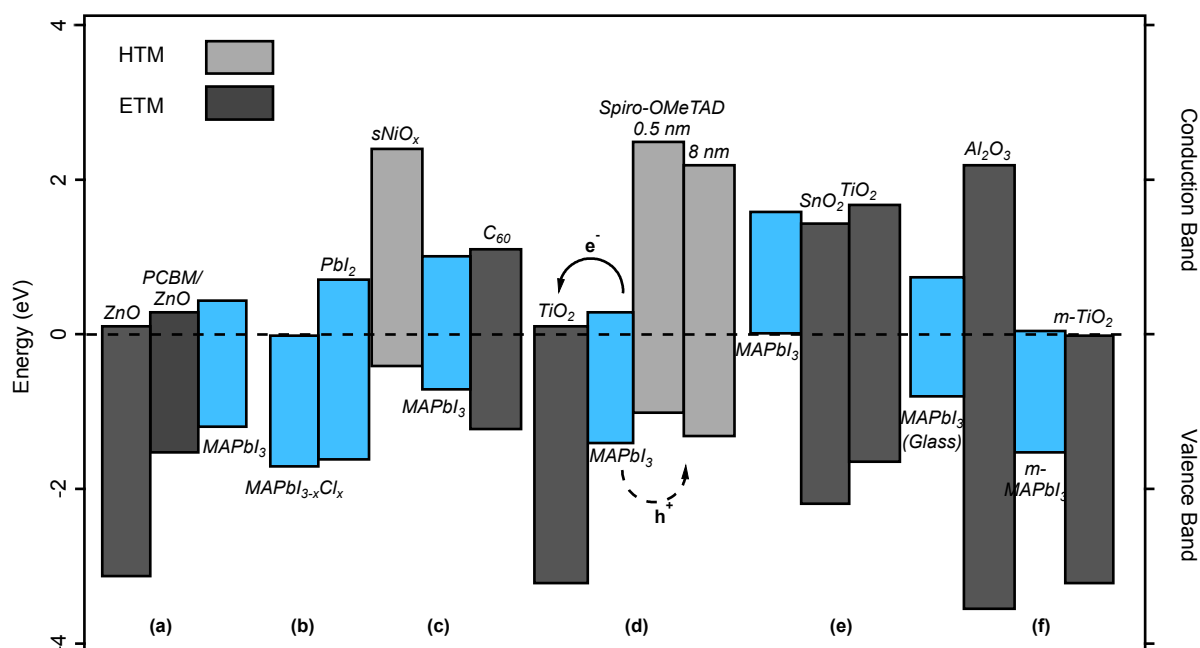


Figure 2.6 Interfacial energetics and electronic structure of MAPbI₃ samples and bi-layers. Energy levels indicated here are CB_{min} (top) and VB_{max} (bottom), vacuum levels have not been included. (a): Ref [58], (b): Ref [59], (c): Ref [60], (d): Ref [61] (e): Ref [62], (f): Ref [63], note that Al₂O₃ VB_{max} extends to -6 eV but has been truncated in this illustration. E = 0 eV is the Fermi level (E_F) in this case.

Hole-Transport Materials

A higher highest occupied molecular orbital (HOMO) or VB_{max} for that of a HTL than that of MAPbI₃ facilitates hole transport. A higher CB_{min} is preferred to prevent electron recombination from MAPbI₃ to the transport layer. However, too much of an offset reduces V_{oc}. Current organic HTL that have been studied are poly(3-thiophenyl acetic acid) (P3TAA), Spiro-OMeTAD, poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS), and poly(3-hexylthiophene) (P3HT) to name a few. A range of inorganic materials used are: copper phthalocyanate (CuPc), sol-gel nickel oxide (sNiO_x), copper iodide (CuI). The relative performance of devices utilising different HTM have been investigated purely based

on the effects of theoretical energetics and film morphology on device performance without rigorous studies of the (interfacial) energetics.

According to Bi *et al.* [64], $\text{TiO}_2/\text{MAPbI}_3/\text{Spiro-OMeTAD}$ device structures had significantly higher V_{oc} than P3HT analogues. On the other hand, Heo *et al.* [65] reported that P3TAA-based devices had higher V_{oc} than Spiro-OMeTAD analogues (0.997 eV and 0.855 eV respectively) which was attributed to P3TAA's better VB_{max} alignment with MAPbI_3 at an offset of 0.2 eV. However, this may also be attributable to a large number of factors such as morphology of the transport material, $\text{MAPbI}_3/\text{HTM}$ interfacial area, and electron lifetimes.

It was also found that Spiro-OMeTAD had recombination rates that were slower by a factor of 10 than P3HT and therefore, the latter had smaller electron lifetimes [64]. While they attributed the difference in device metrics solely to this, it may be that energy level offset also contributes significantly.

Schulz *et al.* [61] measured energies for Spiro-OMeTAD on MAPbI_3 of up to 80 Å thickness. At 5 Å, the HOMO is 0.4 eV higher than the VB_{max} of MAPbI_3 . At 80 Å, this offset was reduced to 0.1 eV, indicating a slight downward bending of 0.3 eV. It should be noted that they did not observe any bending at the organometallic halide absorber surface. Despite increasing thickness, the LUMO offset remained at > 2 eV higher than the CB_{min} of MAPbI_3 , thus giving Type-II band alignment at the $\text{MAPbI}_3/\text{Spiro-OMeTAD}$ interface **Figure 2.7**—its higher LUMO is favourable for preventing electron recombination and demonstrates the good electron-blocking property of Spiro-OMeTAD.

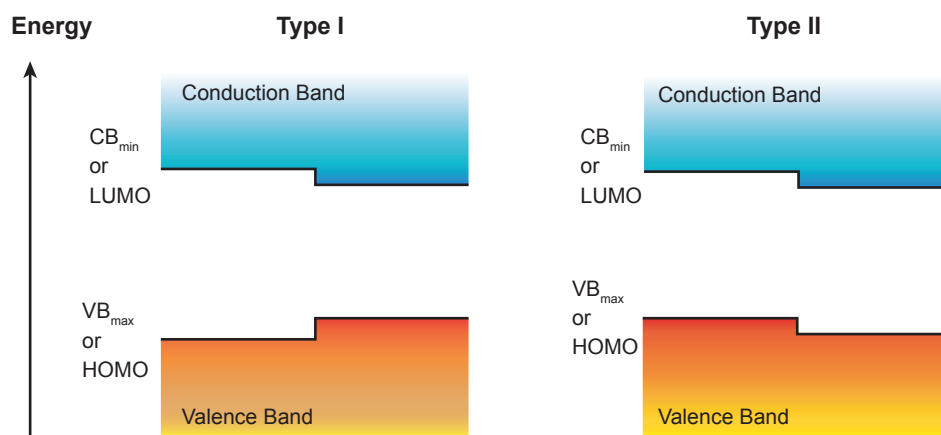


Figure 2.7 Illustration of band alignment between two layers. Type I: where the $\text{CB}_{\text{min}}/\text{LUMO}$ and $\text{VB}_{\text{min}}/\text{HOMO}$ of one layer is higher and lower (respectively) than that of the other layer. Type II: where both the $\text{CB}_{\text{min}}/\text{LUMO}$ and $\text{VB}_{\text{min}}/\text{HOMO}$ of one layer is higher than the other.

Another photoemission investigation into the energy levels showed that the offset between Spiro-OMeTAD and MAPbI_3 was 0.17 eV and that the HOMO of P3HT (against vacuum level) was −4.67 eV

compared to -3.88 eV of MAPbI₃, indicating an offset of 0.79 eV. While the difference in offset is not commensurate with the difference in V_{oc} (approx. 0.2 eV), it stands to reason that the HOMO/ VB_{max} offset sets a fundamental limit to achievable V_{oc} . In agreement with that argument, it was shown that the smallest HOMO/ VB_{max} offset at 0.1 eV for MAPbI₃/PPP showed the highest V_{oc} [66] amongst other materials (PEDOT:PSS, polythiophene, and PPN).

CuPc has also been used as a hole transport material. A PES study of the MAPbI₃/CuPc interface indicated a downward band bending of 0.3 eV within CuPc, with an overall offset of 0.2 eV [67]. Similar to the previously mentioned work [61], no band bending within MAPbI₃ was observed.

Electron-Transport Materials

In inverted *p-i-n* structures, fullerene-based ETLs have been rigorously employed and studied. One such example is [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) which has been used as a 10 nm-thick ETL [15]. It has also been used as an intermediate layer for a more favourable CB_{min} alignment between MAPbI₃ and ZnO [58] in which it was suggested PCBM passivated electron trap-states at the MAPbI₃/ZnO interface. The authors reasoned that the combination of both resulted in increased V_{oc} . Similarly, the addition of a PCBM/C₆₀ passivation bilayer between MAPbI₃/cathode was noted to have reduced surface trap density of states and increased J_{sc} and V_{oc} [54]. Impedance spectroscopic data further suggested that surface recombination processes dominated over bulk recombination. This is plausible considering the non-stoichiometry induced formation of defects discussed in **Section 2.5**.

Such passivation effects have been reported in functionalising compact TiO₂ (c-TiO₂). Functionalising MAPbI₃/c-TiO₂ with a C₆₀-SAM layer was shown to not only increase device metrics but reduce photocurrent hysteresis [68]. They concluded that the passivation of non-radiative trap-states on TiO₂ surfaces improved electron-transport across the interface, based on increased electroluminescence efficiency for functionalised samples. In a separate study, the band-alignment of C₆₀ was determined to be favourable at the MAPbI₃/C₆₀ interface with a LUMO offset of only 0.1 eV with respect to the VB_{max} , and a HOMO offset of 0.7 eV with respect to the CB_{min} of MAPbI₃ [60].

Other metal-oxides have also been used as alternatives to TiO₂. Baena *et al.* [62] used atomic-layer deposition (ALD) to deposit SnO₂ on MAPbI₃. Compared to planar and mesoporous TiO₂, they obtained a near hysteresis-free J-V measurements and higher device metrics for planar SnO₂. This was attributed to the favourably lower CB_{min} of SnO₂ by 0.17 eV. In contrast, they noted mesoporous TiO₂ had a higher CB_{min} than MAPbI₃. However, this is in conflict with previously reported energy level alignment at the MAPbI₃/TiO₂ interface [61, 69].

2.4.2 Effects of Precursor Ratio

Different precursor ratios and processing routes were shown to result in different electronic structure which could be due to the unbalanced ratio of MAI/PbI₂ precursors introducing defects through doping of uncoordinated species. The surface termination could also change due to changes in reaction equilibria. These can be useful in understanding the electronic structure of films with slight deviation from stoichiometry, as well as in deliberate energetics modification of the absorber film.

Emara *et al.* [70] have carried out an extensive and exhaustive study of the effect of precursor ratios (MAI, PbI₂) and fabrication routes. They reported large variations in workfunction, no changes in optical bandgap, no changes in onset/density of states (DOS) of VB, shifts in high binding energy cut-off, and variations in DOS for the range: 4 eV to 6 eV. These imply that the onset of VB and CB must have occurred concurrently, and by the same energy shift. Additionally, they note that with an excess of MAI precursor, there was a reduction in DOS close to the VB. Changes in electronic structure as a function of precursor ratios have also been reported [71, 72]. From an equimolar ratio of precursors, with increasing MAI concentration, the Fermi-level shifted closer to the VB_{max} by about 0.2 eV, an indication of p-doping while an increasing PbI₂ concentration resulted in n-doping [72]. It was also noted that with a PbI₂/MAI ratio of 0.3, there was an increase in metallic Pb (Pb⁰) species of about 3.25% (from about 1.39%) [71] (possible interactions arising from X-ray irradiation are discussed in **Section 2.5.2**).

Further, it has been shown that with annealing, stoichiometric p-doped MAPbI₃ becomes n-doped [72, 73], strongly suggesting that during the process, MAI species are liberated creating I-vacancies, Pb–Pb clusters, and a PbI₂ secondary phase. Similarly, Peng *et al.* [74] reported photoluminescence (PL)-quenching when increasing annealing temperature from 150 °C to 175 °C which indicated the formation of non-radiative trap states. This could mean that increasing annealing temperature causes thermally-activated liberation of MAI and/or formation of defects in the already intrinsically unstable perovskite lattice and therefore, explains why Xing *et al.* [75] did not observe Pb⁰ at an annealing temperature of 50 °C. Further, they suggested that a p-type surface is seen on their films, but it should be noted that there was no experimental evidence.

2.4.3 PbI₂ Secondary Phase

PbI₂ is not a deliberate addition for energetic modification but results have shown that small amounts of it, as a consequence of degradation and/or incomplete conversion to MAPbI₃, reduces hysteresis and charge recombination at interfaces and grain boundaries [76–78]. It has been shown that intergranular

PbI₂ phase exists for both one-step and sequential deposition methods [79]. PbI₂ was also reported on surfaces of organometallic halide-sensitised Al₂O₃ mesoporous substrates [59] and on thick-film samples [71].

Studies have been carried out to determine the effect PbI₂ and annealing time have on device properties. Using Kelvin probe force microscopy (KPFM) [79], it was shown that with a 15 min annealing time at 100 °C, there was a maximum barrier to recombination at the MAPbI₃/TiO₂ interface. Additionally, the deposited film had the highest surface potential and the lowest grain boundary potential. Longer annealing times and temperatures were said to induce surface defects (caused by dangling bonds/under-coordinated atoms in the lattice) which act as trap states for recombination; consistent with the results reported by Peng *et al.* [74]. Whereas an optimum amount of PbI₂ is beneficial in preventing recombination and allowing hole-extraction due to a higher CB_{min} and lower VB_{max} of PbI₂, and is therefore characterised by Type-II band alignment [59] (see **Figure 2.6**). In contrast, a Type-I band alignment was said to persist instead [80].

2.5 Surface & Bulk Composition

There is a real need to quantify surface composition of organometallic halides as one can imagine that any deviation may affect surface electronic properties which will in turn affect interfacial energetics and charge transport properties. Theoretical studies have also discussed the different possible surface terminations. Given that degradation also propagates from the surface into bulk, it is therefore also crucial to understand how different surface terminations and compositions influence device stability inasmuch as it is dominated by degradation of the absorber layer. Here, empirical studies discussing the surface composition of MAPbI₃ are reviewed. **Table 2.2** shows the various peak-fitted core-level spectra for MAPbI₃ and analogues.

Table 2.2 Reported XPS binding energies (eV) of Pb 4f_{7/2}, I 3d_{5/2}, C 1s, N 1s, bandgap (E_v-E_F) where E_v is the valence band onset and E_F is the Fermi edge, and I/Pb stoichiometry.

Composition	Pb 4f _{7/2}	I 3d _{5/2}	C 1s	N 1s	Pb ⁰	E _v -E _F	I/Pb	Ref
CH ₃ NH ₃ PbI ₂ Cl	138.7	-	-	-	136.9	1.62	-	[81]
CH ₃ NH ₃ PbI ₃	-	-	-	-	136.3	-	2.19	[82]
CH ₃ NH ₃ PbI ₃	138.6	619.4	-	-	137.0	1.55	3.3	[83]
CH ₃ NH ₃ PbCl ₃	139.1	619.4	-	-	137.0	2.65	-	[83]
CH ₃ NH ₃ PbI ₃	138.7	619.5	-	-	-	1.6	2.7 to 3.1	[84]
CH ₃ NH ₃ PbI _{3-x} Cl _x	138.7	-	-	-	137.0	1.54	-	[85]
CH ₃ NH ₃ PbI ₃	137.9	618.8	285.9	401.8	136.3	1.54	-	[71]
CH ₃ NH ₃ PbI ₃	138.3	619.6	285.7	402.7	-	-	3.1	[75]
CH ₃ NH ₃ PbI ₃ *	139.1	619.9	285.7	403.0	-	-	2.6	[75]

There are few techniques available to give a reasonable degree of surface composition quantification. The most used is XPS which gives quantification in the form of atomic percentage and is a surface-sensitive technique which provides information from the first few nanometres of the material surface and as such is easily influenced by surface contamination. Quantification by SIMS is also theoretically possible but pose too many challenges on account of matrix effects.

Nevertheless, XPS provides a starting point for compositional quantification. Core-level spectra provide information about composition *i.e.* the type of species and their atomic concentration, in the outermost 5 nm-10 nm of a material [86]. For MAPbI₃, core levels of interest are: Pb 4f_{7/2}/Pb 4f_{5/2}, I 3d_{5/2}/I 3d_{3/2}, C 1s, N 1s, and O 1s—the binding energies indicate the chemical species/oxidation state of Pb, I, C, and N within the perovskite lattice *i.e.* they contribute electrons, and oxygen adsorption (contamination) respectively. Independent measurements yielded similar binding energies for Pb 4f_{7/2} at 138.5 eV to 138.9 eV [59, 69, 81, 83] with a spin-orbit splitting of 4.85 eV. I 3d_{5/2} features are reported at 619.4 eV with a spin-orbit splitting of 11.5 eV [69, 87] (see **Table 2.2**).

For films that have been exposed to air, C 1s features were observed to be dominated by two peaks at (1) 286.6 eV to 286.7 eV and (2) 285.3 eV to 285.5 eV [59, 88], corresponding to C–N bonds in MAPbI₃ and adventitious carbon, respectively. Interestingly, Liu *et al.* [89] observed a secondary C 1s feature at 285.3 eV as MAI was *sequentially* evaporated *in situ* onto PbI₂ which was ruled out as adventitious/aliphatic carbon. This feature was not present when PbI₂ was evaporated onto MAI and they noted that Pb⁰ was observed concurrently with this secondary carbon species. This feature is discussed separately as it could have instrumental interaction origins.

Other publications have also reported significant deviations from the stoichiometric I/Pb ratio of 3, at values of 1.4–2 [90] and 2.29 [57]. On the other hand, a ratio of 3.3 was found using hard X-ray photoelectron spectroscopy (HAXPES) [83]. In the same work, it was discovered that both contact with atmospheric H₂O and storage conditions affected the stoichiometry. In particular, based on an I/Pb ratio of 2, it was suggested during annealing degradation occurred *via* the liberation of CH₃NH₃I species, leaving excess PbI₂ at the surface. often regarded as a degradation product of MAPbI₃, is formed over grain surfaces which has been argued to be beneficial to device properties [91, 92].

Empirically, the surfaces of these materials are almost always not stoichiometric, to a significant degree. Whether this non-stoichiometry is a result of processing, the inherent nature of the material, or of instrumental interactions is not entirely clear. However, non-stoichiometry throughout the bulk of the material has also been elucidated by Matteocci *et al.* [90] and Heo *et al.* [65] using ToF-SIMS and XPS depth-profile measurements. Matteocci *et al.* noted an overall deviation from a ratio of 3 throughout the film, but also noted a changing stoichiometry with depth. Such non-stoichiometry was observed for the different conversion processes used. In agreement with Heo *et al.* [65], their results also show a significant amount of I[−] at the Au contacts, implying diffusion of I across the Spiro-OMeTAD transport layer. This could imply the presence of uncoordinated MAI and Pb species throughout the film. They also observed the presence of additional Pb_xI_y species close to the MAPbI₃/Spiro-OMeTAD interface². The persistence of non-stoichiometric surfaces is a comment on the incomplete formation of precursors to MAPbI₃, regardless of deposition routes; from solution processing to chemical vapour deposition (CVD). Incomplete conversion on account of user error during processing or residual solvents can, in part, explain the observed phenomenon.

However, the effect of the instrument on the measurements cannot be disregarded. Coupled with non-stoichiometry described above, the presence of Pb⁰ in photoemission spectra [59, 69, 71, 81–83, 87, 88, 93] also suggest that X-rays can influence the chemical composition of the material but the degree and significance of this effect have not been quantified or qualified thoroughly. It could also, on the other hand, be a symptom of non-stoichiometry. This is further explored in **Section 2.5.2**.

2.5.1 Effects on Electronic Properties

Theoretical studies suggested that for the tetragonal phase, the valence band is largely influenced by hybridised Pb 6*p* and I 5*p* orbitals, while the conduction band is influenced by Pb 6*p* orbitals [22, 94–97]. This has great significance which has been investigated [22, 24] to show the possibility of defect doping

²Further discussion on diffusion of species in **Section 2.7**

MAPbI₃ based on the relative amounts of precursors, *i.e.* MAI and PbI₂ where I-vacancies in the lattice resulted in p-doping while MA- and Pb-vacancies resulted in n-doping [24].

The electronic structure is influenced by the crystal structure, and if the perovskite phases are intrinsically dependent on operating temperature, so must their electronic structure. But, their electronic structure can also be affected by more *extrinsic* factors such as processing routes, annealing temperatures, and precursor (MAI/PbI₂) ratios that alter the surface composition/stoichiometry which has an indirect effect—through changes in intrinsic properties—on the surface electronic structure. One must also consider the type of surface terminations at the interfacial contacts between the absorber and transport materials; Haruyama *et al.* [95] illustrated that different terminations (e.g. PbI₂-rich, MA-rich, or vacant) of the most stable (110) and (001) faces have significantly different electronic bandgaps of about 1.56 eV to 1.91 eV. A similar bandgap for (001) was reported (MAI: 1.85 eV, PbI: 1.17 eV) by Quarti *et al.* [98]. The authors also suggested that MAI-rich terminations are to be expected compared to Pb-I due to being more thermodynamically stable.

Empirically, vacant and PbI₂-rich terminations are plausible due to the non-stoichiometry composition already reported. This is crucial for interfacial engineering as determining the dominant crystal orientation and relative composition at the surface can optimise interfacial engineering for better charge transport and reduced recombination.

For *intended* stoichiometric films, the measured and calculated electronic bandgaps for different organometallic halide compositions, using a range of analytical techniques are summarised in **Table 2.3**. A PES study also revealed these materials can be p- or n-doped depending on the substrate [94] by shifting of the Fermi-level, consistent with other reported interfacial energetics studies [60, 61, 63, 99].

The optical bandgap is said to decrease with decreasing temperature [45, 100]. This positive correlation with temperature could be attributed to thermal expansion of the perovskite lattice. A comprehensive study by Foley *et al.* [101] for the temperature range 298 K to 358 K was carried out using UPS which are consistent with temperature-dependent XRD measurements by Baikie *et al.* [41]. In another temperature-dependent study [102] a general trend in increasing V_{oc} with temperature from 80 K to 360 K was shown which, can be rationalised with a similar temperature-dependence of bandgap.

Table 2.3 Electronic Band Structure; values in eV. C-P.Cub: Calculated, pseduo-cubic. C-Cub: Calculated, cubic. C-Tet: Calculated, tetragonal. XPS: X-ray photoelectron spectroscopy. HAX-PES: Hard X-ray photoelectron spectroscopy. UPS: UV-photoelectron spectroscopy. IPES: Inverse photoelectron spectroscopy. m: mesoporous-TiO₂

Material	WF(ϕ)	IP	EA	Bandgap	Method	Ref
MAPbI₃						
<i>As-prepared</i>	3.99	5.4	3.7	1.7	UPS/IPES	[61]
		5.7		1.6	C-P.Cub	[103]
<i>As-prepared</i>		6.1			XPS	[70]
<i>Air-exposed</i>		5.9			XPS	[70]
<i>As-prepared (m)</i>				1.55	HAXPES	[83]
		5.9		1.51	UV-Vis	[41]
		5.9		1.43	C-Tet	[41]
		5.9		1.3	C-Cub	[41]
MAPbBr₃						
<i>As-prepared</i>	4.0	5.9	3.6	1.7	UPS/IPES	[61]
		5.96		1.95	C-P.Cub	[103]
<i>Air-exposed</i>	4.89			2.39	UPS	[104]
MAPbCl₃						
<i>As-prepared (m)</i>				3.1	HAXPES	[83]
		6.30		2.46	C-P.Cub	[103]
<i>Air-exposed</i>	4.61			3.18	UPS	[104]
MAPbI_{3-x}Cl_x						
<i>As-prepared (m)</i>				1.55	HAXPES	[83]
<i>As-prepared</i>	4.14		3.7	1.7	UPS/IPES	[61]

2.5.2 Effect of X-ray Irradiation

There have been sufficient reports of instrument material interactions to dictate a thorough review on such effects. Independent observation of Pb⁰ at small concentrations have been reported [59, 69, 71, 81–83, 87, 88, 93]; where films were either solution-processed or evaporated.

Philippe *et al.* [83] reported a Pb 4f_{7/2} peak at 137.0 eV for MAPbI₃, MAPbCl₃, and MAPbI_{3-x}Cl_x. Similar binding energies were also reported for MAPbI₃ at 136.3 eV to 136.9 eV [81, 82], and for MAPbI_{3-x}Cl_x at 137.1 eV [59].

Pb⁰ was also observed *in situ* when MAI was thermally evaporated onto PbI₂ [89]. Here, the formation of Pb⁰ may involve the intercalation of MAI in the PbI₂ matrix which, is the mode of synthesis for most

of the films with an observed Pb^0 feature. With an increased concentration of added MAI precursor with respect to PbI_2 , Xie *et al.* [71] noted a higher atomic concentration of Pb^0 at 3.25% for annealed films than at 1.32% for unannealed films.

Conversely, the absence of Pb^0 has also been reported [75, 87, 105]. Conings *et al.* [88] observed the formation of Pb^0 only under X-ray irradiation; most probably caused by liberation of organic/volatile species. Whereas Xing *et al.* [75] did not report any Pb^0 for pristine or annealed (50 °C) MAPbI_3 films; they also noted non-stoichiometric I/Pb and N/Pb ratios post-annealing, strongly suggesting the formation of PbI_2 caused by liberation of MAI species. It was also found that increasing excitation HAXPES photon energies from 2 keV to 6 keV resulted in an increase in Pb^0 signal in comparison to the Pb^{+2} peak by a factor of 5 [85].

There have been few considerations on temporal changes in photoemission spectra, which can prove insightful on the effects of X-ray irradiation. Steirer *et al.* showed that over a span of 42 h, significant time-dependent depletion of organic and I species from the absorber layer occurred [84] associated with co-ordinated formation of I^- and MA^+ vacancies ($\text{V}_\text{I}^\bullet$ and V'_{MA} , respectively). This was identified by a decaying I/Pb ratio **Figure 2.8(a)**. Despite removal of species from the material, it was suggested that MAPbI_3 retained its surface chemistry based on a constant full-width half maximum (FWHM) within region (i) **Figure 2.8(b)**, due to its inherent defect tolerance. This was supplemented by observing peak-shape changes and peak shifts in $\text{Pb } 4f$ and $\text{I } 3d_{3/2}$ core-levels (**Figure 2.8(c)** and **(d)**, respectively) in which Steirer *et al.* suggested a 1:1 molar ratio of MAPbI_3 and PbI_2 after 9.04 h of X-ray irradiation. Based on changes in valence band onset (*i.e.* changes in VB_{max} , ΔE_v) and with reference to the Fermi edge³ ($E_{\text{VBmax}} - E_{\text{Fermi}}$), a generalised view of the surface electronic structure is obtained. The authors showed that there are three distinct regions in which the surface electronic structure changes (**Figure 2.8(e)**) with respect to surface composition. It can be observed that when I/Pb is more than 2.5, the defect tolerance of MAPbI_3 sufficiently allows the retention of its electronic and crystal structure (*i.e.* chemical bonding) but below that, structural changes occur and eventually complete degradation to PbI_2 occurs.

³In XPS measurements, the Fermi edge is usually defined as 0 eV at the cut-off point of secondary electron emission of a reference material, usually Au, where the Fermi levels of both sample and reference material are said to be the same.

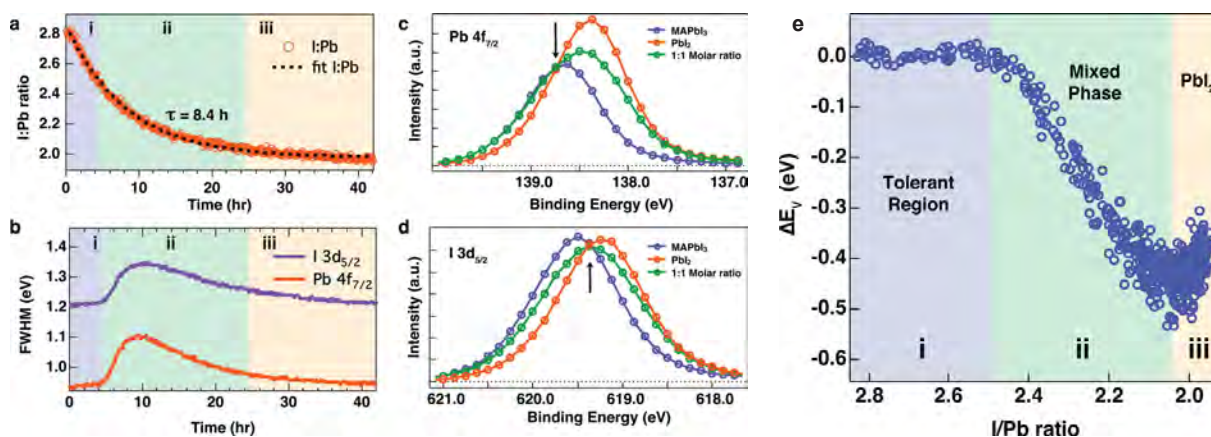


Figure 2.8 (a) Decay of I/Pb ratio fitted with first order kinetics using Avrami analysis. (b) Changes in full-width half maximum (FWHM) of I $3d_{5/2}$ and Pb $4f_{7/2}$ core-levels with time. (c) Pb $4f$ and (d) I $3d_{5/2}$ peak shapes at 0 h corresponding to MAPbI₃, at 42 h corresponding to PbI₂, and at 9.04 h corresponding to a 1:1 molar ratio of MAPbI₃ and PbI₂. (e) Dependence of ΔE_v (change in valence band onset from initial value with reference to the Fermi edge), on I/Pb ratio. Reproduced with permission from [84] Copyright © 2016 American Chemical Society.

In what is also a crucial piece of work in exposing the temporal effects of X-ray irradiation on the defect density and chemistry of MAPbI₃, Das *et al.* [106] performed time-resolved XPS measurements of MAPbI₃ in the dark and under illumination in which they reported slight changes in I/Pb (3.3 to 3.1) and I/N (3.3 to 3.5) ratios after 15 hours in the dark. Comparatively, changes in intensity ratios were more severe under illumination and open-circuit condition: I/Pb (3.0 to 2.2) and I/N (4.0 to 7.4). These observations are indications that ultra-high vacuum (UHV) conditions may be deleterious to organometallic halide materials causing the liberation of volatile chemical species. This behaviour seems to be exacerbated under illumination which suggests that when MAPbI₃ is in a state of excitation with light-induced charge carriers in the absence of a closed-circuit (e.g. in a device), decomposition to MAI and PbI₂ is much more likely. The authors also reported the formation of Pb⁰ under illumination only, that is partly reversible in the dark.

One can, surmise that the presence of Pb⁰ is an indication of the decomposition of MAPbI₃ leaving defects in the crystal lattice or incomplete formation of perovskite from its precursors. The resultant Frenkel defect(s) may cause p-doping [24]. Pb-clusters may also act as electron-donating species, resulting in n-doping [81].

These conflicting reports seem to stem from the fact that it can occur *via* a range of independent factors, e.g. deposition routes, precursor ratios, atmospheric interaction (e.g. humidity), and X-ray irradiation [83]. Minute experimental details such as beam size and measurement time for each core-level spectrum dictate the overall X-ray photon dose to which an area on the sample is exposed. Thus, one can deduce that different measurement parameters potentially affect obtained spectra.

Despite the tolerance of MAPbI₃ to defect generation during X-ray irradiation [84] the observed relationship of surface composition and electronic structure coupled with the large variation in independently reported I/Pb ratios (see **Table 2.2**) underline the importance of identifying the region within which the surface composition exists before any electronic structure measurements (either by UPS or XPS) are carried out as they usually require extended periods to achieve high signal-to-noise ratio.

2.6 Defect Passivation

Generally, point defects are expected in crystalline materials, and MAPbI₃ is no exception. The possible type of vacancies are: ion vacancies ($V_I^\bullet$, V_{Pb}'' , V_{MA}'), interstitials ($MA_i^\bullet$, I_i' , $Pb_i^{\bullet\bullet}$), and antisite substitutions ($I_{MA}^\times$, $I_{Pb}^\bullet$, $Pb_I^\bullet$, $MA_I^\times$). It has been suggested that $V_I^\bullet$, V_{Pb}'' , V_{MA}' , and $MA_i^\bullet$ have low formation energies which introduce shallow trap states, with little effect on non-radiative recombination as they are close (0.5 eV) to the CB_{min}/VB_{max} [22]. Deep trap states leading to non-radiative Shockley-Read-Hall (SRH) recombination are thought to originate from $Pb_i^{\bullet\bullet}$, $Pb_I^\bullet$, $I_{MA}^\times$, $I_{Pb}^\bullet$ and have transition levels deep within the bandgap. The physics of defect formation and their corresponding formation energies have been studied and reviewed relatively extensively [22, 107, 108] and are not within the scope of this thesis. However, knowing the possible type of defects, and that they result in deep trap states which encourage non-radiative SRH recombination and consequently reductions in current density and voltage, various strategies against their deleterious effects can be devised. Surface defects can be found on the surface where undercoordinated atoms are inevitable but result in net charges or at grain boundaries where there is a discontinuity in crystallographic orientation of each grain—as such certain additives that influence the nucleation and growth processes would inevitably influence material properties and not necessarily through defect passivation. Many studies have been published discussing the effects of grain sizes and the effects of grain boundaries but with seemingly contradictory results [109, 110]—such issues are not discussed in this thesis.

Currently, the various routes for defect passivation of MAPbI₃ are: Lewis acids/bases, ionic bonding, and hydrogen bonding where the exact mechanism depends on the species used for passivation. A generalised view of the surface of the grain can be described as having a combination of ion vacancies, and inevitably dangling bonds due to undercoordinated atoms. The consequences of these surface defects are photocurrent hysteresis and degradation.

As mentioned in **Section 2.4.3**, PbI₂ can be observed depending on the processing temperatures and can be beneficial when in controlled amounts. This can be induced also by an excess of PbI₂ precursor in the precursor solution. An excess of MAI precursor has similarly shown improvements in device

properties through defect passivation and by introducing a more favourable energy level. By altering the stoichiometry of the precursor solutions, improvements in device properties and stabilities have been observed.

Enhanced device efficiency has been reported after fullerenes (and its derivatives) were added to MAPbI₃ precursor solutions [111–113]; their stabilising effects were also reported [114, 115]. Halogen containing additives (e.g. iodopentafluorobenzene C₆F₅I, IPFB) have also been shown to be effective in improving device properties and stability employing mixed halide compositions [116]. It was suggested that the higher electronegativity of the surround F atoms causes a re-distribution of electron density thereby inducing a $\delta+$ charge on $-C-I$ in IPFB. Thus, a supramolecular halogen bond occurs between IPFB and undercoordinated halogens (X) with an excess negative charge (X^-) on the crystal surface.

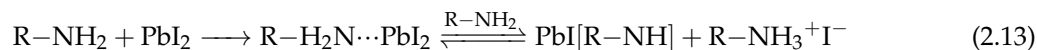
The origins of the enhancing effects from the inclusion of these additives is not yet clear though evidence has shown that they behave as Lewis acids interacting with surface defects such as undercoordinated I (I^-) and PbI₃⁻ antisites [112] by forming coordinate bonds, effectively passivating their trap states. A similar effect has been observed for Lewis base additions. Sulfur-based alkyamines additions to the precursor solution was shown to improve moisture resistance [117]. though it was reported in a *n-i-p* device containing Spiro-OMeTAD as a HTL which is well known for its porosity. Other functional groups have also been explored. For instance, pyridine (C₅H₅N) and thiophene (C₅H₅S) are said to form coordinate bonds with Pb²⁺ which act to reduce deep trap states and therefore SRH recombination [118, 119]. Similar $-S$ functional groups from thiols were also reported to have increased moisture resistance and device performance [120]. Other $-N$ functional group additives include phenylalkyamines (ph-R-NH₂) which are thought to form coordinate bonds with V'_{MA} and Pb²⁺ and show promise not only in improving device efficiency but also stability in air [121].

Apart from Lewis acids/bases, ionic bonding passivation can be effective as well. Metal cations are reported to passivate undercoordinated halide atoms [122–125] while ammonium functional groups ($-NH_3^+$) can form hydrogen and ionic bonds with V'_{MA} and Pb²⁺ [126, 127] and induce morphological changes and the formation of a 2D-layered structure [128, 129].

However, it is also possible that major contributions to the reported improvements may have been by more favourable nucleation and growth processes in which preferential crystallographic orientation is induced during nucleation and formation processes [130] or by a more stoichiometric precursor through the mitigation of I^- oxidation to I₂ [131]. The exact surface terminations have been shown to influence surface electronic structure and overall stability of the material. Thus far, evidence for defect passivation

has been given but there has been little direct observations with a surface-sensitive characterisation approach.

The exact mechanism of bond formation is not clear for these passivation strategies though an attempt has been made to better understand their solution chemistry [132]. It was suggested by the authors that the following reactions take place:



where the acidic nature of PbI_2 when forming a dative bond with the $-\text{N}$ functional group of the amine additive, results in the formation of Pb –amide bonds which is evident from nuclear magnetic resonance (NMR) and XPS of deposited MAPbI_3 samples. In a further study by the same authors, an improvement in MAPbI_3 stability (in terms of the oxidation of Pb^{2+} to Pb^0) under X-ray irradiation and PL features evident of reduced charge carrier recombination [133]. Such observations were a consequence when an optimum concentration of amine precursors were added to a non-stoichiometric $\text{PbI}_2 > \text{MAI}$ precursor solution where an excess destabilised MAPbI_3 .

Direct and empirically obtained observations of the resulting surface terminations and more systematic approaches in identifying bond formation in solution are necessary for a more rational and controlled approach to devising passivating strategies.

2.7 Interlayer Reactions in a Perovskite Solar Cell

The previous section discussed the complexities of quantifying surface composition and the relationship between surface composition and electronic structure. The core developmental issues of organometallic halides—namely, its stability as a photoactive material in the face of environmental stressors such as light, oxygen, water, and thermal energy—were also discussed. Given the various facets of degradation this material (and its compositional analogues) face, the overall stability of a device is certain to be non-trivial especially when one considers possible interactions between the interlayers and the effects of environmental stressors on the individual layers (illustrated in **Figure 2.9**).

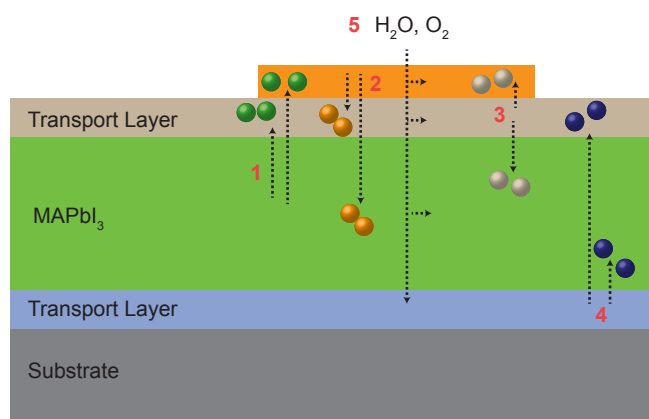


Figure 2.9 Illustration of possible (interfacial) reactions and diffusion pathways within a photovoltaic device employing MAPbI₃ as an absorber. **1:** Diffusion of I[−] into the transport layer and electrode resulting in degradation. **2:** Electrode metal diffusion into the transport layer and MAPbI₃ layer resulting in impurities imparting certain defect levels. **3:** Chemical reactions between the electrode and MAPbI₃ layer as well as diffusion of species into these layers. **4:** Diffusion of species from bottom transport layer to the top transport layer and MAPbI₃. **5:** Diffusion of H₂O and O₂ into the device resulting in oxidation of electrode, transport layer, hydration and superoxide mediated degradation of MAPbI₃.

There have been ample observations and evidence of interfacial effects in organometallic halide-based devices to dictate more rigorous investigation. The predisposition of these materials to surface degradation upon contact with atmosphere complicates this endeavour; *in situ* measurements or systems that prevent atmospheric exposure are thus desirable but are not without limitations—the influence of X-ray irradiation and UHV conditions were discussed in the previous section.

Similar to organic semiconducting devices (e.g. OLEDs) in that organometallic halide-based devices are also, for the most part, solution processed, the conformity of each layer and the interface that they make with each other can have significant influence on the behaviour of the entire device. This effect is exacerbated when one considers the overall thickness of a typical planar device and especially so with a mesoporous device with a large surface area. Thus, efforts should also be directed to understanding interfacial phenomena.

The choice of interlayers and device architectures are intertwined—certain materials are incompatible with organometallic halide-based devices depending on the order of layer deposition. Studies have also shown that degradation can originate from these interlayers or be exacerbated by it which underline the importance of choosing appropriate materials that would be stable under operating conditions in a device. While there are currently no main-stream strategies for predicting such complex chemical, photochemical, or thermally-induced interactions between the different layers, there are still certain chemical and physical requirements for the interlayers: stable under thermal energy and light; resistant

to (photo-)oxidation and moisture; able to form a conformal layer; chemically unreactive (unless intended) with organometallic halides. In addition, their $VB_{\max}$ /HOMO and $CB_{\min}$ /LUMO must match that of the absorber layer for efficient charge extraction. A review into such strategies is out of the scope of this thesis but extensive ones for transport layers can be found separately: [31, 134, 135].

This section aims to tie aspects such as stability, material chemistry, and processing methods with interfacial changes and compositional variations in a device as symptoms or factors in the process of degradation.

2.7.1 Transport Layer/MAPbI₃ Interface

Organic Materials

As discussed in **Section 2.4.1**, Spiro-OMeTAD is widely used in standard *n-i-p* structures but is well reported to be non-uniform in coverage which resulted in easier oxygen and water ingress. Depth-profiles using ToF-SIMS showed compositional variations in particular, I^- migration through and within the Spiro-OMeTAD layer [136] (see **Figure 2.11**). Its temperature stability was lacking with distinct crystallisation at elevated temperatures (100 °C) [137]. It is also necessary to dope Spiro-OMeTAD with 4-tert-butylpyridine (tBP) and lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI) to improve its hole conductivity but Li-TFSI was shown to make the transport layer hydrophilic which can be detrimental to the organometallic halide absorber layer should there be water ingress [138] and Li^+ from Li-TFSI-doped Spiro-OMeTAD was also shown to diffuse to the TiO_2 layer [139] and may have been a contribution to past reports on hysteresis and degradation using TiO_2 as the ETL; tBP was found to be corrosive to MAPbI₃ [140] and can chemically react with certain transport materials (including Spiro-OMeTAD) to form pyridinated products that reduce conductivity [137, 141].

PEDOT:PSS has also been found to be chemically reduced by MAI which further results in oxidation consequently its energy levels were modified leading to unfavourable interfacial energetics [142]. Similarly, PEDOT:PSS was also found to be corrosive towards the absorber layer and while it was shown that in an inverted device, the stability of PEDOT:PSS/MAPbI₃ (in air, 40%RH, and under controlled illumination) was higher than that of a full device (PEDOT:PSS/MAPbI₃/PCBM/BCP/Al) [143] for which was attributed to the increase in MAPbI₃ surface roughness and degradation of both the MAPbI₃ and interfacial contacts. However, the use of Al as an electrode could also be the limiting factor as its instability in air is well established.

In *p-i-n* inverted devices, PCBM is often used as the ETM due to the strict solvent limitations that pre-

vent other materials from being used as the common solvents are detrimental (through dissolution) to processing organometallic halides. While MAPbI_3 decomposition resulting in I^- diffusion and its consequent reaction with electrodes are often regarded as origins of device performance degradation (Section 2.7.2), there is another possible compositional-electronic facet of device degradation.

According to Lee *et al.*, through a process of Ag removal and restoration over time, they argue that the accumulation of I^- , observed from ToF-SIMS depth profiles, at the Ag/PCBM interface results in an electrochemical reaction between I^- and PCBM [144]. The authors suggest that structural ordering of the PCBM layer (see Figure 2.10) from I-C_{71} interactions resulted in higher V_{oc} over time and such interactions resulted in n-doping and produced trap states which partially accounted for a reduction in J_{sc} .

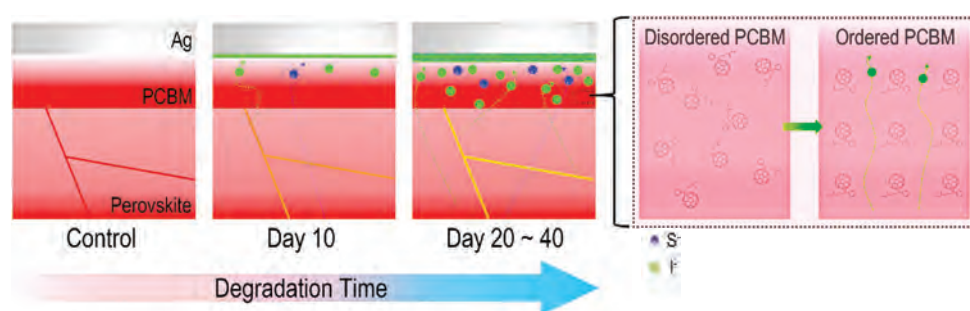


Figure 2.10 Illustration of I^- (green) from MAPbI_3 and S^- (blue) from PEDOT:PSS accumulating at the Ag/PCBM interface over a period of 40 days. Accumulation of I^- results in structural ordering of the PCBM layer through electrochemical interactions. Reproduced with permission from [144] Copyright © 2017 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Additionally, it was shown that oxidation of PCBM results in degradation of MAPbI_3 , causing further degradation through formation of metal-halide compounds with the Ag electrode [145]. Apart from such chemical interactions, oxidation of PCBM has been shown to result in modified energy levels (lower LUMO) which could introduce deep traps [146], and thereby contribute to performance degradation through reduced electron mobility or increased non-radiative recombination.

Given the reported instabilities, the flexibilities in molecular design to improve thermal stability [147] and doping to modify energy levels still make them an attractive material choice for transport layers.

Inorganic Materials

Oxides are generally thought to be chemically inert and electrically superior to their organic counterparts with a main drawback of high processing temperatures. They are also thought to be efficient barriers against oxygen and moisture diffusion into the device. As such, most metal oxides have been

used in *p-i-n* structures (e.g. NiO_x , CuO_x , Cu_2O , MoO_x) and have the ability to be p-doped or n-doped giving them immense flexibility. However, certain oxides have shown to initiate degradation of the absorber layer.

While TiO_2 has been widely used, it was shown that its thermal expansion resulted in degradation of the device [148]. Additionally, oxygen vacancies within the transport layer was shown to exacerbate photoinduced degradation [149–151] where the authors also reported interfacial engineering through defect passivation of TiO_2 .

ZnO has gained popularity as an ETM but has been found to induce degradation when MAPbI_3 was deposited on it during the annealing process [152]. It can also initiate degradation of MAPbI_3 layers through proton transfer [153] which was ascribed to the basic nature of residual $-\text{OH}$ groups on ZnO , effectively deprotonating the methylammonium group and a typical acid-base degradation reaction proceeds [154]. However, there have been efforts to introduce interfacial engineering to prevent physical contact between ZnO and the absorber layer [155–157] and by doping ZnO with Al (AZO) [158] or by introducing a hydrophobic poly(tetrafluoroethylene) (PTFE) layer between MAPbI_3 and ZnO [159]. Intentionally accelerating the degradation between these two layers to form an in-built physical buffer layer of PbI_2 was also reported [160].

Another metal oxide transport layer of note is MoO_x and is attractive in its energy level alignment with MAPbI_3 or compositional analogues. But MoO_x induced degradation was also observed during the deposition and formation processes [99].

The permeability of the transport layer at this interface often results in diffusion of I^- and subsequent degradation of the metal electrodes through formation of halogenated metal compounds. The cross-diffusion of metal into the absorber layer is also affected. Both of these issues are discussed in **Section 2.7.2**. Therefore, there have been significant work in finding suitable diffusion barriers [149, 161, 162].

2.7.2 Electrode-Dependent Degradation

The most widely used counter electrodes are metals due to their high conductivity and high conformity in forming a dense layer but they are often involved in degradation processes. Degradation can occur *via* oxidation of the electrode under atmospheric conditions which can act as additional sources of corrosion from the environment and is known to occur spontaneously for most electrode metals with the exception of Au. Additionally, metal oxides are generally more resistive than their base metals which

can contribute to current density reductions during atmospheric testing [163]. Degradation can also occur *via* metal diffusion (thermally activated or otherwise) into the organometallic halide absorber layer which has been directly observed by several independent work. Additionally, the reactivity of certain metals with halides (specifically I^-) is a major concern [164].

Metal Diffusion

A major concern in the diffusion of metallic species is the formation of clusters within the active layer that introduce deep traps [23].

Using scanning transmission electron microscopy (STEM), Liu *et al.* observed Ag diffusion into $(FA)_{0.5}(MA)_{0.5}Sn_{0.5}Pb_{0.5}I_3$ (where FA^+ : $CH(NH_2)_2^+$) after thermal evaporation of Ag electrodes. By contrast, no Ag was detected when a 40 nm thick layer of ZnO was deposited between PCBM and Ag (see **Figure 2.11(a)**) [165].

Using energy dispersive X-ray spectroscopy (EDX) in STEM high angle annular dark field (HAADF), clusters of Au have also been observed within the active layer after subjecting a ITO/m-TiO₂/MAPbI₃/Spiro-OMeTAD/Au device to 200 h of LED illumination and MPP-tracking (**Figure 2.11(b)**) [166]. It was theorised that the dynamic field within the device as employed during MPP, induced diffusion of Au.

Au diffusion for the structure m-TiO₂/MAPbI₃/Spiro-OMeTAD/Au is also shown by Busby *et al.*. They showed that after deposition of Au, limited but non-trivial extension of the Au interface into the Spiro-OMeTAD could be observed which worsened after undergoing constant LED illumination at 1000 W m⁻² **Figure 2.12(a)** and a subsequent suppression of said diffusion after interfacial engineering **Figure 2.12(b)** [167].

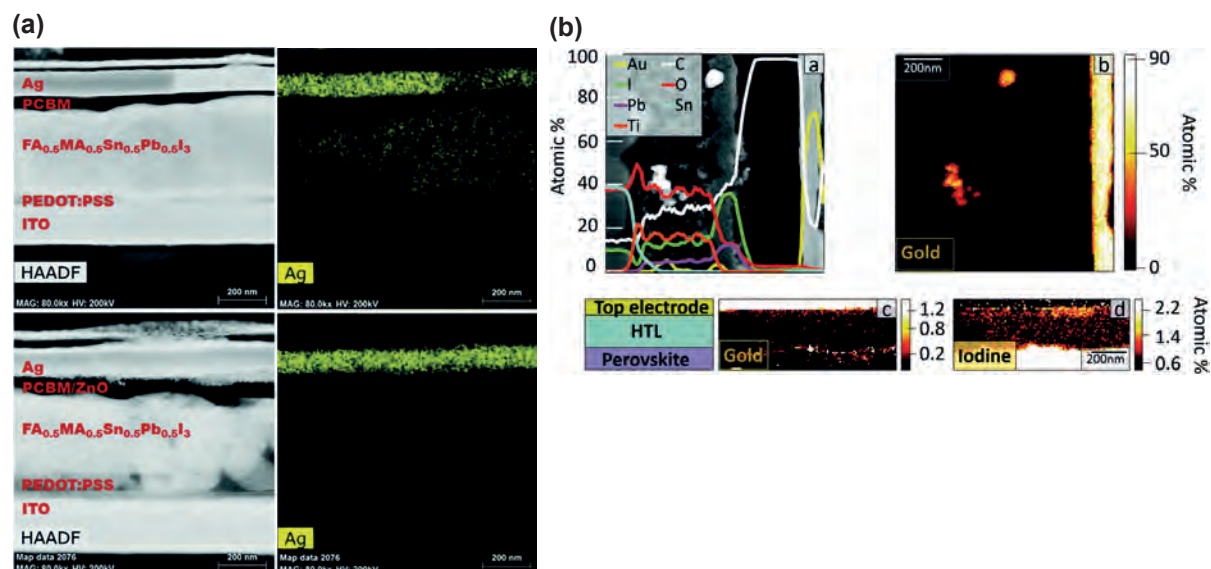


Figure 2.11 (a): Cross-sectional STEM energy dispersive X-ray spectroscopy (EDX) showing the presence of Ag within the $(\text{FA})_{0.5}(\text{MA})_{0.5}\text{Sn}_{0.5}\text{Pb}_{0.5}\text{I}_3$ active layer below PCBM/Ag while an absence below PCBM/ZnO (40 nm)/Ag after thermal evaporation of Ag [165]. (b): (a) Quantitative elemental profiles using STEM HAADF EDX showing distribution of species throughout cross-section of device. Quantitative EDX mapping showing (b) Au clusters within active layer, (c) Au distribution in HTL, and (d) I distribution in HTL [166]. Reproduced and adapted with permission. Copyright © 2019 Royal Society of Chemistry, Copyright © 2017 Royal Society of Chemistry, respectively.

Diffusion was also reported after thermally ageing ITO/m-TiO₂/(FA)_{0.83}(MA)_{0.17}P(I_{0.83}Br_{0.17})₃/Spiro-OMeTAD/Au at 70 °C for 15 h under LED illumination and MPP tracking **Figure 2.12(c) and (d)** [168] and even though replacing the electrodes showed some degree of recovery, irreversible degradation in device performance still occurred. Coupled with the observation of Au at the TiO₂ layer there is reason to believe that degradation was mainly contributed by said diffusion. However, the effects of energetic changes in the transport layer (as was reported [144] and discussed in **Section 2.7.1**) as a result of I⁻ accumulation or the process of thermal evaporation of Au repeatedly, were not considered in this work. The authors also noted that depositing a layer of Cr (10 nm) between Spiro-OMeTAD and Au resulted in enhanced stability which was attributed to the suppression of Au diffusion, though no direct evidence was provided.

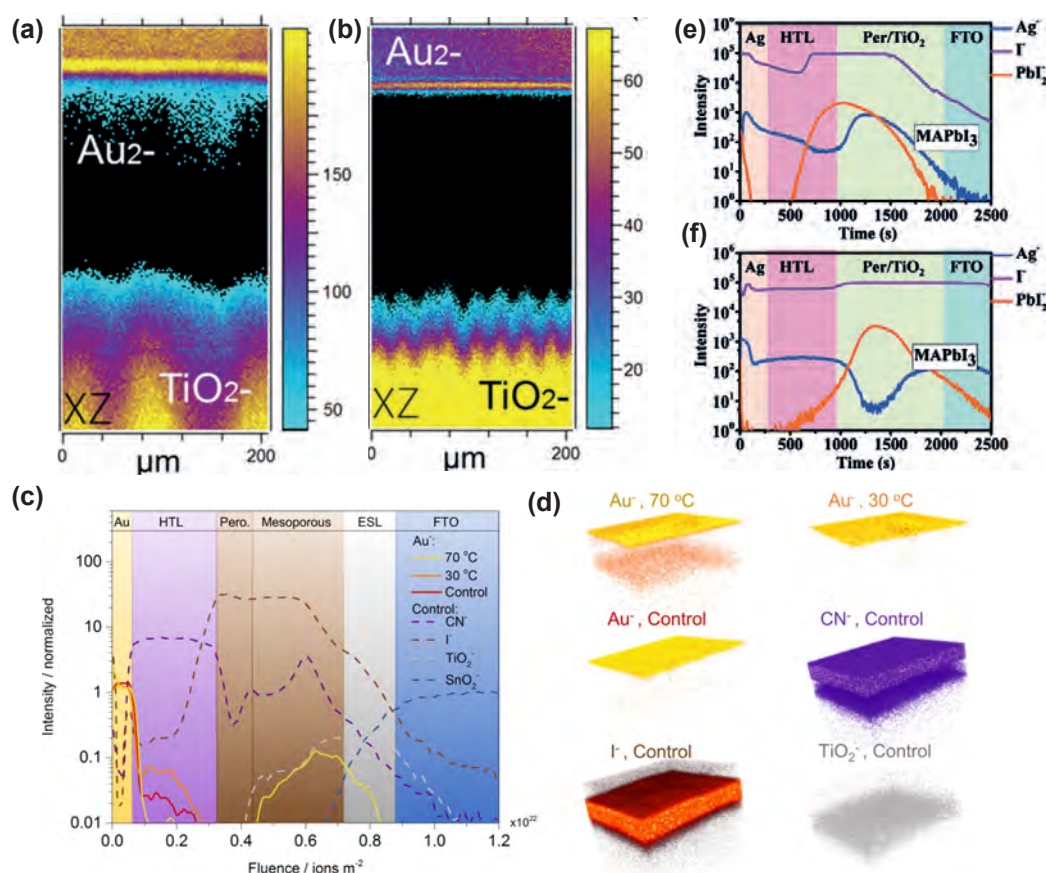


Figure 2.12 ToF-SIMS ion intensity map showing Au (Au_2^-) and TiO_2 (TiO_2^-) layers, cumulative over one lateral axis showing Au diffusion for (a) a fresh device and (b) suppression of said diffusion after interface engineering [167]. (c): ToF-SIMS depth profile of fresh and degraded devices, with (d) 3D reconstruction showing presence of Au^+ within the TiO_2 layer after thermal annealing [168]. ToF-SIMS depth profiles of MAPbI₃-based devices, using Spiro-OMeTAD as a HTM (e) kept in a dry box for a month and (f) left in ambient laboratory conditions both showing the apparent mobility through and retention of I^- in the HTM and differences in Ag^+ profiles [136]. Reproduced and adapted with permission. Copyright © 2018 Elsevier, Copyright © 2015 American Chemical Society, Copyright © 2017 Royal Society of Chemistry, respectively

Analysing depth profiles from a *p-i-n* FTO/ TiO_2 /MAPbI₃/Spiro-OMeTAD/Ag device **Figure 2.12(e)** and (f), the presence of Ag^+ within the HTL and MAPbI₃ is apparent [136]. On the contrary, thermally ageing FTO/NiO/MAPbI₃/PCBM/Ag devices at 85 °C for 24 h showed no visible Ag diffusion [169]. Comparing with [167, 168], both cite the use of a Cs⁺ sputter beam in ToF-SIMS depth profiling which should rule out any beam-related effects influencing ionisation probabilities of Au. Therefore, the discrepancies between these observations could arise from the following: (1) Spiro-OMeTAD was used as the transport layer which is well known to be a poor barrier and can form pin-holes, (2) the combined action of light and a bias within the device could be necessary factors, (3) the difference in device energetics (*n-i-p* vs. *p-i-n*) coupled with the use of m- TiO_2 could have resulted in favourable conditions for metal diffusion, (4) Ag does not diffuse to the same extent as Au on account of activation barriers, (5) the process of using a focussed ion beam (FIB) for STEM sample preparation, as is the case for the works

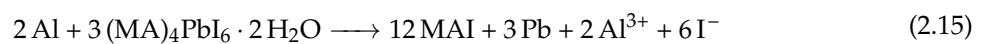
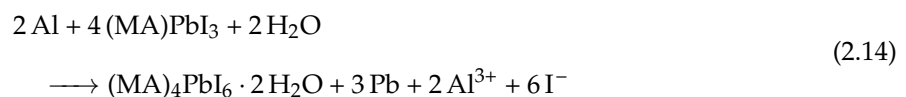
mentioned above, may have induced artefacts during ablation, (6) incorporation of Au clusters within the absorber layer occurred during the thermal deposition process of Au on Spiro-OMeTAD. Such issues need to be systematically investigated before reconciling said discrepancies.

Chemical Reactions

The presence of CuI for PTAA/MAPbI₃/Cu samples thermally aged at 100 °C for 16 h was not observed [170]. In fact, it was reported to be a highly stable electrode material though it was only tested under N₂ environment. In an *in situ* experiment of Ag deposition directly on MAPbI₃ and photoemission measurements, based on Ag 3d and I 3d_{5/2}, it was observed that AgI was formed as the main species in thin overlayers (< 16 Å). This scenario changes with increasing Ag thickness resulting in metallic Ag (Ag⁰) having a higher intensity. Coupled with observations of PbI₂ in XRD data and Pb⁰ in Pb 4f, they concluded some form of Ag induced MAPbI₃ degradation occurred [171]. This interfacial chemical reaction was attributed to the cause of this degradation. However, even though low photon excitation energies were used (<480 eV), the possibility of X-ray induced degradation (as discussed in **Section 2.5**) cannot be disregarded.

Li *et al.* also suggested that with Ag as an electrode, there exists an Ag-induced degradation mechanism. They observed vastly different MAPbI₃ morphology for samples (using PCBM as a HTM) with and without Ag after subjecting them to thermal stress (85 °C for 24 h) [169]. They argued that due to the chemical potential gradient of forming AgI at the electrodes, degradation of the absorber layer occurred more rapidly. Based on conductive atomic force microscopy (c-AFM), lower conductivity at grain boundaries were observed, indicating the presence of PbI₂ for thermally aged samples with Ag which supports their hypothesis that formation of AgI accelerates degradation of the absorber layer.

This electrochemical driving force was proposed by Zhao *et al.* though instead exemplified with Al as an electrode. They note that depositing Al directly on MAPbI₃ resulted in irreversible degradation and observed Pb 4f core-level features when various metals were directly deposited onto MAPbI₃ [172] and theorised that Al and Pb²⁺ undergo a redox reaction given by:



Their results suggest that interfacial redox reactions take place spontaneously for all reported

metal/MAPbI₃ interfaces (**Figure 2.13**) with the exception of Au/MAPbI₃ whose Pb 4*f* core-level shows partial charge transfer between Au and Pb [172]. The same group further show that underpotential deposition (UPD) reactions occur between Au and, I and Pb [132] when Au is deposited directly on MAPbI₃ (**Equation 2.16** and **Equation 2.17**).



The result is the formation of surface species/adsorbates on Au and the formation of Pb⁰ at the Au/MAPbI₃ interface. This scenario changes when Au is deposited directly on PbI₂ which showed the presence of two different oxidation states of I.

These phenomena are deserving of further investigation due to their potential implications in device stability employing metal electrodes, though it is unclear if a physical barrier—such as the scenario in a solar cell employing transport layers—would prevent such underpotential reactions or if such reactions would occur at the Au/MAPbI₃ interface.

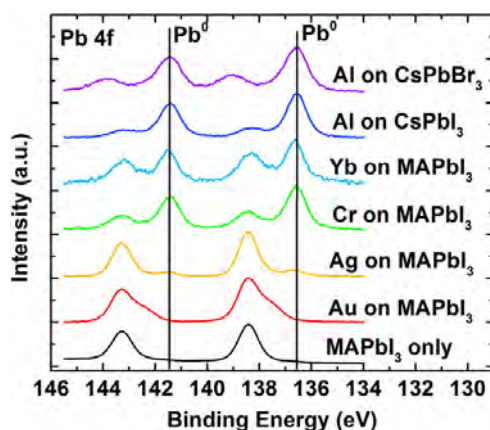


Figure 2.13 XPS: Pb 4*f* core-level spectra for various metal/organometallic halide composition interfaces. All interfaces (except Au) show presence of Pb⁰ peak [172]. Copyright © 2016 American Chemical Society.

2.8 Concluding Remarks

The effects of different precursor ratios and processing routes on the energetics and surface composition has been discussed. There is reportedly a large variability in empirical observations of surface compo-

sition which can be explained by a largely different surface composition compared to the bulk due to degradation of the surface from environmental conditions, processing routes, and the effects of X-ray irradiation; in particular the presence of anomalous Pb^0 can also be explained by the same mechanisms. While additives in MAPbI_3 precursor solutions have been hypothesised to terminate surface defects, direct observations have yet to be provided. Finally, the dependence of device stability on the choice of interlayers—and consequently interlayer reactions—and metal electrodes has been discussed. Additionally, interfacial phenomena such as metal diffusion and chemical reactions at the metal electrodes require further investigation.

As such, the following chapters aim to experimentally investigate instrumental (XPS, ToF-SIMS, LEIS) effects on acquired data (**Chapter 4**), the stabilising effects of organic additions and their corresponding surface composition (**Chapter 5**), and finally electrode dependent and thermal degradation of devices (**Chapter 6**).

Chapter 3

Materials & Methods

3.1 Sample Fabrication & Device Testing

Organometallic halide film and device fabrication were performed by Mr. Chieh-Ting, Lin⁴. Light-soaking stability (**Chapter 5**) and thermal ageing (**Chapter 6**) experiments were also carried out by Mr. Chieh-Ting, Lin.

3.1.1 Thin Film Preparation and Deposition

MAPbI₃ Precursor Solution

The different compositions of organometallic halide film samples (**Chapter 5**) were fabricated using solution-processing methods. Precursor solutions were prepared by dissolving 1.5M methylammonium iodide (MAI; Greatsolar, Inc) and 1.5M lead iodide (PbI₂; Tokyo Chemical Industry, Inc.) in a binary solvent system of dimethyl formamide (DMF):dimethyl sulfoxide (DMSO) in a 9:1.1 volume ratio.

Where organic additives were used (**Chapter 5**), solutions were prepared by adding them directly into the MAI:PbI₂ precursor solutions in controlled amounts: 1-naphthyl methylamine iodide (NMA-I) (0.05 vol %), glycine (5.0 vol %), β -alanine iodide (5.0 vol %), γ -aminobutyric acid iodide (5.0 vol %), 5-aminovaleric acid iodide (5.0 vol %).

Where excess precursor ratios were investigated (**Chapter 5**), the respective precursor was added in

⁴Imperial College London, Materials Department.

excess of mol%. The following precursor solutions were used: MAI in excess of 1.5 mol% and 3.0 mol% and PbI_2 in excess of 1.5 mol%, 3.0 mol%, and 6.0 mol%.

All precursor solutions were stirred at 60 °C for 1 h prior to sample fabrication.

$(\text{FA})_x\text{Cs}_{1-x}\text{Pb}(\text{I}_y\text{Br}_{1-y})_3$ Precursor Solution

Precursor solutions for the composition $(\text{FA})_{0.85}\text{Cs}_{0.15}\text{Pb}(\text{I}_{0.9}\text{Br}_{0.1})_3$ were prepared by dissolving formamidinium iodide (FAI, GreatCell Solar), cesium iodide (CsI, Alfa Aesar), PbI_2 and lead bromide (PbBr_2 , Tokyo Chemical Industry, Inc.) in the pre-determined stoichiometric molar ratios, in a binary solvent system (8:2 volume ratio) of DMF and N-methyl-2-pyrrolidone (NMP) with a molar concentration of 1.25M.

$(\text{FA})_x\text{Cs}_{1-x}\text{PbI}_3$

Precursor solutions for the composition $\text{FA}_{0.85}\text{Cs}_{0.15}\text{PbI}_3$ were prepared by dissolving FAI, CsI, PbI_2 in the predetermined stoichiometric molar ratios in a binary solvent system (8:2 volume ratio) of DMF and NMP with a molar concentration of 1.25M.

$(\text{MA})_x\text{Cs}_{1-x}\text{PbI}_3$

Precursor solutions for the composition $(\text{MA})_{0.95}\text{Cs}_{0.05}\text{PbI}_3$ and $(\text{MA})_{0.8}\text{Cs}_{0.2}\text{PbI}_3$ were prepared by dissolving MAI, CsI, and PbI_2 in the predetermined stoichiometric ratios in a binary solvent system (8:2 volume ratio) of DMF and NMP with a molar concentration of 1.25M.

MAPbI₃ & Analogues Deposition Steps

Precursor solutions were deposited directly on indium tin-doped oxide (ITO) patterned glass substrates (10 mm × 10 mm) and spin-cast at 4000 rpm for 30 s and 0.7 ml of diethyl ether (Sigma-Aldrich) was used as the anti-solvent which was added after 7 s of spinning. After this step, as-deposited samples were thermally annealed at 100 °C for 1.5 h to remove residual solvents and drive crystallisation of as-deposited samples. All samples were fabricated and annealed within an N_2 filled glovebox.

3.1.2 Device Fabrication

All devices were fabricated in an inverted *p-i-n* architecture: ITO/PTAA/PFN/APbX₃/PCBM/BCP/electrodes (where A: MA, Cs, FA, X: I, Br). The deposition steps are described below (in order):

1. PTAA (Ossila, Inc.) was dissolved in toluene at a concentration of 2 mg ml⁻¹ and spin-cast on ITO at 3000 rpm for 20 s which was left to dry for (5 min).
2. PFN solution (0.05 wt. % in methanol, (1-Material, Inc.) was spin-cast on ITO/PTAA at 5000 rpm for 30 s.
3. MAPbI₃ (& compositional analogues) deposition follows the steps described in **Section 3.1.1**.
4. PCBM (Ossila, Ltd.) at a concentration of 40 mg ml⁻¹ in chlorobenzene was spin-cast at 1500 rpm for 30 s subsequently.
5. BCP (Lumtec) in methanol (0.5 mg ml⁻¹) was spin-cast at 4000 rpm for 20 s.
6. Counter electrodes were thermally deposited onto the samples with a mask containing 6 pixels. Deposition was performed in a vacuum chamber (1×10^{-6} mbar). The thicknesses of the various electrodes are: Au: (100 ± 5) nm, Cr: 3.5 nm, Cu: (100 ± 5) nm, Ag: (100 ± 5) nm. The deposition times were calibrated (by using a profilometer on the electrodes) to obtain desired thicknesses of the electrode.

3.1.3 J-V Characterisation

Solar cell device current density-voltage (J-V) characteristics and performance were characterised under Air Mass 1.5 global (AM 1.5G) illumination by a Xe lamp; calibration was performed by using a national renewable energy laboratory (NREL) certified Si reference cell.

3.2 Stability Testing

Where devices underwent thermal stability testing, samples were placed in an aluminium foil covered (to prevent light soaking) petri dish on hotplates. Testing was done within an N₂ filled glovebox to rule out effects of moisture and oxygen. Samples were transported to instruments via encapsulated sample boxes but were exposed to atmosphere during sample mounting for ToF-SIMS measurements.

Device stability under maximum power point (MPP) was measured by an MPP tracker system (Candle Light). During testing, a device's maximum power point is tracked under 1 sun intensity illumination (provided by an LED) in dry air or N₂ atmosphere. The light intensity of the LED is calibrated by achieving the same short circuit current density (J_{sc}) obtained for such devices under an AM 1.5G solar simulator.

3.3 Time-of-Flight Secondary Ion Mass Spectrometry

3.3.1 Theory

Secondary ion mass spectrometry (SIMS) is a surface sensitive technique that relies on the use of a *primary* ion beam to bombard the surface of a material. This process results in the fragmentation of molecules from the matrix, a portion of which are ionised as cations and anions. It is the detection of these ions that give SIMS its sensitivity to variations in surface chemistry and surface contaminants. Within SIMS, there are a number of analysers each with a different method of detecting and separating the ions such that ions of different masses can be resolved. Different analysers have varying degrees of mass resolving power and the three most common detectors are time-of-flight (ToF), magnetic, and quadrupole. ToF-SIMS is probably the most widely used configuration as it provides high mass resolution about $\Delta M/M$ 10,000. It works on the principle of accelerating secondary ions through an extractor with a known potential V through a flight tube of known length L (**Figure 3.1**).

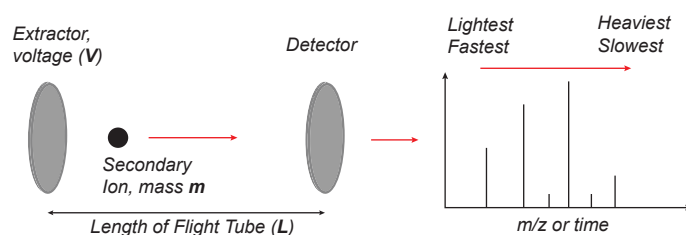


Figure 3.1 Basics of separating ions of different masses based on the time taken for them to travel through the flight tube.

Since the secondary ions are accelerated by the same electric potential, their kinetic energies (E_{KE}) must be equivalent given by:

$$E_{KE} = \frac{1}{2}mv^2 = \frac{1}{2}m\left(\frac{L}{t}\right)^2 = zeV \quad (3.1)$$

where z is the charge of the ion, $e = 1.6 \times 10^{-19}$ C and V is the electric potential of the extractor with

reference to the sample. Thus, ions of different masses travel to the end of the tube at different times and given that this time t is recorded, they can be then separated based on their mass-to-charge ratio (m/z) [173]. Rearranging the equation, we get:

$$\frac{m}{z} = \frac{2Vt^2}{L^2} \quad (3.2)$$

Generation of secondary ions can be classified into two regimes: the first is the emission of secondary ions directly from the point of impact from the primary ion (recoil sputtering), the second is the implantation of an energetic primary ion into the material, transferring its energy to the surrounding lattice (laterally and depthwise), a portion of which will be sufficient to emit secondary ions from a point at the surface away from the original impact point [174]. By detecting these secondary ions, mass-resolved data are obtained and mass spectra analysis enables understanding of the chemistry and composition of samples, provided some prior knowledge of the sample/material exists.

The intensity (I_s) detected from a particular species (x) takes the form [175]:

$$I_s^x = I_p \cdot \theta_x \cdot S_x \cdot \alpha^+ \cdot \eta \quad (3.3)$$

I_p = Primary ion beam current

θ_x = Fractional concentration of x

S_x = Sputter yield of x

α = Ionisation probability of x

η = Transmission of the analysis system

If one were able to empirically obtain values for all parameters for a particular species, then quantification of its fractional concentration becomes possible. However, the question as to whether the concentration of said species is indicative of the target molecule/atom cannot be answered as this is influenced by both beam interactions and surface chemistry. Thus, quantification in SIMS is generally not pursued to any great lengths.

The initial basis for SIMS is the acquisition of surface mass spectra. But considerations have to be made for analysis of pre-bombarded areas as secondary ions obtained would be from an already (chemically and physically) modified surface and therefore, not representative of the material.

Every collision event can be thought to introduce an area of damage on the sample, with a cross-section

σ . Suppose the area of analysis is A , then the proportion of total damaged area to analysis area is $\frac{\Sigma\sigma}{A}$. One can then say that this is the probability of an ion impact within an area that has already been damaged by other ion impact events. Benninghoven describes *static* condition in which this probability is $\ll 1$ [174, 176]. Mass fragments obtained within this limit are considered to be chemically true of the surface inasmuch that the fragmentation is influenced by the chemistry of the surface. Practically, the flux density or dose (ions/cm²) limit beyond which static analysis is no longer applicable is often regarded as 1×10^{13} ions/cm² for inorganic surfaces and 1×10^{12} ions/cm² for organic ones [175].

Thus, *static-mode* is one in which the primary ion beam is used to analyse the surface⁵ of the material using a low-current (0.1 pA to 1.2 pA) primary ion beam. Analysis in this mode is performed *per pixel* which means that in an analysis square of 256 pixels $\times$ 256 pixels, there are 14,336 spatially resolved mass spectra giving a large amount of information.

Inherent to SIMS is the influence of the matrix on the ionisation yield of certain species (e.g. dopants); where certain matrices enhance or suppress the yield. the phenomenon is known as ‘matrix effect’. This phenomenon is translated to dynamic SIMS in that at certain interfaces within a multilayer sample, the yield of ions can be evidently modified from reality [177, 178].

3.3.2 Ionisation and Molecular Mass Fragmentation

Ionisation of inorganic materials has been studied to great lengths and there are two widely accepted models for providing mechanistic explanation of the emission of secondary ions: (1) the nascent ion molecule model by Gerard and Plog [179, 180] which was formed to explain secondary ion emission from inorganic materials, particularly metal oxides. The model posits that most sputtered particles from the surface are neutral, and only a portion will dissociate into ions a short distance away from the surface [175] and (2) the desorption ionisation model by Cooks and Busch [181] on the other hand describes the emission of secondary ions (mostly molecular ions) *via* the transfer of vibrational energy to pre-formed molecular ions on the surface, desorbing them or by fragmentation of neutral molecules and subsequent dissociation. Evidently, this model seems to better explain formation of secondary ions from molecular solids such as polymers where molecular ions dominate observed mass spectra.

Molecular fragmentation behaviour of organic materials is far more relevant to organometallic halides and related organic additives discussed in this thesis. The fragmentation and detection of ionised (cations/anions) parent molecules $[M]^{\pm}$ is said to occur *via* electron transfer [175] (**Equation 3.4**), producing a parent molecular ion with an unpaired electron.

⁵Surface in this instance refers to first atomic layer of the material.



The formation of parent-like ions $[M-H]$ and $[M^{+}H]$ occur via Brönsted reactions resulting in the deprotonation or protonation of the parent molecule, respectively. However, it is also possible for the desorption of already ionised organic molecules present on the surface [182], as described above by desorption ionisation model.

3.3.3 Dynamic SIMS

The biggest advancement in SIMS is the generation of elemental or molecular concentration profiles, calibrated against depth or sputter/erosion time. Dynamic or dual-beam mode in which a second beam (usually called sputter beam) of a much higher current (from 1 nA to 250 nA) is used in conjunction with a primary beam such that a sputter cycle removes material from a predetermined area and a primary beam bombards a smaller area within the sputter crater for analysis. This interlaced process of sputtering and analysis produces depth-resolved mass spectra using which one can reconstruct data showing the variation of ion concentration/intensity as a function of depth. In this mode, data is acquired in *voxels* (three dimensional pixel).

However, interpretation of these profiles is not straightforward. The scenario described above has an added complexity that ion bombardment on a surface with energetic particles results in various collision events that introduce damage beyond the analysis surface ('collision cascades'). Thus, both beams introduce damage and ultimately influence ionisation yields and require systematic studies to deconvolute their effects. These damage mechanisms have been studied extensively for inorganic materials. But with the evolution of new materials (e.g. inorganic-organic hybrid materials or even functional polymeric materials), and the use of ion-beam based techniques to characterise them, such interactions (including matrix effects) are still the subject of research [183, 184]. These collision events can be broadly categorised into:

1. Primary ion implantation and collision cascades resulting in recoil implantation and mixing of target atoms. Consequently, vacancies and interstitials are formed and the extent of which depends on the range of ion implantation. This value varies for different ion species, accelerating voltages,

and target materials and can be theoretically modelled by using stopping range of ions in matter (SRIM) discussed by Ziegler *et al.* [185] with an available software package [186, 187].

2. Structural changes due to energy transfer of atoms.
3. Chemical alterations by bond breaking and bond forming [173, 188]. These are not the only processes that take place as a result of particle bombardment, events such as photon/electron emission and ion neutralisation can occur and carry useful information about the chemistry and structure of the surface. For example, ion scattering can be a powerful surface sensitive characterisation that is reviewed in **Section 3.4**. This can be particularly relevant for polymers (e.g. poly(methyl methacrylate) (PMMA) and poly(styrene) (PS)) where cross-linking between chains has been observed with C₆₀ cluster sputter beams [189, 190].

Compared to elemental solids or those with binary constituents, the scenario is more complex for compounds and multilayer samples—issues such as preferential sputtering [191], surface roughening [192], and interfacial matrix effects [193–196] influence the overall profiles and any interfacial features. These processes are inherent in the limitations in the determination of elemental or molecular concentration profiles and in the characteristics of concentration (‘depth’) profiles. Typical profiles involve analysing intensity changes of pre-selected secondary ions with increasing dose (or depth, provided calibration is performed) giving the ability to identify compositional changes as a function of depth. In a typical depth profile of a multilayer **Figure 3.2**, the following features are present:

1. A surface transient region that is an artefact of the initial sputtering process and is often found in molecular sputtering of organic films. These features have been modelled by using an erosion model [197] that is relevant for understanding the steady-state region.
2. A steady-state region is expected where a horizontal profile is characteristic of an artefact free profile. It indicates that damage (e.g. collision cascades) from ion bombardment at the surface of the analysis area causes accumulation of damage beyond the surface that is sufficiently removed such that undamaged material is revealed after subsequent sputter cycles. This occurs when the damage range of the bombardment process is smaller than the volume of material removed (*i.e.* sputter yield) [197, 198].
3. Finally, when subsequent underlying layers are revealed as a result of the physical sputtering process, an exponential rise in intensity from secondary ions characteristic to the underlayer can be observed. In an ideal interface where no pre-existing mixing between the layers has occurred (pre-bombardment), the decrease in intensity from the first layer should be exponentially trailing.

However, the roughening effects of the sputter beam imparts signal broadening, resulting in a wider-than-expected interface.

While this is not a crucial issue in elemental solids (e.g. metals) or metal oxides where elemental homogeneity is expected, application of depth-profiling measurements to organics and hybrid materials become more challenging.

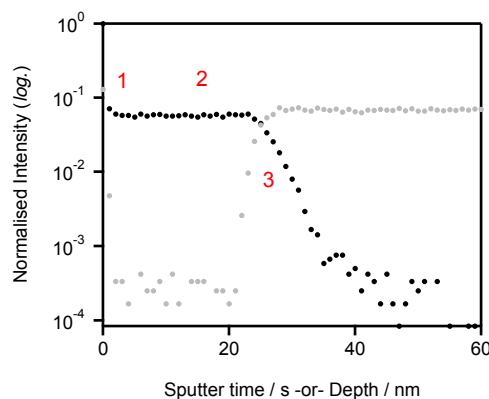


Figure 3.2 An illustrated example of distinct regions expected in a concentration profile of a multilayer sample showing (1) a transient region .

3.3.4 Instrumentation

Mass spectrometry data were obtained from the TOF.SIMS5 (IONTOF) instrument. It is fitted with a reflectron mass analyser and a multi-channel plate (MCP) within the detector module to amplify the conversion of secondary ions to electrons. It has a differential vacuum system: a load-lock at 1×10^{-7} mbar feeding to the main chamber at 1×10^{-9} mbar. Thus samples are measured under ultra-high vacuum (UHV) conditions.

Primary-ion beam is generated from a liquid metal ion gun (LMIG) with Bi metal at an accelerating voltage of 25 kV. Three different primary ions are available: Bi^+ at approximately 0.8 pA to 1.2 pA, Bi_3^+ , and Bi_3^{2+} with the larger clusters at approximately 1/3 the current. Various columns and sputter beams are available in the instrument: a dual-ion source column (DSC) providing a thermally ionised Cs^+ beam at four optimised voltages (0.25 kV, 0.50 kV, 1.0 kV, 2.0 kV) and an electron impact (EI) source for the generation of O_2^+ at four optimised voltages (0.25 kV, 0.50 kV, 1.0 kV, 2.0 kV); and a gas cluster ion beam (GCIB) column for variable clusters of $\text{Ar}_{500-3000}$ at a maximum accelerating voltage of 20 kV. A low-energy electron flood gun (0 eV to 21 eV) is also available for charge compensation when measuring highly insulating samples.

There are two measurement modes: static and depth-resolved measurements as described in the theory

section. Within each mode, two options are available: interlaced and non-interlaced modes. In the non-interlaced mode, one can control individual sputter and analysis times as well as dictating a pause interval, during which no sputtering or analysis takes place. This is usually done in conjunction with an electron flood gun for highly insulating samples. In the interlaced mode, the process of sputtering and analysis is done without pause and occurs sequentially.

3.3.5 Measurement Parameters

Three primary-ion analysis modes exist: high-current bunched mode (HCBM), burst alignment mode (BAM), and extreme imaging mode. HCBM was selected for all mass spectra acquisition due to its higher mass resolving capabilities but sacrificing lateral resolution. Generally, one uses BAM for higher lateral resolution but sacrificing mass resolution (unit mass) rendering analysis of organic species inaccurate. The extreme imaging mode is based on BAM but has the highest lateral resolution.

For static measurements, a 25 kV Bi_3^+ primary ion beam was used to raster an analysis area of $150\text{ }\mu\text{m} \times 150\text{ }\mu\text{m}$ with $128\text{ pixels} \times 128\text{ pixels}$ and was run in the 'interlaced' mode.

The choice of sputtering and analysis areas is crucial in minimising beam-induced artefacts. Generally, as the sputtering process does not result in a well-defined crater with sharp vertical edges, the sputter area should therefore be sufficiently larger than the analysis area such that the sputter crater edges are not included in the analysis area (**Figure 3.3**). Larger sputter areas may result in a less spatially-localised view of the compositional profile but it also result in slower sputter times. Additionally, it is necessary to adjust the analysis area such that the primary ion dose from the analysis beam is a few orders of magnitude lower than that of the sputter beam. This is to ensure primary ion induced damage is sufficiently removed from each sputter cycle whose effects can otherwise be evident in the profiles. A smaller sputter area—while resulting in faster sputter times and therefore higher sample throughput—results in larger sputter volume per sputter cycle and may mask important interfacial features. Therefore, careful optimisation of sputter and analysis areas to ensure measurement cycles are not prohibitively long and profiles obtained are representative of the compositional variations in a multilayer device.

For depth-profile measurements, (unless otherwise stated) an O_2^+ sputter beam at 1 kV and approximately 220 nA was rastered over an area of $300\text{ }\mu\text{m} \times 300\text{ }\mu\text{m}$ within which a Bi_3^+ primary ion beam was rastered over a $150\text{ }\mu\text{m} \times 150\text{ }\mu\text{m}$ area with $128\text{ pixels} \times 128\text{ pixels}$ and was run in the 'interlaced' mode—no sample charging was observed. Under these conditions, because the current of the primary ion beam is much lower than the sputter beam current, the dose in depth profile measurements are approximately $1 \times 10^{10}\text{ ions/cm}^2$ and $1 \times 10^{15}\text{ ions/cm}^2$ respectively. This means that damage cascades

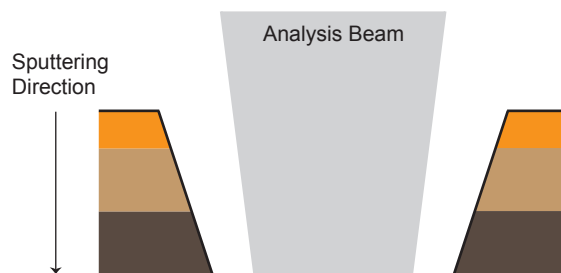


Figure 3.3 Illustration of crater edge effects, underlining the need for a sufficiently small analysis area.

imparted by the more energetic primary ion beam (25 kV) should be sufficient removed by subsequent sputtering cycles and is thus mitigated. The bombardment of primary ions on the analysis area is now on an undamaged area as opposed to an area that is dominated by primary ion damage (or a combination of both sputter and primary ion beams)—as discussed in **Section 3.3.3**.

Dose density (or dose) can be calculated using the equation below:

$$\text{Dose (ions/cm}^2\text{)} = \frac{I_{\text{beam}}}{D \cdot e} \times t \quad (3.5)$$

where, I_{beam} is the beam current (A), D is the area of beam impact (cm^2), e is the elementary charge $1.6 \times 10^{-19}\text{C}$, and t is the total beam irradiation time (s).

3.3.6 Data Analysis

Data processing and analysis were performed in IONTOF SurfaceLab 6 software [199]. In depth profiles, mass calibration was done individually first for each spectrum with secondary ions tabulated in **Table 3.1**. When comparing depth profiles between samples, a single mass calibration spectrum (from a reference sample) was used to apply to all spectra for consistency. Same mass fragments between samples were identified using the same peak margins to ensure peak integral quantification was consistent and any change in normalised intensities was therefore due to sample differences; peak intensities were normalised either to the total counts for each data point to limit artefacts or to a constant signal (electrode or substrate signal as these proved to be most consistent) when a feature in the profile was to be differentiated more clearly.

Table 3.1 ToF-SIMS: Secondary ions used for mass calibration, with nominal m/z values, in both negative and positive polarities.

Positive	Negative	m/z
H ⁺	H ⁻	1
C ⁺	C ⁻	12
CH ⁺	CH ⁻	13
CH ₂ ⁺	CH ₂ ⁻	14
CH ₃ ⁺	CH ₃ ⁻	15
O ⁺	O ⁻	16
-	OH ⁻	17
-	F ⁻	19
C ₂ ⁺	C ₂ ⁻	24
C ₂ H ₅ ⁺	-	29
-	Cl ⁻	35
C ₃ H ₇ ⁺	-	43
C ₄ H ₉ ⁺	-	57
C ₅ H ₁₁ ⁺	-	71

3.4 Low-Energy Ion Scattering

3.4.1 Theory

Low-energy-ion scattering (LEIS) is, fundamentally, a non-destructive method of surface analysis that has the ability to detect atomic species on the first atomic layer of the surface. It can also provide in-depth information. It has been widely used on oxides, specifically atomic-layer deposited (ALD) samples [200, 201]. It involves the bombardment of a sample with a low energy (primary) ion beam (0.5 keV to 10 keV). There are several processes that occur when such a low energy ion interacts with the sample: (1) binary collisions between surface atoms and primary ions resulting in backscattering of said ions, (2) ion neutralisation, (3) scattering of neutral atoms. An illustration of these processes is given in **Figure 3.4** [202, 203].

For binary collisions between the incident ion and target atom of masses m_2 and m_1 respectively, one can expect the final energy of the backscattered ion E_F scattering at an angle (θ) (with momentum conserved) [203]:

$$E_F = \left(\frac{\cos \theta + \sqrt{r^2 - \sin^2 \theta}}{(1 + r)} \right) \cdot E_0 \quad (3.6)$$

$$r = m_2/m_1 > 0$$

m_1 = Mass of incident primary ion

m_2 = Mass of target atom

E_0 = Initial energy of incident primary ion (eV)

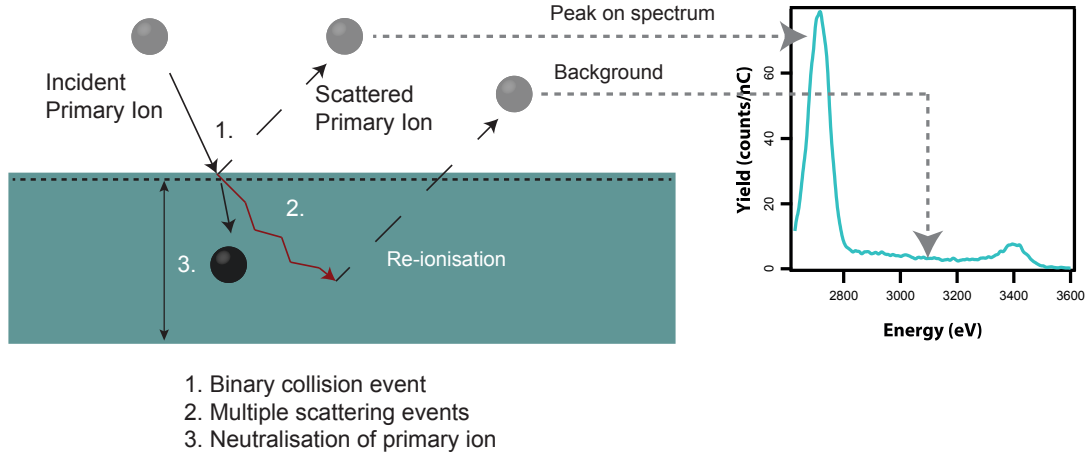


Figure 3.4 Illustration of binary and non-binary scattering events leading to obtained spectrum in LEIS. Only backscattered ions are detected, removing any detected neutral atoms. Background intensity comes from inelastically scattered ions from beyond the surface of the sample and neutralised atoms that undergo reionisation.

Thus, given that different target atoms have different masses, backscattered ions detected are expected to have an energy spectrum corresponding to the binary collisions between the different surface target atoms. Furthermore, it was shown that most incident ions reaching deeper into the material are neutralised which means that ion backscattering from the underlayers are severely suppressed, giving LEIS its extreme surface sensitivity.

In reality, the scenario described is more complex and involves the interaction of the different atomic potentials which is crucial in quantifying scattering cross-sections used in absolute atomic quantification. However, it is generally accepted that *matrix effects* from the chemistry of the surroundings are absent and one can accept that the obtained LEIS energy spectrum does not possess artefacts as that in SIMS, though there are methods in which to ascertain the presence of matrix effects. Generally, one can expect negligible effects of the matrix on backscattering of Ne^+ ions [202].

The intensity (S_i) of a scattering peak from a target atom i is given by:

$$S_i = \frac{I_p}{e} \cdot T_i \cdot R \cdot t \cdot N_i \cdot P_i^+ \cdot \left(\frac{d\sigma_i}{d\Omega} \right) \quad (3.7)$$

I_p = Primary ion current

e = Elementary charge of $1.6 \times 10^{-19}C$

T = Instrumental factor

R = Roughness factor, with a value of 1 for a smooth surface

t = Acquisition time

N = Atomic concentration

P^+ = Ion-fraction (ratio of detected ions to sum of ions and neutrals) $\frac{S_i^+}{S_i^+ + S_i^0}$

$\frac{d\sigma_i}{d\Omega}$ = Differential cross-section

Based on **Equation 5.1**, one can theoretically obtain absolute atomic concentration of the target atom species i on the sample surface if the other parameters are known; $\frac{d\sigma_i}{d\Omega}$ can be calculated based on Coulombic interaction potential⁶; t and I_p are measurement parameters; T should be constant for any instrumental set-up; P^+ should be constant for a specific E_0 .

To circumvent obtaining absolute values for these parameters, comparing intensities can provide relative quantification as all parameters (except N_i) cancel out eventually. A direct relationship $S_i \propto N_i$ can be obtained where any increase in surface concentration results in a linear increase of peak intensity, *ceteris paribus*.

3.4.2 Instrumentation

Low-energy ion scattering (LEIS) data were obtained with the Qtac100 IONTOF instrument (**Figure 3.5**). It is equipped with $^4\text{He}^+$, $^{20}\text{Ne}^+$, and $^{40}\text{Ar}^+$ primary-ion sources. Non-reactive monatomic Ar gas can also be used for sputtering. The instrument can be operated under 'static' conditions where only the primary-ion beam is used to obtain atomic information from the topmost atomic layer. It can also be operated under 'dynamic' conditions by using a dual-beam (primary and sputter) mode, providing highly sensitive atomic scattering information as a function of depth.

⁶Widely used calculation methods include Thomas-Fermi-Moliere and the Universal Potentials

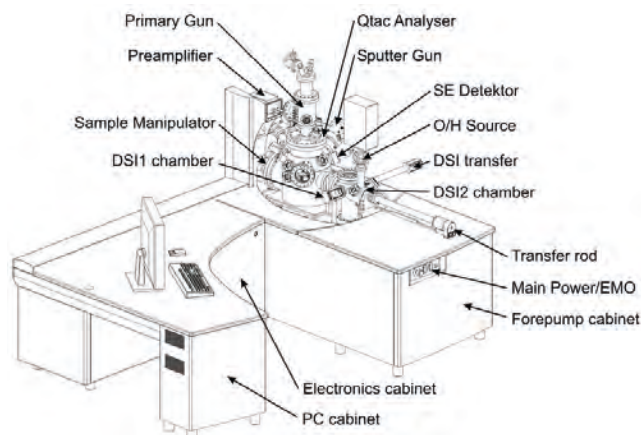


Figure 3.5 Illustration of LEIS instrument obtained from manual [204].

The instrument operates under UHV conditions (base pressure 10^{-10} mbar) and samples are fed into the instrument and analysis chamber via a dual load-lock system (10^{-4} mbar and 10^{-7} mbar). A time-of-flight (ToF) filter is also available for lower mass elements (e.g. C, N, F, O) which is useful, particularly for organic materials or for identifying surface contamination.

3.4.3 Measurement Parameters

For $\text{CH}_3\text{NH}_3\text{PbI}_3$ (and Cs-substituted compositions), elements that can be detected are C ($\sim 12 u$), N ($\sim 14 u$), I ($\sim 127 u$), Cs ($\sim 133 u$), and Pb ($\sim 207 u$). The choice of primary ion species are dependent on their respective binary scattering peak energies as shown in **Table 3.2**. Generally, one desires mass resolution in terms of sufficient scattering peak energy separation ΔE ; this results in the following ion choice for different target atom masses $^4\text{He}^+$: $< 40 u$, $^{20}\text{Ne}^+$: $< 100 u$, $^{40}\text{Ar}^+$: $< 200 u$ [200].

In this case, scattering energies for $\text{He} \rightarrow \text{Pb}$ and $\text{He} \rightarrow \text{I}$ are too close that make background subtraction difficult for peak fitting, as a result, $^{20}\text{Ne}^+$ and $^{40}\text{Ar}^+$ beams are preferable. For Cs-substituted compositions, ΔE for $\text{Ar} \rightarrow \text{Cs}$ and $\text{Ar} \rightarrow \text{I}$ is larger compared to other primary ion species.

When acquiring data, a limited pre-defined energy range for backscattered ion detection is provided so that unnecessary dose is applied. For static measurements, primary ions were rastered over an analysis square of $1000 \mu\text{m} \times 1000 \mu\text{m}$ with $64 \text{ pixels} \times 64 \text{ pixels}$.

Table 3.2 Theoretical scattering energies (eV) for C, N, Cs, I, and Pb *(For most abundant isotope. Scattering energies for lower abundance isotopes are different). These values are based on theoretical calculations and dependent on the instrument detector angle. Real values are expected to be lower due to inelastic losses.

Pri. Ion	Voltage (kV)	C*	N*	I	Pb*	Cs
$^4\text{He}^+$	3	846	1027	2674	2797	2688
$^{20}\text{Ne}^+$	5	N/A	N/A	2804	3520	2879
$^{40}\text{Ar}^+$	8	N/A	N/A	2436	3939	2580

Based on **Equation 5.1**, primary ion currents scale peak intensities linearly, thus obtaining accurate current values are crucial. Fluctuations during measurements are unavoidable but care was taken to ensure currents were stable to within a few nA over an extended period of time before measurements were performed. Additionally, currents were measured before and after each measurement for an average value.

3.4.4 Data Analysis

Analysis was performed on IONTOF SurfaceLab 6 software [199]. Static spectra were retrospectively obtained by re-running measurements with a dose limit of 1×10^{13} ions/cm². Peak integrals (area) were obtained by fitting each peak with a Gaussian peak with an error function for background contribution. It should be noted that these values have been corrected for beam currents, yielding values with counts/nC.

Primary data that are obtained are represented as a spectrum of intensity *vs.* scattering energy (eV). When attempting to illustrate changes in spectra as a function of cumulative ion fluence (secondary data), intensity plots are used; they are a series of spectra obtained from each consecutive scan, whose intensities are normalised and represented by a colour scale (**Figure 3.6**).

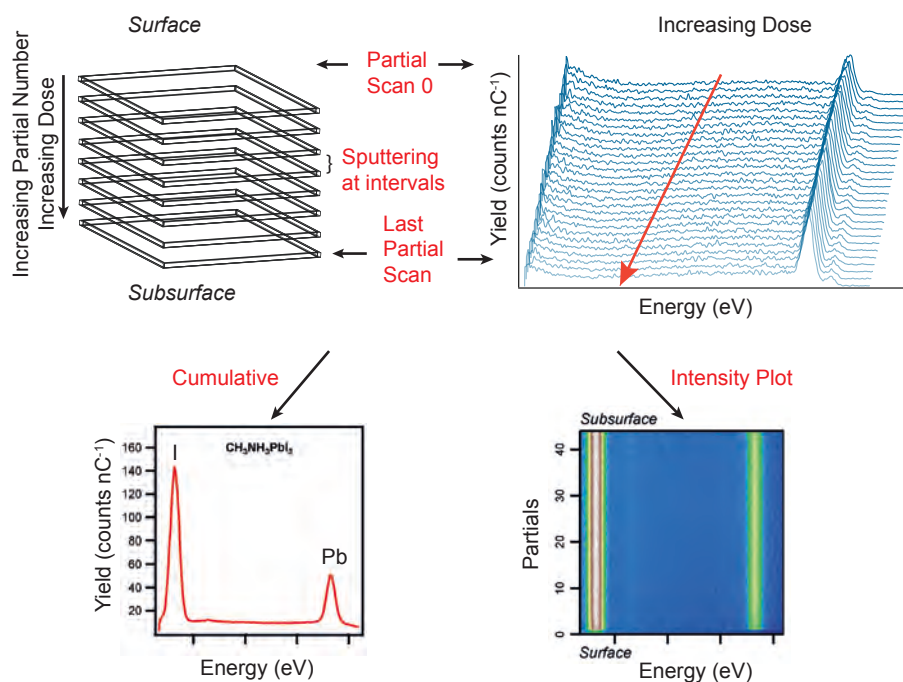


Figure 3.6 Data acquisition methodology. Each *partial* is a scan of a pre-determined ion fluence. Each successive partial obtains a discrete and new scattering spectrum with cumulatively increasing ion fluence applied to the area. These partials/scans are stitched together to obtain an image plot of spectral intensities (**Intensity plot**). The average of these scans produce a single scattering spectrum (**Cumulative**).

Peak Fitting Procedures

Peak fitting for scattering peaks from $^{40}\text{Ar}^+$ and $^{20}\text{Ne}^+$ were performed by two different procedures, depending on the composition (**Figure 3.7**). Procedure 1 involves fitting lead and iodine peaks with a Gaussian peak with a background intensity correction trailing the peak at lower energies. The rationale being inelastic scattering from these atoms result in said background intensity. This is important for fitting iodine scattering peaks as inelastic scattering from $\text{Ne} \rightarrow \text{Pb}$ resulting in background intensity at energy values lower than 3520 eV can influence intensities of iodine scattering peaks. Procedure 2 was used when a shoulder feature off the iodine scattering peak is evident from the scattering of cesium atoms. An error function to account for background signal from lead scattering was added and an exponential decay was added to achieve a more meaningful fit with better background correction. Pure Gaussian peaks were used to fit scattering peaks of iodine, lead, and cesium. Fitting this spectrum with procedure 1 leads to over calculation of iodine peak integrals and difficulty in obtaining a good fit for cesium scattering peak. Where consecutive LEIS spectra were obtained (intensity plot, **Figure 3.6**) as a function of dose, each spectrum was fitted with the same peak fitting procedure and parameter constraints.

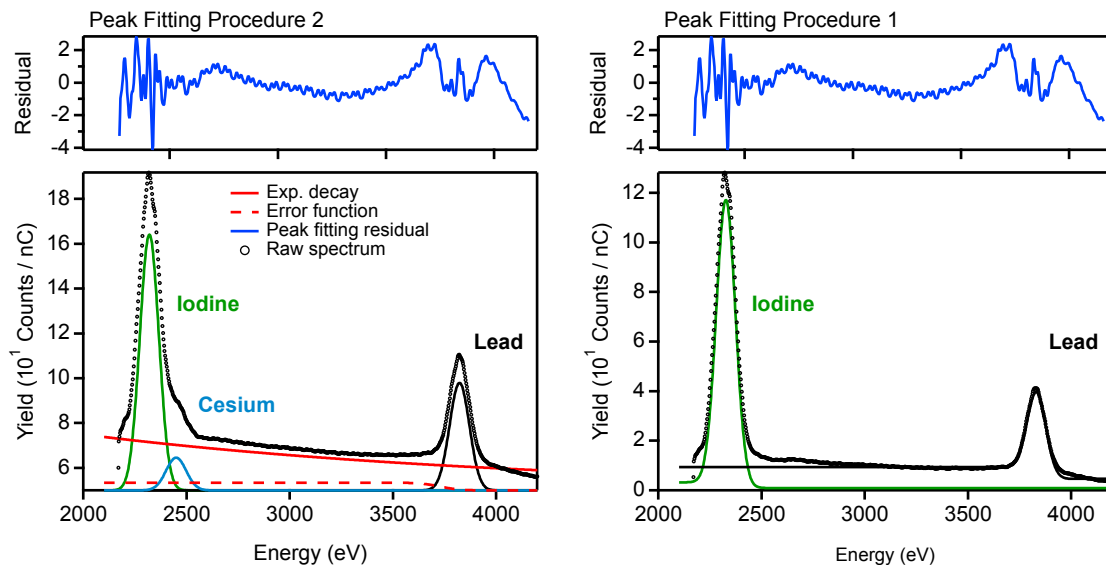


Figure 3.7 Peak fitting procedures for MAPbI₃. Peak fitting procedure 2: used where a shoulder feature, attributed to cesium, on the left of the scattering peak of iodine can be observed; pure Gaussian peaks, an exponential decaying intensity and an additional error function are used to achieve a better fit. Peak fitting procedure 1: used for MAPbI₃ or where a shoulder feature cannot be observed; pure Gaussian peaks with background intensity correction are used for fitting spectra.

3.5 X-ray Photoelectron Spectroscopy

3.5.1 Theory

Performed first by Robinson and developed into electron spectroscopy for chemical analysis (ESCA) by Siegbahn *et al.* [205, 206], the basics of X-ray photoelectron spectroscopy (XPS) lie in the exploitation of the photoelectric effect—whose mathematical description was developed by Einstein—in which the wave-particle duality of light was exemplified [207]. In the photoelectric effect, light is shown to be discretised packets of light (“photons”) each with an energy E_{photon} :

$$E_{\text{photon}} = hf \quad (3.8)$$

where h is Planck’s constant ($6.63 \times 10^{-34} \text{ J s}^{-1}$) and f is its frequency which is related to the speed of light v , and its wavelength λ by $v = f\lambda$. Thus, we have:

$$E_{\text{photon}} = \frac{hv}{\lambda} \quad (3.9)$$

Given a photon has sufficient energy, exciting an electron would result in its emission, overcoming the sample's workfunction (ϕ_{sample}). The photoemitted electron ("photoelectron") will have a kinetic energy whose value is a consequence of the incident photon energy and the sum of its original binding energy (E_{BE}) and workfunction. Thus we have,

$$E_{KE} = h\nu - E_{BE} - \phi_{sample} \quad (3.10)$$

where E_{KE} is the kinetic energy of the photoelectron. However, in the case of XPS, there is no real way of knowing E_{KE} with respect to the vacuum level of the sample, but measured with respect to the work function of the spectrometer (ϕ_{spec}) instead. Thus, given that the Fermi level (E_F) of both sample and spectrometer are equalised and assuming that ϕ_{spec} is higher than that of ϕ_{sample} , the binding energy of the electron in its rest-state within the sample can be obtained by [86]:

$$E_{KE} = h\nu - E_{BE} - \phi_{sample} - (\phi_{spec} - \phi_{sample}) \quad (3.11a)$$

$$E_{BE} = h\nu - E_{KE} - \phi_{spec} \quad (3.11b)$$

E_{BE} therefore gives information about the element and orbital from which the photoelectron was generated. A typical survey XPS spectrum, giving the whole range of binding energies, is shown in **Figure 3.8**.

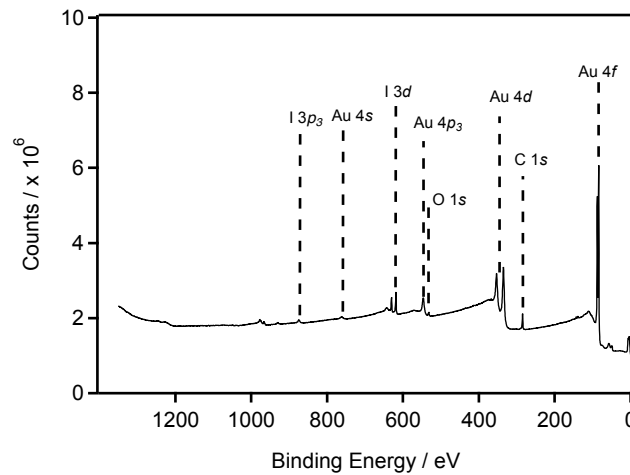


Figure 3.8 A typical survey spectra with photoemission peaks corresponding to the core-levels of the detected elements within the information depth.

The scenario described above is one that can be described as an elastic process where the photoelectron does not interact with its surroundings once escaping the sample and one of several other processes that

occur. The photoelectron can undergo inelastic processes that results in energy loss and contributes to background signal. Generally, because of the inelastic mean free path (IMFP) of photoelectrons which is sample dependent, the information depth (*i.e.* the depth from which elastic processes dominate) is up to 10 nm from the surface of the material; beyond which, detected photoelectrons contribute merely to the background intensity. Contribution to background intensity also comes from photoemission with *Bremsstrahlung* radiation. Thus, in a spectrum, characteristic peaks originate from "elastic" processes without energy loss. In reality the width of these peaks are broadened due to instrumental factors and slight chemical shifts. Additionally, other features such as Auger photoemission peaks, plasmon losses, and satellite peaks are present in an XPS spectrum. These can provide interesting characteristics (structurally and electronically) of the material but are not discussed in any detail in this thesis.

Photoelectrons generated from all orbitals are detected but only those that are deeper (in energy) than the valence band are analysed in greater detail to identify chemical species and oxidation states. One can deduce that should the chemical environment/bonding change, E_{BE} shifts accordingly and it is this shift that confers XPS its ability to determine chemical speciation. With relevance to the this thesis, the main elements of interest and their electronic structure are as follows: Pb: [Xe]5d¹⁰6s²6p², I: [Kr]4d¹⁰5s²5p⁵, C: [He]2s²2p², and N: [He]2s²2p³.

In the case of XPS, quantification is more straightforward than ToF-SIMS or LEIS. Peak intensities (I) are used in quantification and they are linearly dependent on the concentration and is described by the following simplified equations:

$$I_x = J \cdot n_x \cdot d\sigma \cdot T \cdot \lambda_{IMFP} \quad (3.12a)$$

$$I_x = S_x \cdot n_x \quad (3.12b)$$

J = X-ray flux (cm⁻²)

n_x = Concentration of element x in the sampled volume

$d\sigma$ = Photoemission cross-section, specific for element x

T = Constant embodying all instrumental factors

λ_{IMFP} = Inelastic mean free path for photoelectrons within measured sample

S_x = Sensitivity factor encompassing all factors less n_x

Accurate quantification using these absolute values can prove to be easily erroneous and many factors need to be considered. A simpler method of quantification would be relative concentration of the element of interest against all measured elements *i.e.*

$$n_x = \frac{I_x/S_x}{(I_y/S_y) + (I_z/S_z) + \dots} \times 100\% \quad (3.13)$$

A limiting factor with quantification in XPS (or any surface sensitive technique in general) is the effect of surface contamination. One can conclude that with an overlayer of surface contamination, photoemission peak intensities would be attenuated which would give a lower than expected intensity and lead to erroneous quantification; this necessitates appropriate sample handling. Generally, one can expect a detection limit of 0.1 *at. %*.

3.5.2 Instrumentation

Instrument used is the Thermoscientific K-Alpha High-Throughput XPS. It is equipped with a load-lock chamber (10^{-7} mbar) and a main chamber where the sample is analysed at UHV conditions (10^{-10} mbar) which are necessary to allow for faster sample transfer from atmospheric conditions and to obtain good signal-to-noise ratio spectra.

3.5.3 Measurement Parameters

The prepared and deposited MAPbI₃ films on ITO substrates were transferred, with exposure to air/atmosphere, to a sample stage and subsequently to the XPS chamber. Ion-beam flooding was used to limit photoemission charging effects.

Spectra were measured with an Al K α source gun at 1486.68 eV photon energy. Survey spectra were measured with a 400 μm spot size, a 200 eV pass energy at an energy step size of 0.5 eV. Survey spectrum acquisition used to ascertain the chemical species present before more specific core-level spectra were measured. Core-level spectra measurements were done with a 400 μm spot size with a pass energy of 20 eV and a step size of 0.1 eV. The region of interest was positioned roughly in the middle of each film, where no visual defects were seen.

3.5.4 Data Analysis

Peak-fitting procedures for individual core-level spectra were carried out using the *Smart* background type which is a variation of the *Shirley* routine. This specific peak-fitting routine found in the *Avantage* data processing software [208] prevents over-calculation of background signal which would otherwise

result in a higher intensity over the measured spectrum. A Voigt (Lorentzian-Gaussian mix) function was used for all peak fitting and was constrained between 10 to 40% (*i.e.* a peak shape that is a convolution of both Lorentzian and Gaussian peak shapes where 100% would be a pure Lorentzian peak shape and 0% would be a pure Gaussian peak shape). For simplicity, only peak-fits for lower energy doublet peaks are shown for core-levels exhibiting spin-orbit doublets (*i.e.* p , d , and f). However, to fit spin-orbit doublets, lower energy doublet peaks (e.g. $\text{I } 3d_{5/2}$ and $\text{Pb } 4f_{7/2}$) are first fitted, then peak-splitting energy values, which are already known in literature, are applied as constraints to obtain spin-orbit coupled fitted core-level spectra.

Where relative atomic concentrations are given, sensitivity factors used were obtained from the instrument manufacturer's library whose values were obtained from reference elemental samples.

The sampling depth as a function of electron kinetic energy for the material MAPbI_3 is plotted in **Figure 3.9**. A maximum of 10 nm sampling depth was calculated, based on the Tanuma, Penn, and Powell (TPP-2M) relation that calculates the mean free path of an electron before undergoing an inelastic scattering event, as a function of kinetic energy:

$$\lambda_{\text{IMFP}} = \frac{E_k}{U^2 [\beta \ln(0.191 \cdot \rho^{-0.5} \cdot E_k) - (C/E_k) + (D/E_k^2)]} \quad (3.14a)$$

where

$$\text{Sampling Depth} = 3 \times \lambda_{\text{IMFP}} \cdot \cos \theta \quad (3.14b)$$

$$U = 28.8 \left(\frac{N_v \cdot \rho}{M} \right)^{-0.5} \quad (3.14c)$$

$$\beta = -0.0216 + 0.944(U^2 + E_g^2)^{-0.5} \quad (3.14d)$$

$$C = 1.97 - 0.91 \left(\frac{U^2}{829.4} \right) \quad (3.14e)$$

$$D = 53.4 - 20.8 \left(\frac{U^2}{829.4} \right) \quad (3.14f)$$

and

N_v = Number of valence electrons: 48

E_k = Kinetic energy (eV)

ρ = Density (g cm^{-3}): 4.15 g cm^{-3}

M = Atomic weight (g mol^{-1}): $619.98 \text{ g mol}^{-1}$

E_g = Bandgap (eV): 1.5

θ = Take-off angle: 90°

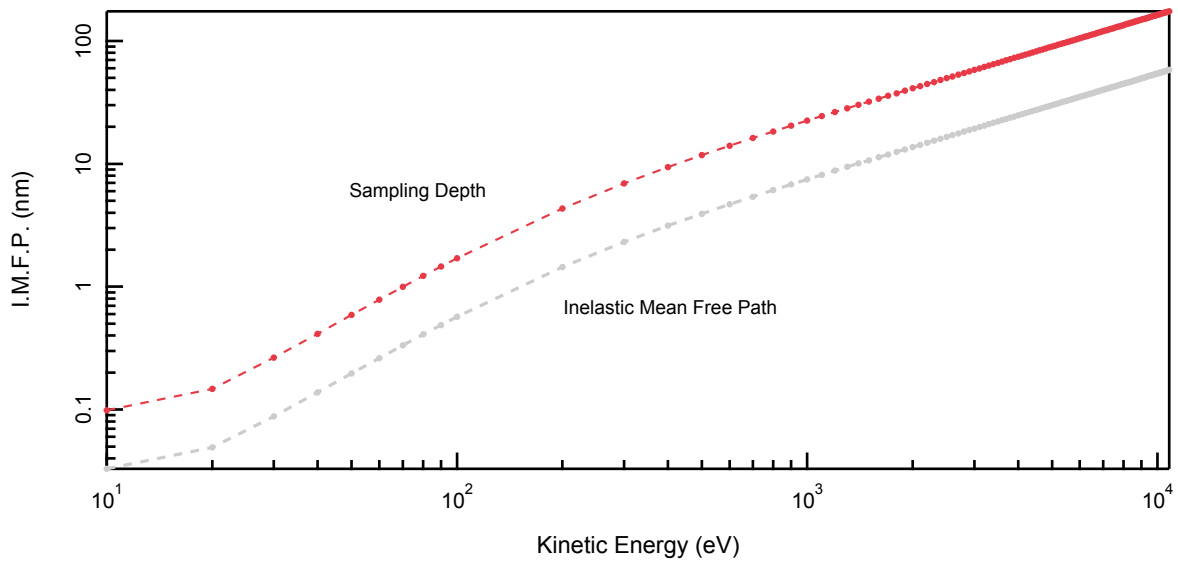


Figure 3.9 The inelastic mean free path and sampling depth are calculated using the Tanuma, Penn, and Powell (TPP-2M) relation plotted against the kinetic energy of the electron. Sampling depth = $3 \times \text{IMFP}$. Both axes in logarithmic scale.

3.6 X-ray Diffraction

3.6.1 Theory

X-ray diffraction (XRD) is a structural technique used to characterise physical and by extension, some level of chemical properties (e.g. secondary phases). It relies on the fact that in a crystalline sample, there is some level of periodicity. In short range order, this is the lattice unit cell which has some fixed lattice spacing d_{hkl} , where (hkl) is miller indices notation used to describe crystallographic planes of atoms. In long range order, this can be thought of as an increased orientation of crystallographic planes along some direction. When an X-ray is incident on an atom, its electrons will interfere and scatter it. Thus, when short-range order is present *i.e.* a periodic structure of atoms, the interference and scattering of X-rays by these regularly spaced atoms within the lattice will result in constructive and destructive

interferences that produce a diffraction pattern.

This can be described by the well known Bragg diffraction equation,

$$n\lambda = 2d_{hkl} \sin \theta \quad (3.15)$$

n = Integer value that corresponds to the order of diffraction

λ = Wavelength of X-rays

d_{hkl} = Lattice spacing

θ = Diffraction angle

which states that for constructive interference to occur for parallel planes of regularly spaced atoms with lattice spacings of d_{hkl} , the path difference ($2d_{hkl} \sin \theta$) of the incident light and reflected light must be integral multiples of its wavelength λ .

In a polycrystalline sample, one can expect that all the crystallites are randomly orientated. Therefore, by varying the angle between the incident X-ray (of known wavelength), sample, and detector the intensity of the detected X-rays will produce all possible peaks at certain angles corresponding to constructive interference that satisfy Bragg's equation. The result is a diffraction pattern containing all the crystallographic planes of a sample which allows certain conclusions about the sample to be made (e.g. crystal structure, crystallite domain orientation, crystallinity, strain within the crystallites, secondary phases).

3.6.2 Measurement Parameters

XRD characterisation and analysis were carried out by Ms. Zhongyao, Jiang⁷.

MAPbI₃ samples (and devices) that underwent XRD characterisation were all spin-cast on a 10 mm × 10 mm glass (or ITO patterned glass) substrate. Samples were mounted onto the sample holder and secured with an adhesive. Additionally, the level of each sample was kept consistent throughout to prevent sample tilting and its effect on the diffraction data.

Data was acquired using a Cu K α X-ray source at 40 kV and tube current of 40 mA in a PANalytical X'Pert Pro diffractometer. A step size of 0.0167 was used to acquire diffraction data for a 2θ range of 6 to 80(°). Measurements were performed in the 'spinning' mode to obtain diffraction data from randomly oriented crystallographic planes.

⁷Imperial College London, Materials Department.

3.7 Scanning Electron Microscopy

Scanning electron microscopy (SEM) is highly useful characterisation tool that produces highly spatially resolved (order of a few nm) images of samples. Its underlying principle is the detection of emitted secondary electrons (SE) by bombarding a sample with a highly focussed e^- beam. As opposed to instruments that use light as a probe, an electron beam can be focussed to a much smaller spot size giving it better spatial resolution than other imaging techniques.

Bombarding a material with a highly energetic electron beam produces a range of electrons and X-rays that can be used to obtain more information about the sample (see **Figure 3.10**).

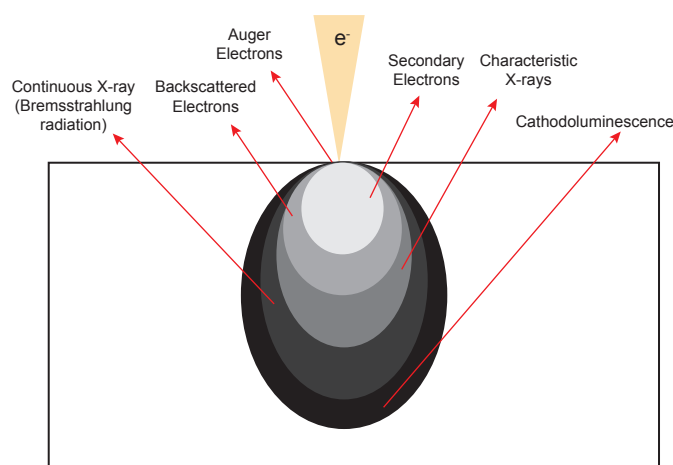


Figure 3.10 Illustration of effects of bombarding a sample with a highly focussed electron beam with their corresponding (non-scaled) information depth.

In an SEM instrument, this gives the user different options for analysis; elemental identification using characteristics X-rays (called energy dispersive X-ray (EDX) analysis)), topographical/morphological information from backscattered electrons (BSE) and SE. However, only topographical information obtained from SE are of interest in this thesis.

Generation of SEM images are predicated upon the emission of valence electrons from the surface (up to a few nm from the surface) of the sample and have lower energies than BSE. Secondary electrons generated from beyond that are either annihilated or undergo inelastic scattering which are not detected. BSE are usually of higher energies and therefore have different trajectories. This difference allows the placement of different detectors to obtain two different sources of information. Electron to image conversion comes from the conversion and amplification of electrons to light by use of a scintillator.

Images generated from SE are surface sensitive, though with a larger interaction volume on the order of a few nm. Increasing the accelerating voltage of the electron beam increases interaction volume

which reduces the surface sensitivity but it also reduces aberrations resulting in a more focussed beam. Considerations also have to be made for electron-beam induced damage which has been shown to be a concern for organometallic halide materials.

3.7.1 Instrumentation & Measurement Parameters

SEM characterisation was carried out by Mr. David L.M. Poussin⁸.

Instrument used was a LEO Gemini 1525 field emission gun (FEG) SEM. Accelerating voltage used was 5 kV.

Samples were imaged without a conductive layer coating, instead silver paste was applied such that a conductive pathway was made between the sample and the sample holder to avoid charging. Top-down and cross-section images were obtained via the secondary-electron (SE) imaging mode.

⁸Imperial College London, Materials Department

Chapter 4

Instrument Material Interactions

4.1 Motivation

Given that X-ray photoelectron spectroscopy (XPS), time-of-flight mass spectrometry (ToF-SIMS), and low energy ion scattering (LEIS) are the main characterisation techniques used in this thesis, this chapter aims to better understand the interactions between the mentioned instrumentation and organometallic halide materials, specifically $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI₃).

There have been few extensive studies in regards to the effects of X-ray irradiation on these materials. In particular, there have been only a handful thus far, describing time-resolved effects [84, 106]. However, the work described have only reported cumulative spectra at specific time-intervals and not necessarily the effects of irradiation in the time-scales of each core-level measurement.

Additionally, the use of energetic beams for depth profiling such multilayer devices or for surface mass spectrometry on organometallic halides is not well established. There exists a number of published work exploring the interactions of such beams on multilayer devices employing organometallic halides [193–195]. It was shown that several matrix effects in depth profiles exist, especially that of I^- and organic mass fragments. While it is a substantial leap in understanding how such beams interact with these materials, such matrix effects may change in multilayer samples employing different interlayers.

Finally, the use of low energy ion beams (less than 10 kV) on inorganic surfaces has had an extensive historical basis but there has been no published work investigating the interaction of low-energy ion beams on inorganic-organic hybrid materials.

4.1.1 Scope of Work

This chapter aims to address the effect(s) of X-ray irradiation and ultra-high vacuum (UHV) on acquired core-level spectra in XPS, in the timescales of normal data acquisition. This is achieved by obtaining time-resolved core-level spectra of MAPbI₃ (Pb 4*f*, I 3*d*, C 1*s*, N 1*s*). By observing the evolution of spectra with time, associated chemical changes, whether from the effects of UHV or X-ray irradiation, are analysed.

Next, chemical and morphological effects of ⁴He⁺, ²⁰Ne⁺, and ⁴⁰Ar⁺ bombardment on MAPbI₃ surfaces are examined by performing XPS measurements on ion bombarded areas.

Finally, mass fragment analysis of MAPbI₃ is given followed by analysis of depth profile quality, using Ar₁₀₀₀, Cs⁺, and O₂⁺ sputter beams.

4.2 X-ray Photoelectron Spectroscopy

Photoelectron spectroscopy is a crucial and relatively accessible technique for surface characterisation, especially when quantifying relative atomic concentration and determining chemical states of novel organometallic halide compositions e.g. cation-substituted, doped, or compositionally engineered analogues are needed. Given the importance, it is necessary to understand and if possible, quantify the interactions of X-rays and the sample. An *in situ* photoemission study of MAPbI₃ under bias showed that [106] under dark and UHV conditions the surface composition did not change significantly. The authors obtained cumulative core-level spectra at regular time intervals to track changes in atomic concentration. However, the evolution of spectra with increasing X-ray irradiation was not captured or considered.

In this section, the combined effects of UHV exposure and X-ray irradiation from an XPS instrument are investigated. A single sample of MAPbI₃ was used and different areas were irradiated, each with increasing irradiation time. An iterative measurement procedure was carried out for core-level measurements. This was used to record any change in core-levels with increasing irradiation time and/or UHV exposure time.

The number of iteration loops for each core-level are determined by the pre-set irradiation times. A total of five different irradiation times (t_{rad}) were used: 0.5 h, 1.0 h, 1.5 h, 2.0 h and 3.0 h. Owing to the energy range of the spectrometer for each core-level measurement, the acquisition time (t_{acq}) for each of the core-levels are as follows: C 1*s*: 57.3 s (6 scans); N 1*s*: 54.3 s (6 scans); I 3*d*: 45.2 s (3 scans); Pb 4*f*:

30.2 s (3 scans), giving a cumulative t_{rad} of 187.0 s for each iteration loop. The procedure is illustrated in **Figure 4.1**.

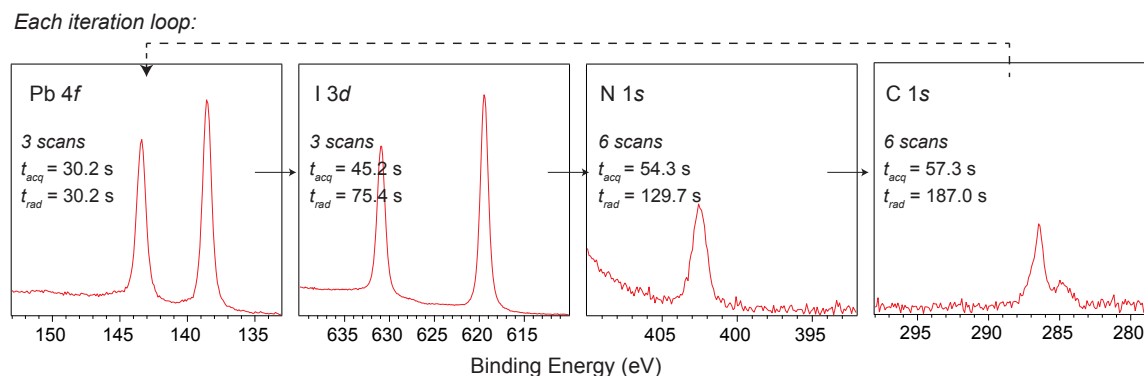


Figure 4.1 XPS: Measurement protocol and timescales of each iteration loop and core-level acquisition where the total acquisition time t_{acq} and cumulative X-ray irradiation exposure time t_{rad} for a single iteration loop are 187.0 s.

The lowest possible t_{acq} (equivalent to a single scan) is governed by the pass energy, energy step size, and energy range which are fixed for all core-level acquisition. Determination of t_{acq} used in this experiment arises from minimising the number of scans for each core-level. The strategy for doing so lies with attempting to minimise X-ray irradiation for each core-level to a point just before the spectra would be visibly dominated by noise and therefore, impossible to provide any useful information. This then allows each core-level spectrum to capture any temporal effects from X-ray irradiation and UHV exposure with sufficient time-resolution.

However, as data is acquired energy stepwise from lower to higher binding energies, core-level spectra at higher binding energies are inherently exposed to larger X-ray doses and is a limiting factor in spectral analysis. Additionally, because core-level acquisition is performed sequentially, minimising t_{acq} is doubly crucial in reducing any ‘hidden’ spectral evolution (e.g. any changes in Pb 4f would be masked during acquisition of C 1s). Therefore, one can also equate *cumulative* t_{acq} to t_{rad} and will be crucial in the following spectral analysis. Finally, the order of core-level acquisition in the iteration loop was determined by order of importance where chemical changes to Pb and I are weighted over C and N.

In this study, five different areas (A, B, C, D, and E) were irradiated each with increasing exposure time to X-ray irradiation where t_{rad} for each of these areas are: 0.5 h, 1.0 h, 1.5 h, 2.0 h and 3.0 h (**Figure 4.2**). Due to the nature of the experiment, one can deduce that the vacuum exposure times (t_{vac}) for subsequent areas are therefore cumulative: 0.5 h, 1.5 h, 3.0 h, 5.0 h and 8.0 h, respectively. Thus, each iteration loop is a representation of both the cumulative effects of vacuum exposure and X-ray irradiation.

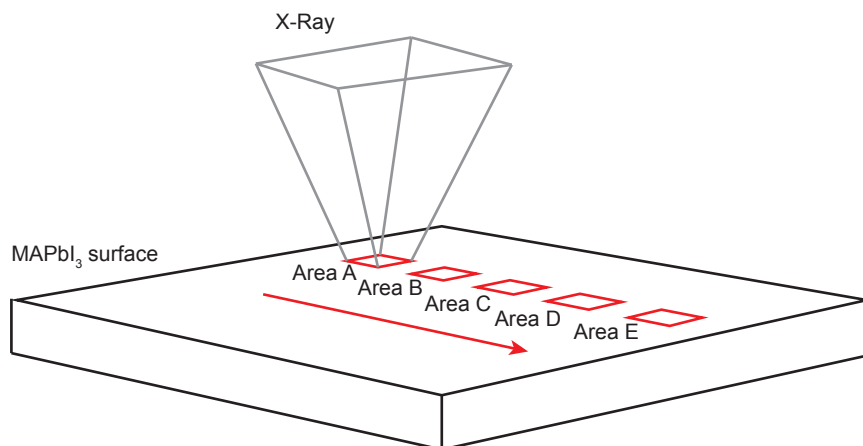


Figure 4.2 Illustration of XPS experiment on a single MAPbI₃ sample on five different areas: Area A ($t_{rad} = 0.5$ h, $t_{vac} = 0.5$ h), Area B ($t_{rad} = 1.0$ h, $t_{vac} = 1.5$ h), Area C ($t_{rad} = 1.5$ h, $t_{vac} = 3.0$ h), Area D ($t_{rad} = 2.0$ h, $t_{vac} = 5.0$ h), and Area E ($t_{rad} = 3.0$ h, $t_{vac} = 8.0$ h)

4.2.1 Irradiation Effects

Core-level spectra intensity plots for all areas are shown in **Figure 4.3** and their individual spectra are shown in **Figure B.1** to **Figure B.4** in the appendix. **Figure 4.4** shows spectra and intensity plots for Area E ($t_{rad} = 3.0$ h).

Based on intensity plots of core-level spectra from the different areas, there are no significant changes in peak positions or presence of secondary peak features for Areas A to D ($t_{rad} = 0.5$ h to 2.0 h). However, in Area E after $t_{rad} = 2.4$ h, secondary features for both I 3d and Pb 4f at lower binding energies from the main peak can be observed. Additionally, there is an apparent decrease in peak intensity for C 1s and N 1s with increasing t_{rad} .

These features are more closely seen in **Figure 4.4** which shows spectra from Area E ($t_{rad} = 3.0$ h). Evidently, the peak shapes of Pb 4f and I 3d change after iteration loop 43 ($t_{rad} = \sim 2.4$ h) and attenuation of C 1s and N 1s are observed. In order to quantify such changes, each core-level was fitted for all iteration loops and their respective normalised peak areas and elemental ratios based on calculated atomic concentrations are plotted (**Figure 4.5**).

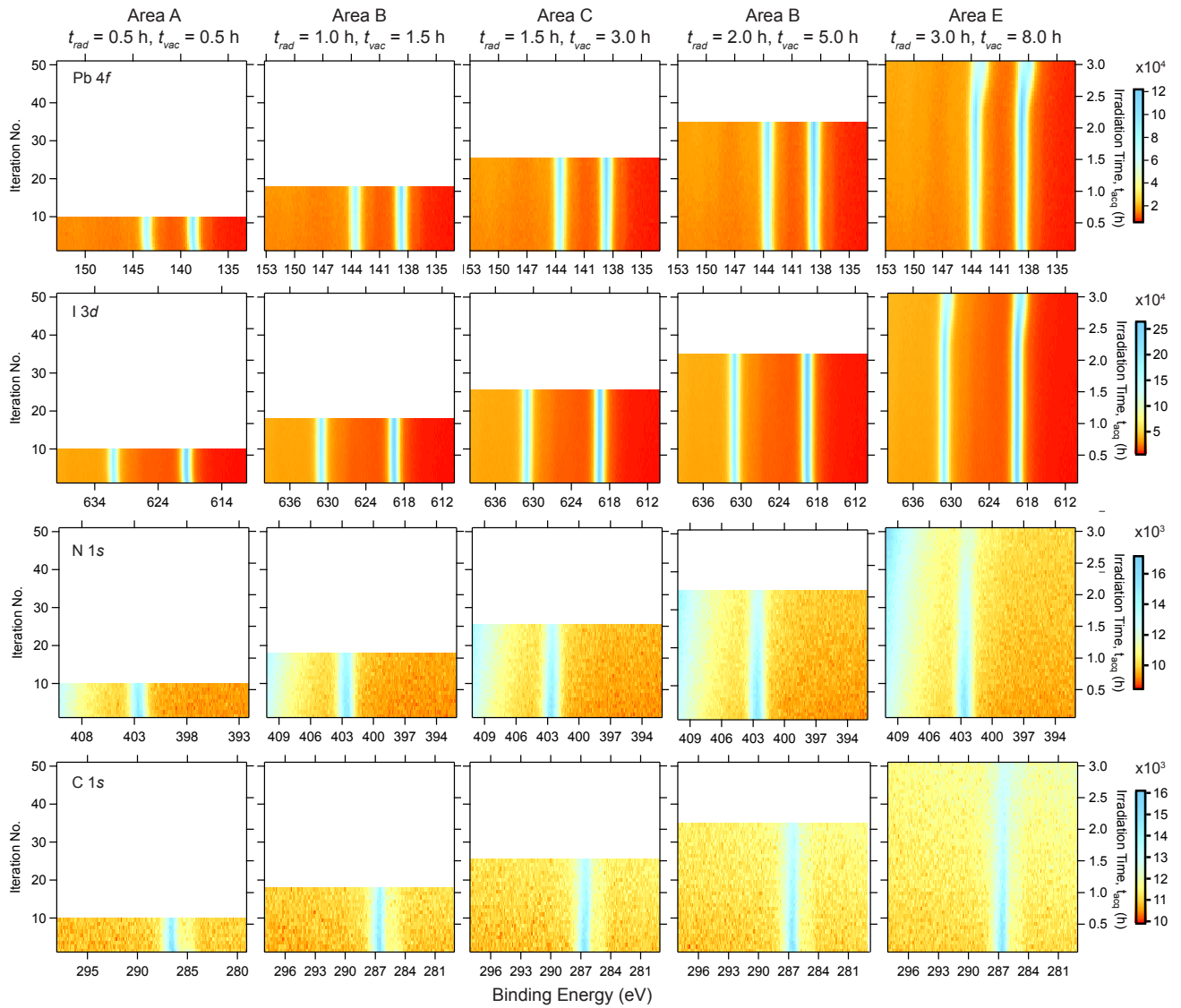


Figure 4.3 XPS: Intensity plots of all raw core-level spectra for all irradiation areas (A, B, C, D, E). Colour-scale range of each core-level group is set constant to a constant value. Attenuation of C 1s and N 1s peaks can be observed while secondary features at lower binding energy to the main core-level peak for I 3d and Pb 4f can be observed.

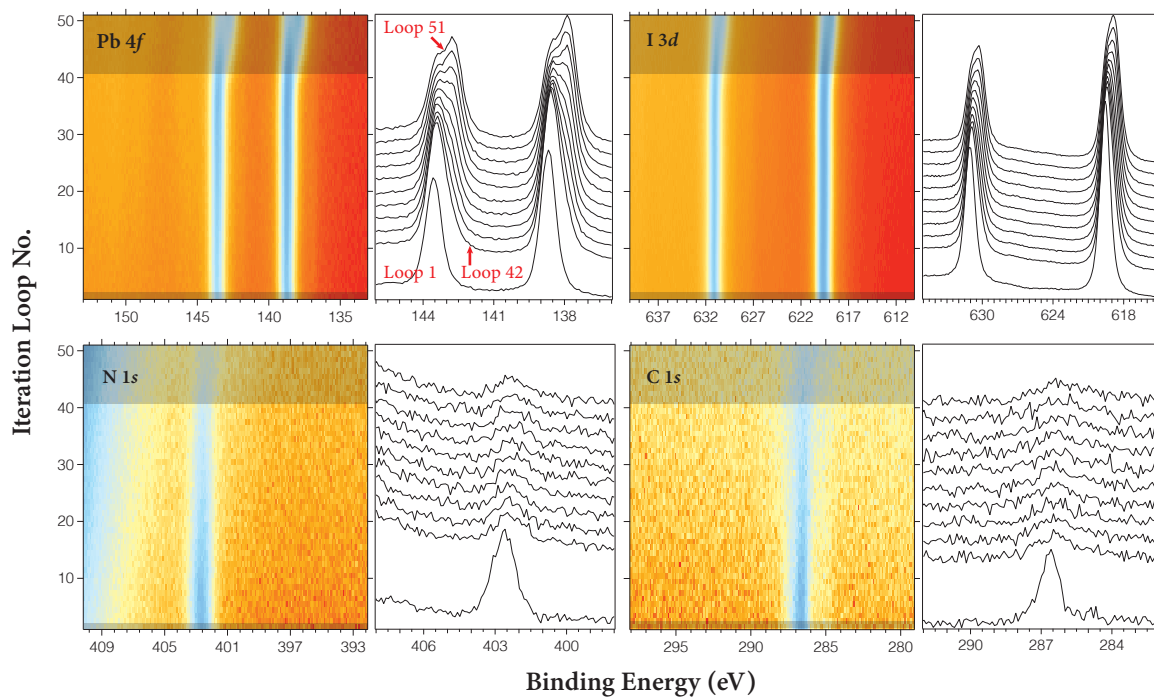


Figure 4.4 XPS: Core-level spectra of Area E ($t_{rad} = 3.0$ h). Each core-level spectrum makes up an iteration loop with a total t_{acq} of 187.0 s. Image plots were obtained by using spectral intensity as colour intensity. On the right of each image, spectra from iteration loop no. 1 and no. 42 to 51 are shown.

It should be noted that peak fitting for Pb 4f and I 3d is based on fitting two peaks (even at earlier t_{rad} where no secondary features are seen): peak 1 (Pb 4f_{7/2}: 138.7 eV and I 3d_{5/2}: 619.6 eV, in agreement in previously reported values in **Table 2.2**) and peak 2 (Pb 4f_{7/2}: 137.8 eV and I 3d_{5/2}: 618.3 eV). The peak fitting procedure is as stipulated in **Section 3.5.4** with the addition of constraining the full-width half maximum (FWHM) and L/G mix (%) of both peaks to the same value, though these values were not kept the same *between* iteration loops. Additionally, it should be noted that the peak attributed to adventitious carbon at ~284.8 eV is not included in analysis of C 1s core-level.

Relative atomic concentrations (n) are weighted based on the sum of normalised peak areas of selected elements:

$$n_x = \frac{I_x/S_x}{(I_y/S_y) + (I_z/S_z) + \dots} \times 100\% \quad (4.1)$$

Where I_x is the peak intensity of element x and S_x is the sensitivity factor of element x . The normalised peak area (A_x) is therefore simply an unweighted n_x ,

$$A_x = \frac{I_x}{S_x} \quad (4.2)$$

and is used to quantify the reduction in peak intensities. Considering that no peak shifts are observed, one can draw conclusions on physical processes behind the observed trends in normalised peak areas. While the data does not allow one to draw conclusions about the exact *amount* of species, relative atomic concentrations provide evidence for deviation of sample (surface) stoichiometry and any apparent relationship between the species.

Based on **Figure 4.5(a)**, there is a linear reduction in normalised peak areas for C 1s and N 1s throughout the measurement time. This observation is indicative of the removal of organic species with t_{rad} from at least 10 nm from the surface (based on the information depth of XPS) with a constant rate. The reduction in C 1s and N 1s intensities is accompanied by a linear increase in normalised peak areas of peak 1 for Pb 4f_{7/2} and I 3d_{5/2} which could simply have arisen from lesser attenuation of Pb and I signals.

After $t_{rad} = \sim 2.2$ h, a decrease in normalised peak areas for peak 1 for Pb 4f_{7/2} and I 3d_{5/2} is observed which is accompanied by an increase in normalised peak areas for peak 2. Thus, the decrease in peak 1 intensities is brought about by a change in the oxidation states or chemical environment of Pb and I, resulting in additional photoemission peaks (peak 2). Such a feature suggests that chemical changes occurred after $t_{rad} = \sim 2.2$ h where oxidation and reduction of I⁻ and Pb²⁺, respectively, would result in

observed secondary features.

Further analysis of the I/Pb ratio (**Figure 4.5(b)**) shows a decreasing trend and reflects a deviation of I/Pb stoichiometry from $t_{rad} = 0$ h which is in agreement with [84]. While the initial ratio is much higher than expected (at 3.0), it is not unexpected as has been previously reported (**Table 2.2**). At $t_{rad} = 2.5$ h coinciding with the reduction of normalised peak areas for peak 1 in both Pb $4f_{7/2}$ and I $3d_{3/2}$ and increase in normalised peak areas for peak 2, a sharp increase in I/Pb ratio to is observed. I/Pb ratio increases to a maximum of 4.7 at $t_{rad} = \sim 2.7$ h and is followed by a sharp drop to 3.4 at $t_{rad} = 3.0$ h. However, following I/Pb ratio using both peaks (1 and 2), this feature is suppressed and a linear decrease in its value is observed instead.

Therefore, using peak 1 leads to erroneous stoichiometry calculations and artificially created features. This is likely due to the difficulty of fitting a convoluted peak shape with unknown number of contributions. It is likely that there are multiple peaks corresponding to various chemical states of I between $t_{rad} = 2.5$ h to 2.7 h. Thus, fitting the peak shape with only two peaks leads to underfitting and overestimation of stoichiometry calculations.

Additionally, increasing I/N and Pb/N ratios (**Figure 4.5(b)**) with increasing t_{rad} confirm the removal of N from the sample surface while C/N ratio is kept almost at a constant value suggesting that the removal of organic species occurs at a similar rate. At later irradiation times, this value increases which is likely due to the much higher noise in the spectra resulting in imprecise fitting.

However, even though total peak areas for I $3d$ and Pb $4f$ increase with t_{rad} (**Figure 4.5(a)**), it is not clear from these results if the variations in I/Pb stoichiometry are caused by redistribution of species on the surface or if I has been liberated from the sample surface (as has been previously suggested in other published work).

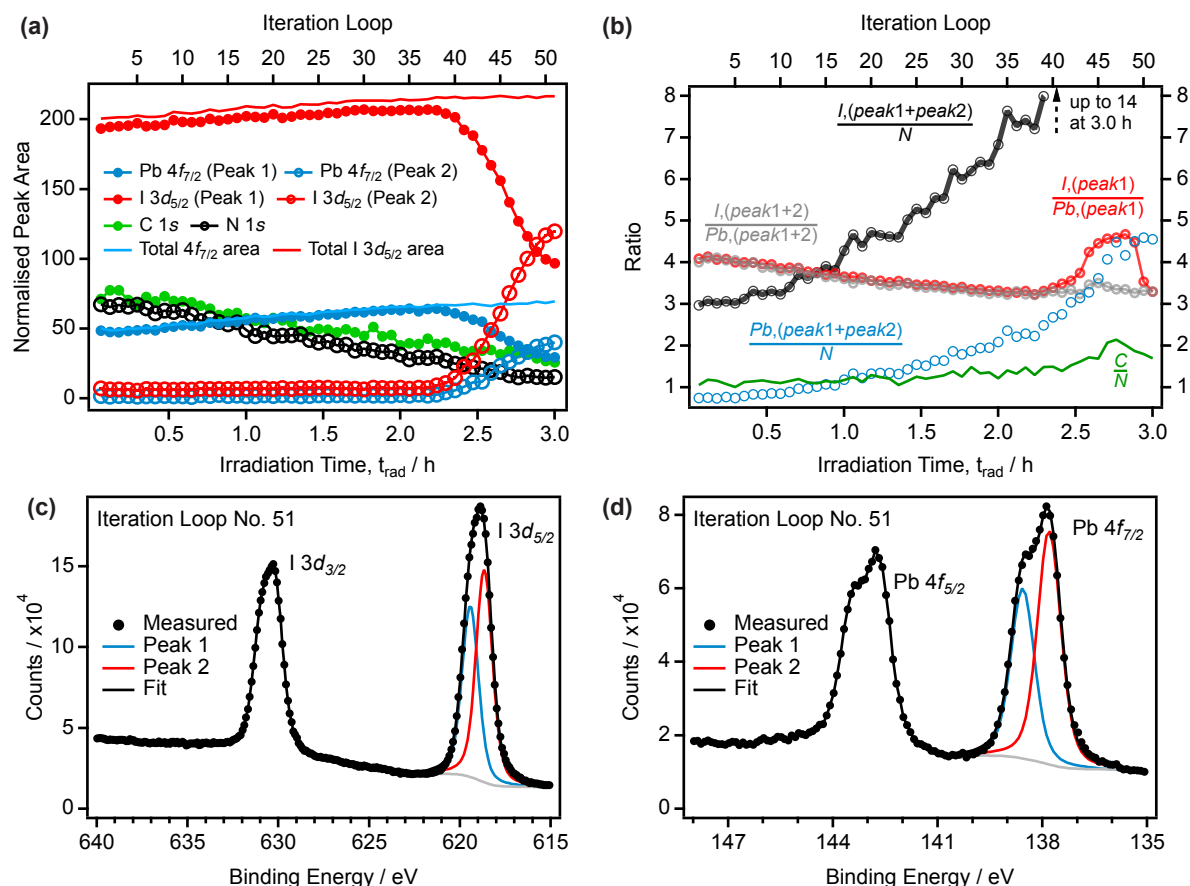


Figure 4.5 XPS: of Area E ($t_{rad} = 3.0$ h). **(a)** Normalised peak areas for all core-levels, showing a decrease for N 1s and C 1s while an increase for Pb $4f_{7/2}$ and I $3d_{5/2}$ and the appearance of a secondary feature at lower binding energies after $t_{rad} = 2.2$ h. **(b)** Elemental ratios based on relative atomic concentrations. **(c)** Fitted core-level from iteration loop 51 of I $3d_{5/2}$. **(d)** Fitted core-level from iteration loop 51 of Pb $4f_{7/2}$.

4.2.2 Ultra-High Vacuum Effects

The effects of instrument's pressure conditions are also considered. The pressure within the analysis chamber is approximately 6.0×10^{-7} mbar with a base pressure of less than 5.0×10^{-8} mbar. Such low pressures are necessary in increasing detection of photoelectrons without unwanted scattering.

Since subsequent analysis areas are subjected to cumulative UHV exposure, the effects of UHV on the spectra are shown by observing trends in the changes in normalised peak areas from the different analysis areas (**Figure 4.6**). Evidently, normalised peak area values and associated trends with respect to t_{rad} , for N 1s and C 1s, are reproduced in all areas. These data clearly indicate that within these timescales (8.0 h), UHV exposure has little effect on the removal of organic species which is in agreement with an earlier reported work [106]. Whereas, the formation of metallic Pb (Pb^0) at 137.0 eV [81, 83, 85] seems to be dependent on vacuum exposure and the surface defect density (see **Section 4.3.2**).

Finally, normalised peak area trends for Pb $4f_{7/2}$ and I $3d_{5/2}$ are similar in all areas except area E ($t_{vac} =$

8.0 h). This is due to the addition of peak 2, where even at lower iteration loop number is of non-zero value, which serves to reduce peak 1 intensity.

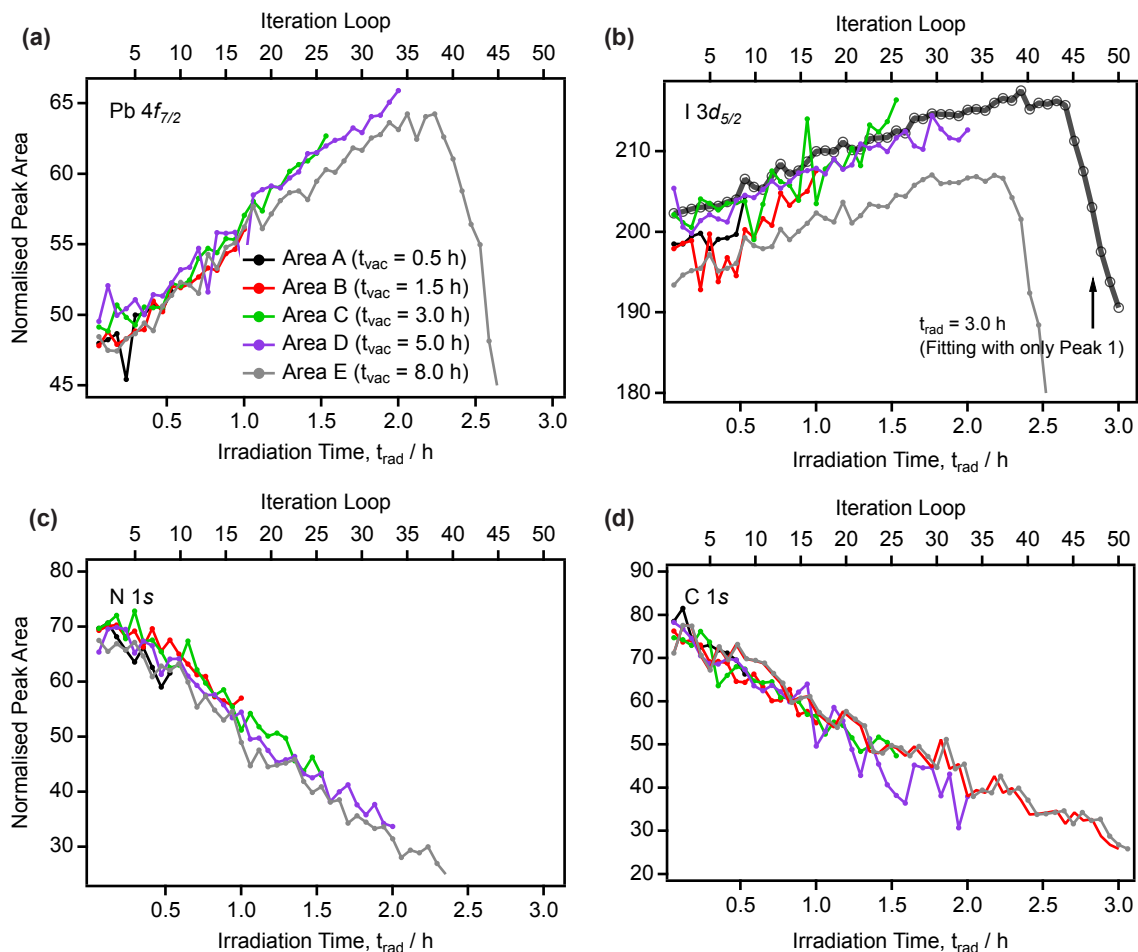


Figure 4.6 Effects of UHV exposure by observing normalised peak area values and their trends. Normalised peak areas for Pb $4f_{7/2}$ and I $3d_{5/2}$ are for peak 1. N 1s and C 1s show consistent behaviour throughout all t_{vac} while Pb $4f_{7/2}$ and I $3d_{5/2}$ show similar behaviour except reduced normalised peak area values for $t_{vac} = 8.0$ h, which is due to the addition of peak 2 in peak fitting procedures, and therefore reduction in peak 1 intensity.

4.2.3 Cumulative vs. Iterative

If their cumulative (and averaged) spectra are analysed instead (**Figure 4.7**), a systematic drop in peak intensities with increasing t_{rad} can be observed for both N 1s and C 1s. Peak shapes of N 1s are observed to be similar in all irradiation times whereas the main peak feature of C 1s at around 284.8 eV shows a decrease which is related to the removal of adventitious carbon from the sample surface.

From $t_{rad} = 0.5$ h to 2.0 h, peak shapes of Pb $4f$ and I $3d$ core-levels are similar with the exception of the presence of a secondary feature at 137.0 eV in Pb $4f$ that can be attributed to Pb⁰ [81, 83, 85], previously discussed in **Section 2.5**. However, this feature is not clearly defined in spectra obtained from iteration

loops in the previous section.

Further, at $t_{rad} = 3.0$ h both core-levels also show some degree of peak broadening that could be attributed to secondary features at lower binding energies. These features were also captured by the iteration loop procedure and showed the gradual evolution over time. Unfortunately, they have intrinsically high noise due to the low number of scans, making accurate peak-fitting difficult. Should identification of chemical species be required, cumulative spectra are preferred. Often, data reported for these materials are cumulative and little attention is paid to the amount of irradiation time. The data shown here could partly explain the deviation of atomic quantification from stoichiometry of these materials.

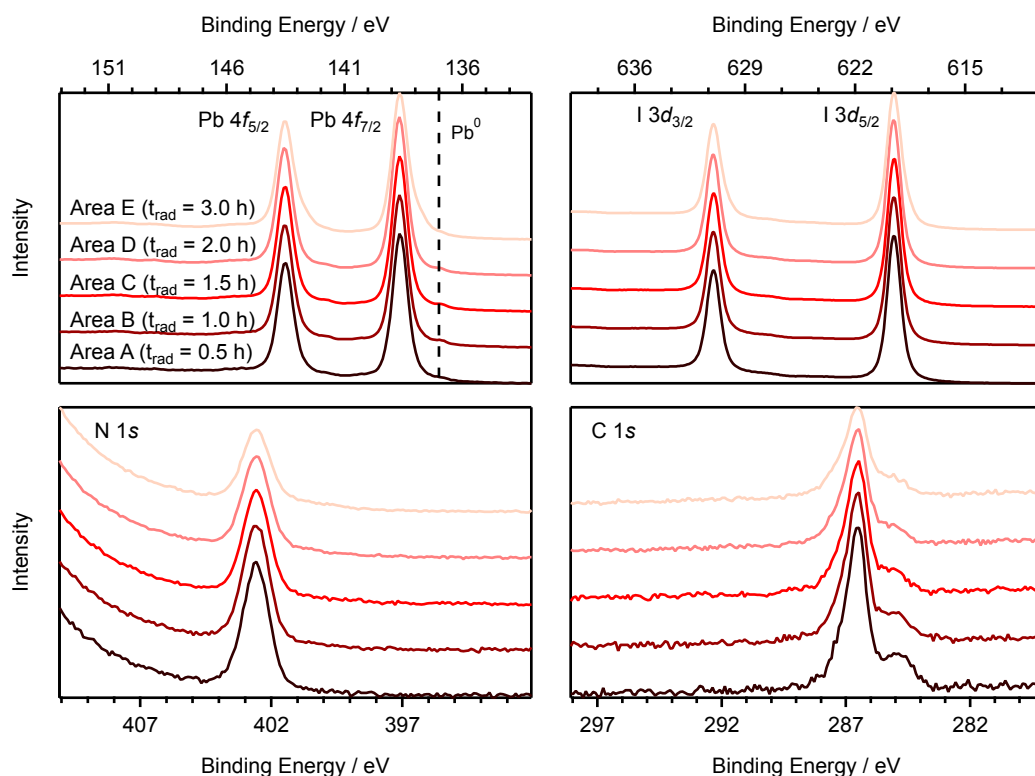


Figure 4.7 XPS: Cumulative core-level spectra of all five different areas. Each spectrum has been vertically offset. Attenuation of N 1s and C 1s peak intensities are evidently significant while secondary features at lower binding energies for Pb 4f_{7/2} and I 3d_{5/2} are not as prominent (and are visibly suppressed), highlighting the need for careful consideration of measurement times. Dashed line indicates theoretical peak binding energy for Pb⁰.

4.3 Low Energy Ion Scattering

The effects, both physical and chemical, of different gas sources for primary-ion beams used in the instrument are presented here. Investigating ion-material interactions and their possible effects on the sample's chemical and physical states provide a better understanding of the limitations of such mea-

surements. The static-limit has been defined as the dose density associated with removing at most 1% of the atomic layer with the caveat that the material chemistry is unchanged. However, the use of such techniques on hybrid materials such as organometallic halides is not as prolific as other more readily available ones. The interactions of these instruments with the material is not well understood and its effect(s) not thoroughly investigated. This section attempts to provide morphological and chemical analyses of any interactions.

4.3.1 Morphological Effects

On a single MAPbI₃ film, primary-ion beams, each at a total dose density of 1.0×10^{16} ions/cm² were bombarded on the surface. The selection of such a dose value was based on dose-dependent measurements in **Section 5.5** where doses of up to 1.6×10^{16} ions/cm² were used. SEM in the SE-imaging mode was then used to capture top-down images of these areas. It is apparent that rectangular features and elliptical features are present in all bombarded areas corresponding to the analysis areas of LEIS and XPS, respectively (**Figure 4.8**). The area within the elliptical areas show significant differences between each ion bombarded areas. The observed lighter features are likely due to Pb⁰ as discussed in **Section 4.3.2** where XPS spectra from the area bombarded by ⁴⁰Ar⁺ were acquired the last, thus being exposed to UHV conditions the longest.

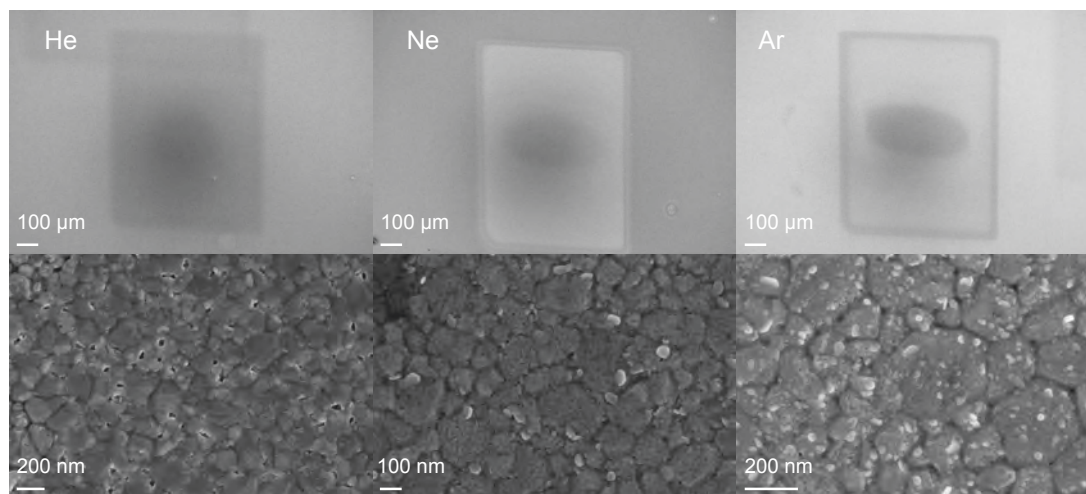


Figure 4.8 SEM SE-Imaging: Top down images of areas bombarded by ⁴He⁺, ²⁰Ne⁺, ⁴⁰Ar⁺, post-XPS measurements. Images show morphological artefacts introduced by the XPS instrument (elliptical feature, corresponding to the elliptical analysis area) and the LEIS instrument (rectangular feature, corresponding to the ion-beam analysis area).

That the analysis area of the LEIS beam can be observed at such low magnification is indicative of its effects on the morphology. Higher magnification images in the area bombarded by the ion beam and away from the elliptical mark were acquired (**Figure 4.9**). Qualitatively, one can conclude that ⁴He⁺

shows least modification to the surface while $^{40}\text{Ar}^+$ exhibits the most significant surface modification.

Upon closer look, one can observe the presence of pin-holes in the morphology of the area bombarded by $^4\text{He}^+$ compared to the pristine area. However, grain morphology remains similar overall. On the other hand, the area bombarded by $^{20}\text{Ne}^+$ shows significant changes with a uniform distribution of pin-holes. MAPbI₃ grains are also now less defined with some smearing effect present which could be due to surface modification introduced by the beam. Finally, the morphology of $^{40}\text{Ar}^+$ bombarded area shows the most significant modifications; pin-holes have visibly increased in size and density. These images show proof of surface modification from ion bombardment for the applied dose.

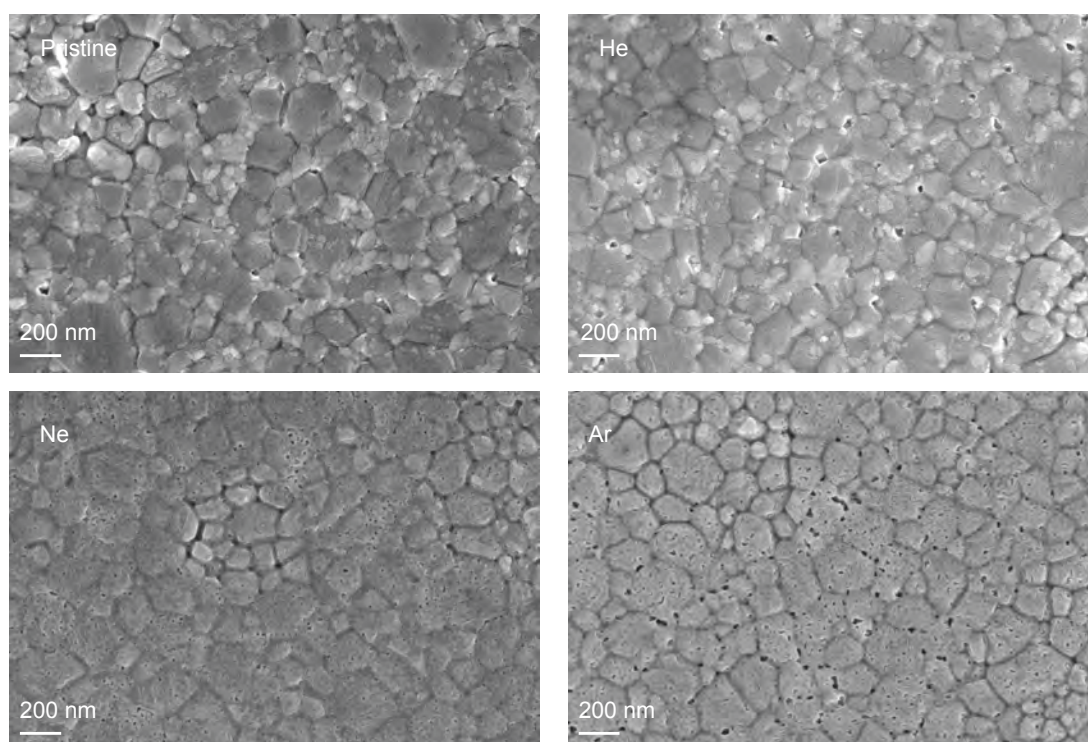


Figure 4.9 SEM SE-Imaging: Top down images of areas bombarded by $^4\text{He}^+$, $^{20}\text{Ne}^+$, $^{40}\text{Ar}^+$. Dose density of all beams were set to 1.0×10^{16} ions/cm².

4.3.2 Chemical Effects

Photoemission spectra were obtained from each bombarded area. Their respective core-level spectra are illustrated in **Figure 4.10**. It can be observed that modification to surface chemistry occurred after $^{20}\text{Ne}^+$ and $^{40}\text{Ar}^+$ beam bombardment. The following observations can be made: (1) C 1s peak shapes and intensities are different, (2) N 1s core-levels are absent and, (3) secondary Pb 4f features can be observed at lower binding energies. These prove that at those dose densities, the sample's surface composition has significantly changed in the Ne and Ar spectra. In particular, the secondary Pb 4f features can be attributed to Pb⁰.

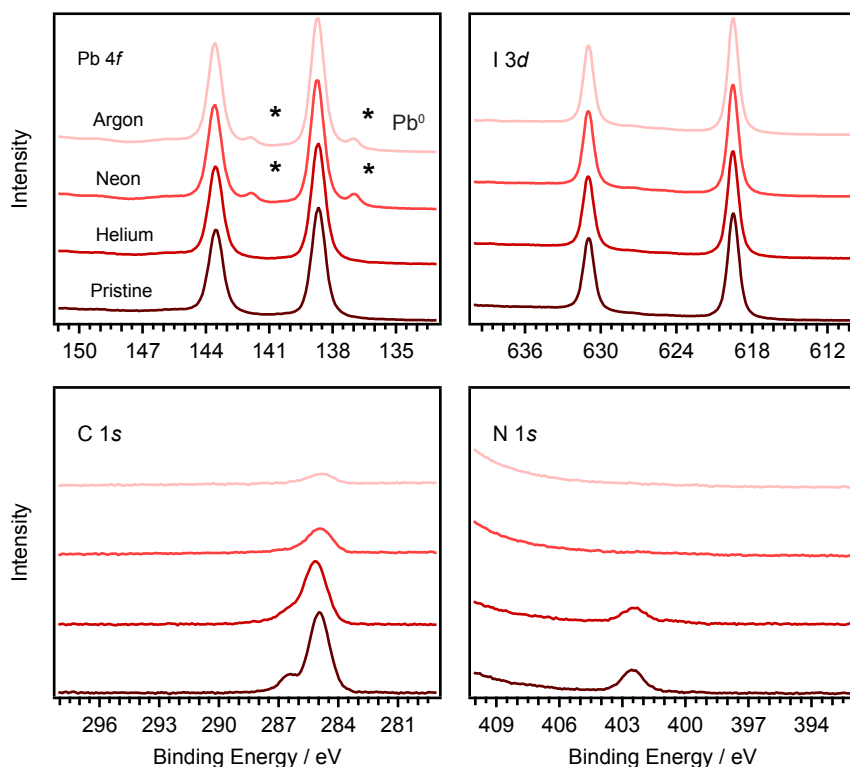


Figure 4.10 XPS: Core-level spectra obtained within the areas bombarded by $^4\text{He}^+$ (1 kV), $^{20}\text{Ne}^+$ (5 kV), $^{40}\text{Ar}^+$ (8 kV) beams at 1.0×10^{16} ions/cm² over a $1000 \mu\text{m} \times 1000 \mu\text{m}$ area. (*) indicates metallic Pb (Pb^0).

It can be concluded that with a dose above 1.0×10^{16} ions/cm², the bombarded surface consists of material accumulated with beam damage. Further, noting the larger information depth of XPS, it can be concluded that the damage extends from the first atomic layer to approximately 5 nm to 10 nm. There is a strong possibility that the increasing degree of C and N removal from the sample surface (< 10 nm) with $^{20}\text{Ne}^+$ and $^{40}\text{Ar}^+$ is related to beam energies (accelerating voltages are 5 kV and 8 kV, respectively) where ion implantation and therefore recoil cascades and related beam-induced vacancies become more severe with increasing beam energy. It is unsure if these atoms from the organic component of MAPbI_3 are predominantly sputtered away as neutral particles or exist as recoil cascades deeper within the material.

To further qualify the effects of increasing dose densities, $^{20}\text{Ne}^+$ beam of different dose densities were bombarded onto a sample. Photoemission spectroscopy was then performed on each area. The spectra are shown in **Figure 4.11**. Pb^0 is present in areas bombarded with lower ion dose densities which may seem contradictory initially, but this seems to arise from the amount of time the sample was kept in UHV condition. As is the case for XPS spectra of different beams where $^{40}\text{Ar}^+$ and $^{20}\text{Ne}^+$ were the last two measurements, spectra containing (Pb^0) were also the last measurements to be made *i.e.* measurements where the sample has been in UHV conditions for a cumulatively longer period of time. This may appear

to disagree with the data reported in **Section 4.2** where no Pb^0 was detected in $\text{Pb } 4f$ core-levels but can be reconciled by considering the increased number of defects ($V'_{\text{MA}}, V_I^\bullet, V''_{\text{Pb}}$ and coupled interstitials) on the surface of MAPbI_3 —extending to some depth corresponding to collision cascade processes of $^{20}\text{Ne}^+$ in MAPbI_3 . It is likely that the defect density in the MAPbI_3 sample of the previous section was initially low but with a sample that has an already elevated defect density (post ion bombardment), further exposure to UHV conditions resulted in accelerated removal of volatile species. Thus, increasing its defect density to a level that induced formation of Pb^0 [84]. SEM images discussed in **Section 4.3.1** are in support of this hypothesis.

It can be surmised that with increasing time in UHV conditions, the likelihood of (Pb^0) formation is increased in this instance and is not affected by the quality of the sample or fabrication process. This can be further explained with the high volatility of the MA group suggesting that these organic cations could have been liberated, resulting of the reduction of Pb^{2+} to Pb^0 .

As expected with increasing dose, there seems to be increasing influence on the removal of organic species on the surface. Based on calculated relative atomic concentrations, plotted in **Figure 4.12**, atomic concentrations of N and C decrease with increasing applied dose. While atomic concentrations of I and Pb can be observed to increase. It should be noted that Pb^0 was not included in the quantification but was included in peak fitting due to possible intensity convolution.

Despite observing slight compositional changes with the various primary ion species and with increasing $^{20}\text{Ne}^+$ dose, no significant chemical shifts can be observed: peak binding energies for $\text{I } 3d_{5/2}$ and $\text{Pb } 4f_{7/2}$ remain at 619.5 eV and 138.7 eV, respectively. With the exception of the presence of Pb^0 on select spectra, no secondary features can be observed in all spectra that would be indicative of a change in chemical oxidation state. Thus, one can conclude with reasonable certainty that despite removal of organic components, the overall chemical states of Pb and I remain unchanged.

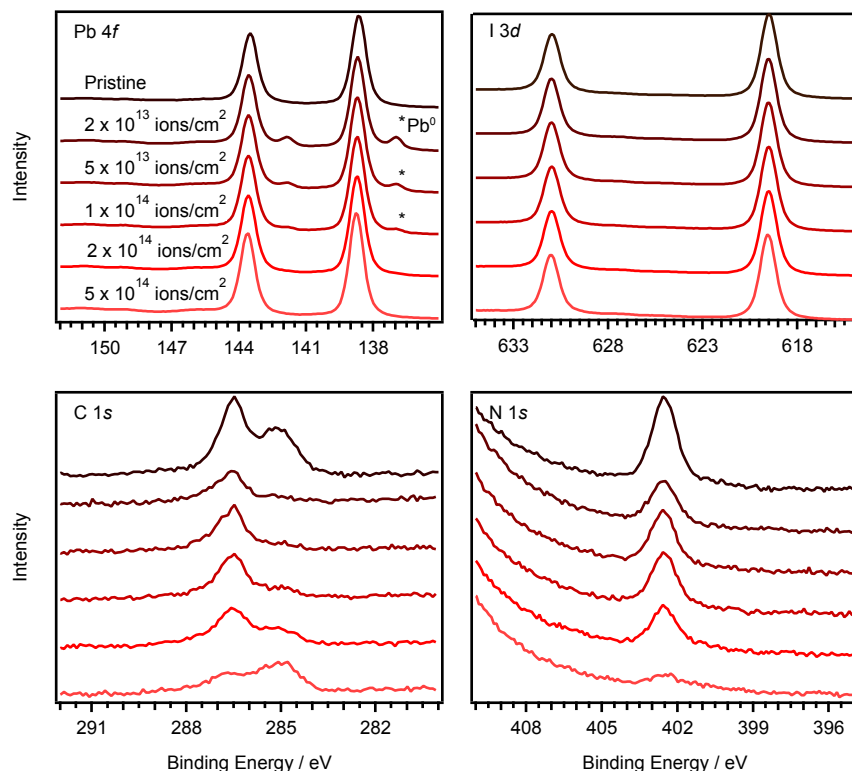


Figure 4.11 XPS: Core-level spectra obtained within the areas bombarded by $^{20}\text{Ne}^+$ beam of different dose densities. (*) indicates metallic Pb (Pb^0).

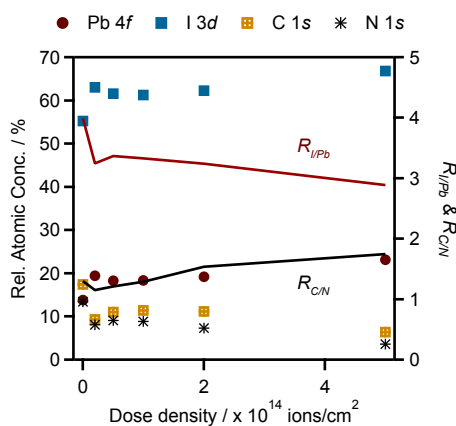


Figure 4.12 XPS: Core-level spectra obtained within the areas bombarded by $^{20}\text{Ne}^+$ beam of different dose densities.

4.3.3 Static Limit

The determination of the static limit for ion bombardment during the development of SIMS as a widely used surface sensitive characterisation technique was previously qualitatively described [174, 176]. It was analytically described as the dose below which the total amount of damage, by defining the damage cross-section of each incoming projectile, is such that all incoming projectiles bombard only a pristine surface. This corresponds to the removal of 1% of the top atomic layer. As a result following values

have been predicted: 1.0×10^{12} ions/cm² for organic materials and 1.0×10^{13} ions/cm² for inorganic materials [175]. However, these values vary from material to material. It has been shown that this limit can be 1.0×10^{14} ions/cm² for organics and varies largely according to its chemical structure.

Considering the results shown in this section, and the weakly bound organic component of MAPbI₃, it is not surprising to learn that the dose density limit for static measurements is less than 2.0×10^{13} ions/cm². This value has been approximately determined by deducing the dose density above which, the organic component of MAPbI₃ is significantly removed through the action of beam bombardment. It would be ideal to apply a dose less than 1.0×10^{13} ions/cm² but based on the signal-to-noise ratio of the obtained scattering data, all data from which surface stoichiometry is obtained, are subjected to a dose 1.0×10^{13} ions/cm².

While the static limit for ion beam interactions developed for SIMS should be the same for LEIS, the section qualifies the effects of ion beam interactions relevant to the inorganic-organic hybrid framework in MAPbI₃ which has not been studied to any reasonable degree. Additionally, the physical processes underpinning the detected particles are different. Notably, LEIS detects backscattered incoming ions and provides elemental information not influenced by the chemistry of the surface. On the other hand, ToF-SIMS relies on the detection of generated secondary ions which are destructive in nature and therefore provides information that is based on the chemistry of the surface.

4.4 Time-of-Flight Mass Spectrometry

Different sputter sources were used to profile devices using MAPbI₃ as an absorber layer to determine the possible beam effects on the profiles and any sources of matrix effects.

Argon clusters are thought to be effective in profiling organic materials [209, 210] but ineffective for inorganic materials while cesium ion (Cs⁺) has been widely used in profiling inorganic materials for its more uniform depth profiles. But a low-energy Cs⁺ beam has also been shown to produce smoother profiles of organic materials by avoiding accumulation of significant beam damage on the surface [211].

However, in the case of multilayer devices with a combination of organic and inorganic materials, the choice of beam and its energy becomes crucial in ensuring no beam-induced artefacts are introduced in the profiles. A 500 eV monoatomic Cs⁺ has been suggested to be a suitable candidate for depth profiling samples with inorganic and organic layers [212] although many artefacts exist at such inorganic-organic interfaces. Noel *et al.* [194] used varying sizes of argon clusters and Ar⁺ and Cs⁺ monoatomic beams for profiling through multilayer devices but were hard-pressed to find an opti-

mal beam condition. Instead, they found that the choice of beam depends largely on the area of interest in the device (*i.e.* the layer of interest). Specifically, they performed measurements on simple bilayers and on indium tin-doped oxide (ITO)/TiO₂/Cs_xFA_{0.83}(MA_{0.17})_{1-x}Pb(I_{0.83}Br_{0.17})₃/Spiro-OMeTAD/Au devices. However, a multilayer device is complex and can have different matrix effects and differential erosion rates, therefore whether their model systems can be applied to other device structures cannot be for certain.

In the subsequent results shown, mass fragments are analysed to determine characteristic ions for depth profile analysis on the following device structure: ITO/MAPbI₃/C₆₀/Ag. Subsequently, depth profiles obtained from Ar₁₀₀₀ 10 keV, Cs⁺ 1 keV, and O₂⁺ 1 keV are given. The different profiles are analysed to deconvolve any material-beam induced artefacts.

4.4.1 MAPbI₃ Mass Fragment Analysis

Secondary ions used for analysis can be found in **Table 4.1**. Generally, as one would expect, mass spectra from MAPbI₃ are dominated by a fragmentation pattern of m/z values whose chemical identity can be attributed to Pb_xI_y and I_x species. In particular, ionisation of I⁻ ($m/z = 126.92$) occurs efficiently and saturates the detector when Cs⁺ sputter beam is used.

Table 4.1 ToF-SIMS: Secondary ions used for layer identification in the following device structure ITO/MAPbI₃/C₆₀/Ag.

Silver Electrode	m/z	C ₆₀ Layer	m/z	MAPbI ₃ -absorber	m/z
Ag ⁻	107	C ₃ ⁺	36	CH ₆ N ⁺	32
CsAg ⁻	240			Pb ⁺	208
Cs ₂ Ag ⁻	373			I ⁻	127
Ag ⁺	107			I ₂ ⁻	254
Ag ₂ ⁺	214			PbI ⁻	335
Ag ₂ O ⁺	230			I ₃ ⁻	381
CsAg ⁺	240			PbI ₂ ⁻	462
¹⁰⁹ AgAg ₂ O ⁺	341			PbI ₃ ⁻	589
CsAg ₂ ⁺	347				
Cs ₂ Ag ⁺	373				
Cs ¹⁰⁹ AgAg ₂ ⁺	589				

Mass spectra (positive and negative polarities) obtained from O₂⁺ on the device described above, are given in **Figure 4.13** and **Figure 4.14**. The mass range between 0 and 200 m/z contains C_xH_y⁻ fragments and elemental ions (e.g. H, F, C, N, O, Cl) used for mass calibration. As can be observed, I⁻ ($m/z =$

126.92) dominates this mass range. The mass range between 200 and 400 m/z shows more I-based and Pb-based fragments (including isotopic fragments). It should be noted that there are fragmentation patterns alluding to isotopic fragments but are likely due to fragmentation from Ag and are not thoroughly identified. Finally, the mass range between 450 and 600 m/z is dominated by PbI_2^- ($m/z = 461.80$) and PbI_3^- ($m/z = 588.71$) fragments. On the other hand, PbI_2^+ and PbI_3^+ cannot be detected at the expected m/z value in the positive polarity. Furthermore, other secondary ions such as metal-halide fragments are not as easily ionised in the positive polarity, as such much of the potential chemical information for identification of interfacial species is lost. Despite the lower ionisation yield of metals in the negative polarity, as shown in the next section, Me^- show more consistent profiles with minimal interfacial matrix effects.

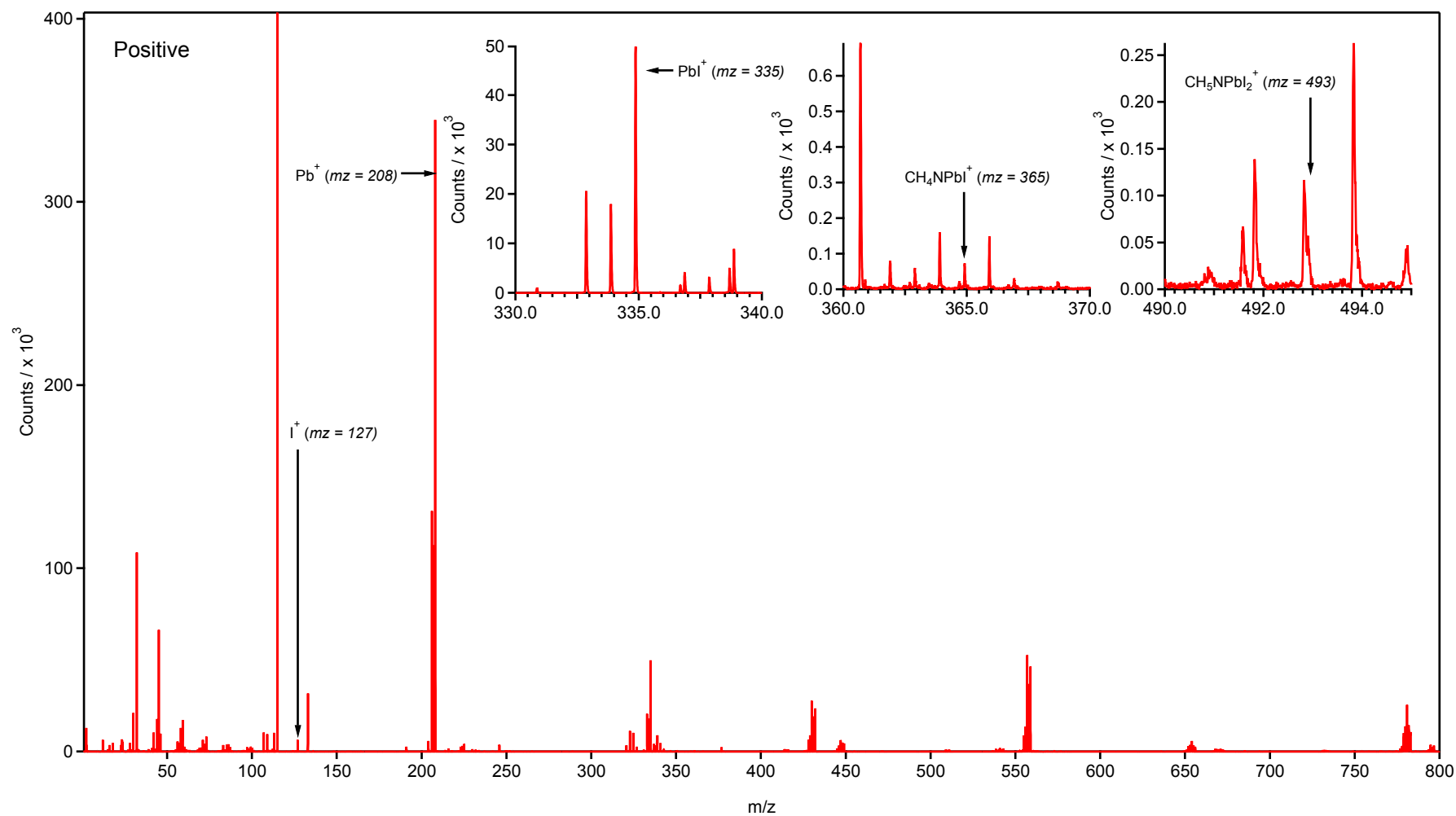


Figure 4.13 ToF-SIMS: Mass spectrum obtained from a ITO/MAPbI₃/C₆₀/Ag device profiled using O₂⁺ sputter and Bi₃⁺ analysis beams in the positive polarity for the m/z range 0 to 800 m/z . Note that m/z values of indicated fragments have been rounded up to unit mass resolution.

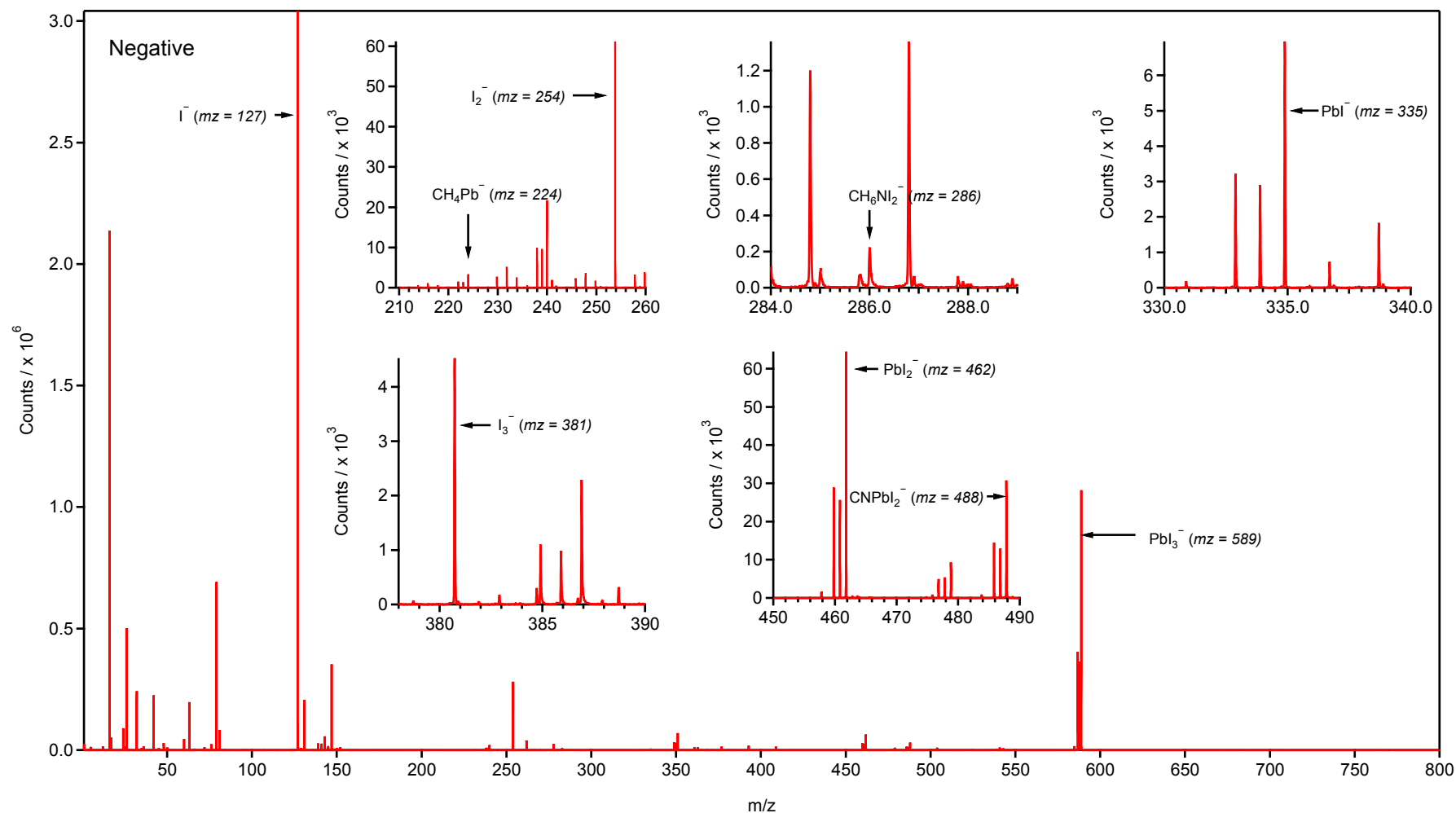


Figure 4.14 ToF-SIMS: Mass spectrum obtained from a ITO/MAPbI₃/C₆₀/Ag device profiled using O₂⁺ sputter and Bi₃⁺ analysis beams in the negative polarity for the m/z range 0 to 800 m/z. Note that m/z values of indicated fragments have been rounded up to unit mass resolution.

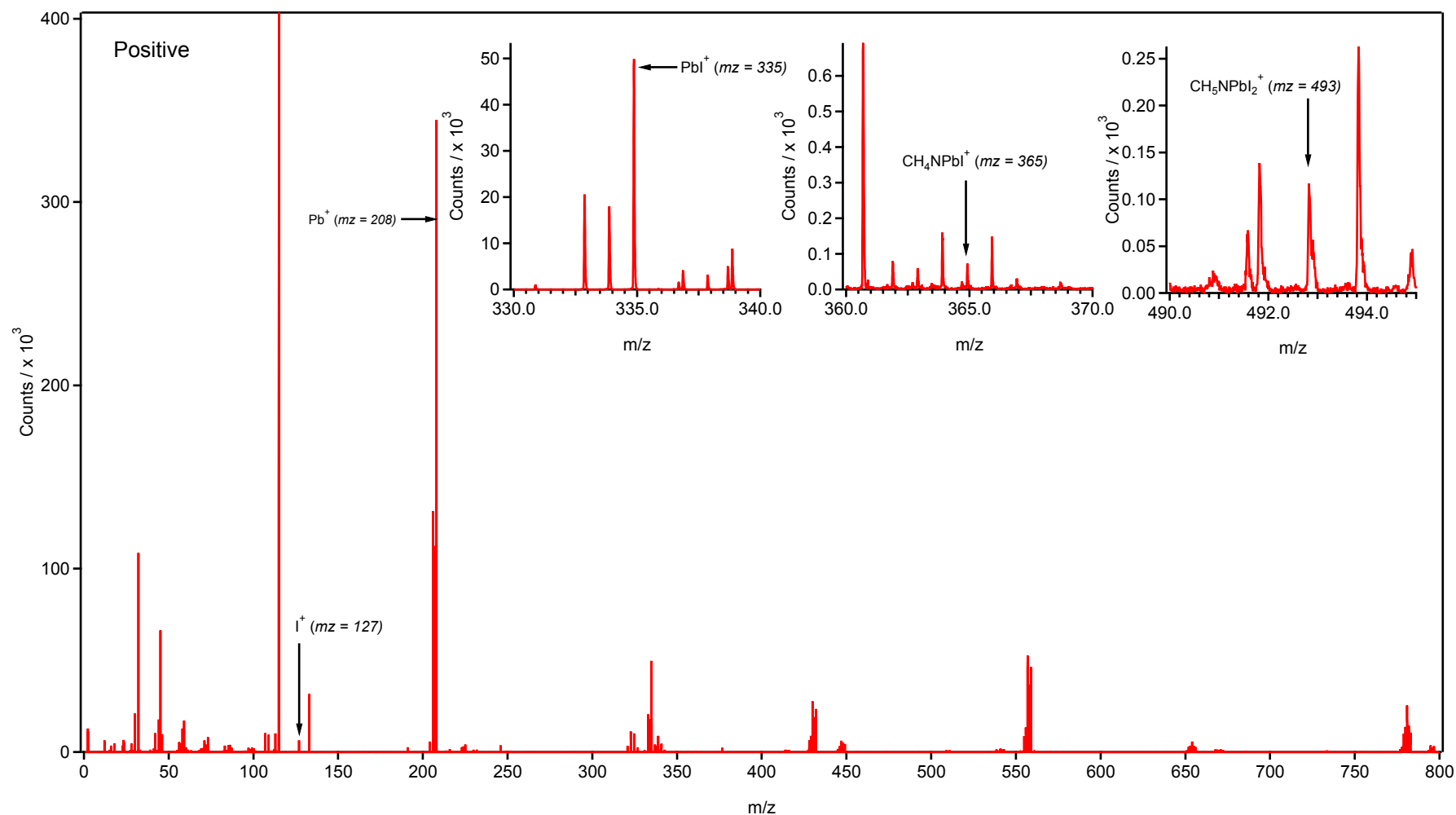


Figure 4.15 ToF-SIMS: Surface mass spectrum obtained from a ITO/MAPbI₃ sample in the positive polarity, analysed using a Bi₃⁺ analysis beam for the m/z range 0 to 800 m/z. Note that m/z values of indicated fragments have been rounded up to unit mass resolution.

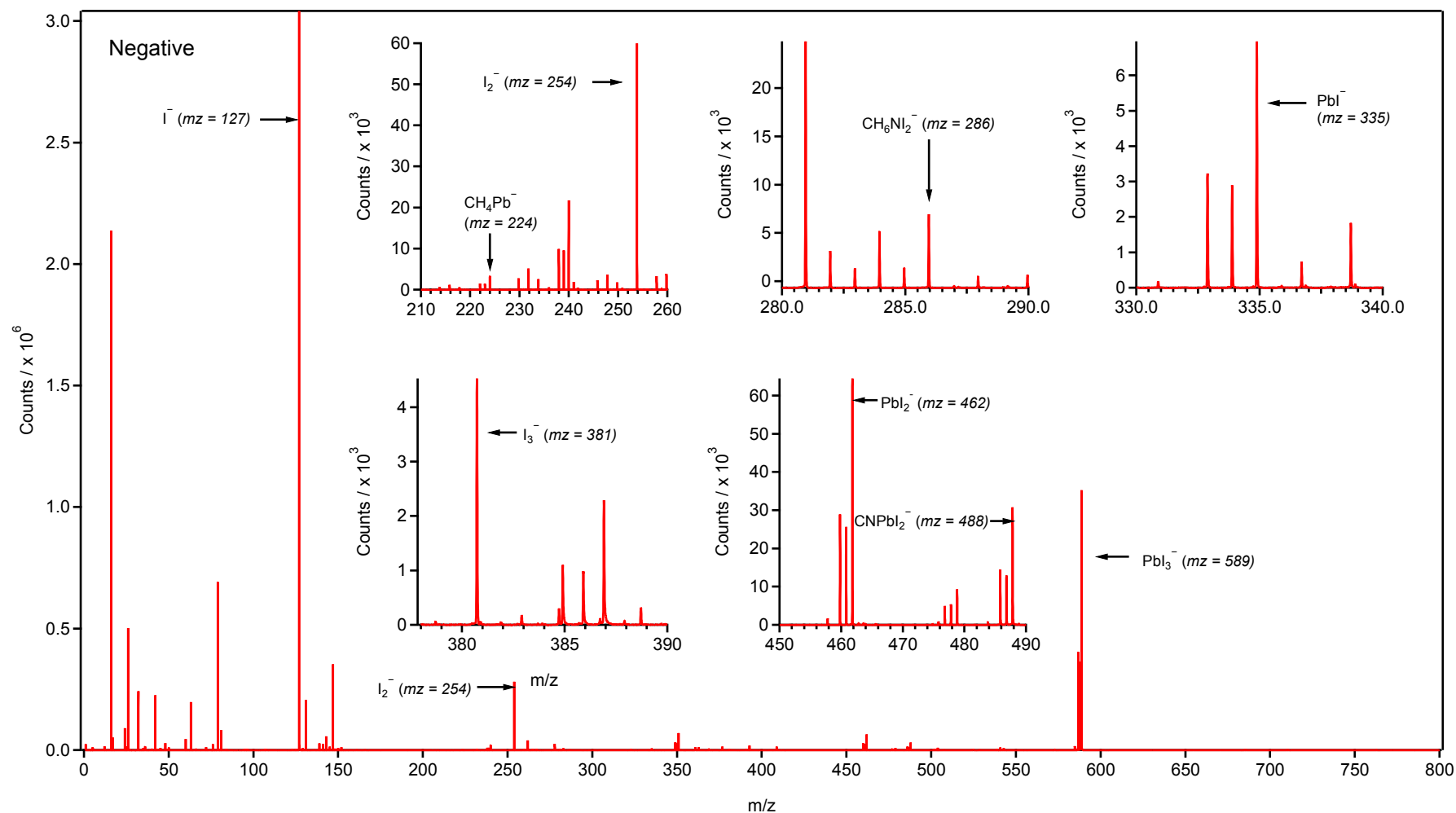


Figure 4.16 ToF-SIMS: Surface mass spectrum obtained from a ITO/MAPbI₃ sample in the negative polarity, analysed using a Bi₃⁺ analysis beam for the m/z range 0 to 800 m/z . Note that m/z values of indicated fragments have been rounded up to unit mass resolution.

As a comparison, surface mass spectra obtained from a simple MAPbI₃ sample are also given in **Figure 4.15** and **Figure 4.16**. It can be observed that certain fragments are more intense, for instance PbI⁻ ($m/z = 334.9$), I₃⁻ ($m/z = 380.7$), CH₄NPbI⁺ ($m/z = 364.9$) while other fragments in the larger m/z range such as CH₅NPbI₂⁺ ($m/z = 492.8$), CNPbI₂⁻ ($m/z = 487.8$), CH₆NI₂⁻ ($m/z = 285.9$), CH₄Pb⁻ ($m/z = 224.0$) while other fragments show suppressed intensities. These differences indicate the reactive nature of O₂⁺ and suggest the following fragments to be used for depth profile analysis: PbI⁻ ($m/z = 334.9$), PbI₂⁻ ($m/z = 461.80$), PbI₃⁻ ($m/z = 588.71$), I⁻ ($m/z = 126.92$), I₂⁻ ($m/z = 253.8$), I₃⁻ ($m/z = 380.7$) but further considerations need to be made when using different sputter beam species.

To verify that such MAPbI₃ specific secondary ions are identified with certainty (in **Table 4.1**), isotope distributions were obtained for Pb_xI_y⁻ using an O₂⁺ sputter beam (**Figure 4.17**). Evidently, there is strong evidence that secondary ions picked are accurate in their chemical identity in that the calculated abundance based on peak intensities of secondary ions with m/z values equal to the indicated isotopes have good correlation to theoretical values. As an exception, there is some incongruence with theoretical and measured isotope abundance distribution for the following isotopes: ²⁰⁴Pb₂I₃⁻, ²⁰⁶Pb²⁰⁴PbI₃⁻, ²⁰⁷Pb²⁰⁴PbI₃⁻. That only three isotopes for Pb₂I₃⁻ do not have matching abundance values suggest that this deviation is not from a Pb-based secondary ion. Instead, mass interference from beam-induced formation of organic secondary ions (C, N, H) at these m/z values contributing to overvalued peak intensities seem to be the likelier reason.

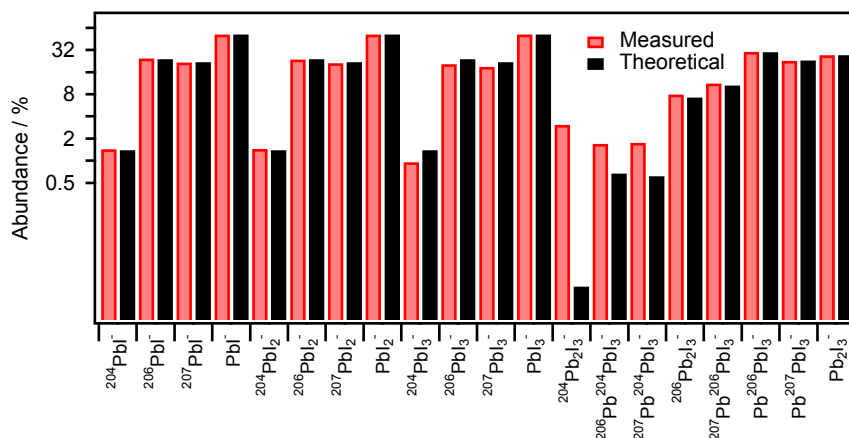


Figure 4.17 ToF-SIMS: Pb_xI_y⁻ isotope abundance distribution based on measured and theoretical values, from O₂⁺ sputtering of ITO/MAPbI₃/C₆₀/Ag. Most isotopes have good agreement between measured and theoretical values, with the exception of ²⁰⁴Pb₂I₃⁻, ²⁰⁶Pb²⁰⁴PbI₃⁻, ²⁰⁷Pb²⁰⁴PbI₃⁻ where oversampled intensities are present.

4.4.2 Ag/C₆₀ Interface

Figure 4.18 shows the depth profiles of the electrode, hole-transport layer, and the start of the MAPbI₃ layer.

Analysing depth profiles obtained from Ar₁₀₀₀, at first glance, it can be noted that while the electrode profile can be described as linear, the cluster beam is inefficient in sputtering the metal electrode: Ag⁻ ($m/z = 106.91$) signal has an extended decay while Ag⁺ ($m/z = 106.91$) signal is enhanced and extends beyond the actual layer. The former is probably due to fragments of Ag being repeatedly embedded within the sputter crater during each sputter cycle, while the latter is likely to have come from the creation of a positive surface charge assisted by the matrix that repels Ag⁺ ($m/z = 106.91$) ions beyond the sampling area. Despite that, sharply defined interfaces are obtained for PbI₃⁻ ($m/z = 588.71$) and Pb⁺ ($m/z = 208$) which indicate that sputter induced roughening is likely not to be a factor in these beams for sputtering metal/C₆₀ interfaces.

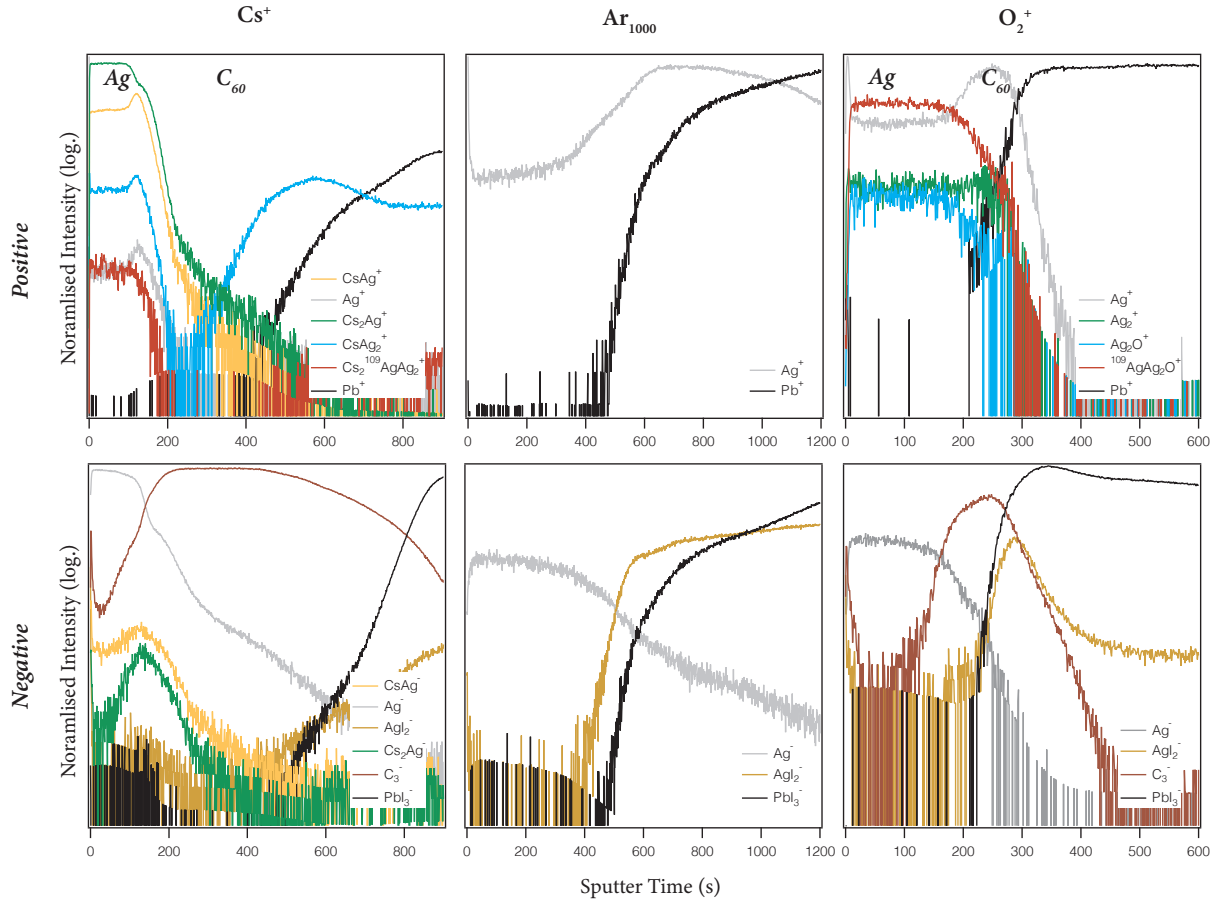


Figure 4.18 Dynamic ToF-SIMS: Depth profiles of the Ag/C₆₀ interface of ITO/MAPbI₃/C₆₀/Ag device obtained using monoatomic Cs⁺ 1 keV and O₂⁺ 1 keV, and Ar₁₀₀₀ 10 keV sputter sources with both polarities shown. Black profiles belong to the MAPbI₃ layer. Profiles indicate that O₂⁺ in the positive and negative polarities are least affected by interfacial matrix effects. Each datapoint is normalised to the total counts of all corresponding detected secondary ions.

On the other hand, Cs⁺ seems to be more uniform and efficient in sputtering the electrode. Ag⁻ ($m/z = 106.91$) still extends beyond C₆₀ and MAPbI₃ layers, but to a lesser degree than with Ar₁₀₀₀. Similarly, an extended decay lengths of Ag⁻ ($m/z = 106.91$) into the MAPbI₃ layer is observed. This effect has been reported in Cr and Au/Tyrosine/SiO₂ multilayers [212]. However, if one were to note the difference in decay lengths of Ag⁺ ($m/z = 106.91$) and Ag⁻ ($m/z = 106.91$), they suggest different contributions to broadening of profiles for the different ions where the negative polarity is likely to be dominated by residual charges at the sampled surface [213] while that of Ag⁺ ($m/z = 106.91$) likely to be dominated by physical processes—the collision cascade of Cs sputter atoms causes Ag atoms to be physically embedded deeper into the softer underlayers.

There also seems to be an enhancement of Ag⁺ ($m/z = 106.91$) at the Ag/C₆₀ interface that is likely due to interfacial matrix effects. Such artificial enhancements are also observed for CsAg⁺ ($m/z = 240$)

and CsAg_2^+ ($m/z = 347$) while a slight suppression is evident in Cs_2Ag^+ ($m/z = 373$). On the other hand, $\text{Cs}^{109}\text{AgAg}_2^+$ ($m/z = 589$) can be observed to be unaffected by the matrix at this interface. Utility of these diatomic secondary ions is called MCs_n^+ -SIMS (where M is the target element) and has been confirmed to produce Cs_xAg_y^+ secondary ions least affected by the matrix [214]. This is largely due to the different ionisation processes of Ag^+ and Cs_xAg_y^+ ions where the former is brought about by charge transfer processes between the ionised particle and the matrix and the latter is produced with the direct reaction between Cs^+ and Ag^0 on the surface of the sample [215].

These observations, support the conclusion that the extension of Ag^- ($m/z = 106.91$) beyond the Ag/C_{60} interface is artificial. Considering the fact that a similar extended decay length is observed in profiles obtained from Ar_{1000} and may be a chemical or charge effect at this interface affecting ions.

Finally, profiles obtained from O_2^+ show a similar Ag^+ ($m/z = 106.91$) sputtering profile to that of Cs^+ which can be characterised by a narrow interface width and Ag^+ ($m/z = 106.91$) and Ag_2^+ ($m/z = 347$) enhancement at the Ag/C_{60} interface. Enhancements evident only in the positive polarity suggests that during the sputtering process, the electronegative C_{60} layer contributes to the ionisation process of Ag to Ag^+ ($m/z = 106.91$) and Ag_2^+ ($m/z = 347$) thus, increasing their ionisation yield. Similar to analysis of MCs_n^+ ions, Ag_yO_x^+ ions, particularly $^{109}\text{AgAg}_2\text{O}^+$ ($m/z = 341$) and Ag_2O^+ ($m/z = 230$)—show absence of any yield enhancement at the interface.

When analysing the profiles of C_3^- ($m/z = 36$), the profile obtained from Cs^+ sputtering shows an extended decay length—comparative to its initial electrode/ C_{60} interface which is sharply defined—in which concentration of C_3^- is oversampled for an extended depth. This suggests some degree of accumulation of material modification from Cs-implantation in the C_{60} layer that alters its properties and given the energy of the sputter beam (1 kV), it is likely that physical processes dominate chemical ones [216] (e.g. surface roughening).

In the negative polarity, it can be observed that signal enhancements are absent and ionisation of Ag^- ($m/z = 106.91$) produces a sharp decaying profile. Furthermore, C_3^- ($m/z = 36.00$) shows well-defined interfaces. Consequently, the use of O_2^+ to sputter devices where the electrode is of interest, is preferred. Certain ions in the positive polarity can be used without concern for matrix effects but the negative polarity is more representative of the elemental distribution.

4.4.3 C_{60} /MAPbI₃ Interface

Based on the same samples as above, depth profiles of mass fragments from MAPbI₃ are shown in **Figure 4.19**. Their profiles and any influence from the matrix and beam is discussed in this section.

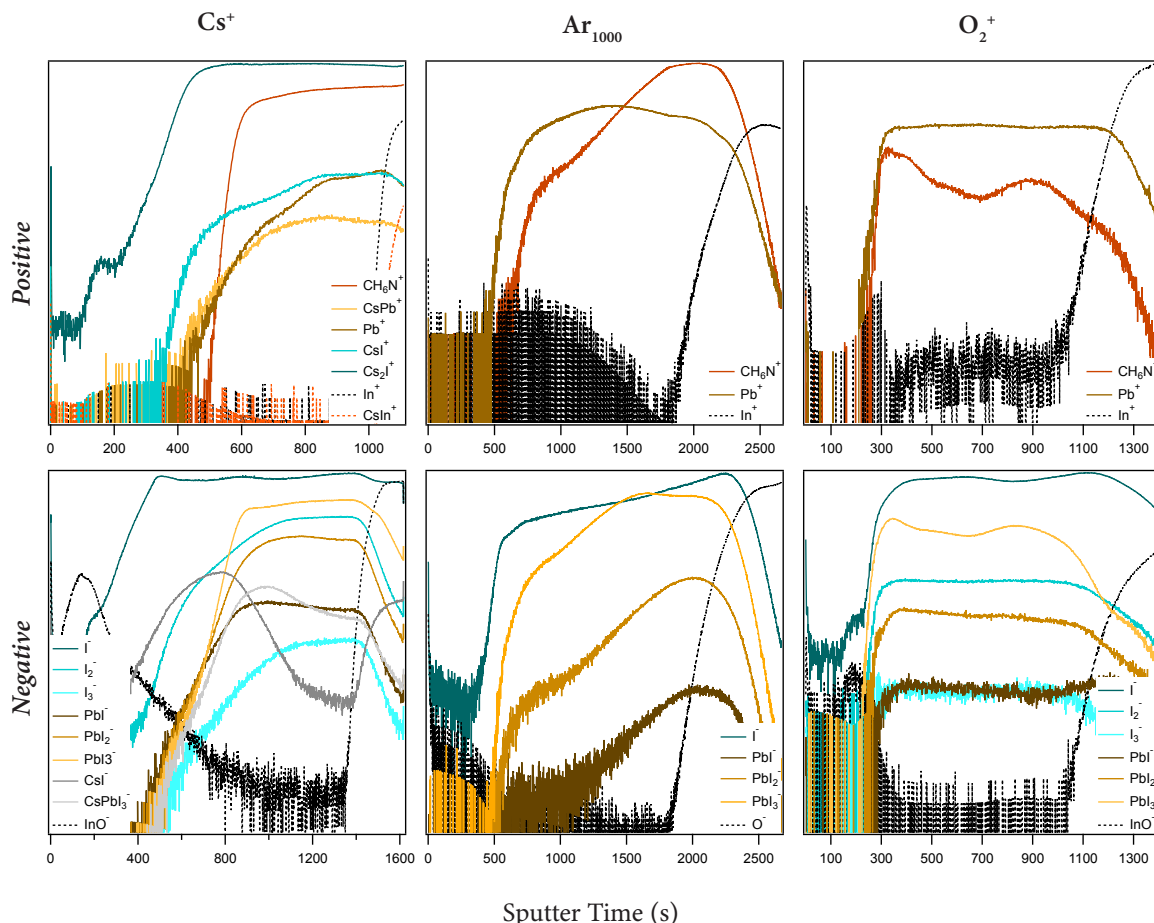


Figure 4.19 **Dynamic ToF-SIMS:** Depth profiles of the C_{60} /MAPbI₃ interface of ITO/MAPbI₃/ C_{60} /Ag device obtained using monoatomic Cs^+ 1 keV and O^- 1 keV, and Ar_{1000} 10 keV sputter sources. Profiles indicate that O_2^+ in the positive and negative polarities have the sharpest interfaces and most linear profiles. Each datapoint is normalised to the total counts of all corresponding detected secondary ions.

Using Cs^+ , ionisation of I^- ($m/z = 126.92$) occurs readily but the different iodine species have dissimilar profiles. It can be observed that I^- ($m/z = 126.92$) occurs earlier in the profile within the C_{60} layer. Whereas I_2^- ($m/z = 253.8$) occurs slightly later and I_3^- ($m/z = 380.72$) occurs with Pb_i^{2+} , PbI_2^- ($m/z = 461.80$), and PbI_3^- ($m/z = 588.71$) mass fragments from the MAPbI₃ layer. Given that all three beams were performed on the same sample, the possibility of anomalous device-specific degradation causing such diffused profiles—as one would expect for a degraded MAPbI₃ layer—can be disregarded. Thus, the extension of these mass fragments to regions closer to the device surface is likely beam induced in which roughening effects of Cs^+ on the C_{60} layer result in apparent intermixing of species and conse-

quently profile broadening.

It can also be observed that the steady-state regions of I_x^- and PbI_x^- mass fragments do not coincide. Comparing negative and positive mass fragment profiles, $Cs_xI_y^+$ species identified by CsI^+ and Cs_2I^+ mass fragments occur at similar times with I_2^- ($m/z = 253.8$) and I^- ($m/z = 126.92$), respectively. CH_6N^+ ($m/z = 32$) mass fragment has a much sharper interface width and a linear profile but occurs slightly later into the profile. Pb^+ and $CsPb^+$ can also be seen to start at similar times with PbI_x^- . These features suggest that Cs^+ causes ionisation of species to different extents during ion implantation. It is likely that during cascade mixing processes, fragmentation and ionisation of I^- occurs much more easily and possible residual positive charges on the sample surface induced by Cs^+ causes its pre-mature emission.

When comparing I_x^- and PbI_x^- profiles from O_2^+ , such broad profiles are not observed, though some diffusion of I^- ($m/z = 126.92$) can be observed within the C_{60} layer. Therefore, the enhancement of I^- ($m/z = 126.92$) by Cs^+ could be exacerbated by slight I^- diffusion already present in the sample, artificially broadening an already diffused profile.

With Ar_{1000} sputtering, PbI_x^- profiles have narrower interface widths but do not have well-defined linear regions like Cs^+ —profiles can be seen to slowly increase at the $C_{60}/MAPbI_3$ interface, peaking at the $MAPbI_3/ITO$ interface. This suggests that the beam energy and/or cluster size used was not optimal, most likely being too energetic resulting in subsurface layers with an increasing degree of damage accumulation. Similarly, Pb^+ ($m/z = 208$) and CH_6N^+ ($m/z = 32$) mass fragments have narrow interface widths but do not have linear sputter profiles.

O_2^+ seems to provide the most linear depth profiles for I_x^- and PbI_x^- mass fragments with narrow interfacial widths. Some oscillatory behaviour in profiles can be observed in CH_6N^+ ($m/z = 32$) and PbI_3^- ($m/z = 588.71$). Unlike Cs^+ and Ar_{1000} sputtering, profiles from O_2^+ start at similar times which suggests that the incongruent apparent interfaces from the different I_x mass fragments seen in the other sputter beam profiles are likely beam-induced due to preferential sputtering/ionisation.

4.5 Conclusions

Based on three different surface sensitive characterisation techniques, instrument-sample interactions are complicated and may influence data. In the case of X-ray irradiation and UHV conditions, minimal exposure to X-rays are recommended as even 0.5 h irradiation was shown to remove methyl groups on the surface. Extended irradiation provides better signal-to-noise ratio but will affect the quantification of the true surface composition. Further, given that valence-band measurements and work-function

measurements in XPS generally take more than an hour, the user should be wary of the effects X-rays have on the sample composition which would consequently affect the measured spectra. Data presented above showed that even after averaging the spectra, the effects are still significant. Using noble-gas ions for LEIS requires the use of extremely low-dose of less than 1.0×10^{13} ions/cm² for non-destructive measurements. For depth profiling of organometallic halide based devices, Cs⁺ and Ar₁₀₀₀ beams produce profiles that are influenced by the beam and matrix, particularly at the interface. O₂⁺ provides the most linear profiles and least affected by matrix effects for all layers. When matrix effects are present within some mass fragments, they can be absent in others that are directly ionised by the sputter beam (e.g. Cs- and O- based fragments).

Chapter 5

Surface Composition of MAPbI₃ & Analogues

5.1 Motivation

The surface composition of CH₃NH₃PbI₃ (MAPbI₃) has been studied to some extent but often with the use of photoemission measurements or based on density functional theory simulations. There has been an increase in the number of compositional analogues that are touted to be much more stable than the standard composition which often rely on substituting the CH₃NH₃⁺ (MA⁺) cation with an inorganic (e.g. Cs⁺) or larger organic cation CH(NH₂)₂⁺ (FA⁺).

Defect passivation has also shown promise which is predicated on using Lewis bases/acids, small molecules (e.g. C₆₀). Published reviews of various organic molecules used to improve device stabilities can be found in Refs [217, 218].

The addition of 5-aminovaleric acid (AVA) and 1-naphthyl methylamine (NMA) to MAPbI₃ precursor solutions have been published [219, 220], respectively. The additions show markedly improved MAPbI₃ film stability in the presence of oxygen and light. The presence of water has been shown to behave as an accelerant by creating metastable hydrated phases within the organometallic halide absorber layer. Thus, in the absence of water and in the presence of light and oxygen, degradation should occur only via the creation of superoxide species that induce degradation at surface defects [38]. This accepted route of degradation underpins the prevailing hypothesis here: the slower degradation kinetics (see **Figure 5.1**) are due to the removal of surface defects through which generated superoxide initiates degradation.

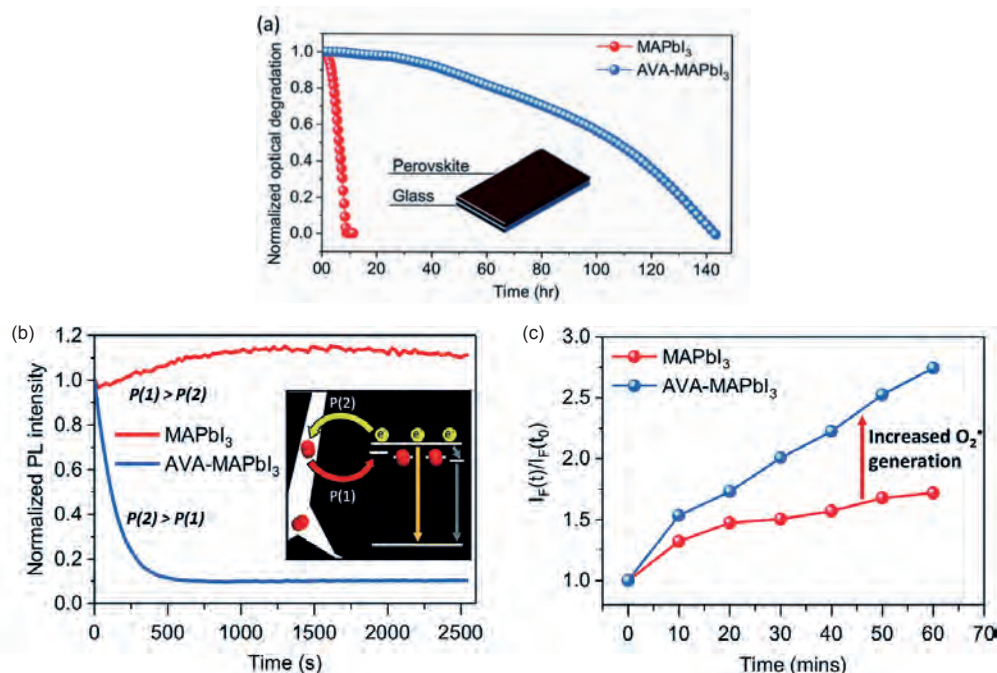


Figure 5.1 (a) Optical stability of MAPbI₃ and MAPbI₃-AVA with the latter exhibiting much more delayed degradation kinetics (for more information of experimental details, refer to publication). (b) Photoluminescence (PL) intensities of both samples with MAPbI₃ showing an increase due to binding of oxygen to surface defects (pathway 1), while reduction/quenching of PL intensity is observed for MAPbI₃-AVA which is indicative of electron transfer from MAPbI₃ to bound oxygen between grains (pathway 2). (c) Y-axis shows PL intensity of solution containing said samples and has a direct relationship with concentration of unbound superoxide in the sample. A higher intensity for MAPbI₃-AVA suggests that these species are 'free' within the bulk unable to induce degradation. Reproduced from [219].

As discussed in **Section 2.3.2**, the size of I vacancies ($V_I^\bullet$) reasonably accommodates that of oxygen molecules and it has been shown that defect density is correlated with superoxide diffusion within the MAPbI₃ [36] and that a [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) overlayer suppresses superoxide formation [221]. The presence of $V_I^\bullet$ also directly follows the number (area) of grain boundaries. Thus one can reasonably conclude that the defects also exist between grain boundaries. Complete discussion of the physical processes behind the photostability enhancement of these samples and the resulting photoluminescence (PL) features, which have been provided in their corresponding published articles, is not covered in this thesis.

Photostability experiments and PL measurements (**Figure 5.1(b)**) suggest a scenario in which the resistance of MAPbI₃, made from precursors containing organic additives, to light and oxygen degradation is a consequence of removal of these surface defects through passivation, by the organic molecules. If superoxide no longer has access to as many defect sites to initiate degradation, then its stability is surely to improve.

Based on work by Lin *et al.* [222], longer chain organic additives was shown to result in reduction in

short-circuit current (J_{sc}) and therefore, may not be applicable in efficient devices. However, it was noted that glycine offered the same enhancement in photostability with minor, if not negligible reduction in J_{sc} . On the other hand, NMA was shown to improve device metrics, particularly open-circuit voltage (V_{oc}) with an easily attainable power conversion efficiency (PCE) of $\sim 18\%$ [220].

5.1.1 Scope of Work

Five different organic additives were added to the MAI:PbI₂ precursor solutions as described in **Section 3.1.1**. Their structures and corresponding X-ray diffraction data (XRD) are shown in **Figure 5.2**. Samples made with precursors with organic additives are given the following identifiers: MAPbI₃-Gly (glycine), MAPbI₃- β (β -alanine), MAPbI₃- γ (γ -aminobutyric acid), MAPbI₃-AVA (5-aminovaleric acid), MAPbI₃-NMA (1-naphthyl methylamine).

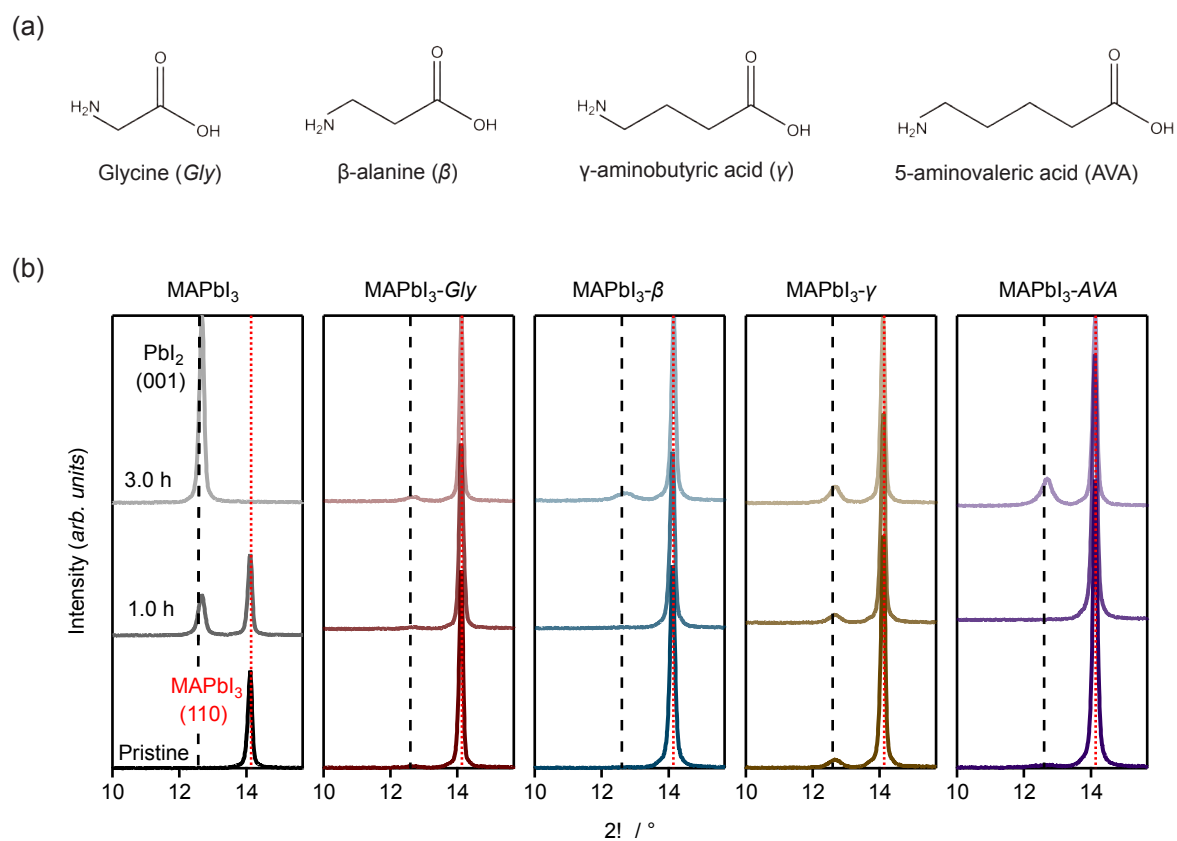


Figure 5.2 (a) Chemical structure of carbon-chain addition precursors. (b) XRD data of the various samples at different ageing times under 1 sun illumination (provided by a UV enhanced LED source) and in dry air [222]. Complete conversion to PbI₂ is observed for MAPbI₃ based on the disappearance of the diffraction peak from the (110) plane of tetragonal MAPbI₃ and the presence of a peak from (001) plane from PbI₂. Samples containing organic additives show higher stability.

Additionally, by examining XRD diffraction peaks (**Figure 5.2**) at 14.14° assigned to (110) planes of MAPbI₃ in the tetragonal phase (predominant stable phase under standard conditions) and at 12.60°

assigned to (001) planes of PbI_2 (a degradation by-product of MAPbI_3 degradation), MAPbI_3 samples made with organic additives in the precursor solution exhibit higher structure stability. In particular, the disappearance of (110) planes for the pristine sample just after 3 h shows the complete conversion of MAPbI_3 to PbI_2 . Whereas it can be observed that complete conversion from MAPbI_3 to PbI_2 is not observed for the other samples, attesting to their enhanced photostability.

Scanning electron microscopy (SEM) images (from secondary electrons - SE) of their surface morphologies are shown in **Figure 5.3**. Based on calculated grain size values MAPbI_3 , $\text{MAPbI}_3\text{-H}_2\text{O}$, and $\text{MAPbI}_3\text{-Gly}$ seem to have a similar average grain size at ~ 300 nm while there seems to be a trend of decreasing grain size with increasing additive carbon backbone chain length ($\text{C}_x\text{H}_y\text{-COOH}$): $\text{MAPbI}_3\text{-}\beta$ (2C, ~ 180 nm), $\text{MAPbI}_3\text{-}\gamma$ (3C, ~ 150 nm), and $\text{MAPbI}_3\text{-AVA}$ (4C, ~ 100 nm). Considering that there is evidence for a correlation of increased grain boundaries with lower film stability [38], such a contradiction must come from the passivating effect of the organic additives.

Despite the supporting evidence, there has been no previously reported *direct* evidence of such organic molecular bonding on the surface or at the grain boundaries. Therefore, the surfaces of these materials are characterised to a greater extent to show empirical evidence. Low energy ion scattering (LEIS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) in the static mode are the main techniques used to better understand how surface stoichiometry differed between the samples. However, the limitation of these techniques in providing only surface information is acknowledged and caution is given when drawing any conclusions.

Additionally, surface composition of MAPbI_3 , $(\text{MA})_{0.95}\text{Cs}_{0.05}\text{PbI}_3$, $(\text{MA})_{0.8}\text{Cs}_{0.2}\text{PbI}_3$, and $(\text{FA})_{0.85}\text{Cs}_{0.15}\text{PbI}_3$ are investigated in greater detail using dose density scattering information.

In this instance, the information obtained from the “surface” is different between ToF-SIMS and LEIS. LEIS provides elemental scattering information from the first atomic layer (at sufficiently low dose density) that is not affected by the chemistry of the surface (‘matrix’) and therefore only provides elemental information. While ToF-SIMS provides chemical information about the first atomic layer, the nature of physical processes resulting in secondary ion formation is largely affected by the matrix. This is the reason relative, much less absolute, quantification is not trivial and requires extensive systematic studies to deconvolve such effects. In comparison with static ToF-SIMS, X-ray photoelectron spectroscopy (XPS) which has been used in great extents to characterise surface composition, has a much larger information depth. Thus, by using LEIS, the relative concentration of I and Pb on the surface can more easily be obtained as the obstacles surrounding ToF-SIMS are absent.

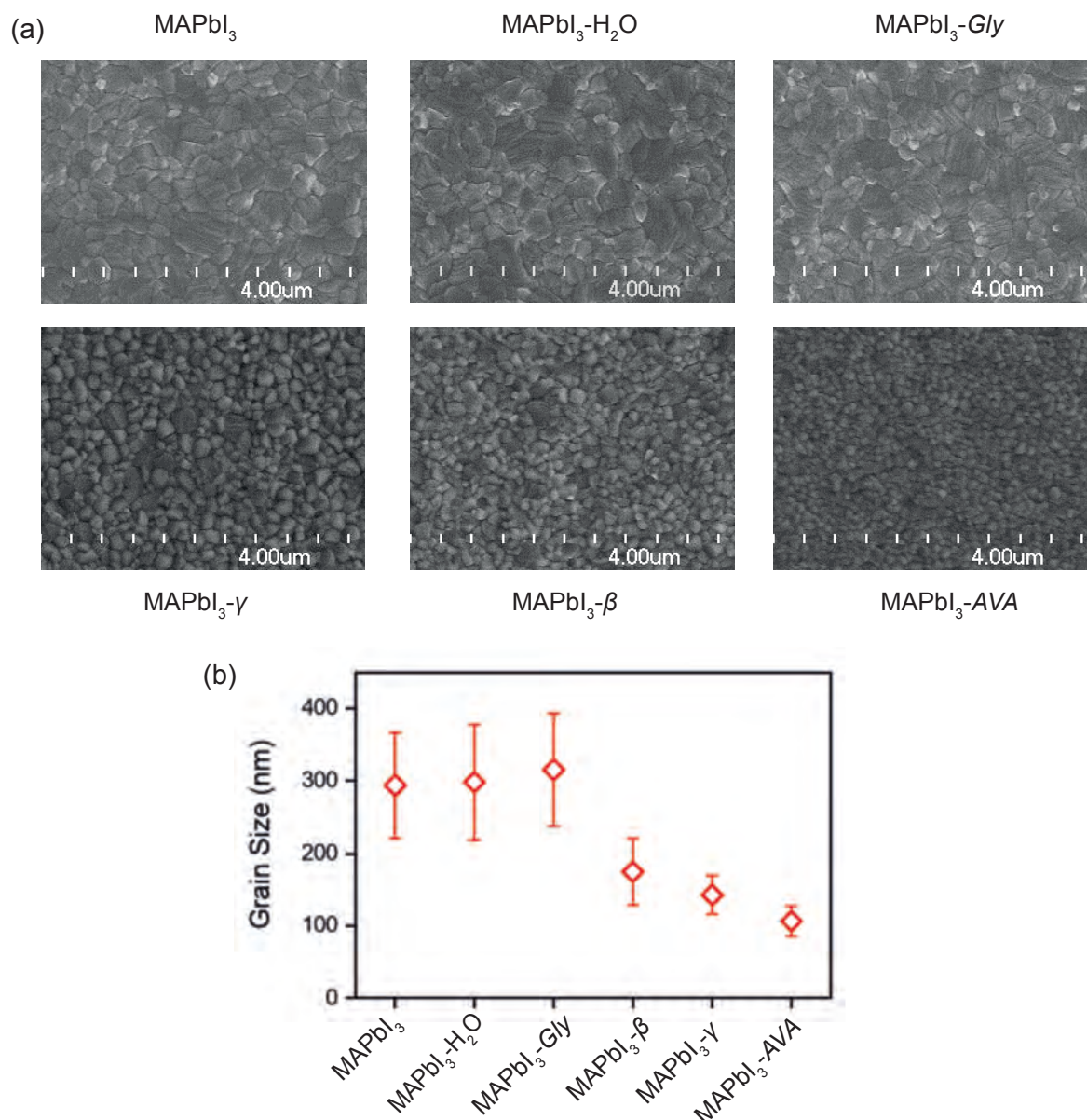


Figure 5.3 (a) SEM (SE-Imaging): Top-down images of the different MAPbI₃ samples fabricated using precursor solutions with organic additives. (b): Average grain size calculated from SEM images. Note that samples were coated with 5 nm of Cr.

5.2 Stabilising Effects of Organic Additives

Device stabilities of samples made only with MAPbI₃ and MAPbI₃-Gly absorber layers are investigated. Both samples were exposed to light soaking under bias (maximum point point (MPP) tracking) and their device data over time are shown in **Figure 5.4**. MAPbI₃-Gly has a higher initial J_{sc} but a lower initial V_{oc} . Even though its J_{sc} drops over time, as is expected, it still maintains a higher value than MAPbI₃. Interestingly, its V_{oc} can be seen to increase by about 1% after 120 h compared to a 2% drop seen in MAPbI₃. MAPbI₃ can be seen to have three different regions of degradation kinetics: (1) a sharp

drop after the first 10 h, (2) an increasing rate of degradation until 40 h and (3) a fairly linear decaying region. In the case of $\text{MAPbI}_3\text{-Gly}$, PCE reduction tends to be slower and owing to the increase in V_{oc} , PCE increases during the first few hours and can then be described by a smaller increasing rate of degradation followed by a similar linear region. Analysing their normalised (to their initial PCE) PCEs, there does not seem to be significant changes in stability, which suggests that there are no significant changes in degradation kinetics where the consistently higher PCE of $\text{MAPbI}_3\text{-Gly}$ arises from its higher initial PCE.

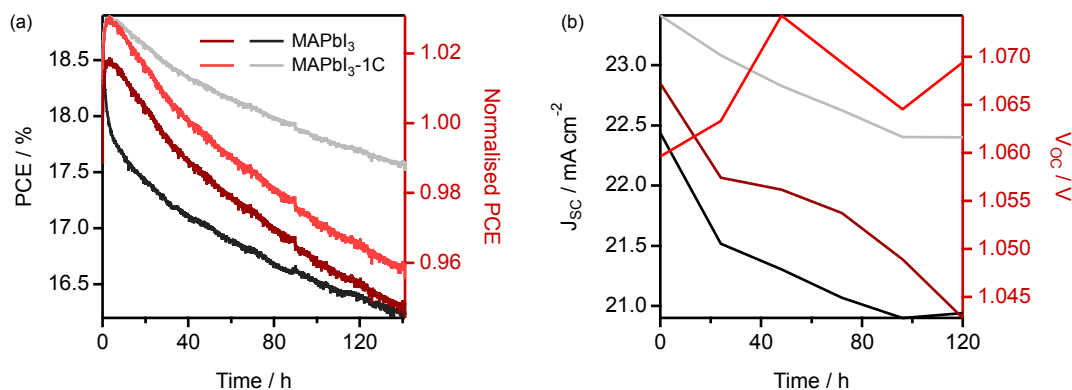


Figure 5.4 Device data: (a) Normalised PCE over time for MAPbI_3 and $\text{MAPbI}_3\text{-Gly}$. Red: normalised PCE. (b) J_{sc} and V_{oc} over time. Red: V_{oc} .

5.2.1 Iodine Diffusion

To understand how the addition of the organic additives affects stability, glycine was added to various MAPbI_3 composition analogues: MAPbI_3 , $(\text{MA})_{0.95}(\text{GA})_{0.05}\text{PbI}_3$, $(\text{FA})_{0.85}\text{Cs}_{0.15}\text{PbI}_3$. The stability of these samples are analysed after light soaking under bias. A total of six different compositions were subjected to testing and their depth profiles measured: MAPbI_3 , MAPbI_3 (+5 vol.% glycine), $(\text{FA})_{0.85}\text{Cs}_{0.15}\text{PbI}_3$, $(\text{FA})_{0.85}\text{Cs}_{0.15}\text{PbI}_3$ (+5 vol.% glycine). These profiles are shown in **Figure 5.5** (Au_x^-), **Figure 5.6** (I_x^-), and **Figure 5.7** (Pb_xI_y^-).

This section thus aims to provide insights into the vertical distribution of ions of the aforementioned sample compositions as a function of operational time. Device stability data for $(\text{FA})_{0.85}\text{Cs}_{0.15}\text{PbI}_3$ -based devices are not available due to instrumental errors. As such, chemical depth profiles of these compositions are not used to correlate any improvements in device stability. Instead, they are analysed for the purpose of furthering the understanding of how organic additives influence chemical depth profiles, particularly the susceptibility of ion diffusion.

Purely based on their depth profiles, there seems to be some degree of correlation between the addition of glycine to the concentration of AuI_2^- ($m/z = 450.73$). This is especially pronounced in

(FA)_{0.85}CS_{0.15}PbI₃-based devices (see **Figure 5.5**).

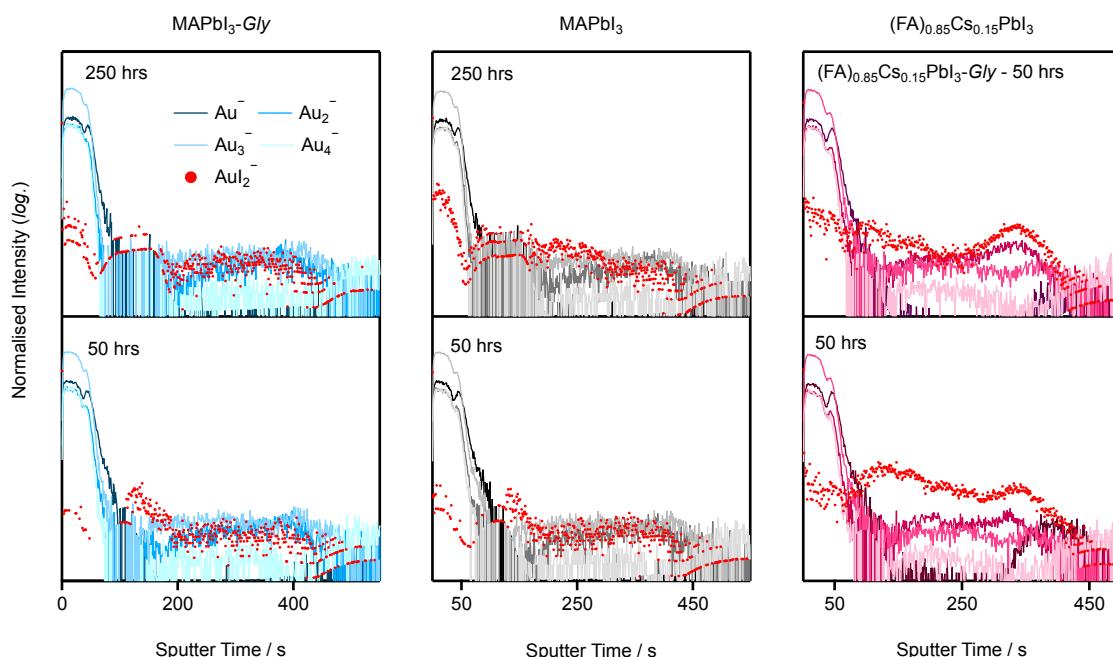


Figure 5.5 **Dynamic ToF-SIMS:** Depth profiles of Au_x^- in devices subjected to lightsoaking and MPP tracking degradation for MAPbI₃, MAPbI₃-Gly, and (FA)_{0.85}CS_{0.15}PbI₃ for periods of 50 h and 250 h.

In fact, one can observe a larger Au^- ($m/z = 196.97$) interfacial width compared to the other devices which is an indication of the breakdown of the electrode/BCP interface which could have arisen from degradation (chemically and morphologically) of the absorber layer resulting in formation of secondary species within the device. I_x^- profiles (**Figure 5.6**) show particular features for I^- ($m/z = 126.92$) and I_2^- ($m/z = 253.8$) at the electrode/BCP interface; the extent of which is not seen in other compositions. These features support the present argument as they may induce morphological changes at the interface that result in a wider Au^- ($m/z = 196.97$) interfacial width.

For all devices, similar to thermally degraded devices as discussed in **Section 6.3**, one can observe accumulation of I^- ($m/z = 126.92$) on the surface of electrodes and both I^- ($m/z = 126.92$) and I_2^- ($m/z = 253.8$) at the electrode/BCP interface (**Figure 5.6**). In particular, in compositions without organic additives, concentration of I^- ($m/z = 126.92$) is much higher within the electrode/BCP/PCBM layers with the exception of FACsPI. The suppressed diffusion of I^- ($m/z = 126.92$) is symptomatic of a more stable absorber layer as it is unlikely to be a measurement artefact of the organic additives during the depth profiling process.

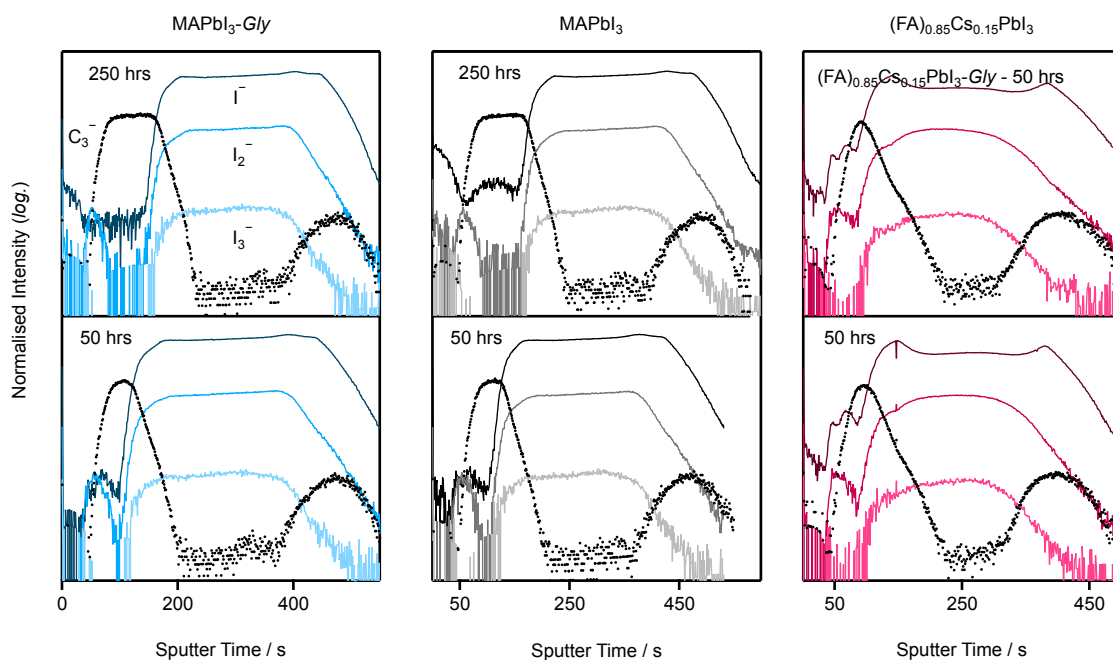


Figure 5.6 Dynamic ToF-SIMS: Depth profiles of I_x^- in devices subjected to lightsoaking and MPP tracking degradation for MAPbI₃, MAPbI₃-Gly, and (FA)_{0.85}Cs_{0.15}PbI₃ for periods of 50 h and 250 h.

The origin of this increased stability and suppression of I^- ($m/z = 126.92$) diffusion is likely to be the passivation of defects/vacancies, specifically $V_I^\bullet$, that would otherwise promote ion diffusion and the formation of superoxide under the action of light.

Analysing $Pb_xI_y^-$ profiles (**Figure 5.7**), there are no significant differences that can be observed. Considering the ratios of Pb-based mass fragments, there does not seem to be any chemical changes within the absorber layer between the samples. Thus, given that significant differences in only AuI_2^- ($m/z = 450.73$) and I^- ($m/z = 126.92$) were observed, diffusion of I^- ($m/z = 126.92$) is likely to be only partly accountable for the reduction in measured device stabilities but are not discussed further. It should be noted that while there is a PbI_2^- interfacial feature at the electrode/BCP/PCBM interface, such a feature was not observed in Au-based devices and based on XPS survey spectra of peeled off electrodes, Pb could not be detected—though this may be due to it being below the detection limit of XPS or that it was removed during the electrode removal process (**Section 6.3.3**).

Finally, the mass fragment $[Gly-H]^-$ from glycine, as reported in **Section 5.3**, is not seen to be distinct in devices made with MAPbI₃-Gly. This is likely due to the reactive nature of the O_2^+ sputter beam and any associated beam-induced damage that introduce mass interferences thus, making detection of $[Gly-H]^-$ difficult.

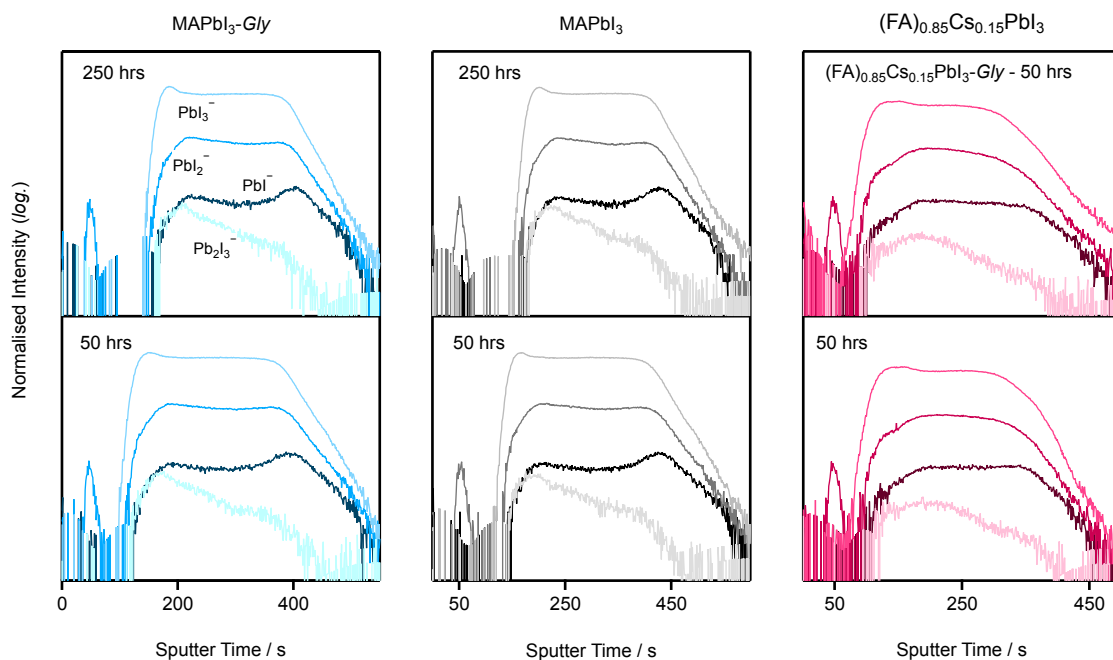


Figure 5.7 Dynamic ToF-SIMS: Depth profiles of $Pb_xI_y^-$ in devices subjected to lightsoaking and MPP tracking degradation for $MAPbI_3$, $MAPbI_3-Gly$, and $(FA)_{0.85}Cs_{0.15}PbI_3$ for periods of 50 h and 250 h.

5.2.2 Thermal Stability

Thermal stabilities of standard $MAPbI_3$ and $MAPbI_3$ with amino acid additives are investigated in this section. Two devices with $MAPbI_3$ and $MAPbI_3-Gly$ underwent thermal annealing at various temperatures for a total of 5 h. Their depth profiles at the electrode region are shown in **Figure 5.8**. There is no apparent difference between the depth profiles at the electrodes and at the absorber layer; in particular there are no observable differences in I_x concentrations or any indication of suppressed I^- ($m/z = 126.92$) diffusion in $MAPbI_3-Gly$. Device data show that at higher temperatures, the FF of $MAPbI_3$ drops drastically while that of $MAPbI_3-Gly$ is more gradual (**Table 5.1**).

That the organic additive has had inconclusive if not, minute, effects on $MAPbI_3$ thermal stability suggests that the energetic barrier against I^- ($m/z = 126.92$) diffusion imparted by $-Gly$ is easily overcome by thermal energy.

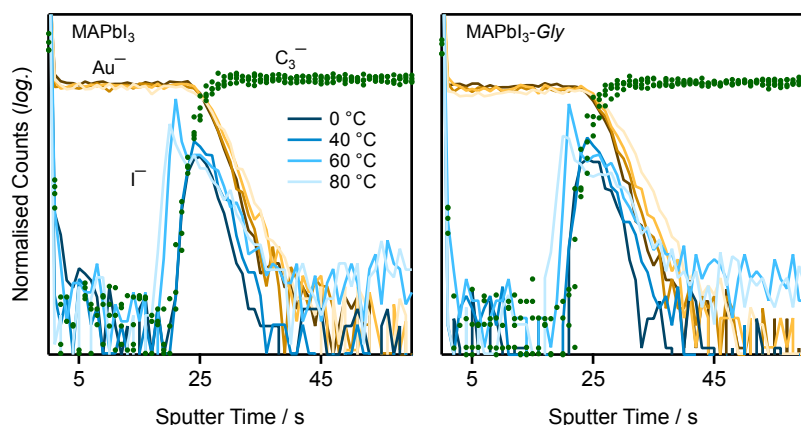


Figure 5.8 **Dynamic ToF-SIMS:** Depth profiles of devices made with (left) MAPbI₃ and (right) MAPbI₃-Gly after thermal ageing at 80 °C for 5 h.

Table 5.1 **Device data:** Measured after thermal ageing for Au-based devices using MAPbI₃ and MAPbI₃-Gly absorber layers. Values are averaged over the number of pixels. Values in brackets are standard error.

Temp. (°C)	Time (h)	V _{OC} (V)	J _{SC} (mA cm ⁻²)	Fill Factor	PCE (%)
ITO/PTAA/PFN/MAPbI ₃ /PCBM/BCP/Au					
0	5	1.07 (±0.001)	19.87 (±1.26)	0.78 (±0.01)	16.59 (±0.97)
40		1.06 (±0.004)	18.81 (±1.58)	0.60 (±0.03)	12.11 (±0.87)
60		1.02 (±0.02)	20.31 (±0.89)	0.36 (±0.09)	7.65 (±2.33)
80		1.01 (±0.01)	19.43 (±0.87)	0.67 (±0.02)	13.39 (±0.30)
ITO/PTAA/PFN/MAPbI ₃ -Gly/PCBM/BCP/Au					
0	5	1.10 (±0.001)	20.07 (±0.51)	0.77 (±0.01)	17.13 (±0.29)
40		1.10 (±0.001)	19.91 (±0.30)	0.74 (±0.013)	16.35 (±0.52)
60		1.04 (±0.02)	19.04 (±1.58)	0.55 (±0.02)	11.02 (±0.71)
80		0.84 (±0.31)	17.06 (±0.48)	0.52 (±0.26)	8.69 (±5.42)

5.3 Mass Spectra Analysis

To show empirical evidence of the presence of these organic additives on the surface of these samples, their mass spectra were obtained from ToF-SIMS. The fundamentals of this technique can be found in **Section 3.3**.

In this measurement, to achieve statistically sound data—given the large number of variables that could influence mass spectra—three indium tin-doped oxide (ITO)/poly(triaryl amine) (PTAA)/MAPbI₃-x samples from each precursor solution were fabricated. In each sample, mass spectra were obtained from four different areas giving a total of twelve mass spectra for each precursor solution. A total of four different precursor solutions were analysed: MAPbI₃, MAPbI₃-Gly (C₂H₅NO₂), MAPbI₃-AVA (C₅H₁₁NO₂), MAPbI₃-NMA (C₁₀H₉N) where chemical composition of each organic additive is given in brackets, and their structures are given in **Figure 5.9**.

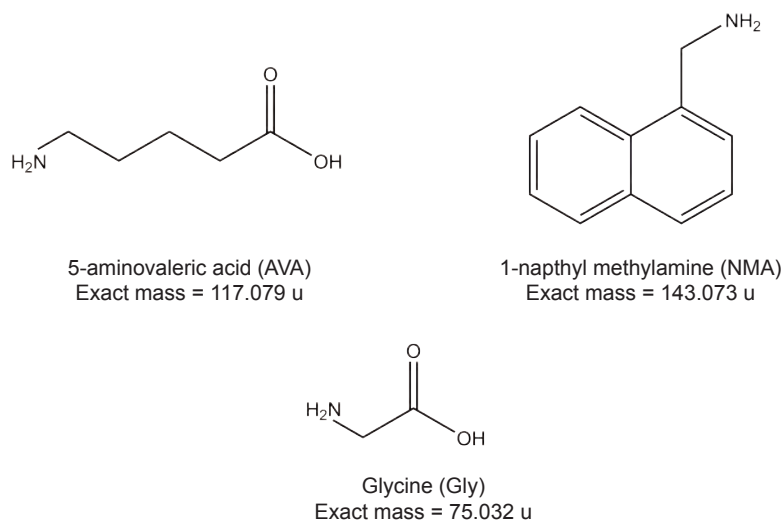


Figure 5.9 Chemical structures of organic additives used for mass spectra analysis with their respective calculated atomic masses.

Measurements were performed with low applied ion dose densities of less than 1.0×10^{12} ions/cm² for all obtained mass spectra, achieving static conditions in which mass spectra obtained are representative of the true surface instead of pre-bombarded areas.

Possible mass fragments (*i.e.* those that are not singly deprotonated/protonated or the parent molecular ion) that produced a mass peak in their mass spectra, from each organic additive are tabulated in **Table 5.2**. The respective fragments that appear to be highest are indicated (*). Their mean peak intensities are shown from **Figure B.5** to **Figure B.12**.

The mean peak intensities of negative and positive mass fragments obtained from different mass fragment references, including those not containing the full backbone carbon chain, are compared. Reference peaks are obtained by identifying peaks in mass spectra whose m/z values correspond to possible permutations of C_wH_xO_yN_z of the organic additives with chemical structural considerations (see **Figure 5.2**).

Table 5.2 Static ToF-SIMS: Tabulation of mass fragments that contain fewer carbon, oxygen, or nitrogen atoms than the respective parent organic molecule. Selection rules: deviation of less than 100 ppm and a minimum peak intensity of 200 counts. (*) Indicates fragment that has highest mean yield from samples made from the respective precursor solution.

MAPbI ₃ -AVA		MAPbI ₃ -Gly		MAPbI ₃ -NMA	
Ion	m/z	Ion	Mass m/z	Ion	Mass m/z
C ₅ H ⁻	61.010	C ₂ HO ⁻	41.004	*C ₇ H ₂ N ⁻	100.030
C ₅ H ₂ ⁻	62.018	C ₂ H ₃ O ⁻	43.019	*C ₈ H ₂ N ⁻	112.031
C ₅ H ₃ ⁻	63.025	C ₂ H ₃ NO ⁻	57.018	*C ₈ H ₄ N ⁻	114.040
C ₅ H ₄ ⁻	64.031	C ₂ H ₂ O ₂ ⁻	58.007	C ₆ H ⁺	73.004
C ₅ H ₅ ⁻	65.041	C ₂ H ₃ O ₂ ⁻	59.015	*C ₆ H ₂ ⁺	74.011
C ₅ H ₆ ⁻	66.047	C ₂ H ₂ O ⁺	42.008	*C ₆ H ₃ ⁺	75.022
C ₅ O ⁻	75.993	C ₂ H ₃ O ⁺	43.018	*C ₆ H ₄ ⁺	76.028
C ₅ H ₅ O ⁻	81.036	[Gly-OH] ⁺	58.023	*C ₆ H ₅ ⁺	77.034
*C ₅ HNO ⁻	91.000	[Gly-O] ⁺	59.031	*C ₆ H ₆ ⁺	78.041
C ₅ HO ₂ ⁻	93.000			C ₆ H ₇ ⁺	79.051
C ₅ H ₂ O ₂ ⁻	94.000			C ₆ H ₈ ⁺	80.054
*C ₅ N ₂ O ⁻	104.006			C ₆ H ₉ ⁺	81.070
C ₅ H ₂ NO ₂ ⁻	108.002			C ₇ H ⁺	74.00
C ₅ H ₃ NO ₂ ⁻	109.009			*C ₆ N ⁺ , *C ₇ H ₂ ⁺	86.008
C ₅ H ⁺	61.012			*C ₆ HN ⁺ , *C ₇ H ₃ ⁺	87.022
C ₅ H ₂ ⁺	62.010			C ₆ H ₂ N ⁺	88.021
C ₅ H ₃ ⁺	63.019			*C ₆ H ₃ N ⁺ , *C ₇ H ₅ ⁺	89.034
C ₅ H ₄ ⁺	64.026			*C ₆ H ₄ N ⁺ , *C ₇ H ₆ ⁺	90.040
C ₅ H ₅ ⁺	65.036			C ₆ H ₅ N ⁺ , C ₇ H ₇ ⁺	91.051
C ₅ H ₆ ⁺	66.041			C ₆ H ₆ N ⁺	92.054
*C ₅ H ₇ ⁺	67.054			C ₆ H ₈ N ⁺	94.064
C ₅ H ₈ ⁺	68.055			C ₈ H ⁺	97.00
C ₅ H ₉ ⁺	69.072			*C ₈ H ₃ ⁺	99.026
C ₃ H ₂ O ₂ ⁺	70.005			*C ₇ N ⁺	98.012
C ₄ H ₆ O ⁺	70.030			*C ₇ HN ⁺	
*C ₃ H ₃ O ₂ ⁺	70.989				
*C ₄ H ₁₀ N ⁺	72.079				
*C ₃ H ₅ O ₂ ⁺	73.023				
C ₃ H ₇ O ₂ ⁺	75.048				
*C ₅ HO ⁺	76.998				
*C ₅ H ₃ O ⁺	79.013				
C ₅ H ₈ N ⁺	82.066				
*C ₅ H ₇ O ⁺	83.056				
C ₅ H ₁₀ N ⁺	84.083				
*C ₅ H ₃ O ₂ ⁺	95.006				
C ₅ H ₈ NO ⁺	98.059				

Mass fragments that contain the full carbon chain of the parent molecules (either deprotonated/protonated or parent ions) and that are distinct to the sample from which they were obtained, are shown in

Figure 5.10 and Figure 5.11.

Using MAPbI₃-NMA as a reference, there seems to be a mass fragment pattern that can be attributed to the addition of NMA to the precursor solution that is distinctly different to that of other precursor solutions. Perhaps due to the structure of NMA, emission of deprotonated parent-like cations and anions, [NMA - xH]⁺ (x = 1 to 5) and [NMA - xH]⁻ (x = 1 to 7), can be observed. Protonated parent-like cations, [NMA + xH]^{+/-} (x = 1 to 2), are also evident in the mass spectra. The formation mechanism(s) are likely to be from already preformed ions, though Brönsted acid-base reactions are possible as well. Additionally, [NMA]⁺ (m/z = 143.066) also appears in the mass spectrum. In particular, it is evident that cationisation processes seem to result in higher cation yield than the yield observed for anions for these samples. The mean intensities of these ions are observed to be higher for MAPbI₃-NMA samples compared to others, strongly suggesting that these ions are derived from NMA additives.

In addition, [C_xH_yN_z]⁺ (x: 6 to 8, y = 1 to 9, z = 0 to 1) fragments also appear in the mass spectrum. This is likely due to the fragmentation of the aromatic functional group of NMA resulting in higher yield of these ions. In comparison, the total number of carbon in glycine and AVA are 2C and 5C, respectively. Thus, formation of [C_xHN]⁺ would not come from fragmentation of the parent molecule(s) and would depend on intermolecular reactions during ion beam-material interactions that are far less likely.

Analysing mass spectra from MAPbI₃-AVA, [AVA + xH]⁺ (x = 1 to 2) and [AVA - H]⁻ (m/z = 116.07) and [AVA]⁻ can be observed. Based on these peak intensities, they are observed to be characteristic to samples made from MAPbI₃-AVA precursors. Similarly, yield of cations seem to be higher than anions.

However, MAPbI₃-Gly is only distinguishable by a small mass peak assigned to [Gly - H]⁻ (m/z = 74.024). Other ions obtained from the parent glycine molecule do not generate mass fragments that are distinct to MAPbI₃-Gly. In fact, possible mass fragments, such as [Gly]⁺ and [Gly - H]⁺ from glycine have mean peak intensities that are highest in samples made from other precursor solutions. A possible explanation is that these fragments can also be found from AVA, NMA, and the organic component of MAPbI₃. The added possibility of the presence of matrix effects where the chemistry of the surfaces in MAPbI₃-AVA and MAPbI₃-NMA enhancing ionisation of these fragments cannot be discounted but in itself confirms the change of surface chemistries through the addition of these organic molecules to precursor solutions.

Based on these organic mass fragments, it can be concluded that the mass spectra of MAPbI₃-Gly, MAPbI₃-NMA, and MAPbI₃-AVA can be distinguished from the others and that the addition of glycine, NMA, and AVA to precursor solutions has an effect on their overall surface composition.

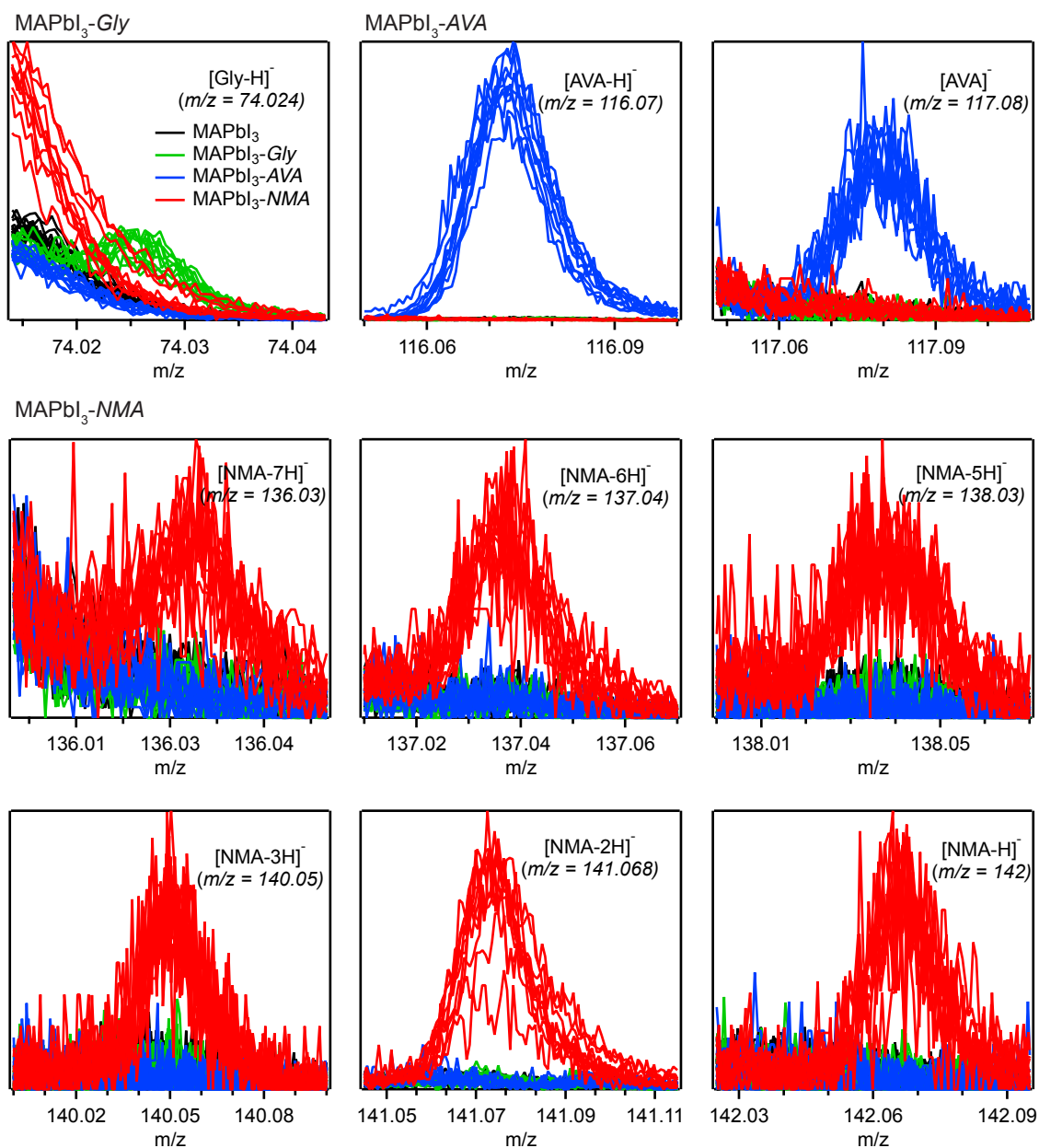
Negative Polarity

Figure 5.10 Static ToF-SIMS (negative polarity): Selected organic peaks identified from fragmentation of or ionisation of organic additives. Mass spectra show that peaks from different organic additives have the highest intensities for samples made from the respective precursor solution. Intensities have been normalised to total counts from each mass spectrum.

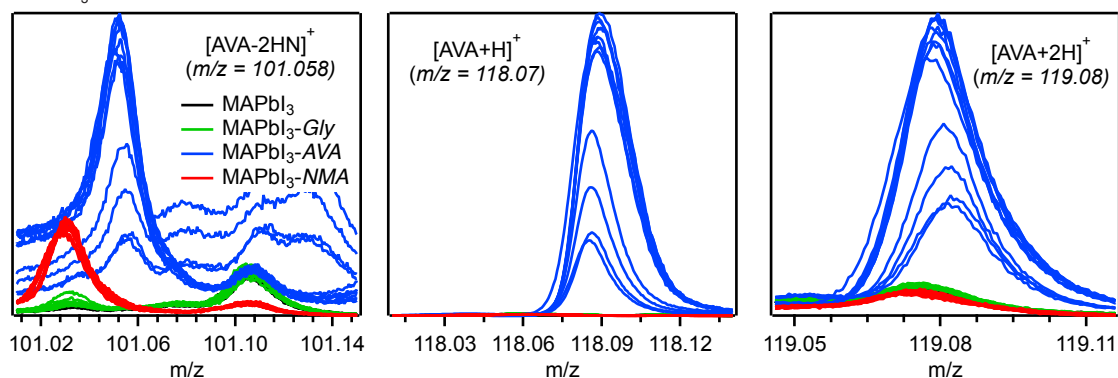
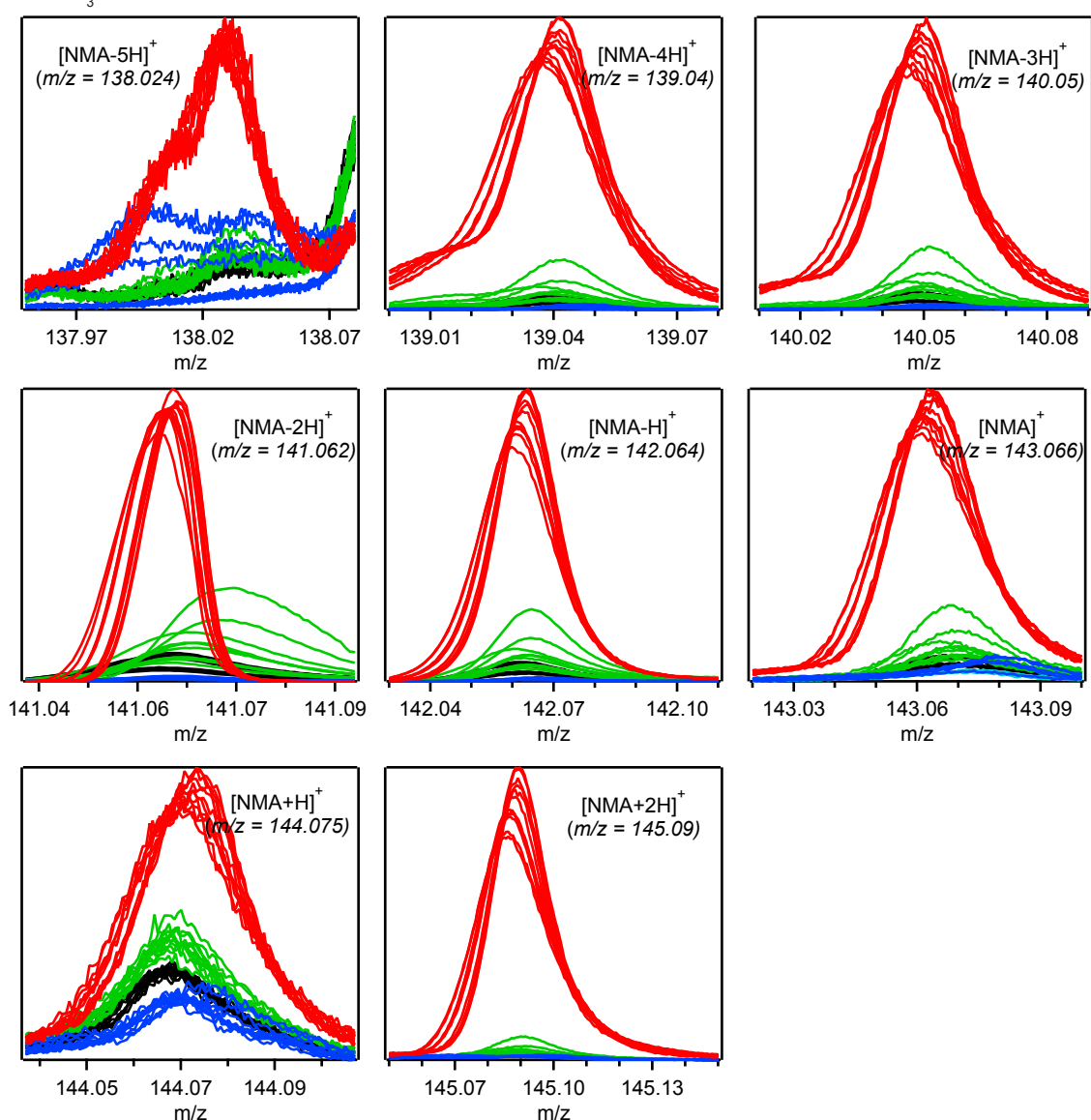
Positive PolarityMAPbI₃-AVAMAPbI₃-NMA

Figure 5.11 Static ToF-SIMS (positive polarity): Selected organic peaks identified from fragmentation of or ionisation of organic additives. Mass spectra show that peaks from different organic additives have the highest intensities for samples made from the respective precursor solution. Intensities have been normalised to total counts from each mass spectrum.

Referring to **Figure B.5** and **Figure B.6**, the yield of these MAPbI₃-based fragments show some trends, in that certain fragments show a lower/higher yield. In the negative polarity, CHI⁻, PbHI⁻, Pb⁻ PbI⁻, PbI₂⁻ ($m/z = 461.80$) are observed to be highest for MAPbI₃ samples while a seemingly contradictory trend is seen for I⁻ ($m/z = 126.92$). In the positive polarity, mass fragments from the organic component of MAPbI₃ suffer mass interferences with the fragmentation and ionisation of organic additives. As such, certain fragments such as CH₄N⁺ and CH₅N⁺ are highest for MAPbI₃-AVA. Given that the matrix of these materials have yet to be thoroughly examined, any further deduction on the surface composition based on these fragmentation patterns would be inaccurate.

Thus, as a final note, using mass fragments derived from MAPbI₃ as reference, there does not seem to be any significant conclusions that can be drawn. Since the ionisation process exploited by ToF-SIMS is inherently influenced by the chemistry of the material surface, further qualification/quantification of matrix effects is necessary. As an extension to this experiment, the evolution of mass spectra of time-resolved degradation of these samples may be able to provide insights into possible degradation pathways. In the next section, MAPbI₃ made from these precursor solutions, including β -alanine and γ -aminobutyric acid additives, are subjected to ion scattering experiments (LEIS).

5.4 Organic Molecules Additives

To exclude the complexity of secondary ionisation probabilities and possible matrix effects, ion scattering was used to further characterise the surface composition of these samples, with the addition of β -alanine, and γ -aminobutyric acid.

Absolute quantification of atomic concentration is not undertaken in this work, rather, relative quantification is given where the ratios of the different scattering peak intensities are calculated which provides inferences about the effects of organic additions on the stoichiometry of Pb and I.

5.4.1 Peak Integral Ratio $R_{I/Pb}$

As mentioned in **Section 3.4**, peak integral scales linearly with concentration of the element of the target atom and that using a ²⁰Ne⁺ beam, no matrix effects should be present, thus one would expect that any decrease in peak integrals should be the result of lower concentration of the element on the surface; since the applied dose was kept at a minimum for good noise-to-signal ratio, thus, sputtering effects are negligible. Consequently, scattering data obtained can be said to be from the first (few) atomic

layers of the sample surface. However, due to the extreme surface sensitivity of the technique, any slight contamination may attenuate peak signals.

Figure 5.12 shows peak integrals from LEIS scattering peaks of all the compositions. The intensity of a scattering peak takes the form:

$$S_i = \frac{I_p}{e} \cdot T_i \cdot R \cdot t \cdot N_i \cdot P_i^+ \cdot \left(\frac{d\sigma_i}{d\Omega} \right) \quad (5.1)$$

I_p = Primary ion current

T = Instrumental factor

R = Roughness factor, with a value of 1 for a smooth surface

t = Acquisition time

N = Atomic concentration

P^+ = Ion-fraction (ratio of ions to sum of ions and neutrals detected) $\frac{S_i^+}{S_i^+ + S_i^0}$

$\frac{d\sigma_i}{d\Omega}$ = Differential cross-section

Thus, I_p , T , and t are constant for all experiments, and can be treated as constants. P^+ has to be obtained empirically and $\frac{d\sigma_i}{d\Omega}$ was calculated from an online calculator [223] ($\frac{d\sigma_{Pb}}{d\Omega} = 0.01030$ and $\frac{d\sigma_I}{d\Omega} = 0.006906$). However, given that P^+ for both elements are unknown and that these parameters should hold constant with the exception of N_i , for which is being calculated, it may be just as meaningful to use peak integral ratios of I : Pb ($R_{I/Pb}$). Therefore, it stands to reason that using $R_{I/Pb} = \frac{S_I}{S_{Pb}} = \frac{I_{int}}{Pb_{int}}$ between measurement runs and between samples is appropriate even without *a priori* knowledge of the parameter values.

5.4.2 I/Pb Stoichiometry

LEIS measurements were performed on multiple samples of six different compositions: MAPbI₃, MAPbI₃-Gly, MAPbI₃-β, MAPbI₃-γ, MAPbI₃-AVA, MAPbI₃-NMA, and PbI₂. Average peak integral values and $R_{I/Pb}$ values are shown in **Figure 5.12**. It should be noted that measurements for all compositions, with the exception of NMA, were performed on multiple samples. Therefore, the peak integral and $R_{I/Pb}$ values are averaged and the standard deviation of the data are reflected in the error bars. $R_{I/Pb}$ was calculated from raw peak integral values (not average), similarly error bars reflect the standard deviation of the ratio between I_{int} and Pb_{int} .

At first glance, one can observe that there are large variations, based on calculated standard deviation

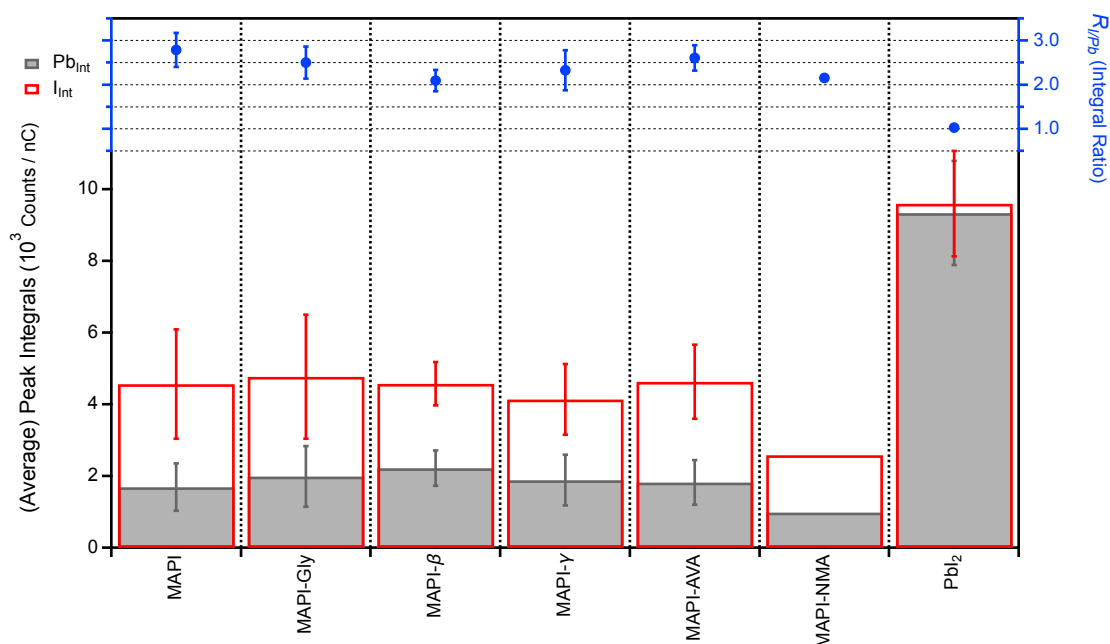


Figure 5.12 LEIS: (Average) I and Pb peak integrals from various MAPbI₃ precursor solutions and average I : Pb ratios ($R_{I/Pb}$) from raw integrals. Error bars obtained from standard deviation of peak integrals and their calculated $R_{I/Pb}$. Data were obtained by $^{20}\text{Ne}^+$ at 5 kV; dose density at 1×10^{13} ions/cm².

values, of peak integrals (Pb_{int} , I_{int}) for all samples, with the exception of PbI₂ (origins of these variations are discussed in further detail in **Section 5.4.3**). However, $R_{I/Pb}$ does not reflect that degree of standard deviation. For instance, the average values (and standard deviation) of I_{int} and Pb_{int} in MAPbI₃ are 4566 ± 1521 nC/counts and 1696 ± 659 nC/counts while its $R_{I/Pb}$ is 2.79 ± 0.38 .

An initial analysis of data from PbI₂ shows that despite variations in peak integral values, the variation in $R_{I/Pb}$ value is negligible and therefore supports the following evaluation of $R_{I/Pb}$ on MAPbI₃ and related compositions and therefore suggests that the factors affecting changes in I_{int} and Pb_{int} occur to similar extent. Also, it should be noted that while its $R_{I/Pb}$ has a value of ~ 1.0 and is not used to infer the relative atomic concentration of I and Pb.

Thus, by comparing the average values of $R_{I/Pb}$ between samples, insights into variations in surface stoichiometry can be obtained—any change in surface concentration of I and Pb *between* samples will scale corresponding peak integrals linearly. Considering that the survivable probabilities of $\text{Ne} \rightarrow \text{I}$ and $\text{Ne} \rightarrow \text{Pb}$ are likely to be different and have not been included in the calculation of $R_{I/Pb}$, that the average $R_{I/Pb}$ for MAPbI₃ ≈ 3.0 is purely coincidental and not a comment of the relative atomic concentration of I and Pb *within* a sample.

Based on illustrated mean $R_{I/Pb}$ and respective standard deviation, there is still a large uncertainty and limits interpretation of any associated trends. Though, one can assert that adding organic additives into

MAPbI₃ precursor solutions has an effect on the surface stoichiometry of the I and Pb. Additionally, MAPbI₃- β and MAPbI₃ have distinctly different surface stoichiometry of I and Pb, beyond the uncertainty of the dataset. A similar conclusion can be made about MAPbI₃- β and MAPbI₃-AVA.

However, given the overlapping $R_{I/Pb}$ variability of MAPbI₃-Gly and MAPbI₃- γ , any possible trends or relationship between $R_{I/Pb}$ and the backbone carbon chain length of the organic additives is limited.

Additionally, it can be observed that mean $R_{I/Pb}$ for all precursor solutions are different from PbI₂ which is an indication that the surface is devoid of a crystalline layer of PbI₂—often regarded as a degradation product and can occur when thermal annealing persists for an extended period of time.

A deviation of $R_{I/Pb}$ from that of MAPbI₃ can only come from a non-concomitant change in concentration (N) of Pb and I atoms on the surface. Thus, a decrease in relative concentration suggests either N_I is lower or N_{Pb} is higher. As the latter seems improbable, the likelier reason for a lower $R_{I/Pb}$ is a lower concentration of I detected on the surface. A point of distinction: it is not known if the global surface composition of the sample has changed *i.e.* a preferential growth of grains in certain crystallographic directions, however, if it were the case, a change from say, an MAI-rich surface to a PbI-rich surface [98] would still induce a change in $R_{I/Pb}$.

Taking that preferred grain orientation has not occurred during the nucleation and growth processes, a lower $R_{I/Pb}$ in this case would have occurred due to the organic additives preferentially bonding to I atoms. As a consequence, the effect of such bonding would be the attenuation of the scattering peak intensity for I with Ne→I suppressed by the organic molecule on the surface.

Location of Organic Molecules

A further note: spatial variations cannot be captured in these measurements as the beam conditions have not been optimised for it. Even when optimised, the highest spatial resolution that can be obtained is on the order of microns. The discussed scattering data and mass spectra thus only provide evidence of their presence on the surface of the sample but are unable to spatially resolve their location *i.e.* whether they exist as secondary phases or if they completely coat the surface of a grain. However, noting that V_{oc} is enhanced with MAPbI₃-NMA, and a reduction in J_{sc} is only observed with increasing concentration [220], increased photostability is observed with MAPbI₃-AVA [219], and the observed changes in $R_{I/Pb}$, the bonding of these molecules on surface defects are likely, though not necessarily discounting the possibility of secondary phases.

Possible bonding mechanisms are suggested for hydrogen and ionic bonding between functional groups

and the dangling bonds on the surface that would explain the observed increased photostability and enhancement in device properties [219, 220].

Carboxyl groups ($R\text{-COOH}$) can undergo hydrogen bonding with I atoms on the surface due to being under-coordinated which is inevitable for surface atoms. Amine groups ($R\text{-NH}_2$) are protonated in solution ($R\text{-NH}_3^+$) and can undergo hydrogen bonding with atoms with dangling bonds. Furthermore, ionic bonding can occur between -COO^- and V_I^* /under-coordinated Pb (**Figure 5.13**).

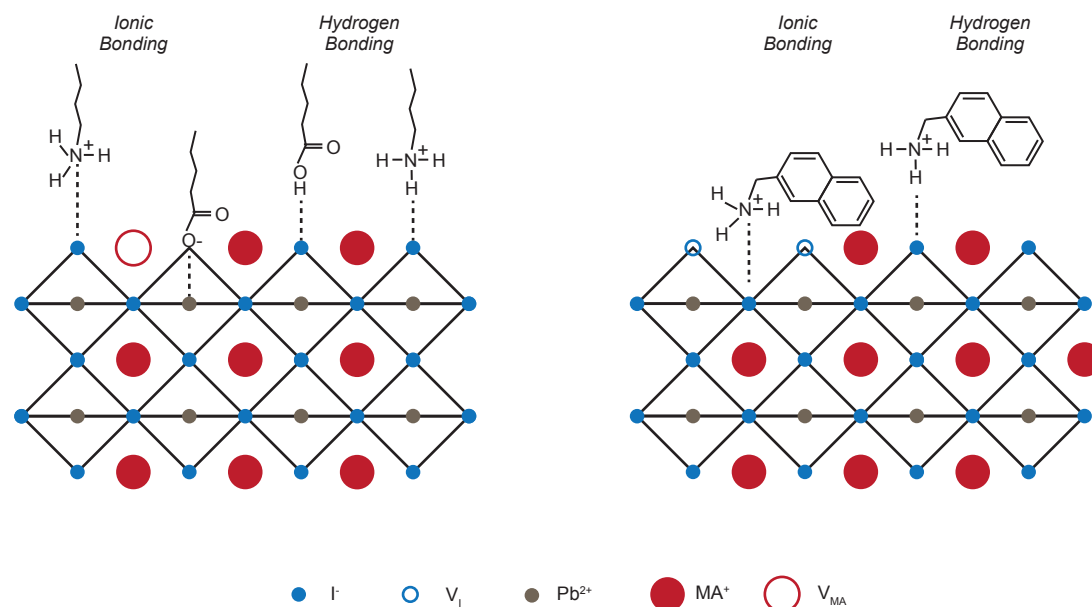


Figure 5.13 Illustration of suggested bonding mechanisms of organic molecules on the surface of MAPbI₃.

With an organic molecule bonded to a surface undercoordinated I (I^-), the $\text{CH}_3\text{NH}_3^+\text{-I}$ bonding may be stabilised and may not take place in acid-base reactions resulting in the deprotonation of the MA group and oxidation of I^- ($m/z = 126.92$) to I_2 in solution [131]. Finally, the apparent behaviour of increasing $R_{I/Pb}$ from MAPbI₃- γ may be related to the increasing carbon chain length and its efficacy in forming $I\cdots\text{HOOC}$ bonds where it has been shown that with increasing alkyl chains, the dimerisation constant of carboxylic acids in polar solvents increases [224]. This suggests that AVA and γ -aminobutyric acid may form a higher concentration of dimers in solution and therefore compete with forming ionic or hydrogen bonds with crystal defects. It is also possible that -CONH intermolecular bonds are more preferably formed with a separate amino acid molecule in solution, which further reduces the probability of forming MAPbI₃-amide or hydrogen bonds. Additionally, ionic bonding between the positively charged sites of the molecules with under-coordinated I or V_{MA}' may occur.

5.4.3 Peak Integral Variations

This section discusses the variability of peak integrals and by consequence $R_{I/Pb}$ of MAPbI₃ samples, between samples and measurement runs. These variations are illustrated in **Figure 5.14(b)**. Each Pb_{int} and I_{int} pair is identified by S_xT_y where S_x is the sample number and T_y refers to the measurement run. Thus, recurrences of the same identifier (e.g. S₁T₁) refer to repeat measurements on different areas of the same sample.

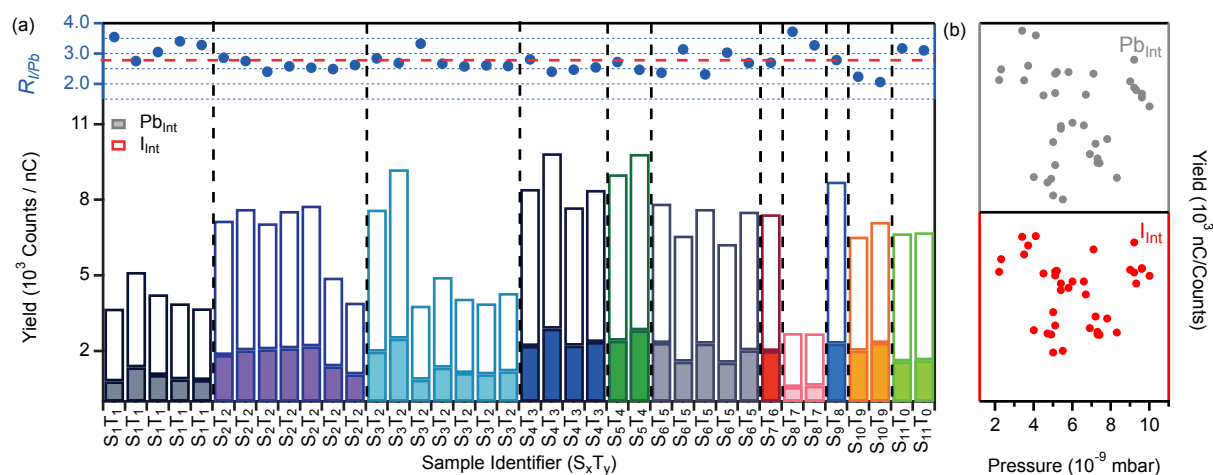


Figure 5.14 LEIS: (a) Peak integral and integral ratio variations between samples and measurement runs where repeated measurements on different areas on the same sample are identified by S_xT_y (x = Sample, y = Measurement) (b) Peak integrals as a function of main chamber pressure. Vertical lines demarcate different samples while colour is used to group samples in the same measurement run. Red dashed line indicates average $R_{I/Pb}$ (2.78).

Based on the illustrated data, there are large peak integral variations between samples and measurement runs. The possible influence of varying vacuum conditions in the main analysis chamber is further shown in **Figure 5.14(b)** where peak integrals are plotted against the pressure of the analysis chamber during the measurement run. One might expect that a lower pressure would yield higher peak integrals due to better detection conditions. However, the plots show a random distribution with no physically meaningful trend. Thus, it can be safely concluded that the reported chamber pressures have little effect on the observed variations.

Therefore, it is likely due to:

1. Exposure to atmosphere during sample preparation leading to adsorption of organic compounds onto the surface which is unavoidable as there is no current solution in the instrumentation that allows for sample transfer without atmospheric exposure and may explain the observed variability. This is especially so when LEIS has extreme surface sensitivity to the the top atomic layer of the surface.

2. Length of time in ultra-high vacuum conditions which could be a large contributor as time-resolved XPS measurements show that volatility is exacerbated under vacuum conditions and higher defect density brought about by particle bombardment **Figure 4.11**, though only under X-ray irradiation, but as these measurements have a much larger information depth, the volatility of species on the first atomic layer would not yield any photoemission spectral differences. This can be confirmed by performing a time-resolved scattering experiment.
3. Primary beam current fluctuations during measurement. Despite measuring beam current before and after the experiment, and setting dose densities to below 1×10^{13} ions/cm² which also rules out concerns of beam damage inasmuch as any beam damage persists to the same extent for all reported peak integrals, any significant fluctuations during measurement would influence the overall dose and yield (which is normalised by the beam current) and therefore influence peak integrals.

On the other hand, $R_{I/Pb}$ for PbI₂ shows negligible variations even though peak integrals show otherwise (**Figure 5.12**). Further analysis of $R_{I/Pb}$ variations show that it is more forgiving, though variations are observed as well and rationalises the use of $R_{I/Pb}$ trends when such factors have yet to be quantified. This may be due to the fact that variations of peak integrals are likely influenced by surface contamination which would attenuate I and Pb scattering peaks to the same extent.

5.5 Surface Composition of MAPbI₃ and Analogues

To better understand how organic molecules can affect MAPbI₃, the surface composition of MAPbI₃ has to be better investigated. There exist numerous works on photoemission studies. They often report non-stoichiometry (see **Table 2.2**), though often—with a few exceptions—the effects of vacuum and X-rays have not been taken into consideration. Even so, the information depth of X-ray photoemission measurements can be up to several nanometres and not the *true* surface of the sample (first atomic layer). By analysing $R_{I/Pb}$ as a function of dose density (ions/cm²), one can obtain scattering information from the first atomic layer where dose density $\rightarrow 0$ ions/cm² and depth-sensitive scattering information with increasing dose. Measurements were performed on MAPbI₃ and PbI₂ (**Figure 5.15**).

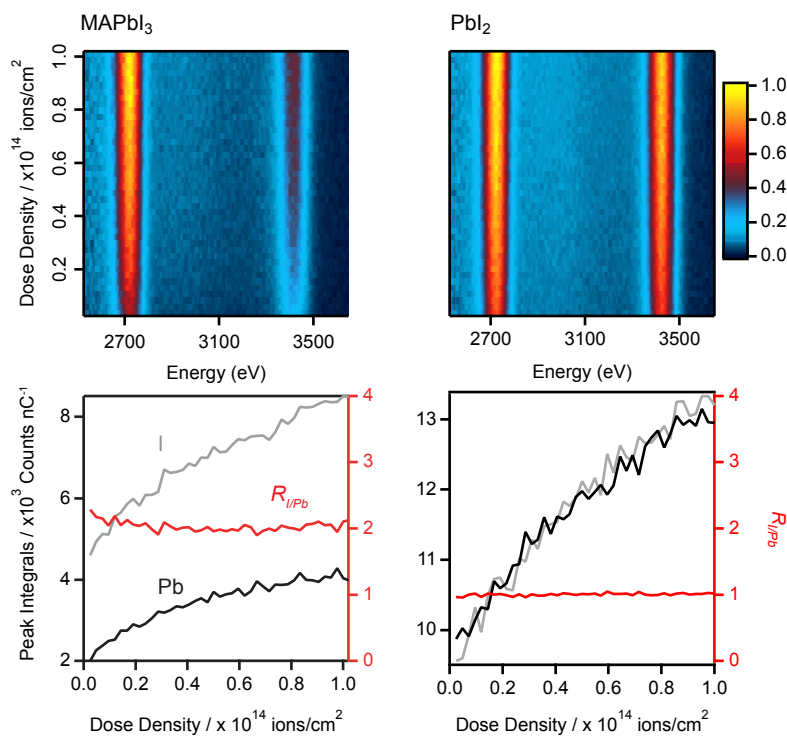


Figure 5.15 LEIS scattering data obtained from MAPbI₃ and PbI₂. (Top) Intensity plots of normalised (to maximum height) LEIS scattering data and corresponding (bottom) peak integrals and peak integral ratio ($R_{I/Pb}$). Spectra obtained from $^{20}\text{Ne}^+$ at 5 kV.

Naturally, $R_{I/Pb}$ for PbI₂ is different from that of MAPbI₃ as their crystal structures and therefore the surface compositions are different. Furthermore, $R_{I/Pb}$ for PbI₂ remains unchanged over the dose density range applied while that of MAPbI₃ shows a slight decay and reaches a plateau at around 0.4×10^{14} ions/cm². It is unclear if this plateau is the scenario where the interaction of $^{20}\text{Ne}^+$ beam $\rightarrow$ MAPbI₃ reaches a steady state. Though, if one considers that the degradation of MAPbI₃ leads to PbI₂, one might expect $R_{I/Pb}$ to approach that of PbI₂, especially so with the surface sensitivity of LEIS. Additionally, based on photoemission spectra of post- $^{20}\text{Ne}^+$ bombarded areas (Section 4.3)—also noting that Ne atoms may penetrate deeper into the material causing cascade mixing and taking into consideration the larger information depth of XPS—chemical bonding of Pb and I from 10 nm up to the surface remains relatively unchanged with the exception of the attenuation of C 1s and N 1s signals. This is likely due to beam effects.

Thus far, only Pb and I have been analysed. An attempt was made to characterise scattering peaks from C and N where $^4\text{He}^+$ is required due to its lower atomic mass based on equation **Equation 3.6**. Because of the large concentration of organic components (MA^+) with H atoms in organometallic halide materials, a large exponential decay at lower energies from the ionisation and detection of H^+ is observed which may mask any C or N scattering peaks. To circumvent this issue, a time-of-flight filter (ToF-filter) was

used to remove any ionised H⁺ secondary ions (**Figure 5.16**). Based on the spectra, the large H⁺ decay is now suppressed and a scattering peak from C can be observed at an energy slightly lower than the value due to minor energy losses from inelastic processes. Evidently, despite using the ToF-filter, N is still undetectable which is likely due to the large in-depth background signal which underlines the limitation of probing inorganic-organic hybrid materials using LEIS.

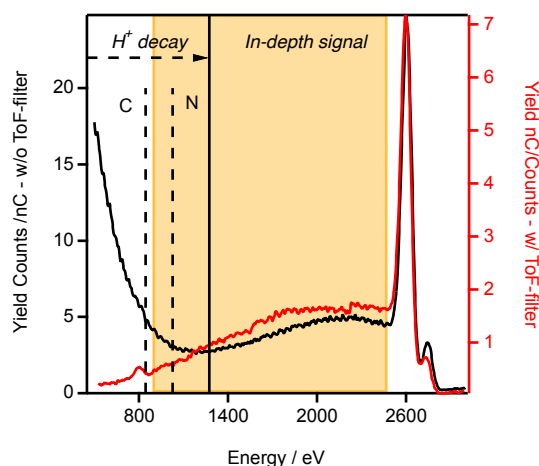


Figure 5.16 LEIS Spectra obtained from $^4\text{He}^+$ at 3 kV with and without the ToF-filter. Only C can be observed. Dose density at 1×10^{15} ions/cm².

However, as Cs is often used in substituting MA⁺ cations for a more stable crystal structure, these mixed compositions are further analysed to overcome the aforementioned limitation. Due to the narrow energy difference (ΔE) between Cs and I scattering peaks from both $^4\text{He}^+$ and $^{20}\text{Ne}^+$ (**Section 3.4**), $^{40}\text{Ar}^+$ was used instead. In **Figure 5.17**, it can be observed that all three compositions have two distinct regimes in which absolute peak integrals increase linearly until 2×10^{14} ions/cm², followed by a relatively flatter region in which Pb_{Int} remains fairly constant while I_{Int} has a slow increase with increasing dose. Interestingly, $R_{I/Pb}$ is more than 15 at very low dose which arises from a very low initial Pb_{Int}. Without knowing the survivable probability of backscattered $^{40}\text{Ar}^+$ (P^+) for Pb, a judgement on the actual surface composition becomes tricky. However, having observed a similar $R_{I/Pb}$ trend for $^{20}\text{Ne}^+$ scattering (to a lesser degree), it is highly likely that there could be a concentration gradient of I from the surface to subsurface regions.

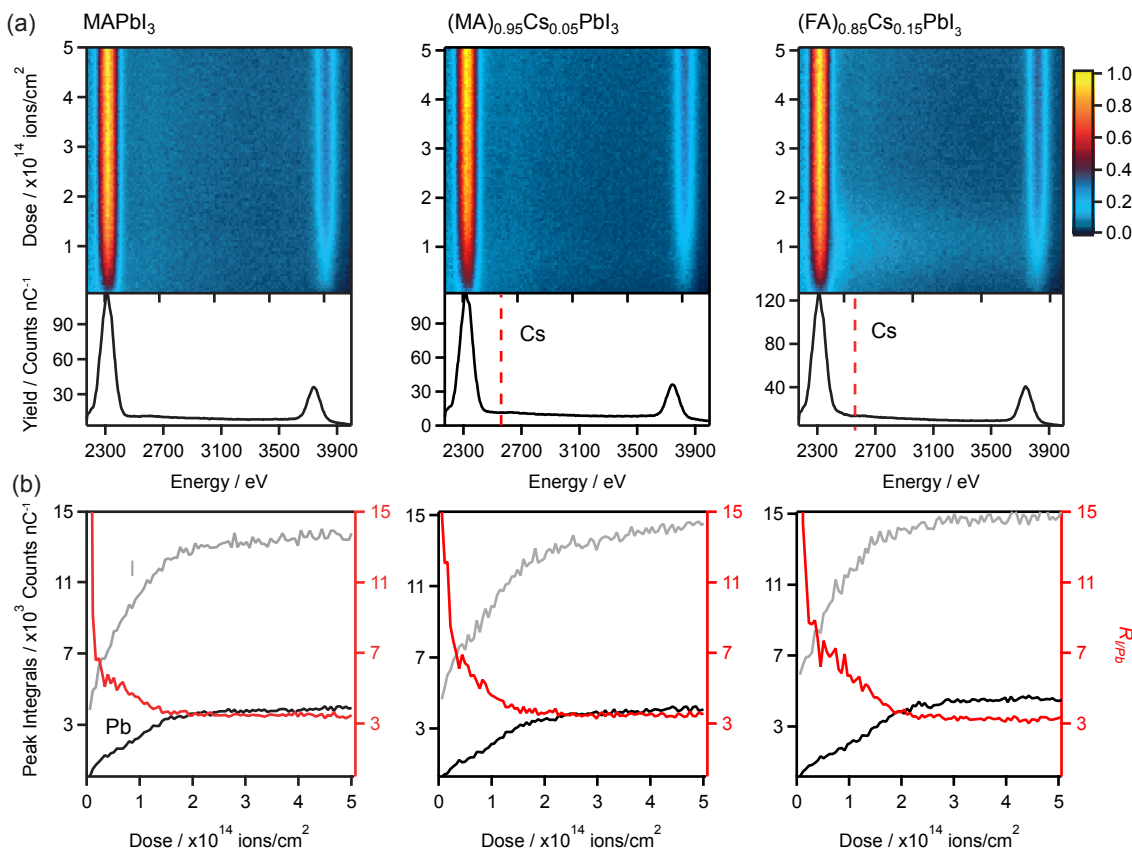


Figure 5.17 LEIS Spectra: (a) Intensity plots of normalised (to maximum height) LEIS spectra and corresponding (b) peak integrals and peak integral ratio ($R_{I/Pb}$). Scattering data obtained from ⁴⁰Ar⁺ at 8 kV.

5.5.1 'A'-Site Identification

The scattering peak for Cs (indicated with a red dashed line) cannot be detected in both (MA)_{0.95}Cs_{0.05}PbI₃ or (FA)_{0.85}Cs_{0.15}PbI₃ which could be due to the overlapping background intensity from scattering on Pb atoms and in-depth inelastic scattering, but it could suggest that the composition on the surface is devoid of any Cs atoms. Though, it should be noted that I_{Int} increases slightly for both compositions compared to MAPbI₃ at higher doses; Cs could be convoluted in the scattering peak of I where its background signal is contributing to the apparent increase in I intensity. These samples underwent oxygen plasma treatment for a total of 15 min and intensity plots are shown in **Figure 5.18**.

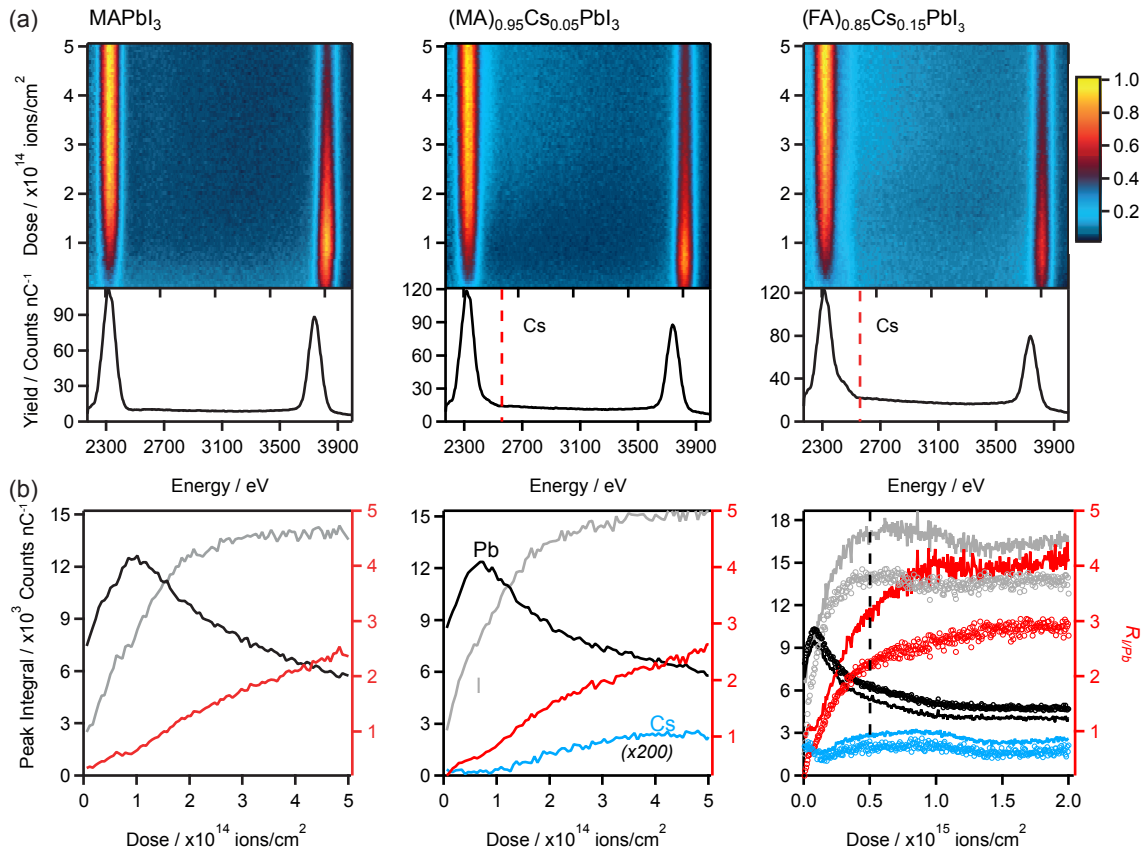


Figure 5.18 LEIS Spectra: Post-O treatment. **(a)** Intensity plots of normalised (to maximum height) LEIS spectra and corresponding **(b)** peak integrals and peak integral ratio ($R_{I/Pb}$). Spectra obtained from $^{40}\text{Ar}^+$ at 8 kV. Unfilled markers show integrals from peak fitting procedure 2.

A few features stand out:

1. I_{Int} reaches the same maximum at approximately the same dose which suggests that the oxygen plasma treatment has had little effect on it.
2. Pb_{Int} at low dose is much higher than before and peaks at around 1×10^{14} ions/cm² followed by a gentle decrease. The physical process behind this phenomenon is unclear and understanding of ion beam interactions in the emission of secondary ions is not applicable as they are fundamentally different techniques though actual sputtering of surface atoms by the incident $^{40}\text{Ar}^+$ is likely to occur with increasing dose, leading to surface or chemical modification.
3. At sufficiently high dose densities (1×10^{15} ions/cm²), $R_{I/Pb}$ plateaus at a value of approximately 3, similar to pre-oxygen treatment. This may suggest that despite possible surface modification as discussed in (2), and based on a lack of chemistry modification when using $^{40}\text{Ar}^+$ (Section 4.3.2), sample surface stoichiometry is I-rich compared to bulk and that $R_{I/Pb} \approx 3.0$ for bulk when using $^{40}\text{Ar}^+$.

4. A shoulder off the scattering peak of I attributable to scattering from Cs atoms can be observed which exhibits a similar trend with Pb_{Int} pointing to oxidation of Cs atoms. However, it is surprising that the scattering peak for Cs is only obtained after surface modification though it provides a clue as to the composition of the surface.
5. By using a higher current monoatomic Ar ion beam as a sputter source, higher dose densities can be obtained which provides more in-depth information (**Figure 5.19**) and that is applied to a sample that has a higher concentration of Cs substitution (20%). Each spectrum obtained constitutes one scan; analysing the first scan (3.4×10^{14} ions/cm²), it can be observed that the scattering peak from Cs is absent and only appears after the second scan (6.8×10^{14} ions/cm²). In comparison, the very first scan shows definitive I and Pb scattering peaks. Thus, the profile seen in post-oxygen treatment can be rationalised as having the same effect as applying a sufficiently high dose to remove the surface (and possibly a few atomic layers). Consequently, these observations suggest that the surface (in Cs-substituted compositions) are devoid of any Cs atoms.

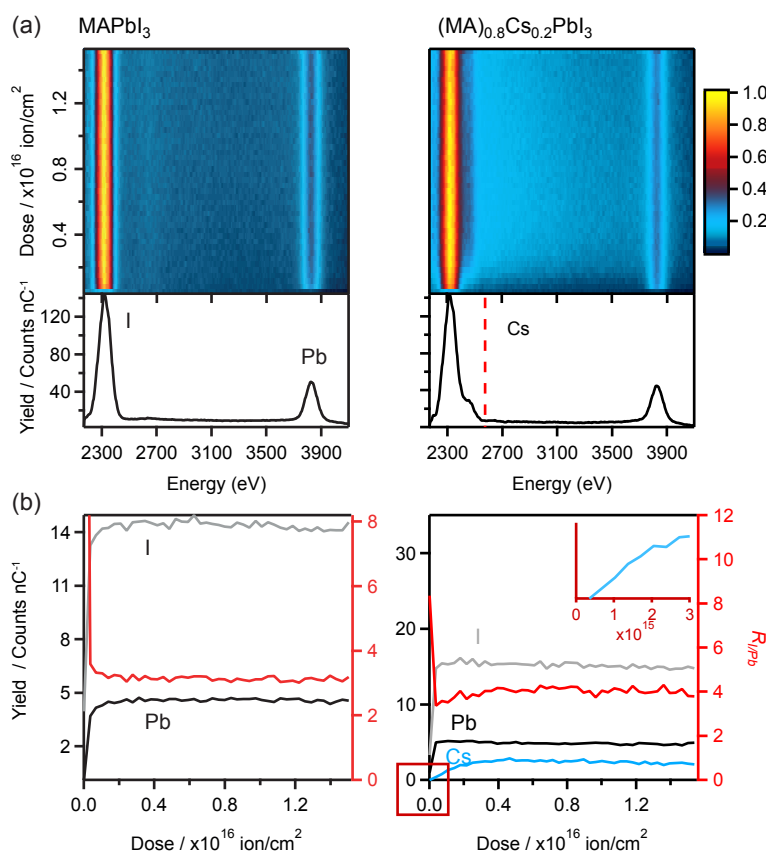


Figure 5.19 LEIS Spectra of MAPbI₃ and (MA)_{0.8}Cs_{0.2}PbI₃. (Top) Intensity plots of normalised (to maximum height) LEIS spectra and corresponding (bottom) peak integrals and peak integral ratio ($R_{I/Pb}$). Spectra obtained from ⁴⁰Ar⁺ at 8 kV.

5.6 Conclusions

The effects of adding organic molecules to the precursor solutions on the surface composition of MAPbI₃ have been explored in greater detail in this chapter. Depth profiles obtained from ToF-SIMS showed that with addition of glycine to MAPbI₃ precursor solution, devices made with these absorber layers showed markedly reduced I⁻ diffusion when tested under MPP-tracking and light and oxygen environmental stressors. Thermal stabilities seem to be largely unaffected, though, further testing needs to be carried out for more conclusive results.

Based on static ToF-SIMS measurements which provide surface sensitive chemical information, mass fragments from organic molecules are detected at higher mean normalised-intensities for the corresponding samples. This provides evidence for their location within the MAPbI₃ sample. For a more detailed analysis on the relative stoichiometry of I and Pb ($R_{I/Pb}$) between the various samples, scattering data from LEIS was analysed. It showed that precursor solutions with organic additives were characterised by I-deficient scattering data suggesting an I-deficient surface. However, no trends (in relation to the backbone carbon chain length of the organic additives) could be deduced from the dataset due to observed variability in $R_{I/Pb}$.

The results discussed here are in agreement with the *hypothesis* that such organic molecules with various functional groups of (–COOH) and (–NH₃⁺) when used as an additive in MAPbI₃ precursor solutions, passivate surface defects [219, 220]. This was reasoned in the hypothesis because the consequence of adding organic additives is an enhanced stability against the action of light and oxygen degradation mechanisms. However, as the instrument has a poor spatial resolution, the presence of such organic molecules as secondary phases between MAPbI₃ grains cannot be disregarded.

Finally, there are difficulties in the detection of organic components (MA⁺) on the sample surface which makes *absolute* quantification of surface composition near impossible. This may be circumvented by using a pure inorganic composition (e.g. CsPbI₃) but may not be relevant to the surfaces measured in these hybrid materials. Further analysis of Cs-substituted compositions showed that the surface is likely MA⁺-deficient *i.e.* a surface that is dominated by Pb–I.

More extensive characterisation should be performed on different excess precursor ratios and to better qualify the effect of carbon chain length on the bond-formation (with MAPbI₃) probabilities, further scattering experiments should be carried out on MAPbI₃ samples fabricated from different carbon chain length additives and different functional groups.

Chapter 6

Degradation and Diffusion in Organometallic Halide Devices

6.1 Motivation

There are many factors that contribute to degradation of organometallic halide based devices; many of which are a result of the (intrinsic) instability of the material to (extrinsic) factors such as hydration, oxygen, light, and a combination of these. Electrode metal-migration and halide-migration are of particular interest as the factors controlling them are both external (temperature, illumination, operational time, atmosphere) and internal (choice of interlayers, material composition, processing method).

For a standard *p-i-n* structure, indium-doped tin oxide (ITO)/c-TiO₂/m-TiO₂/(FA)_{0.83}(MA)_{0.17}Pb(I_{0.83}Br_{0.17})₃/2,2',7,7'-tetrakis[*N,N*-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (Spiro-OMeTAD)/Au, it was argued that the reduction in device performance after thermal ageing at 70 °C for a period of 24 h was due to accumulation of Au clusters within the absorber layer. When a thin (10 nm) Cr layer was deposited between the Au contact and hole-transport layer (HTL), marked improvements in device stability and temperature resistance were observed [168]. Based on minimal changes in the X-ray diffraction (XRD) pattern and with time-of-flight secondary ion mass spectrometry (ToF-SIMS), it was suggested that the inhibition of diffusion and consequent agglomeration of Au⁻ ($m/z = 196.97$) provided a direct improvement in device stability. A similar effect was observed by Cacovich *et al.* [166] where they observed Au clusters using scanning transmission electron microscopy high-angle annular darkfield (STEM-HAADF) at the mesoporous TiO₂ and defect sites for which an

electric-field induced mechanism of Au diffusion was hypothesised.

There have also been strategies to improve stability of devices by preventing oxygen and water ingress through the non-uniform HTL (e.g. Spiro-OMeTAD) using barrier layers between the electrode e.g. MoO_x [225]. Yang *et al.* showed that with poly(3-hexylthiophene) (P3HT) as the HTL, the device had better retention of its optical properties compared to poly(triarylamine) (PTAA) or Spiro-OMeTAD which, was attributed to the inhibition of water ingress [154]. These suggest that both morphology and chemistry of the interlayers greatly affect device stability but they are not covered in greater detail in this thesis. The formation of metal-halide compounds have been shown to be detrimental to device performance thus, the choice of counter electrodes therefore becomes critical as there are additional routes for degradation should a non-uniform transport layer be used or through thermally-induced or electrically-induced diffusion.

In a more fundamental study, Zhao *et al.* investigated the degradation reaction of a range of metals deposited onto MAPbI₃ and observed the formation of metallic lead on Al/CsPbBr₃ and Al/CsPbI₃ samples, and to a lesser degree Ag/MAPbI₃ [172]. Consequently, it was suggested that redox reactions of metal and Pb²⁺ occur readily under ambient conditions resulting in *electrochemical* degradation of the MAPbI₃ layer. Such findings imply that the more stable lead-based analogues (e.g. FAPbI₃) are not exempt from metal-induced degradation, should metal from the top electrodes diffuse into the absorber layer.

Indeed, ion-diffusion (mostly, iodide anions I⁻) readily occurs throughout a device [226–228] but can also be accelerated by temperature and degradation of the organometallic halide absorber layer. Thus, a large issue to overcome is the apparent mobility of I⁻ under operation and even storage. It has been shown that this is accelerated by environmental stressors such as hydration and temperature [168]. Diffused halide ions have the ability to form metal-halide compounds with the top metal electrode [164] that are wholly undesirable. It is possible to inhibit the intrinsic volatility of iodide by using more stable composition, for instance halide migration in FAPbI₃ occurs to a lesser degree than MAPbI₃ due to the larger FA⁺ cation providing a more stable crystal structure [136] however, they are generally less efficient than MAPbI₃ devices.⁹

For inverted *p-i-n* structures, it was observed that devices employing Al, Ag, and Au electrodes are characterised by an *s-shape* J-V curve after 4 h of constant illumination [229]. They attributed this feature to the creation of a permanent dipole from the reaction of I⁻ with the metal electrode at the electrode/[6,6] phenyl-C61-butyric acid methyl ester (PCBM) interface. Boyd *et al.* [161] reported Ag diffusion into the absorber layer of an inverted device structure (ITO/NiO_x/FA_{0.75}Cs_{0.25}Sn_{0.5}Pb_{0.5}I₃/C₆₀-

⁹The effects of such stabilising strategies are not considered to any reasonable extent in this work.

PCBM/SnO₂/ITO/Ag) after 1000 h of thermal ageing at 85 °C in the dark and under N₂ atmosphere. They observed that with metal electrodes (Au, Ag, Cu), the devices inevitably degrade. The authors further suggest that metal diffusion can be inhibited through morphological engineering to obtain higher quality interlayers.

6.1.1 Scope of Work

It has been shown that degradation processes from metal electrodes and the absorber-layer are pressing concerns in device operational and storage stabilities. There have been many studies of standard *n-i-p* planar and mesoporous devices but a thorough investigation, with a detailed examination into the resultant and causal changes at the interfaces, into these processes for inverted *p-i-n* planar devices is lacking.

The following work attempts to uncover additional strategies for inhibiting both metal and halide diffusion that are simpler by nature. By performing X-ray photoelectron spectroscopy (XPS) and dynamic ToF-SIMS measurements, the formation of interfacial species that can be correlated with device degradation is shown. In particular various metal-halide mass fragments that have not been previously reported are examined more thoroughly. Only thermal degradation in the absence of light and atmospheric conditions, and light and voltage bias-induced (in ambient air) degradation processes are investigated. The effects of hydration accelerating the decomposition of organometallic halide absorber layer are not discussed in any detail.

The possible effects of the different matrix and fragmentation and sputtering behaviour of these multilayer devices are discussed insofar as these processes may influence qualitative understanding of the data and related degradation mechanisms. No attempt is made to quantify concentration as it is non-trivial and most quantification methods are known to depend on relative sensitivity factors (RSF) that are empirical by nature, thus, any mention of concentration is done in a qualitative manner and always made in comparison to an untreated pristine sample.

6.2 Electrode Dependent Degradation

There have been a number of studies discussing the suitability of different electrodes on both inverted and standard structure devices. In this section, an in-depth compositional and chemical analysis, into the interfacial effects of illumination and voltage bias, on device degradation is given. Four electrode

configurations of Cu (100 nm), Ag (100 nm), Al (100 nm), and a bilayer of Ag (100 nm) on a thin layer of Cu (10 nm) for the device structure ITO/PTAA/poly[(9,9-bis(3'-(*N,N*-dimethylamino)propyl)-2,7-fluorene)-*alt*-2,7-(9,9-dioctylfluorene)] (PFN)/MAPbI₃/PCBM/bathocuprine (BCP)/electrode, are investigated. An illustration of the device structure and a cross-section SEM SE-imaging are shown in **Figure 6.1(a)** and **Figure 6.1(b)**, respectively. These devices were subjected to maximum power point (MPP) tracking in ambient air with 40-50% RH, under continuous LED illumination—its intensity was adjusted to ensure their J_{sc} was kept at a value that would be obtained from air mass 1.5 (AM 1.5G) illumination. Their PCE(%) as a function of time were obtained and shown in **Figure 6.1(c)**. J-V measurements of pristine devices are illustrated in **Figure 6.1(d)** indicating that initial device properties were similar.

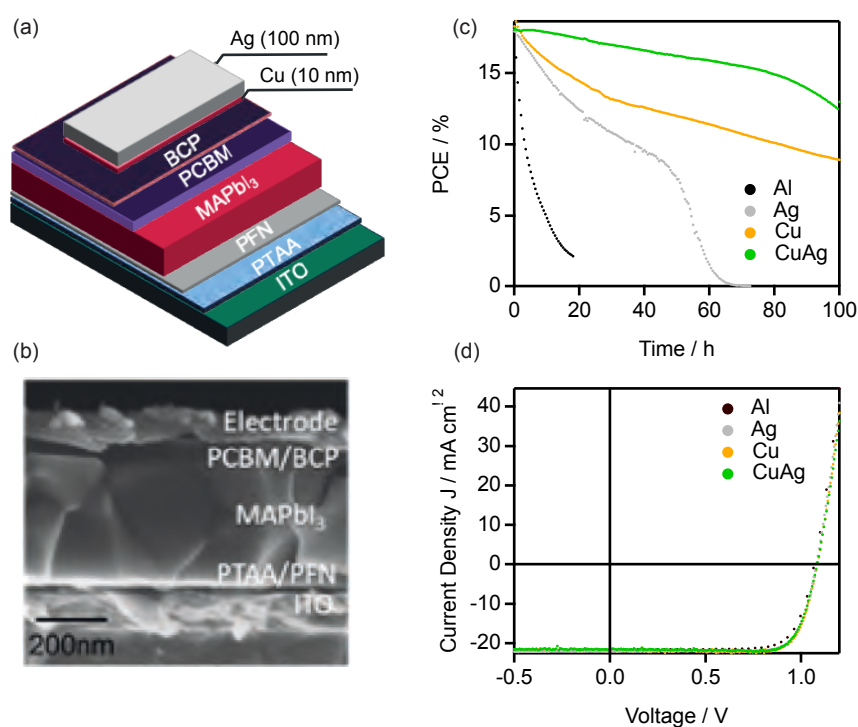


Figure 6.1 (a) Schematics of CuAg device that underwent MPP ageing. (b) Cross-section SEM (SE-Imaging) of a pristine device showing the different layers. (c) J-V characteristics of pristine devices. (d) Stability of PCE (%) a function of time when undergoing MPP ageing.

It is no surprise that Al metal is unsuitable without any form of encapsulation as it is susceptible to oxidation and its operational lifetime is testament to that. Ag metal degrades with two kinetic regimes: first a slow decay from 0 h to 50 h with a 20% reduction of its initial and a drastic linear reduction from 50 h to 60 h. Despite its susceptibility to oxidation, Cu metal degrades with two regimes as well but with a gentler decay in the linear region. With the bilayer configuration of Cu_{10nm}Ag_{100nm}, there is only one linear regime and a 85% retention of its initial PCE after 70 h of ageing.

ToF-SIMS was used to qualify the relative degradation in devices made with these electrode configurations by measuring devices with a minimal period of time after fabrication and devices that have undergone illumination under bias. Mass fragments used for layer identification in the devices are shown in **Table 6.1**.

6.2.1 Single Electrode Configuration

It can be observed that all pristine devices are characterised by sharp profiles which are a good indication that the layers have undergone minimal degradation and/or diffusion throughout the device and that the beam conditions used are optimal. The relatively flat profiles indicate that there is no accumulation of beam damage (from either the sputter or primary beams) on the surface of the material for if it were present, one would expect a profile gradient that is higher at the top and lower towards the end.

Further, their electrode and PCBM layers do not have any signal enhancements at interfaces indicating the absence of matrix effects. However, an apparent increase in intensity of I^- ($m/z = 126.92$) close to the substrate interface is observed and a similar apparent increase of $Pb_xI_y^-$ mass fragments is observed at the PCBM/MAPbI₃ interface. Observing profiles of degraded devices, the decaying gradient of PbI_3^- ($m/z = 588.71$) is less severe, suggesting that this feature is not merely an artefact of the sputtering process.

The calculated interface width—which is a metric for determining the extent of interlayer degradation—is conventionally obtained by calculating the time taken for the profile to decrease from 84% to 16% of the maximum intensity (obtained from the linear steady-state region) [230] and corresponding values for different interfaces are given in **Table 6.2**.

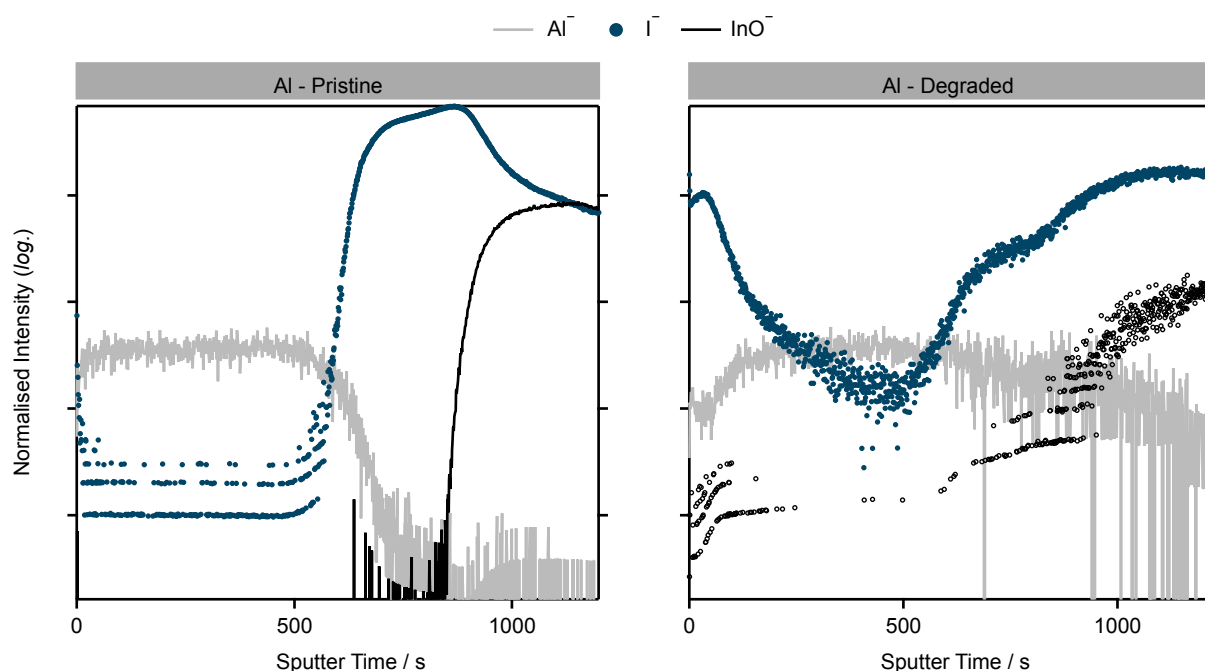
Table 6.1 ToF-SIMS: Secondary ions used for layer identification. *Possible mass interference (discussed further in **Section 6.3.4**).

Mass Fragment	m/z	Device Layer / Compound
Cu^-	62.93	Cu electrode
Ag^-	106.91	Ag electrode
Al^-	26.98	Al electrode
C_3^-	36.00	BCP/PCBM hole-transport layer
I^-	126.92	MAPbI ₃ absorber
PbI_3^-	588.71	MAPbI ₃ absorber
InO^-	130.91	ITO patterend substrate
CuI_2^-	316.77(*)	Metal-halide(II)
AgI_2^-	360.74	Metal-halide(II)

Table 6.2 Interface widths (in seconds) calculated from the width between 16% and 84% of the maximum intensity.

Electrode Config.	Sample	Electrode/-	AgCu/-	-/PCBM	PCBM/MAPbI ₃
Cu	Ref.	29	-	24	27
	Degraded	30	-	24	39
Ag	Ref.	14	-	10	24
	Degraded	26	-	15	33
Cu ₁₀ Ag ₁₀₀	Ref.	14	11	11	16
	Degraded	21	13	21	27

First, profiles obtained from the degraded Al-based device (**Figure 6.2**) confirm the complete device performance degradation. Apart from significant cumulation of I^- ($m/z = 126.92$) at the surface of the device, profile broadening of Al^- , to the extent of the whole thickness of the device is also evident. This suggests that intermixing of the different layers has occurred, likely to be brought about by Al-induced degradation/oxidation.

**Figure 6.2** Dynamic ToF-SIMS: Depth profiles of pristine and degraded Al-based devices. Intensities have been normalised to total counts at each data point and plots have been set to same scale.

Next, consider a single electrode configuration with Cu (**Figure 6.3**): after 70 h of ageing, while the different layers can still be distinguished, their profiles are significantly different; notably at the electrode and at the MAPbI₃ layer. There is significant accumulation of I^- ($m/z = 126.92$) and $m/z = 316.77$ on the surface of the electrode. On the whole, the Cu/BCP/PCBM interface has not changed as interfacial

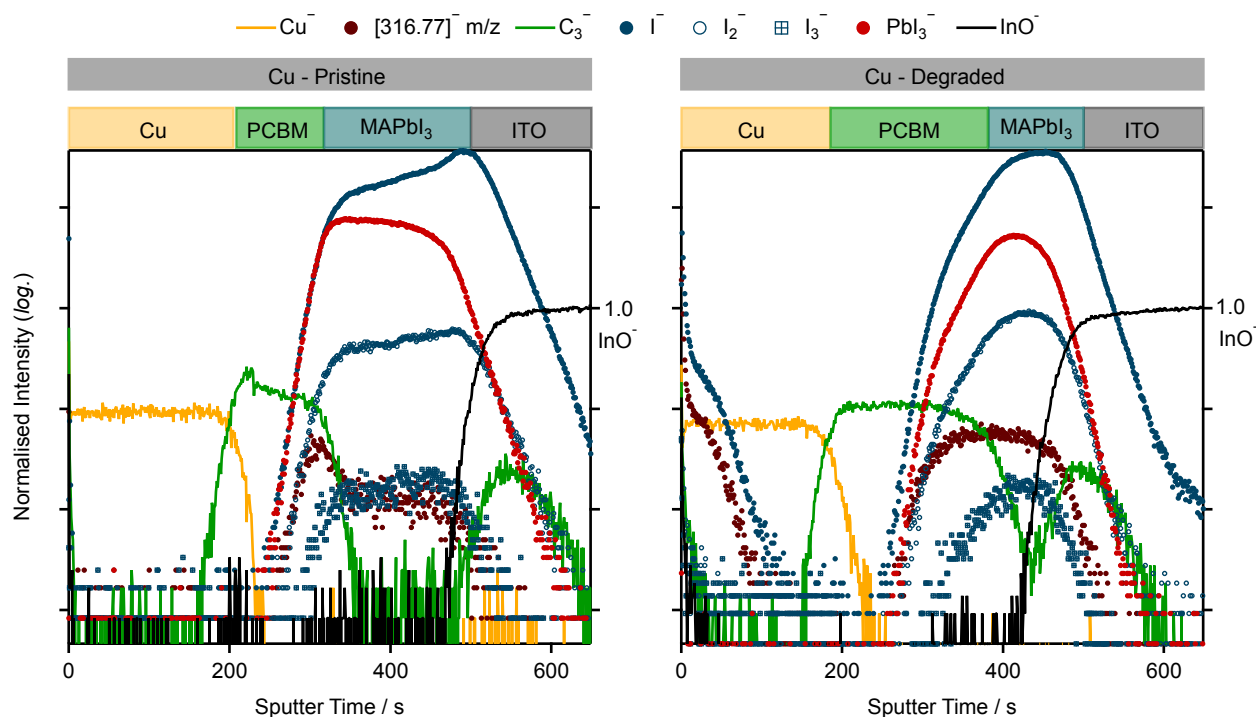


Figure 6.3 Dynamic ToF-SIMS: Depth profiles of pristine and degraded Cu-based devices. Intensities have been normalised to steady-state region of InO^- .

widths (**Table 6.2**) remain largely similar. On the other hand, the interfacial width of C_3^- ($m/z = 36.00$) at the PCBM/MAPbI₃ interface has increased as it can be seen to gradually decay through the MAPbI₃ layer. While $m/z = 316.7667$ has been identified at the PCBM/MAPbI₃ interface in both devices, there is still uncertainty about the compound or if it is a matrix effect but there is an observable increase in its intensity after degradation. Compared to the pristine device, the profile of I^- ($m/z = 126.92$) in the MAPbI₃ layer can be seen to extend towards an earlier sputter time than PbI_3^- ($m/z = 588.71$). I^- , I_2^- ($m/z = 253.8$), I_3^- ($m/z = 380.72$), and PbI_3^- ($m/z = 588.71$) profiles are also visibly less uniform. These features suggest a degraded MAPbI₃ layer.

Comparing Cu profiles to those of Ag (**Figure 6.4**), degraded Ag shows similar features to that in degraded Cu—notably, increased I^- ($m/z = 126.92$) and AgI_2^- ($m/z = 360.74$) intensities at the electrode surface and larger PbI_3^- ($m/z = 588.71$), I^- ($m/z = 126.92$), and I_2^- ($m/z = 253.8$) interfacial widths. On the other hand, the profile of I^- ($m/z = 126.92$) is much more diffused compared to Cu where the concentration at the PCBM layer is *not negligible* as compared to pristine with degraded Ag and Cu-based devices. This also coincides with a larger Ag^- ($m/z = 106.91$) interfacial width (**Table 6.2**). In fact, profiles of PbI_3^- ($m/z = 588.71$), I_2^- ($m/z = 253.8$), I^- ($m/z = 126.92$), and Ag^- ($m/z = 106.91$) now intersect—a strong indication of cross-diffusion between layers which is not seen in Cu (**Figure 6.3**).

From XRD data (**Figure 6.8**), the degraded device with Cu electrodes show a slight diffraction peak

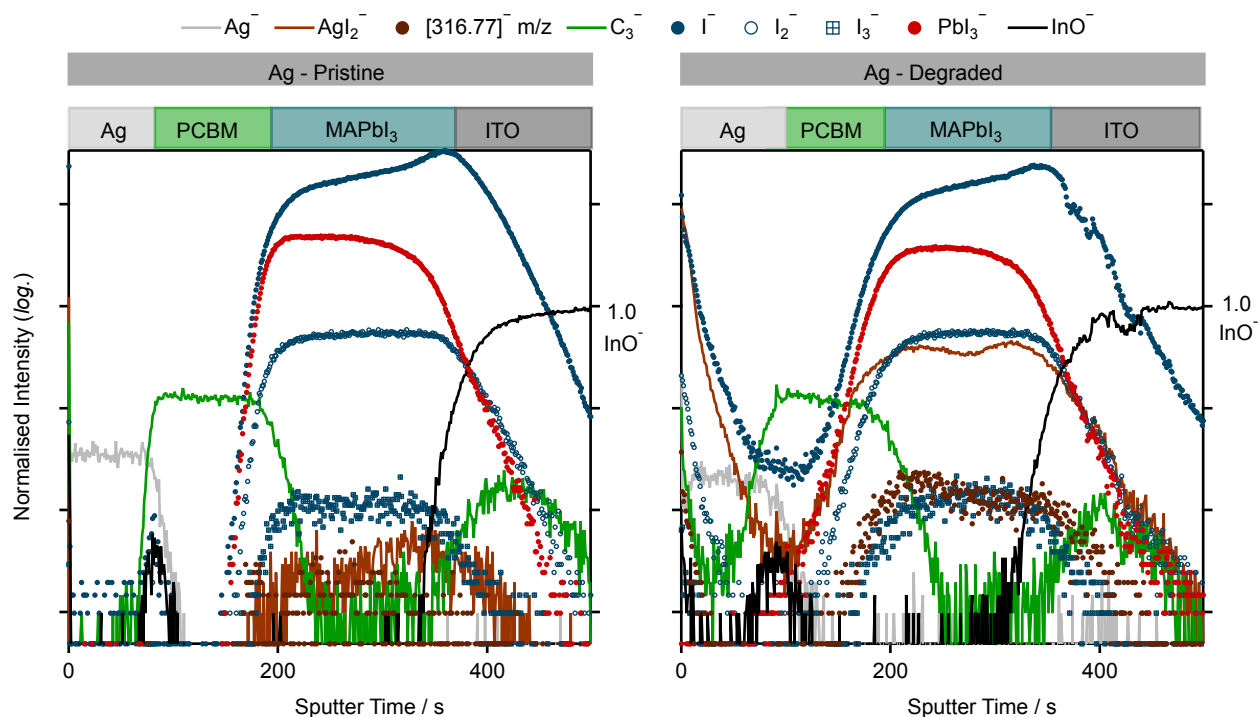


Figure 6.4 Dynamic ToF-SIMS: Depth profiles of pristine and degraded Ag-based devices. Intensities have been normalised to steady-state region of InO^- and plots have been set to same scale.

(111) attributed to CuO which is known to be highly insulating. This would contribute to the overall degradation of the device in terms of its conducting properties. Even though the oxidation of Ag is thermodynamically possible, a peak for Ag_2O was not observed. This could mean that either the oxide layer is amorphous which would not produce a diffraction pattern or that the concentration is below the detection limit for XRD. Even though characteristic peaks for both metal halides are absent in their respective diffraction patterns, the enhanced intensities of I^- ($m/z = 126.92$), CuI_2^- ($m/z = 316.77$), and AgI_2^- ($m/z = 360.74$) at electrode surfaces support the supposition that amorphous AgI and CuI exist within the electrodes. It should be noted that since an O_2 sputter beam was used, oxidation as a result of atmospheric oxygen cannot be analysed without instrumentation interference.

Analysing ToF-SIMS *cumulative over time* ion images (see **Figure 6.5**), the total ion image shows spatial inhomogeneity where certain areas show increased total number of counts. If it were a case of surface contamination, one would expect the propagation of this feature to all ions—through preferential sputtering in those areas—but a lack of any inhomogeneity in C_3^- ($m/z = 36.00$) and Ag^- ($m/z = 106.91$) suggest otherwise. That there is an inverse relationship between the intensities of AgI_2^- ($m/z = 360.74$) and I^- ($m/z = 126.92$) with PbI_3^- ($m/z = 588.71$) and PbI_2 in that area, suggests that the increased intensities originate from the degradation of species with correspondingly decreased intensities.

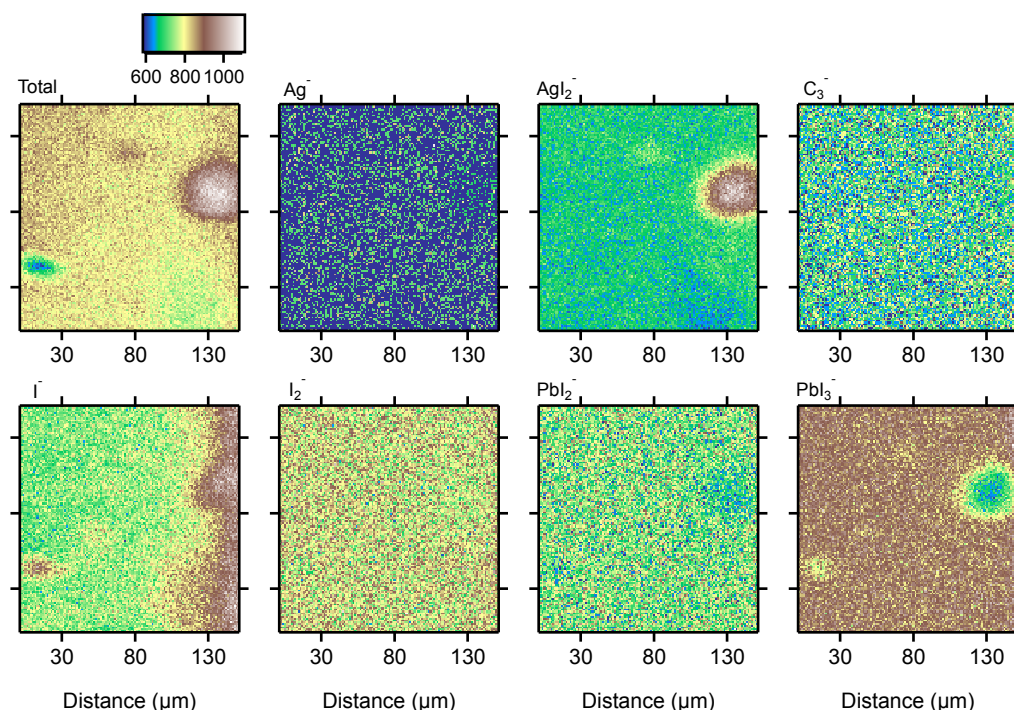


Figure 6.5 ToF-SIMS Ion Images (x,y) of degraded Ag-based device. Cumulative ion images showing spatially resolved inhomogeneities.

A YZ (Z: time) slice was taken as shown in **Figure 6.6** to show cross-sectional ion images, cumulative over the x-axis. Similar to their corresponding cumulative ion images, where PbI_3^- ($m/z = 588.71$) is shown to have suppressed intensity within the absorber layer, there is a correlation with enhancement of I^- ($m/z = 126.92$) and AgI_2^- ($m/z = 360.74$) signals extending to the surface.

It would seem reasonable to argue that the localised inhomogeneity originates from the degradation resulting in the formation of AgI but, it would be unreasonable to conclude that the feature is completely dominated by AgI—a more thorough analysis into possible errors is provided in **Section 6.2.4**. Such inhomogeneity was not observed in the total ion image from the degraded Cu-based device; the caveat being only a small sample area was measured.

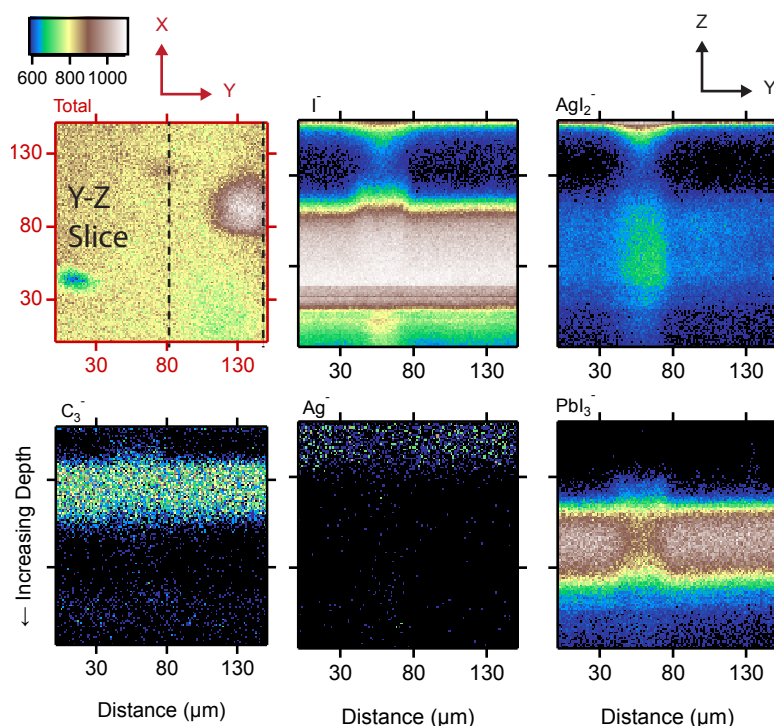


Figure 6.6 ToF-SIMS Ion Images (y,z-depth) of degraded Ag-based device. Cumulative ion images show spatially resolved inhomogeneities. Areas with reduced PbI_3^- ($m/z = 588.71$) intensity correspond to areas with enhanced AgI_2^- ($m/z = 360.74$) and I^- ($m/z = 126.92$) intensities—an indication of the degradation of MAPbI_3 .

Thus, ion diffusion as shown by depth profiles and the related formation of metal-halide compounds at the electrode can certainly contribute to the degradation of devices over time. The formation of an insulating layer of CuO on Cu electrodes is also a contributing factor to its degradation. While Ag_2O was not observed, depth profiles show a larger interfacial width for Ag^- ($m/z = 106.91$) with a more diffused I^- ($m/z = 126.92$) profile. These suggest a breakdown of the Ag electrode and likely contributed to poorer device stability compared to Cu .

6.2.2 Bilayer Electrode Configuration

By depositing a thin layer of Cu (10 nm) first, on BCP then Ag (100 nm) on top (**Figure 6.7**), device stability was improved noticeably. Depth profiles of the degraded device now seem similar to that of Cu . While I^- ($m/z = 126.92$), and AgI_2^- ($m/z = 360.74$) can still be found on the surface of Ag , diffusion of I^- throughout the thickness of the device is suppressed to a larger extent, especially within the PCBM layer. The concentration of AgI_2^- ($m/z = 360.74$) within the MAPbI_3 layer is also lower and the mass fragment 316.7679 m/z can still be found though to a lesser extent than in Cu .

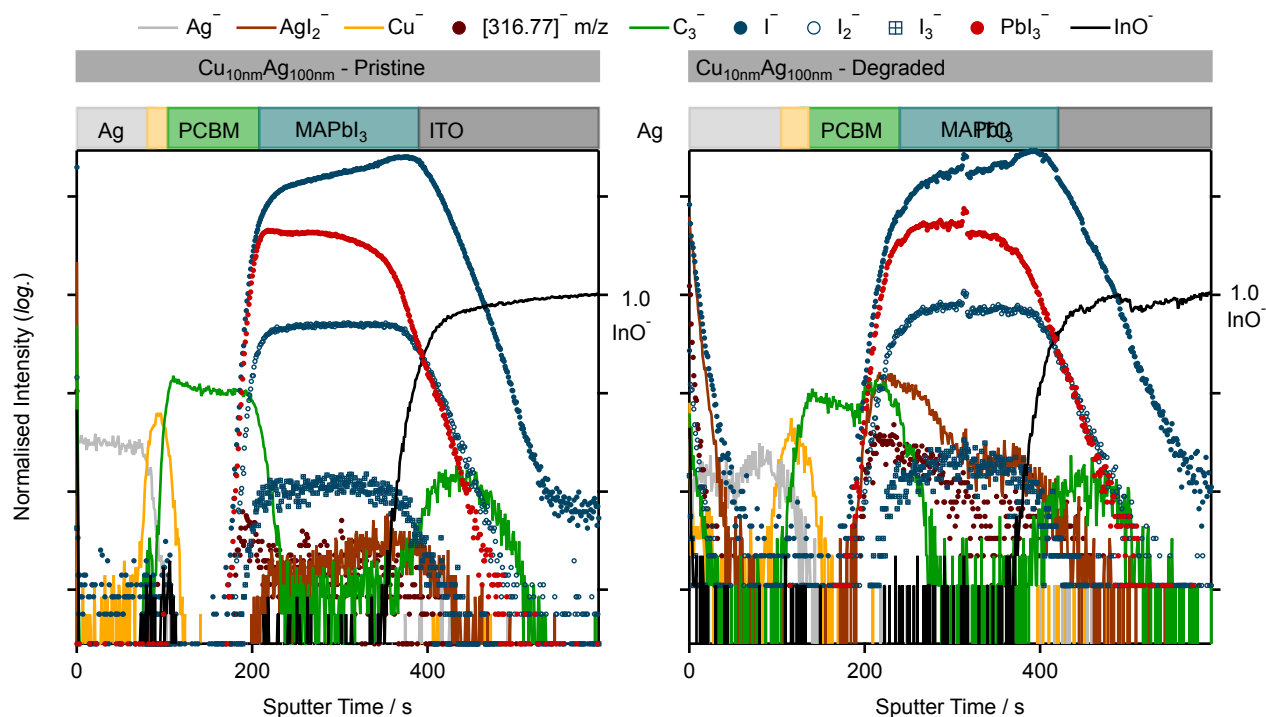


Figure 6.7 Dynamic ToF-SIMS: Depth profiles of pristine and degraded CuAg-based devices. Intensities have been normalised to steady-state region of InO^- and plots have been set to same scale.

Certain conclusions can be obtained from the differences in depth profiles. Whether through the implementation of a thicker electrode (110 nm) or the addition of Cu to Ag, degradation in terms of I^- ($m/z = 126.92$) diffusion is much less severe especially so within the bulk of PCBM and the electrodes, in contrast with that of pure Ag. This relationship seems to be intrinsically tied to the secondary ion AgI_2^- ($m/z = 360.74$) which follows I^- ($m/z = 126.92$) closely. The formation of AgI_2^- ($m/z = 360.74$) is also suppressed significantly in this bilayer configuration suggesting that Cu could have acted as a blocking layer against Ag diffusion into MAPbI_3 . This could mean that the chemistry of the Cu/Ag or (and) the physical Cu/BCP interface(s) prevent(s) the accumulation of I^- . Furthermore, the profiles of Ag^- ($m/z = 106.91$), PbI_3^- ($m/z = 588.71$), I^- ($m/z = 126.92$), now show reduced intermixing. The possibility of Cu acting as a physical barrier that limits beam induced mixing beyond the sampled surface cannot be ruled out (discussed further in **Section 6.2.4**). Regardless of the reported uncertainties, the effects of the addition of Cu is undeniable both in terms of ion diffusion and device stability under operational conditions.

XRD data (**Figure 6.8**) also show the absence of CuO indicating that the bilayer configuration suppresses formation of CuO. There is also no indication of crystalline AgI or CuI (**Figure 6.8** (a)) in all three electrode configurations, while not ruling out the possibility of amorphous secondary phases.

A diffraction peak at $12.7^\circ 2\theta$ corresponding to the crystallographic plane (001) of PbI_2 is present in both

Cu and CuAg configurations but not significantly so in the Ag configuration. This might point towards Cu-related formation of PbI_2 whose presence has been shown to have the potential to be advantageous to device performance [91]. This increased presence of PbI_2 may contribute to the observed enhanced stability for devices containing Cu as an electrode. There could be a phenomenological correlation with the suppressed diffusion of I^- ($m/z = 126.92$) in these electrode configurations whereby PbI_2 behaves as a barrier to I^- ($m/z = 126.92$) diffusion or the reduced diffusion of I^- ($m/z = 126.92$) out from MAPbI_3 is tied to the increased formation of PbI_2 . Based on depth profiles, there is no observable difference in PbI_2 concentrations within the MAPbI_3 layer, which is likely due to the destructive nature of the sputtering process which is not well-studied for these hybrid materials, and not indicative of the absence of local inhomogeneities. Thus, at this juncture it would be premature to provide any conclusive remarks about the origins of this correlation. It is interesting to note, however, while PbI_2 is often regarded as a degradation by-product the stability of the Ag-based device is poorer than that of Cu or CuAg despite the differences in PbI_2 .

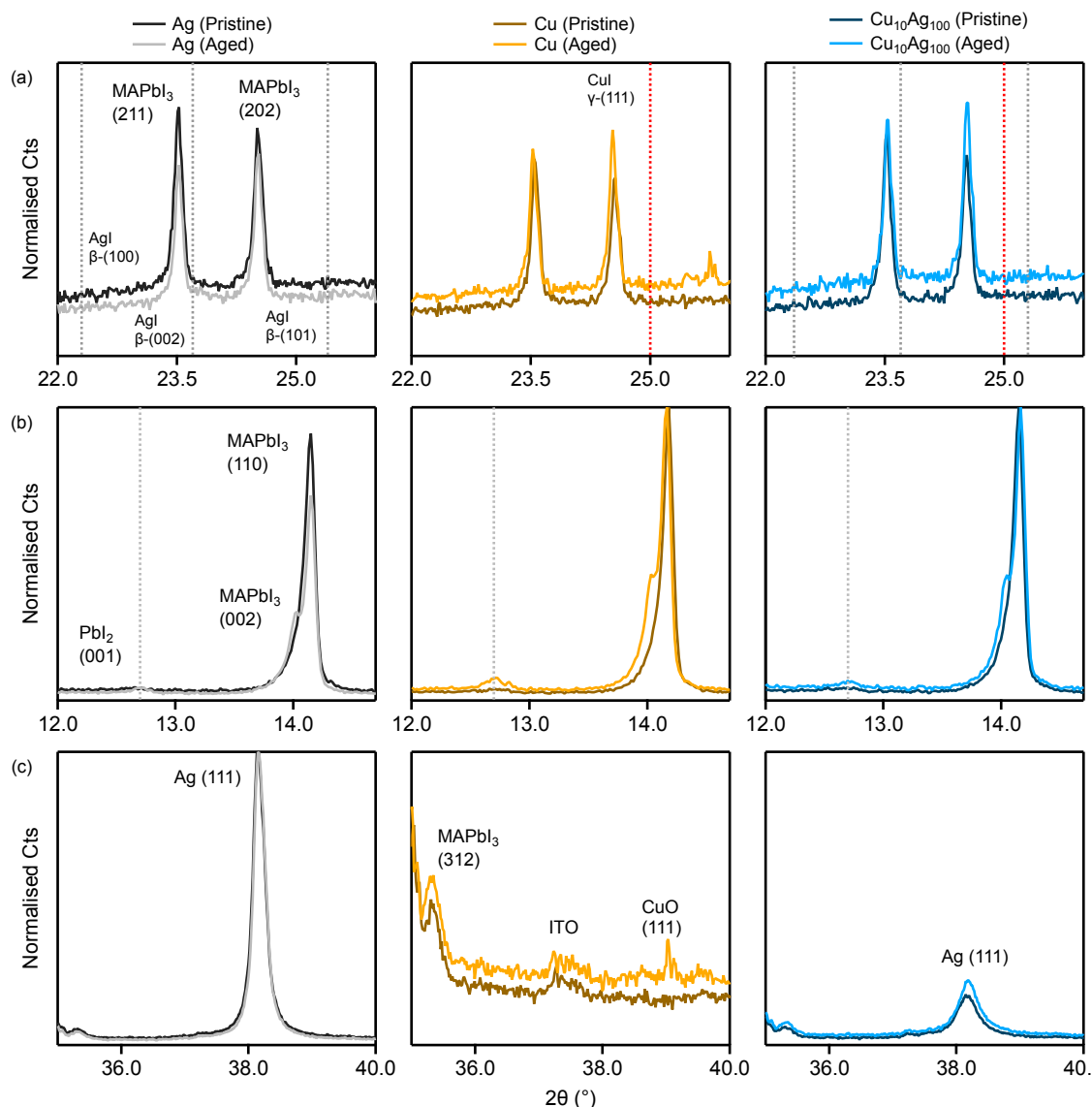


Figure 6.8 XRD: diffraction data showing where diffraction peaks should occur for (a) β -AgI: (100), (002), and (101) and γ -CuI: (111). (b) PbI₂: (001), tetragonal-MAPbI₃: (110)* and (002). (c) CuO (111).

The peak at around 14.14° which is ascribed to the (110) plane and a shoulder peak from the (002) plane is observed at a lower 2θ , 14.04° with the latter exhibiting a larger FWHM than the former. Together with an increased (002)/(110) intensity ratio (regardless of electrode configuration), the pristine MAPbI₃ layer with predominantly ordered (110) planes becomes more disordered with an increased fraction of (002) planes that are more randomly orientated owing to its larger FWHM. The presence of more disordered planes may, in part, contribute to the reduction in device performance, across all samples as charge transport properties can be correlated to the disorder of the crystallites.

One can therefore see that the increased stability of Cu-Ag bilayer configuration comes from a more favourable electrode/BCP interface that seems to work in a synergistic manner: the oxidation of Cu

is suppressed while the breakdown of Ag is retarded through suppression of I^- ($m/z = 126.92$) diffusion. This suppression seems to occur only when Cu is interfaced with PCBM. The possibility of metal impurity diffusion into MAPbI₃ is discussed in the next section.

6.2.3 Diffusion of Metal-Electrodes

Considering the degraded profiles of both single layer electrode and bilayer electrode configurations, neither Cu^- ($m/z = 62.93$) nor Ag^- ($m/z = 106.91$) ions were detected within MAPbI₃ in any electrode configuration. However, a direct correlation exists between intensities of secondary ions AgI_2^- ($m/z = 360.74$) and CuI_2^- ($m/z = 316.77$) with that of I^- ($m/z = 126.92$)—where an increased (or decreased) intensity is seen for all three fragments at the electrode layers. Furthermore, observing suppressed I^- ($m/z = 126.92$) diffusion in the bilayer electrode configuration and a similar suppression of $[Metal-I_2]^-$ fragment intensities in the MAPbI₃ layer, some correlation with the employment of a CuAg bilayer configuration can be concluded though there is insufficient data to draw a direct *causal* relationship with electrode diffusion.

However, the profiles obtained here are in disagreement with a few studies where they reported direct observation of metal diffusion [166, 168] in which they profiled (using ToF-SIMS and STEM-HAADX) a largely different standard structure (ITO/m-TiO₂/MAPbI₃/Spiro-OMeTAD/electrode) whose HTL is known to have pin-holes. They also used a different sputter beam (Cs^+). As to the question of whether the sputter beam may have affected the results, it can be observed that in a thermally aged ITO/NiO/MAPbI₃/PCBM/Ag inverted device profiled with Cs^+ , elemental profiles did not show agglomeration of Ag^- within MAPbI₃ (see **Figure 6.9**) [139]. Additionally, Ag diffusion was reported after thermal ageing an ITO/NiMgLiO/MAPbI₃/PCBM/BCP/Ag device at 85 °C for 100 h [231], though such a claim was an observation of a broad inward Ag^- profile that could have been caused by morphological degradation of the MAPbI₃/PCBM/BCP and/or PCBM/BCP interface(s). Additionally, depth profiles were obtained from Cs^+ which causes beam-induced artefacts in profiling metal/organic interfaces ([212] and **Section 4.4**).

The opposite has also been reported that is in agreement with the work discussed here [165, 170], it should also be noted that impurities of Cu and Ag in MAPbI₃ may not result in the degradation of the material's charge transport properties [23].

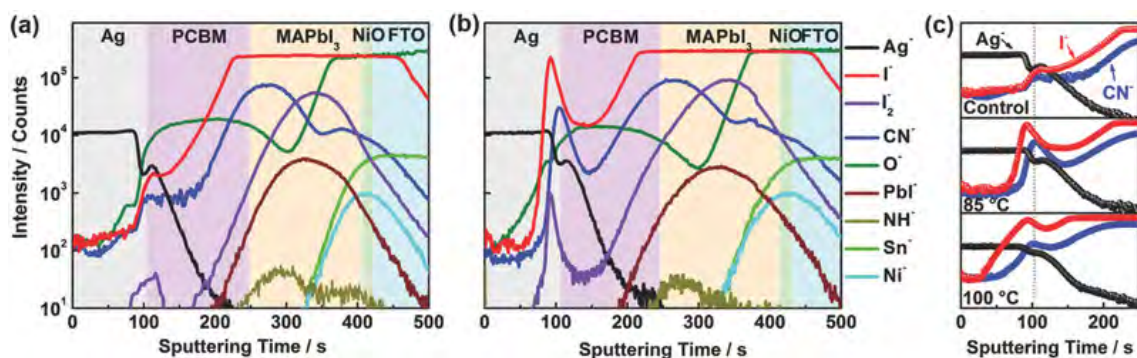


Figure 6.9 Dynamic ToF-SIMS: Depth profiles of (a) pristine and (b) degraded Ag-based devices from thermal aged at 85 °C for 24 h and (c) various ageing temperatures. Reproduced with permission [139]. Copyright © 2017 RSC.

6.2.4 Errors

First, to deconvolute possible preferential sputtering effects from an uneven electrode morphology that would propagate through the depth profile and eventually introduce larger interfacial widths than reality, different region of interests (ROI) from the total ion map were selected based on their visual homogeneity (**Figure 6.10**): (a) was selected to show the profile containing uneven surface morphology, (b) was selected for the profile that has been discussed earlier, (c) was selected to contain a smaller area comparison with (b). Analysing the depth profiles, one can observe that (a) ROI containing localised enhanced intensity shows a more diffused profile with I^- ($m/z = 126.92$) and AgI_2^- ($m/z = 360.74$) extending to the surface. It can even be said that Ag^- ($m/z = 106.91$) has been suppressed significantly while C_3^- ($m/z = 36.00$) still has a reasonably prominent profile with sharp interfaces. These observations are an indication of an I^- based compound throughout the thickness of the Ag electrode. Comparison of ROIs (b) and (c) show minimal differences with the exception of a more suppressed I^- ($m/z = 126.92$) profile within PCBM layer in (c).

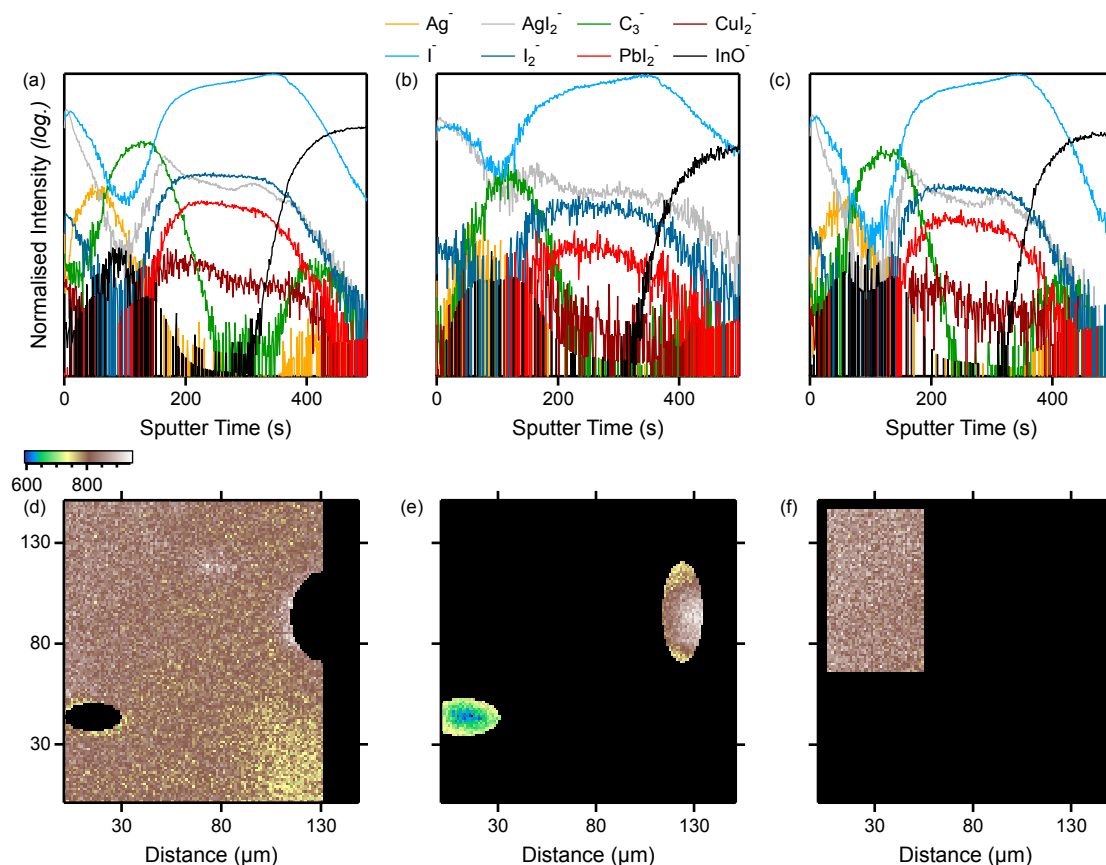


Figure 6.10 ToF-SIMS: (top) depth profiles of degraded Ag-based device with their corresponding (bottom) total ion images containing different region-of-interests (ROI) from a $150\ \mu\text{m} \times 150\ \mu\text{m}$ analysis square. Y-axis shown in log-scale. [(a), (d)] Area used for comparing devices between different electrodes. [(b), (e)] Area containing only inhomogeneities. [(c), (f)] Area that is completely visually uniform. Image intensities have been set to the same colour scale.

Second, the lateral resolution of the total ion map is in the order of microns ($150\ \mu\text{m} \times 150\ \mu\text{m}$ analysis area rastered with 128×128 pixels, where 1 pixel = $1.2\ \mu\text{m} \times 1.2\ \mu\text{m}$ area). Thus, a single pixel provides chemical information acquired cumulative of a few grains (assuming the typical grain size of MAPbI₃ is approximately 400 nm) which offers some level of sensitivity and selectivity. Features (e.g. secondary phases) on the surface of the electrode smaller than $1\ \mu\text{m}$ cannot be spatially resolved. The possible presence of secondary phases, smaller than that which can be spatially resolved, on the electrode cannot be ruled out. This may also contribute to the larger interface widths of profiles through preferential sputtering. However, that any increase in interfacial width is observed at all is sufficient to conclude that there is some degradation (ion diffusion or morphological) between the layers that would have resulted in the profile shown.

Next, even though Ag⁺ ($m/z = 106.91$) was not *directly* detected within MAPbI₃ one could explain significant concentrations of AgI₂⁺ ($m/z = 360.74$) with two possible, though not necessarily *mutually exclusive* mechanisms: (1) Ag diffusion and (2) atomic mixing from sputter damage beyond the information depth

of the primary beam which would occur in the degraded device as the interface width of Ag^- ($m/z = 106.91$) is naturally larger and now intersect profiles of MAPbI_3 . With the data at hand, it would be premature to draw any causal relationship between AgI_2^- ($m/z = 360.74$) and Ag^- ($m/z = 106.91$) diffusion but a correlation to degradation can certainly be made.

That AgI_2^- ($m/z = 360.74$) is detected over Ag^- ($m/z = 106.91$) or AgI^- might be due to beam induced effects and the multiple oxidation states of I as it is unlikely that a divalent metal-halide naturally dominates over pure Ag without external influence. Interestingly, 316.77 m/z is also seen in Ag based devices which also suggests possible mass interference (see **Section 6.3.4**).

There is also an interfacial feature at the Ag/BCP interface that is not observed in the Cu-based device, belonging to the mass fragment InO^- ($m/z = 130.91$). However, seeing as it is improbable for InO^- ($m/z = 130.91$) to exist at just the interface, mass interference is the likeliest culprit. By extracting mass spectra between 0 s and 115 s, calculations were performed on the mass fragment (130.9098 m/z) to determine its identity. Based on possible ions using C, N, O, Ag, and I and considering isotopic abundance, the fragment with the lowest deviation from its theoretical mass is calculated to be C_2Ag^- which has a theoretical mass of 130.9056 u (a deviation of 3.2 ppm), with InO^- having a theoretical mass of 130.9099 u . The difference of 0.0043 u between these two ions requires an instrument with a mass resolution ($M/\Delta M$) of $> 30,000$ which is higher than what is capable with the beam conditions and instrument used. That Cu and CuAg (**Figure 6.7**) profiles do not show the same interfacial feature suggests it is an Ag-based mass fragment or possibly brought about by matrix effects of Ag/BCP.

6.2.5 Conclusions

While Ag or Cu may not necessarily be the best contenders as an electrode, their electrical properties are still very much favourable and have reasonable retention of their initial J-V characteristics. This bilayer electrode configuration approach also allows for streamlining large-scale device deposition, in contrast with other methods that require additional deposition steps and studies into the energy level alignment and possible chemical interactions, such as small molecule (e.g. fullerenes) passivation layers [232], chemical vapour deposition (CVD) of graphene [233], or atomic layer deposition (ALD) of metal oxides [234]. In order to qualify the degree of I^- diffusion as a result of operating the device under 1 sun illumination, a second measurement should be further carried out on a device stored in the dark and in N_2 environment for the same amount of time.

In the bilayer configuration, both Cu oxidation and ion diffusion are visibly suppressed which are certain to have contributed its much longer operational lifetime. AgI_2^- ($m/z = 360.74$) can be seen to have

a lower concentration within MAPbI₃ and at the Ag electrode surface indicating that I⁻ diffusion and the possible diffusion of Ag⁻ ($m/z = 106.91$) into MAPbI₃ were retarded to significant extents. However, whether it is due to a different interface chemistry with Cu being a more stable intermediate layer or physically through the introduction of a thicker electrode cannot yet be said.

To ascertain the origins of this stability increase, the following should be carried out: (1) depth-resolved XPS should be performed to identify with certainty any metallic impurities within MAPbI₃, (2) a bilayer configuration of Cu_{100nm}Ag_{100nm} should be further examined.

Furthermore, the phenomenon where PbI₂ diffraction peak was only observed in devices containing Cu/PCBM interface (*i.e.* in Cu and CuAg configurations) requires further investigation to ascertain its origins and whether the presence of crystalline PbI₂ was a contributing factor to the increased stability of Cu-based devices.

In the next section, Cu and Au-based devices are tested against their thermal resistance to degradation and the effects of adding a Cr blocking layer (as has been reported to inhibit metal electrode diffusion) between the electrode and HTL are discussed.

6.3 Thermally Induced Degradation

Thermal stability is of paramount importance as devices are subjected to thermal stresses, among others in real-world conditions. In this section, the effects thermal stress has on ion migration and the vertical distribution of chemical species and consequently, device performance in inverted devices are investigated. Specifically, the stabilities of electrode and absorber layers in response to thermal stresses are investigated; particularly, Cu and Au as electrode materials in inverted structures are studied.

6.3.1 Instability of Cu and Au-based Devices

In inverted structures, devices employing Cu and Au electrodes have low resistance to thermal degradation. Devices with both electrodes were subjected to thermal stresses (Cu: 50 °C, 80 °C, 100 °C; Au: 40 °C, 60 °C, 80 °C) for a total of 5 h. J-V measurements were performed before and after thermal ageing (Table 6.3.). Chemical depth profiles by ToF-SIMS were performed on these devices post-ageing.

Table 6.3 Device data: Measured after thermal ageing for Cu-based devices. Values are averaged over the number of pixels. Values in brackets are standard error.

Temp. (°C)	Time (h)	V _{OC} (V)	J _{SC} (mA cm ⁻²)	Fill Factor	PCE (%)
ITO/PTAA/PFN/MA Pb I ₃ /PCBM/BCP/Cu					
50	5	1.05 (±0.02)	17.89 (±2.62)	0.72 (±0.04)	13.53 (±2.84)
80		1.01 (±0.01)	15.18 (±1.26)	0.68 (±0.02)	10.42 (±1.234)
100		0.84 (±0.02)	10.03 (±0.69)	0.63 (±0.03)	5.31 (±0.42)
ITO/PTAA/PFN/MA Pb I ₃ /PCBM/BCP/Au					
0	5	1.07 (±0.001)	19.87 (±1.26)	0.78 (±0.01)	16.59 (±0.97)
40		1.06 (±0.004)	18.81 (±1.58)	0.60 (±0.03)	12.11 (±0.87)
60		1.02 (±0.02)	20.31 (±0.89)	0.36 (±0.09)	7.65 (±2.33)
80		1.01 (±0.01)	19.43 (±0.87)	0.67 (±0.02)	13.39 (±0.30)

Cu Electrode

Even after a mere 5 h of ageing, there is a marked reduction in device performance for both Au and Cu based devices, indicating that irreversible degradation occurs only after a short exposure to thermal stresses with 100 °C showing the most severe reduction in device properties.

Considering that there is little change in V_{oc} between 50 °C and 80 °C, it can be surmised that the energy levels between the different layers have not changed significantly thus, interfacial/surface composition of the interlayers have not been affected to an extent that would result in different interfacial energetics. The slight drop in J_{sc} however, points to possible morphological changes at the interfaces or within the layers that might result in higher series resistance.

A significant drop in both J_{sc} (44%) and V_{oc} (20%), however, are observed after ageing at 100 °C which resulted in an almost three-fold reduction in PCE. Looking at their chemical profiles (**Figure 6.11**), the interfacial widths of Cu^- ($m/z = 62.93$) and C_3^- ($m/z = 36.00$) remain constant with increasing temperatures indicating that at these timescales and temperature range there is no inter-diffusion of chemical species arising from the degradation of the Cu/PCBM interface.

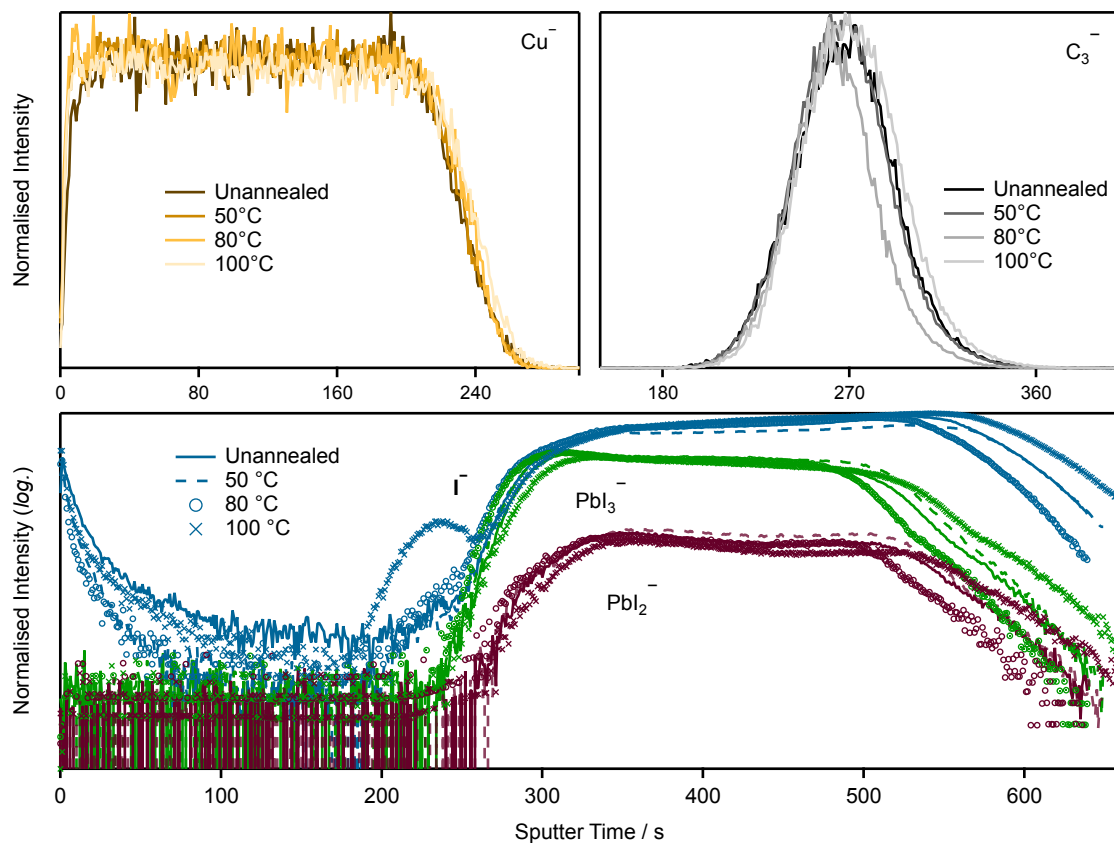


Figure 6.11 Dynamic ToF-SIMS: Depth profiles of ITO/PTAA/PFN/MAPbI₃/PCBM/BCP/Cu devices with thermal ageing at different temperatures, showing the (top left) Cu electrode (Cu⁻), (top right) PCBM layer (C₃⁻), and MAPbI₃ layer (bottom).

It is possible that given the thermal stresses and energy, significant morphological and chemical changes between the interfaces occurred which would explain the significant drop in J_{sc} and V_{oc} after ageing at 100 °C. Based on the chemical depth profile of the absorber layer, an I⁻ ($m/z = 126.92$) feature is observed at the Cu/BCP/PCBM interface and is also accompanied by an increased intensity of the mass fragment identified as CuI₂⁻ ($m/z = 316.77$). This implies a strong possibility of accumulation of I⁻ at the Cu/PCBM interface which could have an adverse effect on interfacial ohmic contact, drastically reducing J_{sc} .

Au Electrode

Surprisingly, the device aged at 60 °C seem to have the poorest device properties. Comparing its current-voltage sweep curve, there is a non-ideal curve shape (*s-shape*) that signifies an interfacial energetic barrier. As a result, the FF is significantly reduced and contributed to the drastic drop in PCE, whilst J_{sc} showed a slight increase and V_{oc} , a slight drop. J-V curves and depth profiles of all thermal ageing temperatures are illustrated in **Figure 6.12**. Similar to Cu-based devices mentioned above, interfacial

widths of Au^- ($m/z = 196.97$) remained constant throughout the ageing temperatures suggesting that the electrode has not broken down to any observable degree.

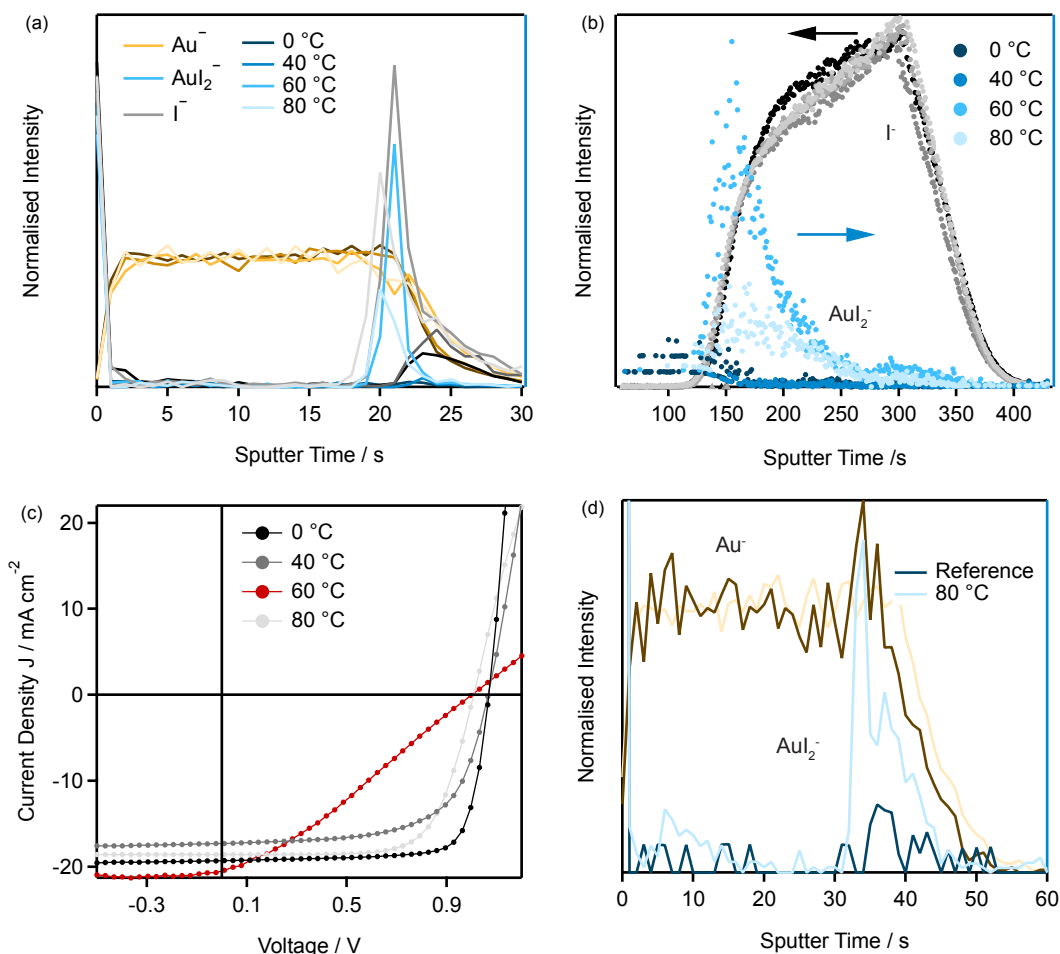


Figure 6.12 (a): **Dynamic ToF-SIMS:** Depth profiles of Au-electrodes, showing the presence of I^- ($m/z = 126.92$) and AuI_2^- ($m/z = 450.73$) at the Au/BCP interface. Dark to light colours: 0 °C to 80 °C. (b): **Dynamic ToF-SIMS:** Depth profiles of MAPbI₃ absorber layer showing the presence of same AuI_2^- ($m/z = 450.73$) detected at the electrode with a higher concentration arising from 60 °C. (c): **J-V characteristics** of devices after thermal ageing. (d): **Dynamic ToF-SIMS:** Depth profiles of Au-based devices using monoatomic Argon sputter beam at 1 kV. Intensities are normalised to the total ion intensity at each data point; vertical axes in linear scale.

Two distinct mass fragments can be observed at the Au/BCP interface regardless of ageing temperatures. One of these mass fragments may be attributed to I^- ($m/z = 126.92$) and as it was not present at the Cu/PCBM interface, its apparent presence may be due to interfacial matrix effects of the Au/BCP interface (for the discussion of this feature, see **Section 6.3.3**). With increasing temperature, both intensity and width of I^- ($m/z = 126.92$) increase suggesting that its presence is not completely artificial; it is also likely to be exacerbated by thermal stresses. The other fragment has the m/z value of $m/z = 450.79$. In samples that were aged at 60 °C and 80 °C, its intensity increased significantly compared to 40 °C and untreated samples.

As to the identity of this mass fragment, it is thought to be AuI_2^- ($m/z = 450.73$) which has a m/z deviation of -1.4 ppm from theoretical value. Concerning the issue of mass interference, possible mass fragments with a maximum theoretical m/z that is within 100 ppm of the recorded value were calculated and yielded no results. To determine whether the reactive nature of the sputter beam is inducing artefacts in the depth profile, a monoatomic Ar sputter beam was used to profile these samples (see **Figure 6.12**). Similar to the oxygen sputter beam, the mass fragment at $m/z = 450.79$ is observed at the Au/BCP interface and at a higher normalised intensity in the sample aged at 80°C . Furthermore, I^- ($m/z = 126.92$) profiles show similar characteristics. Therefore, it is unlikely that its presence is solely from the contribution of matrix or beam-induced effects. It can also be observed that in their cumulative ion images, localised spatial variations of AuI_2^- ($m/z = 450.73$) closely follow that of I^- ($m/z = 126.92$), and total ion images (show images).

However, the presence of interfacial AuI_2^- ($m/z = 450.73$) and I^- ($m/z = 126.92$) may not be sufficient to explain the significantly different J-V curve for 60°C compared to 80°C . Analysing depth profiles deeper into the MAPbI_3 layer, AuI_2^- ($m/z = 450.73$) can be found with a higher intensity at the PCBM/ MAPbI_3 interface and 60°C exhibiting the highest concentration, followed by 80°C whereas profiles from 40°C and 0°C showed no visible differences. Additionally, Au^- ($m/z = 196.97$) cannot be detected within MAPbI_3 suggesting three possible reasons: (1) that pure Au clusters may not have formed within this timescale, (2) its concentration is below the detection limit, (3) the matrix effects of Au^- ($m/z = 196.97$) in MAPbI_3 resulted in preferential fragmentation of AuI_2^- ($m/z = 450.73$) mass fragments only. Thus, it is likely that the differences in current-voltage characteristics come from Au-I species at the PCBM/Perovskite interface.

Given the short thermal ageing time of 5 h, a more extensive approach was adopted, utilising $(\text{FA})_{0.85}\text{Cs}_{0.15}\text{Pb}(\text{I}_{0.9}\text{Br}_{0.1})_3$ as the absorber layer with the addition of a 7.5 nm Cr layer between Au and BCP. This approach was also extended to Cu electrodes. Their chemical depth profiles and J-V curves are supplemented with photoemission spectra. These are reported in the next section. The apparent anomalous result from ageing at 60°C requires further confirmation as it appears counter-intuitive.

6.3.2 Extended Thermal Ageing

$\text{FA}_{0.85}\text{Cs}_{0.15}(\text{PbI})_{2.7}\text{Br}_{0.3}$ -based devices employing Cu and Au electrodes were subjected to extended thermal ageing to better investigate the effects of temperature on the interdiffusion of chemical species and their relationship(s) with device properties. Devices were subjected to thermal ageing at 80°C for a total of 72 h with an interval of 24 h for J-V measurements (**Table 6.4**).

Table 6.4 **Device data:** after thermal ageing for Au and AuCr-based devices. Values are averaged over the number of pixels. Values in brackets are standard error.

Temp. (°C)	Time (h)	V _{OC} (V)	J _{SC} (mA cm ⁻²)	Fill Factor	PCE (%)
ITO/PTAA/PFN/(FA)_{0.85}Cs_{0.15}Pb(I_{0.9}Br_{0.1})₃/PCBM/BCP/Au					
Fresh	0	0.97 (±0.002)	22.33 (±1.47)	0.76 (±0.02)	16.52 (±1.41)
80	24	0.91 (±0.08)	14.91 (±1.86)	0.49 (±0.04)	6.56 (±0.28)
	72	1.00 (±0.03)	20.70 (±2.18)	0.34 (±0.06)	7.05 (±1.44)
ITO/PTAA/PFN/(FA)_{0.85}Cs_{0.15}Pb(I_{0.9}Br_{0.1})₃/PCBM/BCP/Cu					
Fresh	0	0.95 (±0.003)	22.54 (±0.30)	0.73 (±0.01)	15.60 (±0.14)
80	24	1.02 (±0.02)	20.49 (±1.81)	0.64 (±0.02)	13.27 (±0.53)
	72	0.85 (±0.03)	3.96 (±0.82)	0.41 (±0.03)	1.41 (±0.42)

Overall, it can be observed that the device employing Au electrodes degrade more gradually, while that with Cu has better device properties after 24 h but a near complete performance degradation at the end. On the other hand, the Au-based device retained its V_{oc} and J_{sc} after 72 h; while FF drop by about 55% after 72 h of thermal ageing and 44% for the Cu-based one. Notably, in the Au-based device, there is an anomalous trend in J_{sc} between 24 h and 72 h. That it is observed in the Cu-based device suggests that it is not under the direct influence of the absorber layer. Instead, this anomalous behaviour may be an Au-related phenomenon, particularly an interfacial feature observed (**Figure 6.14**).

In the Cu-based device, while V_{oc} increases slightly after 24 h (this behaviour is discussed in **Section 6.3.3**), it drops by about 17% after an additional 48 h of thermal ageing. Whereas its J_{sc} was shown to only have a slight drop. Based on the constant interfacial widths of Cu⁻ (*m/z* = 62.93) and C₃⁻ (*m/z* = 36.00), it can be concluded that thermal ageing has little effect on the cross-diffusion of chemical species at the Cu/PCBM interface when comparing with pristine samples (**Figure 6.13**). After 24 h, there is negligible difference at the Cu surface indicating that iodide-based species are not found. Further, the interfacial width of I⁻ (*m/z* = 126.92) remained the same with a slight feature similar to that in **Figure 6.11**. Thus, reductions in J_{sc} and FF may partly be attributed to I⁻ accumulation at the Cu/PCBM interface. For the case where changes in interfacial morphology might have influenced interfacial contacts, it can be observed that interfacial widths of mass fragments shown did not deviate from pristine samples indicating that the grains/microstructure of each layer did not change significantly (or at least

within the depth resolution of the sputter beam).

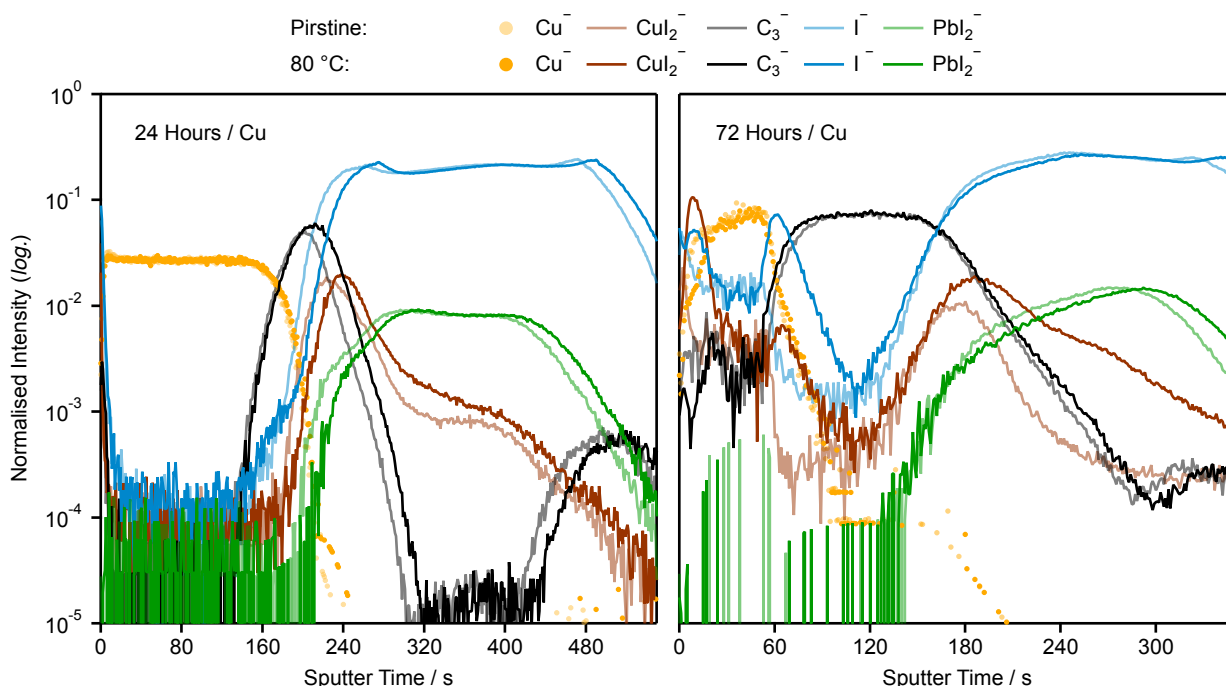


Figure 6.13 Dynamic ToF-SIMS: Depth profiles of ITO/PTAA/PFN/(FA)_{0.85}Cs_{0.15}Pb(I_{0.9}Br_{0.1})₃/PCBM/BCP/Cu devices thermally aged at 80 °C for 24 h and 72 h.

After an additional 48 h of thermal ageing, the profiles are now characterised by three notable features at the following locations: the electrode surface, the Cu/PCBM interface, and the PCBM/absorber interface. An increase in intensities of I^- ($m/z = 126.92$) and CuI_2^- ($m/z = 316.77$) with an associated suppressed intensity for Cu^- ($m/z = 62.93$) to a larger degree than found in the pristine device, are convincing indications of the presence of a Cu-I compound on the electrode surface whose formation is thermally assisted. The Cu/PCBM interface shows significant accumulation of I^- that is not unfamiliar for severely degraded devices as described in the previous section. Finally, at the PCBM/absorber interface an enhanced signal suggests a higher concentration of CuI_2^- ($m/z = 316.77$).

One can thus rationalise the significant drop in device properties after 72 h of thermal ageing. The accumulation of I^- at the Cu/PCBM interface and presence of significant iodine-based compound on the surface are likely to have contributed to an increase in series resistance in the device, reducing J_{sc} . The relatively small drop in V_{oc} suggests that it is likely to have been brought about by energy level changes at the Cu/PCBM and(or) PCBM/absorber interfaces from the accumulation of I_x^- species. These result in less efficient electron transfer, thus a lower V_{oc} .

While the pristine sample did not show the same degree of degradation and diffusion, it is of importance that similar features at the electrode surface were also observed—an indication of the inherent instability

of this mixed cation and mixed halide composition, and by consequence the ease with which I^- diffuses through the device in the absence of environmental stressors.

It has been previously observed that after ageing at 70 °C and under illumination at MPP, Au diffuses through the HTL and accumulated at the mesoporous TiO_2 layer [168]. This phenomenon was observed in a standard structure employing spiro-OMeTAD as the HTL which is well known to be relatively porous and ineffective as a diffusion barrier. Cacovich *et al.* [166] studied I and Au migration in standard structure devices employing spiro-OMeTAD as the HTL and suggested an electric-field induced mechanism of Au diffusion and eventual accumulation at defects (e.g. interfaces); in particular accumulation of Au was observed within the mesoporous TiO_2 .

In samples that were thermally aged for 72 h at 80 °C, Au^- ($m/z = 196.97$) was not observed in their chemical depth profiles, as shown in **Figure 6.14**. I^- ($m/z = 126.92$) and AuI_2^- ($m/z = 450.73$) can be similarly observed at the Au/BCP/PCBM interface as discussed earlier. Higher intensities for both secondary ions are observed after 24 h. Interestingly, the sample that was *stored* for 72 h and the sample that was *thermally aged* for an additional 48 h show similar profiles at the interface which suggests that diffusion of I^- ($m/z = 126.92$) in $(FA)_{0.85}Cs_{0.15}Pb(I_{0.9}Br_{0.1})_3$ occurs inevitably with a low energy barrier. However, the pristine sample shows an anomalous higher normalised AuI_2^- ($m/z = 450.73$) intensity which requires further investigation and confirmation. This may be related to the anomalous J_{sc} values (**Table 6.4**) where the interfacial feature is kinetically controlled and extended thermal ageing causes redistribution of these species and a lesser effect on device properties is observed though additional confirmation is required as it may be due to a device anomaly.

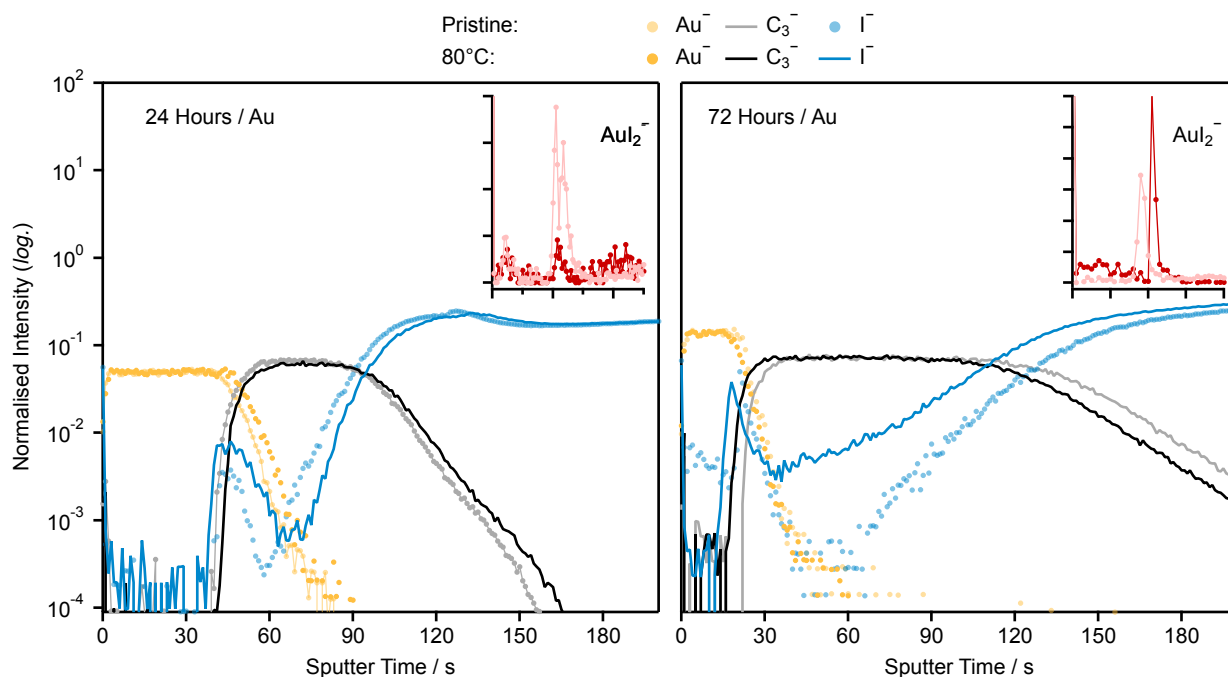


Figure 6.14 **Dynamic ToF-SIMS:** Depth profiles of ITO/PTAA/PFN/(FA)_{0.85}Cs_{0.15}Pb(I_{0.9}Br_{0.1})₃/PCBM/BCP/Au device thermally aged at 24 h and 72 h at 80 °C compared with pristine samples stored in an N₂ environment. Inset figures show AuI₂⁻ ($m/z = 450.73$) profiles at the Au/PCBM interface.

6.3.3 Cr Blocking Layer

The results in previous sections underline the inherent mobility of I⁻ ($m/z = 126.92$). The use of a blocking layer is not uncommon and can be found to inhibit electrode diffusion [168]. In the work described here, while Au⁻ ($m/z = 196.97$) ions have not been observed within the FA_{0.85}Cs_{0.15}Pb(I_{0.9}Br_{0.1})₃-absorber layer, it may have been at a concentration below the detection limit of ToF-SIMS or due to matrix effects. Thus, by depositing a thin layer (7.5 nm) of Cr between the electrodes and BCP, its effect(s) on device stability and diffusion of chemical species is(are) investigated. All devices underwent the same thermal stresses and their device data are shown in **Table 6.5** and they are compared with their pure metal analogues (illustrated in **Figure 6.15**).

Device Stability

Overall, it can be seen that the Au-based device seem to perform better over time than Cu-based ones. In the case of employing a CrAu bilayer, the addition of a Cr-layer between may result in less desirable device properties at 0 h but ultimately results in more stable V_{oc} , FF, and PCE over time with the exception of a lower J_{sc} after 72 h. After 72 h of ageing, both Au and CrAu-based devices have an *s-shape* J-V

curve (**Figure 6.15(a)**) which is indicative of the presence of a permanent dipole [229]. The higher V_{oc} observed after 72 h of annealing is mirrored in the pure Au-device **Figure 6.15(b)** which suggests that a recovery mechanism has occurred after extended thermal ageing causing a spatial redistribution of interfacial species resulting in a more favourable energy alignment between the interlayers. The higher J_{sc} after 24 h compared to the pure-Au device (**Figure 6.15**) and the fact that interfacial AuI_2^- is no longer observed (discussed in a subsequent section) point towards the suppression of an interfacial species. That it is higher than the pristine device may be within standard deviation of measurements; note that even though only a single device was measured, the drastic improvement between CrAu and Au at 24 h is unlikely due to errors.

On the other hand, employing a CrCu bilayer showed minimal (if any at all) improvements in all device metrics. Regardless, significant reduction in device properties after 72 h is still observed in both electrode configurations. A higher V_{oc} is observed after 24 h and is similarly observed in the pure-Cu device with an opposite behaviour observed in CrAu and Au-based devices. Therefore, this must be influenced by the use of Cu in the device. This increase may be due to the formation of CuI which has been previously used as a hole-transport material and has been shown to improve V_{oc} when using PTAA doped with CuI as the HTL in a *p-i-n* device [235]. In the scenario here, according to chemical depth profiles of Cu and CrCu-based devices (discussed in a subsequent section) the presence of CuI_2^- ($m/z = 316.77$) within the absorber layer suggests that Cu diffusion is a possibility. In which case, diffusion to the underlying PTAA layer is possible and forming CuI with redistributed I^- is likely.

Table 6.5 Device data: after thermal ageing for CrAu and CrCu-based devices. Values are averaged over the number of pixels. Values in brackets are standard error.

Temp. (°C)	Time (h)	V_{OC} (V)	J_{SC} (mA cm ⁻²)	Fill Factor	PCE (%)
ITO/PTAA/PFN/(FA)_{0.85}Cs_{0.15}Pb(I_{0.9}Br_{0.1})₃/PCBM/BCP/CrAu					
Fresh	0	0.94 (±0.01)	21.19 (±0.01)	0.73 (±0.002)	14.60 (±0.06)
80	24	0.94 (±0.02)	23.03 (±0.41)	0.74 (±0.01)	15.97 (±0.38)
	72	1.01 (±0.01)	17.60 (±1.69)	0.53 (±0.02)	9.45 (±0.97)
ITO/PTAA/PFN/(FA)_{0.85}Cs_{0.15}Pb(I_{0.9}Br_{0.1})₃/PCBM/BCP/CrCu					
Fresh	0	0.95 (±0.005)	22.60 (±1.27)	0.72 (±0.07)	15.54 (±2.25)
80	24	1.03 (±0.002)	17.34 (±1.06)	0.70 (±0.01)	12.44 (±0.73)
	72	0.88 (±0.03)	6.33 (±1.32)	0.45 (±0.002)	2.56 (±0.62)

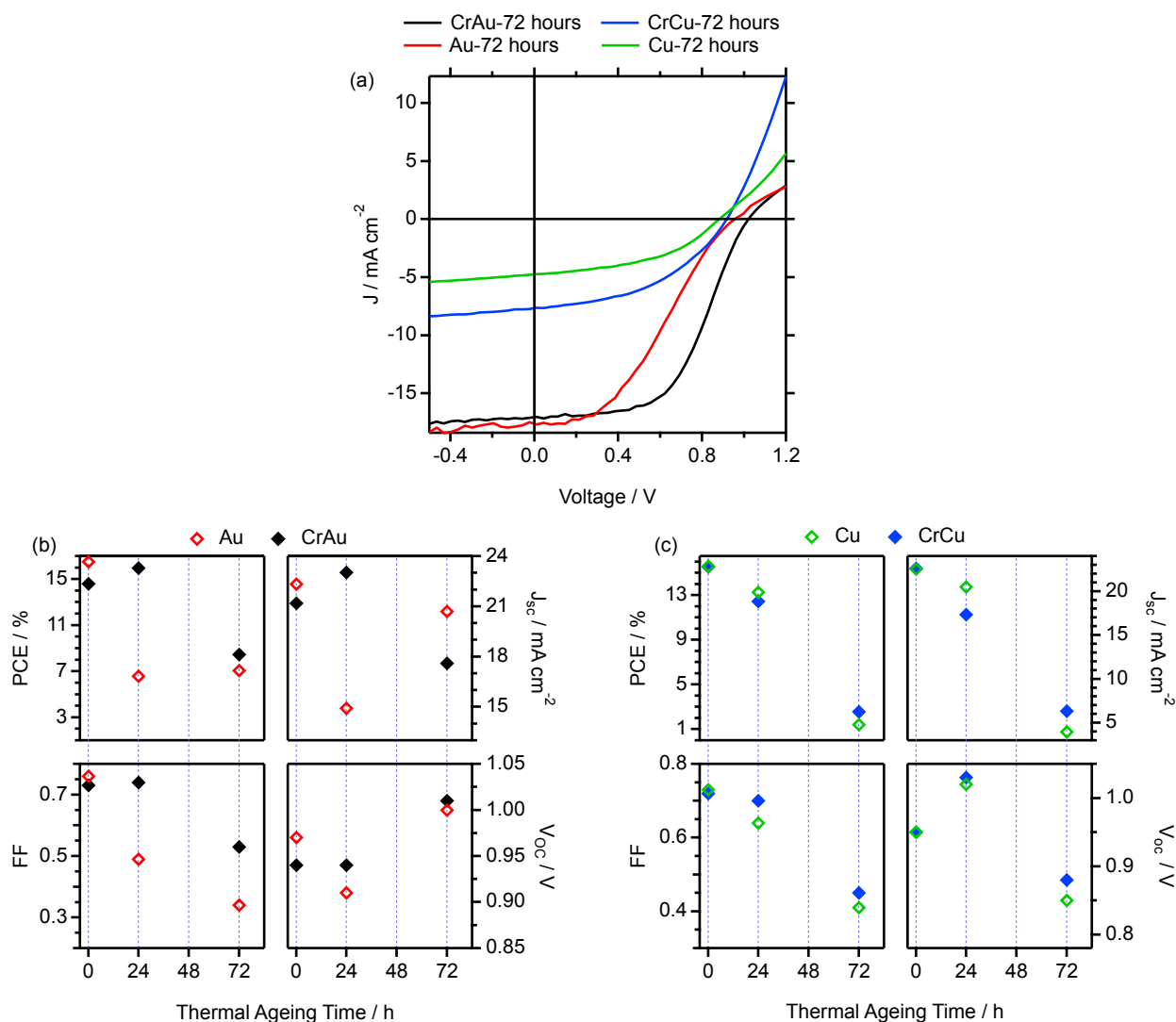


Figure 6.15 (a) Current (J_{sc}) vs. Voltage (V) sweep data. An *s-shape* curve is still observed for the device employing CrAu electrodes. Device data of single layer electrode configurations and bilayer electrode configurations for (b) Au/CrAu and (c) Cu/CrCu.

Chemical Depth profiles

Based on their vertical elemental and chemical distribution (**Figure 6.16**), in both CrAu and CrCu systems, interfacial widths of Au⁻ ($m/z = 196.97$)/Cu⁻ ($m/z = 62.93$) and CrO₃⁻ remain unchanged between pristine and thermally aged samples. At the electrode surface, Cu⁻ ($m/z = 62.93$) intensity can be said to have an indirect relationship with CuI₂⁻ ($m/z = 316.77$) and I⁻ ($m/z = 126.92$) intensities, synonymous to that seen in pure Cu-based device. SEM of the device cross-section shows presence of islands (less than 100 nm) on the surface of Cu (**Figure 6.18**), mirroring its depth profile. This indirect relationship is also seen in Au/Cr but to a much lesser degree however, unlike CuI₂⁻ ($m/z = 316.77$), AuI₂⁻ ($m/z = 450.73$) cannot be observed on the surface. Accumulation of I⁻ ($m/z = 126.92$) at the electrode/BCP interface is also observed in both electrode configurations after 72 h. This suggests that the

mechanism of I^- ($m/z = 126.92$) accumulation at the interface is thermally activated regardless of the nature of the interface. In fact, compared to pure Au, a significant I^- ($m/z = 126.92$) peak is still found at the CrAu/BCP interface yet absent at CrCu/BCP.

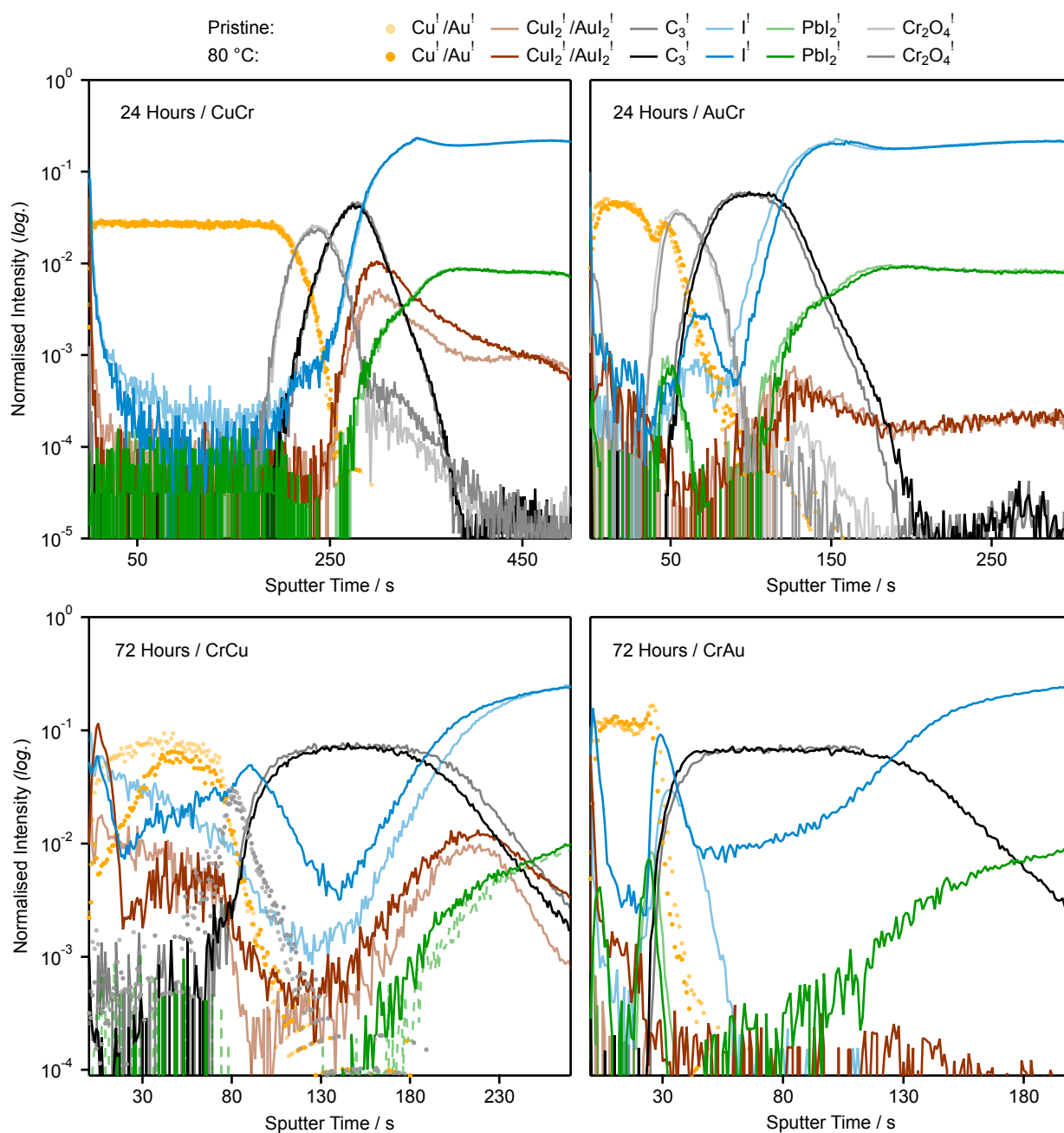


Figure 6.16 Dynamic ToF-SIMS: Depth profiles of devices with 7.5 nm of Cr between Au and BCP/PCBM compared to devices without.

Au Diffusion

Thus, one can deduce that Cr has had no observable influence on the diffusion of I^- ($m/z = 126.92$). Furthermore, since the formation of surface species on Cu is a crucial factor in its poorer thermal resistance compared to Au as discussed earlier, it is natural for the thermal resistance of CrCu to be comparable to that of Cu. Doubly so, it would seem that if metal impurity diffusion into the absorber layer were a source of degradation, the effectiveness of Cr as a blocking layer is limited. To better probe metal impurity diffusion in CrAu, as the process has been shown to induce trap states [23] within the absorber layer, a monoatomic Ar sputter beam was used to profile single layer Au and bilayer CrAu-based devices thermally aged at 80 °C for 24 h (Figure 6.17).

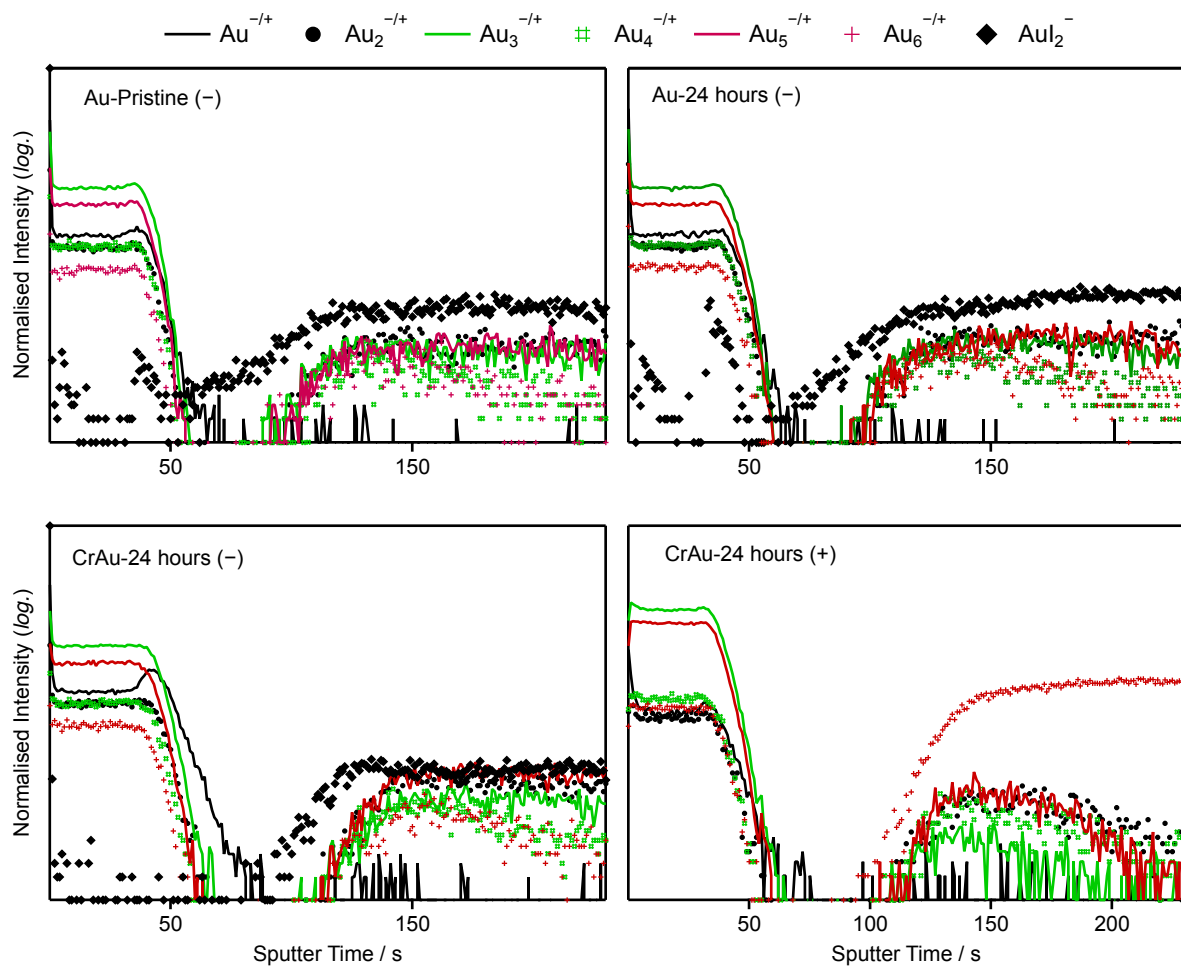


Figure 6.17 Dynamic ToF-SIMS: Depth profiles of Au_x fragments obtained using a monoatomic Ar^+ sputter beam at 1 kV. Intensities have been normalised to linear region of Au^- and Au^+ . Au-device thermally aged at 80 °C for 24 h.

Evidently, $Au_{x,x=2-6}^{-/+}$ ions are detected in the $(FA)_{0.85}Cs_{0.15}Pb(I_{0.9}Br_{0.1})_3$ absorber layer regardless of whether they have been thermally aged. This strongly supports the claim that metal diffusion is largely unaffected in these experiments but confirms the diffusion of Au into the absorber layer as previously

reported [166, 168]. However, it can be concluded that since the concentration of Au has not changed between pristine and aged samples, device degradation did not originate from Au diffusion.

Additionally, AuI_2^- ($m/z = 450.73$) cannot be observed at the AuCr/BCP interface which is an indication that the formation of this species has been suppressed with the addition of a Cr blocking layer. Despite the fact that an *s-shape* J-V curve still persists, the FF can be seen to be significantly better than Au **Figure 6.15**. It can be concluded then there is another source of a permanent dipole within the device which is likely to originate from Au within the absorber layer. Finally, it can be said a Cr-blocking layer is insufficient to inhibit metal diffusion (as reported [168]) and thus is not a source of increased thermal stability of CrAu. Considering that FF and consequently PCE, is observed to be much more affected by thermal stresses the enhancement of thermal stability in CrAu is related to the suppression of AuI_2^- ($m/z = 450.73$) at the electrode/BCP interface.

Cross-sections of the CrAu-based device (**Figure 6.18**) reveal darker contrast features distributed throughout the thickness of the $(\text{FA})_{0.85}\text{Cs}_{0.15}\text{Pb}(\text{I}_{0.9}\text{Br}_{0.1})_3$ layer, mirroring the presence of AuI_2^- ($m/z = 450.73$) and $\text{Au}_{x,x=2-6}^{-/+}$ from chemical depth profiles. Whether the origins of these physical features are directly related to the formation of Au clusters requires more investigation.

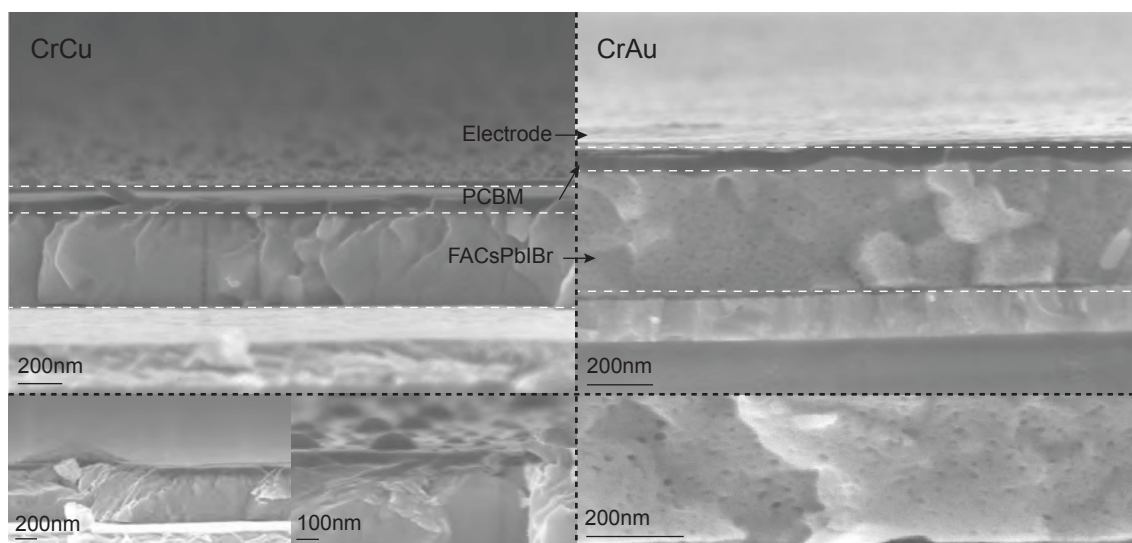


Figure 6.18 SEM SE-Imaging: Cross-section images of CrCu and CrAu-based devices. Islands are observed on the surface of Cu while not observed on Au. Comparison between areas with and without electrodes are shown below. Perovskite layer with CrAu electrode shows darker contrast features distributed throughout the thickness, with a magnified image of a different area below.

Electrode/BCP Interface Analysis

The suppression of AuI_2^- ($m/z = 450.73$) at the interface is posited to have been the source of increased thermal stability in CrAu compared to Au. To provide greater insights into the chemistry of the inter-

face, electrodes of thermally aged devices were peeled off and analysed as illustrated in (Figure 6.19). Due to limitations of ToF-SIMS in the accurate determination of chemical species, especially with the ambiguity of the exact chemical state of the observed interfacial species, XPS was further used to provide unambiguous evidence. It is assumed that peeling off the electrodes with carbon tape does not completely remove the underlying PCBM layer. While there is a presence of a π - π^* shake-up satellite feature at higher C 1s binding energy (Figure B), it is likely due to the adhered BCP layer.

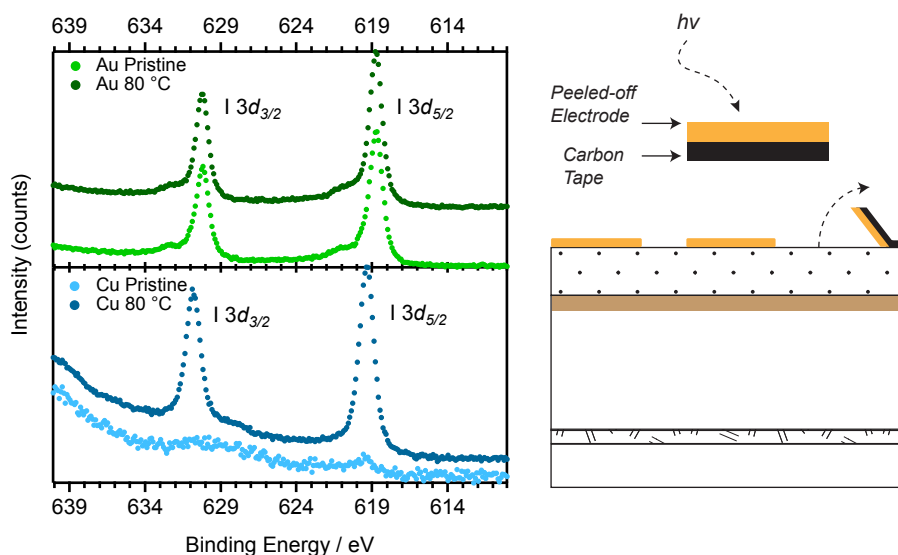


Figure 6.19 XPS: Core-level spectra obtained from XPS of peeled off electrodes. Each spectrum was normalised to the sum of its total counts.

The initial supposition that an Au-I based fragment exists at this interface and is not just an artefact of the sputtering process is supported by I 3d core-level photoemission spectra. The results clearly show that aged and pristine devices containing Au electrodes have within the Au/BCP bilayer I^- with different oxidation states than iodine in the Cu/BCP bilayer; their respective metal core-levels (Au 4f and Cu 2p) have binding energies that are expected for their pure forms. In addition, depth profiles of Cu-based device (Figure 6.13) show that there is minimal I^- at the electrode/BCP interface for the pristine device and which is in agreement with the photoemission spectra of Cu shown (relative atomic quantification is given in Table 6.6).

Turning to literature, Kerner *et al.* posit that underpotential deposition (UPD) occurs at the Au/MAPbI₃ interface in which a redox reaction occurs between the metal electrode and MAPbI₃ resulting in the formation of adsorbate(s)/adlayer at the interface whose oxidation state(s) is(are) altered during the process [132]. By performing XPS, they observed formation of iodine with different oxidation states on the surface of Au/PbI₂ samples and a single oxidation state on Au/MAPbI₃.

Along the same vein, Zhao *et al.* observed spectral changes of Pb 4f at various metal/MAPbI₃ interfaces

and reversible degradation on areas not covered by the electrode [172]. Thus, it would seem that direct contact between these two materials result in irreversible electrochemical degradation. It is apparent then, that the physical separation of the electrode from the absorber layer would hinder this degradation process. Li *et al.* provided elemental depth profiles of FTO/NiO/MAPbI₃/PCBM/Ag devices after thermal ageing for 24 h at 80 °C but focussed on the degradation of the absorber layer [57]. Thus, there are no studies currently available that directly show this phenomenon.

Table 6.6 XPS: Peak fitting parameters and relative atomic concentration for Au 4f_{7/2}, Cu 2p_{5/2}, and I 3d_{5/2} core-level spectra for Au and Cu-based devices. Values in brackets are relative atomic concentrations for the reported core-level spectra.

Core-level	Au 72 h	Au Reference	Cu 72 h	Cu Reference
Au 4f _{7/2}	84.0 eV	84.0 eV	-	-
	(90.2 %)	(90.8 %)	-	-
Cu 2p _{5/2}	-	-	932.6 eV	932.5 eV
	-	-	(92.3 %)	(98.7 %)
I 3d _{5/2} (1)	618.8 eV	618.7 eV	619.3 eV	619.4 eV
	(8.7 %)	(7.9 %)	(7.7 %)	(1.3 %)
I 3d _{5/2} (2)	620.3 eV	619.8 eV	-	-
	(0.6 %)	(0.6 %)	-	-
I 3d _{5/2} (3)	621.3 eV	621.2 eV	-	-
	(0.5 %)	(0.7 %)	-	-

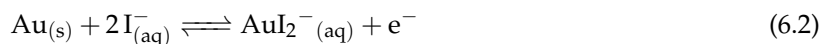
The findings reported here, indicate that a physical and(or) chemical reaction(s) has taken place at the Au/BCP interface in an organometallic halide photovoltaic device. If UPD reaction (**Equation 6.1**) has indeed taken place in this instance, it would seem that the direct contact of both electrodes and absorber layer is not necessary for it to occur. Considering that this reaction is electrochemical by nature, it would be necessary to further investigate by profiling non-thermally aged Au-based devices before and after measuring their current-voltage properties to rule out any possible influence.



It was reported that the bias threshold (V_{th}) for surface reactions is $-0.5 \text{ V} > V_{\text{th}} > 0.9 \text{ V}$ [132]. Thus, given that the concentration of I^- ($m/z = 126.92$) is negligible in Cu electrode from the pristine device, contrary to what is observed in Au electrodes, the formation of I_{UPD}^0 may have been driven by the voltage-current sweep during device measurement.

However, it is possible that the secondary features observed in I 3d_{3/2} arise from an Au-I complex that

is driven by electrochemical forces. In an *in situ* static ToF-SIMS experiment on an electrochemical cell containing an $\text{Au}_{(s)}/\text{KI}_{(aq)}$ system [236], recorded mass spectra show clear evolution of AuI_2^- at the expected $m/z = 450$ value when a voltage of more than 0.2 V was applied across the cell. Thus, the following reaction was proposed:



Thus this shows that the formation of AuI_2^- ($m/z = 450.73$) as discussed in this thesis, could be electrochemically driven. It can also be observed, based on $\text{I } 3d_{3/2}$ and $\text{Au } 4f$ core-levels of CrAu electrodes are given in **Figure 6.20**, that there are no secondary $\text{I } 3d_{3/2}$ features. Taking that either I_{UPD}^0 or Au-I complexes result in different oxidation states of I, it can be said that the chemistry of the Cr/BCP interface prevents either (or both) process(es) from occurring.

Finally, the effect(s) of thermal evaporation of Au on these devices cannot be excluded from possibly contributing to the aforementioned interfacial I^- ($m/z = 126.92$) features.

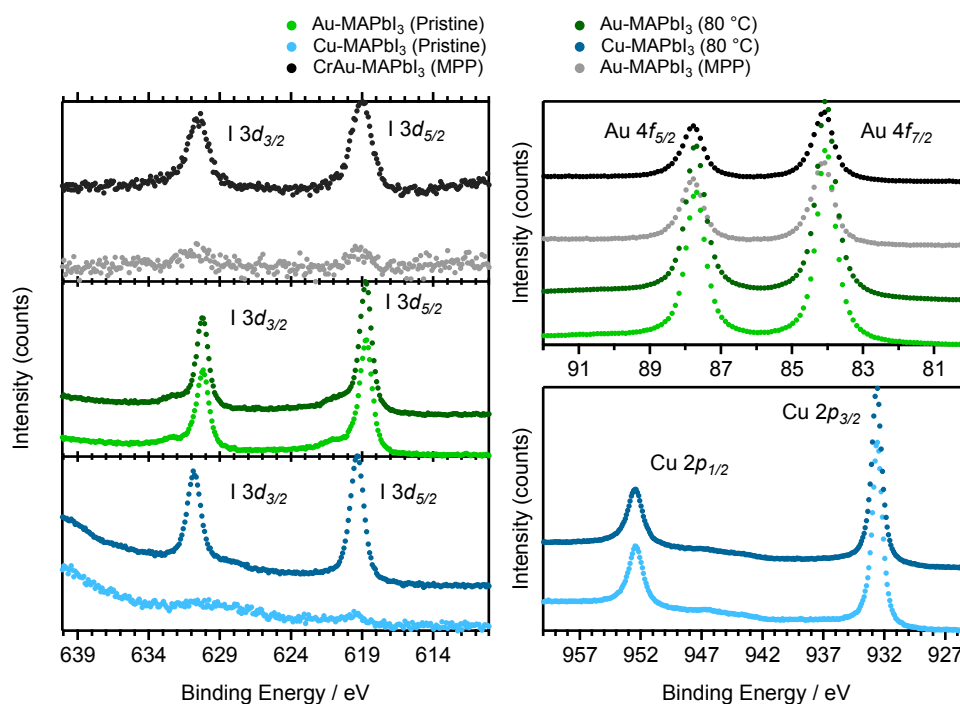


Figure 6.20 $\text{I } 3d$, $\text{Au } 4f$, and $\text{Cu } 2p$ core-level spectra from electrodes of pristine and aged devices. Accumulation of I in Au electrodes (pristine and aged) can be observed while such an accumulation is only observed in Cu electrodes from aged devices. Additional oxidation state of I observed at higher binding energy from main peak is observed for Au electrodes, in agreement with interfacial AuI_2^- ($m/z = 450.73$) observed in ToF-SIMS depth profiles.

6.3.4 Inter-electrode Degradation

More often than not, studies involving thermal degradation and using chemical depth profiles, fail to consider degradation at areas between electrodes. Thus, this section aims to investigate the differences in effects of thermal degradation at the electrode and areas between them.

Using the same device as mentioned in **Section 6.3.1**, chemical depth profiles were measured on areas between electrodes. In order to deconvolute the possible effects of beam-induced migration of Cu, one electrode on the pristine device was peeled off to reveal the underlayer for depth profiling. Their profiles and the illustration of profiled areas are shown in **Figure 6.21**. Note that the profiles show the PCBM/MAPbI₃ interface.

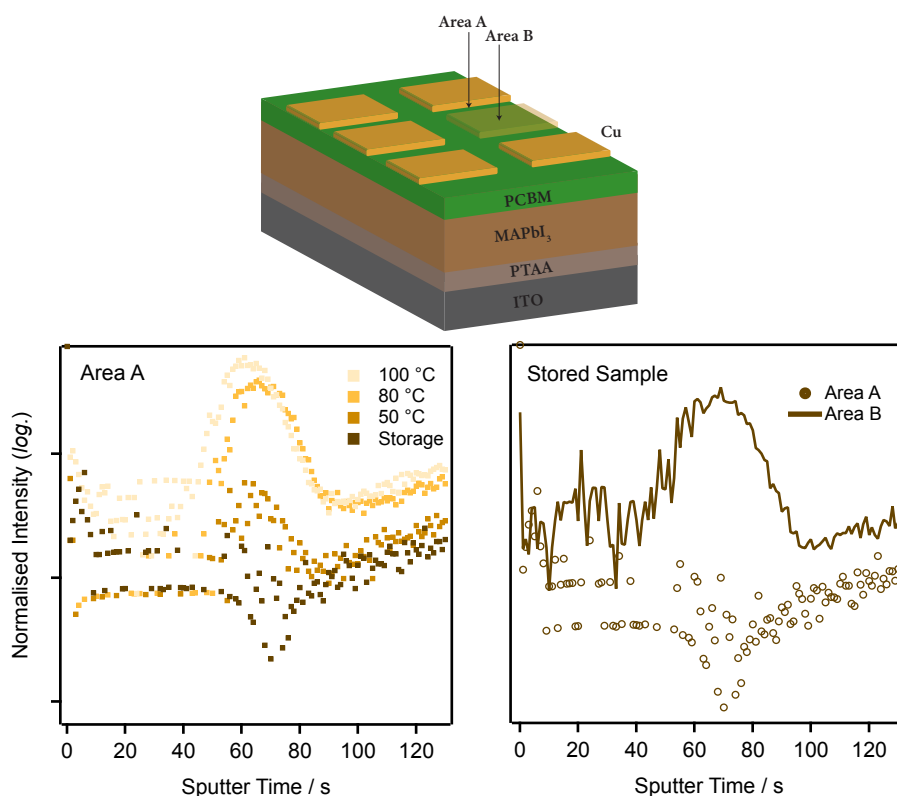


Figure 6.21 **Dynamic ToF-SIMS:** Depth profiles of CuI_2^- (and $m/z = 316.77$) in area A for samples stored (pristine) and thermally aged for 5 h at 50 °C, 80 °C, and 100 °C in the dark and in an N_2 environment. Profiles show that enhancement of this mass fragment is observed at the PCBM/MAPbI₃ interface after thermal ageing at > 80 °C between electrodes. In a stored device, area B shows enhanced signal of this fragment while area A shows a suppression. Observations indicate two origins of mass fragment $m/z = 316.77$: degradation of MAPbI₃ and Cu-based fragment.

From the profiles, Cu^- ($m/z = 62.93$) ions were not detected in all samples, beyond the electrode layer. However, the mass fragment $m/z = 316.77$ was still observed. In the pristine sample, there is a clear difference in intensities between areas A and B where the former shows a suppression of the mass

fragment signal and the latter, an enhancement. Turning towards profiles from area A of the thermally aged samples, increasing temperature enhances this mass fragment. These observations suggest (1) that the mass fragment $m/z = 316.77$ is definitively influenced by temperature *i.e.* its formation must be thermally assisted, (2) that it can be found in the pristine sample in the areas deposited with electrode only, is indicative of its relation with Cu^- ($m/z = 62.93$).

To further investigate this feature, the same measurements were done on Cu and CuCr-based devices (see **Figure 6.22**). In area A, both pristine samples showed a much lower normalised intensity than in thermally aged samples. In area B, the mass fragment is hardly suppressed throughout all samples—it shows a slight increase for thermally aged ones. These observations are similar to what was observed in Cu-based devices which *could* indicate that the thin layer of Cr is unable to completely inhibit Cu diffusion and that the compound/phase associated with this mass fragment has a low formation energy.

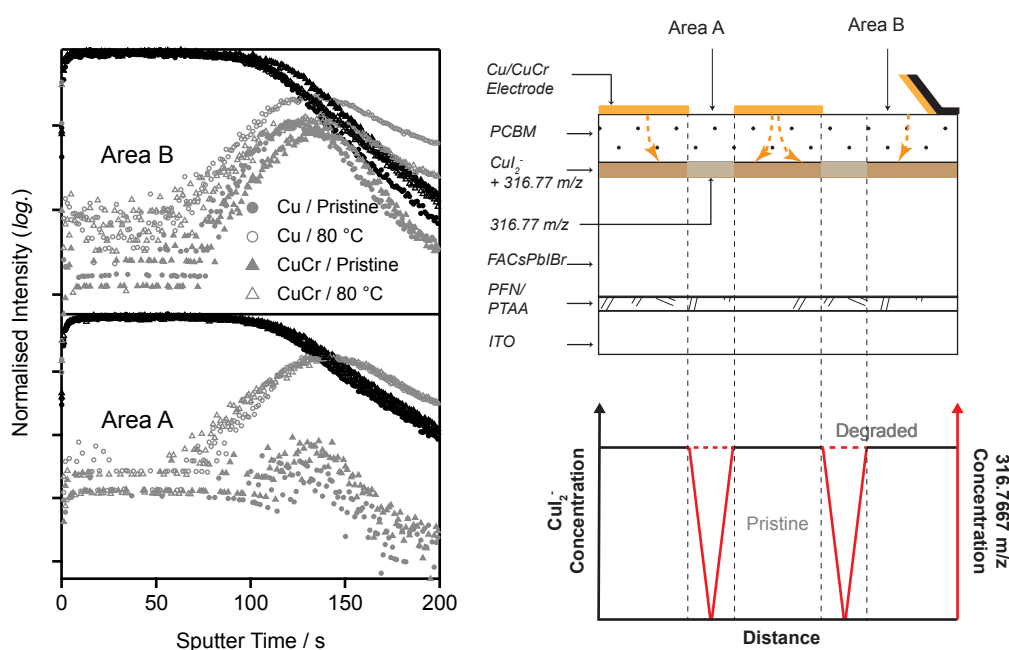


Figure 6.22 Left: **Dynamic ToF-SIMS:** Depth profiles of Cu and CuCr-electrode based devices stored (pristine) and aged at 80 °C in an N_2 environment and in the dark for a period of 24 h. Right: **Illustration** of device depicting analysed area and formation of compound containing Cu-I fragments with suggested corresponding concentration profile of $m/z = 316.7667$ mass fragment.

At this point, it is worth mentioning that there could be mass interference for the selected peak (*i.e.* more than one mass fragment inaccurately identified) that is not a Cu-based fragment and whose formation is also thermally assisted. It is unlikely to be an artefact of the sputtering process as its intensity increases with temperature and a suppression of its intensity in pristine devices between electrodes. To deconvolute these possible interferences, the mass fragment is analysed in degraded Ag-based devices.

The depth profiles of Ag and Cu-based devices that have been degraded by illumination and MPP

tracking in dry air are given in **Figure 6.23**. Both pristine and degraded Cu-based devices show significant presence of the mass fragment, with the degraded device showing a slightly different profile. Interestingly in Ag-based devices, only the degraded sample shows significant concentrations of the mass fragment which strongly suggests that it originates from a by-product of the degradation of the organometallic halide absorber layer. These findings support the hypothesis that the mass peak selected is a combination of at least two mass fragments with one being a Cu-based fragment while the other is likely a degradation (thermal or light-based) product coming from the absorber layer. Therefore, what was observed in area A with increasing temperature (**Figure 6.21**) was likely related to the degradation process of the absorber layer and not entirely related to Cu the inter-electrode diffusion of Cu.

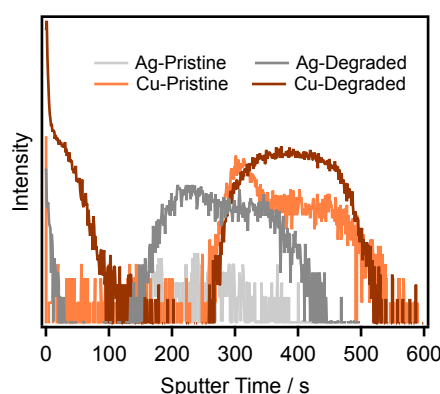


Figure 6.23 Dynamic ToF-SIMS: Depth profiles of $m/z = 316.77$ for pristine and aged Ag and Cu-based devices in their entirety. Profiles show that the mass fragment found in Ag-pristine is almost negligible while Ag-degraded and Cu-pristine show similar profiles.

To provide more definitive examination of the chemistry of this feature, depth profile XPS should be performed as it can provide chemical bonding information. Given the limitations of the available instrument, the nature of this feature could not be explored in greater detail. However, there is no doubt that it is correlated with both Cu-based electrodes and the processes of degradation be it light or thermal based.

6.3.5 Errors

The limitations of the data discussed here are similar to that in the previous section. All profiles shown have had local inhomogeneities removed from depth profile reconstruction.

It should be noted that the sputter times after 72 h thermal ageing are significantly different to profiles after 24 h thermal ageing. This is attributed to a higher sputter beam current (250 nA compared to 230 nA). This difference may result in different depth resolutions due to varying degrees of beam damage/atomic mixing. As such, the same pristine samples (untreated and stored in an N₂ environment and

in the dark) were profiled together to minimise the slight difference in beam conditions. While profiles from pristine samples may possess features from its inherent instability, the purpose of the experiments is to distinguish effects arising from thermal degradation in a non-quantitative manner.

Device properties were measured from a single device for each configuration which may not necessarily be statistically sound. To achieve higher statistical significance, more devices should be measured for their device properties and chemical profiles. All devices were also exposed to air during sample preparation which could result in some degree of oxidation/hydration. However, given that they were exposed to the same extent, its effect can be ruled out in influencing differences in depth profiles.

6.3.6 Conclusions

Based on chemical depth profiles from ToF-SIMS, thermal degradation eventually results in accumulation of I^- ($m/z = 126.92$) at the electrode/BCP interface, regardless of the electrode. Cu-based device exhibited catastrophic reduction in PCE after 72 h of ageing at 80°C while Au-based device showed significantly better thermal stability. Photoemission spectra and chemical depth profiles show that at the Au/BCP interface I^- ($m/z = 126.92$) exists in significant concentration in both pristine (stored) and aged devices. $I3d_{3/2}$ core-levels also indicate the presence of different iodine oxidation states at this interface which is in agreement with the process of an electrochemical degradation of the organometallic halide absorber layer resulting in the formation of an adlayer at the Au/BCP interface through underpotential deposition (UPD). Photoemission measurements of Cu electrodes showed the absence of these features and significantly lower concentration of iodine in the pristine device suggesting that the higher concentration of iodine seen in Au is electrochemically driven.

The origin of the difference in thermal stabilities is likely due to the formation of highly insulating surface species on Cu electrodes and the presence of metal-halide mass fragments within the absorber layer. However, there is still some ambiguity that requires further measurements to ascertain the chemistry at the PCBM/absorber layer interface.

The addition of a Cr interlayer between the electrode and BCP improves FF, J_{sc} , and V_{oc} of Au in response to thermal stresses and Cu, to a limited extent. This may be due to the different degradation mechanisms for both electrodes. Based on depth profiles, it had little effect on the accumulation of I^- ($m/z = 126.92$) at the electrode/BCP interface and electrode surface. The latter feature is exemplified in CuCr electrodes showing an inverse relationship between I^- ($m/z = 126.92$), CuI_2^- ($m/z = 316.77$) with Cu^- ($m/z = 62.93$). Thus, the difference in thermal stabilities between the two metal electrodes comes from the formation of Cu-I secondary phase on the surface of Cu that remains unhindered compared to

Au. Furthermore, the absence of AuI_2^- ($m/z = 450.73$) at the electrode/BCP interface is accompanied by a more stable FF in response to thermal stress. Based on observations of Au_x^- and Au_x^+ ions within the absorber layer and the presence of an *s-shape* J-V curve in thermally aged devices, Au is thought to still have diffused into the absorber layer but may not be the main cause of device degradation under thermal stresses. To provide irrefutable proof, depth-resolved XPS must be performed as mass spectra from ToF-SIMS may be influenced by mass interference.

Cr has been previously reported [168] to improve thermal stability in standard *n-i-p* and mesoporous devices. The results discussed here do not show the same extent in improvements, especially so in the detection of metal impurities in the absorber layer. Additional measurements should be carried out to ascertain the reasons.

Chapter 7

Conclusions & Future Work

7.1 Instrument-Material Interactions

In this thesis, the interaction(s) of X-rays on $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI₃) has been discussed. Morphological and chemical changes were observed after $t_{\text{rad}} = 3.0$ h. Particularly, significant attenuation of C 1s and N 1s are evident and their removal is observed by a reduction in normalised peak areas over irradiation time (t_{rad}), in agreement with previously reported trends. Whereas, Pb 4f and I 3d show increase in normalised peak areas. Upon extended irradiation exposure, significant changes in oxidation states of Pb 4f and I 3d core-levels are present where a convoluted peak shape is apparent after $t_{\text{rad}} = \sim 2.2$ h. While time-resolved XPS measurements have been reported [84, 106], such features have not. Additionally, I/Pb ratio shows a linear drop with t_{rad} indicating a changing surface stoichiometry though, there is insufficient evidence to conclude the liberation of I₂ or redistribution of chemical species throughout the material.

Furthermore, results indicate that within the time-scales of data acquisition, time considerations have to be made for measuring organometallic haldie samples where a limited time-frame (below $t_{\text{rad}} = 2.0$ h) is suggested. This implies that during XPS measurements (including valence band measurements), there might be instrument interactions that influence obtained spectra and may contribute to discrepancies between reported I/Pb ratios (discussed in **Section 2.5**). Finally, there was no apparent change in normalised peak areas as a function of t_{rad} after ultra-high vacuum (UHV) exposure $t_{\text{vac}} = 8.0$ h.

The chemical and morphological effects of ion-beam bombardment ($^4\text{He}^+$, $^{20}\text{Ne}^+$, $^{40}\text{Ar}^+$) are also discussed. Physical surface modification can be observed after applying doses of 1.0×10^{16} ions/cm² from

all three ion beams. Observed metallic lead features with increasing UHV time of post-ion bombarded samples can be explained by the liberation of volatile species, increasing the already elevated defect density, leading to formation of Pb^0 . Through systematic $^{20}\text{Ne}^+$ ion dose increments, it is suggested that the static limit for ion scattering measurements is less than 1.0×10^{13} ions/cm² and is applied to all static LEIS measurements in this thesis. Note that this value should be lower but ion doses with lower dose densities result in high signal-to-noise spectra. The approach in determining the static limit described should also be applied to varying beam energies in order to empirically obtain a more accurate static limit.

Additionally, a systematic investigation into the changes in morphology of MAPbI_3 with increasing dose is of importance. These should be supplemented by calculations of stopping ranges of $^4\text{He}^+$, $^{20}\text{Ne}^+$, and $^{40}\text{Ar}^+$ in MAPbI_3 . While it is theoretically possible to compute such interactions in the SRIM software package [187], computed density value may not be appropriate. Therefore, determination of density value is crucial.

Based on mass fragment analysis of MAPbI_3 , I_x^- and Pb_xI_y^- fragments have the highest yield in the negative polarity, and Pb , PbI^+ , and $\text{CH}_5\text{NPbI}_2^+$ fragments in the positive polarity. CH_6NI_2 ionises with a high yield as well but is not a direct fragment from MAPbI_3 . Analysing the profiles obtained from different sputter beams (O_2^+ , Cs^+ , Ar_{1000}) show that O_2^+ in the negative polarity is preferable due to the consistency in depth profiles and absence of interfacial matrix effects. Consequently, I_x^- and Pb_xI_y^- fragments are used for MAPbI_3 layer identification in all ToF-SIMS depth profiles.

While a cursory approach in mass fragment analysis is provided and is sufficient for the purposes of this thesis, it might be of fundamental interest to conduct a more thorough analysis using different primary ion beams and sputter beams on a simple MAPbI_3 sample. For instance, using Argon cluster, with varying cluster sizes, as an analysis or sputter beam may provide insights into the ionisation probabilities of certain fragments.

7.2 Surface Composition Analysis

The surface composition/stoichiometry of MAPbI_3 is also investigated. Based on previously published work [219, 220], the addition of organic molecules in small concentrations (5.0 vol%) to MAPbI_3 precursor solutions resulted in fabricated MAPbI_3 samples exhibiting improved stability against light and oxygen. It was hypothesised that during the formation of MAPbI_3 , these molecules with functional groups ($-\text{COOH}$, $-\text{NH}_2$) preferentially bond to defect sites from which superoxide initiated degrada-

tion would have occurred.

Using ToF-SIMS in the dynamic mode, depth profiles were obtained from MAPbI₃-based devices (and other compositional analogues) that showed suppressed diffusion of I⁻ for samples whose absorber layer was fabricated with organic additives. These observations indicate that defect sites (e.g. V_I[•]) are no longer accessible for ion migration within MAPbI₃.

7.2.1 Organic Molecules Additives

Static ToF-SIMS-acquired surface mass spectra of MAPbI₃-*Gly*, MAPbI₃-*AVA*, and MAPbI₃-*NMA* showed that the surfaces for these samples can be distinguished by observing mass peak intensities of parent molecular ions (and protonated/deprotonated ones) of the organic additives.

Based on peak integral ratios from LEIS scattering data of MAPbI₃-*Gly*, MAPbI₃- β , MAPbI₃- γ , MAPbI₃-*AVA*, and MAPbI₃-*NMA*, the surface stoichiometry of these samples deviate from that of MAPbI₃ with lower I/Pb ratio ($R_{I/Pb}$) than MAPbI₃ which, is indicative that the surface (first atomic layer) concentration of I and Pb has changed. However, given the large variability in the data, no observable trends can be concluded.

While, based on the scattering data and mass spectra, the location of these organic molecules cannot be ascertained due to a lack of spatial resolution, the increased photostability of these devices [219, 220] suggests that the organic molecules preferentially terminate on grain surfaces (as opposed to predominantly forming secondary phases).

Possible bonding from these organic additives include hydrogen/ionic bonding to V'_{MA}, V_I[•], and under-coordinated I and Pb. However, the non-concomitant change in peak integrals, as reflected by $R_{I/Pb}$ can be inferred to arise from preferential termination of organic molecules on under-coordinated I atoms.

As continuation of the work described above, a time-based degradation experiment could yield insights into degradation pathways. Ideally, one would subject MAPbI₃-*Gly*, MAPbI₃- β , MAPbI₃- γ , MAPbI₃-*AVA*, MAPbI₃-*NMA*, and MAPbI₃ samples to oxygen and light and using static ToF-SIMS and scattering experiments at specific time intervals, the evolution of mass spectra and surface stoichiometry can be obtained. These might provide further evidence for the stabilising qualities of organic additives.

Finally, more statistically sound data for scattering experiments of MAPbI₃ samples fabricated from non-stoichiometric precursor solutions should be obtained. In particular, these experiments should also be complemented by angle-resolved XPS to determine the stoichiometry of I/Pb as a function of depth

in a non-destructive way.

7.2.2 Surface Composition

Finally, an attempt to better understand the surface composition of MAPbI₃ was made. PbI₂ and MAPbI₃ samples were subjected to dose dependent LEIS scattering experiments. A constant $R_{I/Pb}$ value was obtained for PbI₂ while that of MAPbI₃ showed a slight decrease before exhibiting a steady-state region. Such a feature is indicative of an I-rich surface. Further scattering data from Cs-substituted compositions showed that from the first acquisition scan at a dose of 3.4×10^{14} ions/cm² shows an absence of any Cs scattering peak. This strongly suggests a Cs-deficient surface. Further confirmation may be necessary and such scattering experiments should be performed on CsPbI₃.

For absolute quantification of the surface, ion-fractions for Pb and I should be empirically determined by using reference samples. These would allow a more quantified approach in determining both the actual surface composition (supplemented by theoretical calculations of surface atomic densities based on an MA-rich surface and a Pb-I rich surface) and related changes in surface composition from solution processing additives. However, the reported variations in peak integrals require additional investigation and may have been caused in part, by the quality of the precursor solution. Therefore, by preparing a number of precursor solutions with the same molarity, a number of samples from each solution should be fabricated and subjected to scattering experiments for further confirmation.

7.3 Electrode Dependent Degradation

7.3.1 Electrode-Induced Degradation

Device stabilities of four different electrode configurations were examined and reasoned. Single electrode configurations (Al, Ag, Cu) and a bilayer configuration (CuAg) in devices were subjected to MPP-tracking and lightsoaking conditions in ambient air. The PCE of Al-based device was the least stable and reached complete degradation just after 15 h. This was shown to be largely the result of electrode degradation. Comparatively, Ag-based device fared better but was less stable than the Cu-based device. Chemical depth profiles from ToF-SIMS showed that accumulation of I⁻ on the surface of these electrodes were prominent after ageing. In particular, the less stable Ag-based device could be attributed to the degradation of the electrode layer where interface width of Ag⁻ was broader after degradation—indicative of the breakdown of the PCBM interface. Based on ToF-SIMS ion images, it was shown that

an AgI_2^- ($m/z = 360.74$) and I^- ($m/z = 126.92$) rich area extends from the surface to the MAPbI_3 layer which was accompanied by a spatially resolved inhomogeneity involving lower concentration of PbI_3^- ($m/z = 588.71$). This indicates the propagation of degradation from the MAPbI_3 layer to the Ag electrode layer.

On the other hand, the interface width of Cu^- remained the same. In a bilayer configuration of CuAg, device stability showed significant improvements compared the singler layer configuration of its constituents. Notably, it was observed that smearing of Cu^- and Ag^- profiles was absent and the electrode layer can be said to exist as two discrete layers. The aged device exhibited similar accumulation of I^- but to a lesser extent. The broader profiles seen in the Ag-based device are suppressed.

Physical effects of the sputter beam on the obtained depth profiles were not considered e.g. surface roughening which could have a broadening effect, but does not discount the trends observed in profiles and reference samples were always measured together. A more quantified approach would be appealing and would entail obtaining the sputtering yield of each layer and surface roughness values (obtained from a profilometer or atomic-force microscopy), post-bombardment, of each bilayer/multilayer interface. This will allow a more accurate determination of the depth-resolution of the sputter beam for a particular multilayer configuration.

7.3.2 Other Factors

The detection of AgI_2^- ($m/z = 360.74$) and CuI_2^- ($m/z = 316.77$) and absence of Ag^- or Cu^- within the MAPbI_3 layer poses some questions regarding metal diffusion. Namely, whether the metal-halide species detected are indicative of such a reaction between the electrode and MAPbI_3 layer or it is beam induced and therefore indicative of metal diffusion. To resolve these discrepancies, depth-resolved XPS and addition ToF-SIMS depth profiles using a non-reactive sputter beam should be performed on these samples. The strength in XPS lies in its ability to obtain chemical bonding information with quantification of atomic concentration without influence from the matrix. Thus, quantifying iodine concentration within each layer, post-degradation, should be straightforward.

Degradation arising from the breakdown of MAPbI_3 /PFN/PTAA interfaces (morphologically or chemically) were not considered in this thesis but could partly contribute to losses in device properties. These could be supplemented with analysis of a device cross-section by SEM to observe morphological changes at the interface or by scanning transmission electron microscopy (STEM) with elemental analysis for depth-wise diffusion of ions.

7.4 Thermal Degradation

The effects of thermal stresses on device stability by monitoring interfacial chemical species were reported. It showed that significant accumulation of iodine species at the electrode/BCP/PCBM interface was present in all tested devices. Such features were not observed in the profiles obtained from devices aged by MPP-tracking and lightsoaking conditions which indicate that these features are thermally formed. The addition of a Cr-blocking layer between BCP and the electrode for Au and Cu-based devices showed asymmetric improvements between the two electrodes. CrAu bilayer showed much higher FF and J_{sc} values after thermally ageing at 80 °C for 24 h but reached comparable values after 72 h. While improvements in the CrCu bilayer showed minimal improvements throughout. These observations suggest different degradation mechanisms affecting Cu and Au-based devices.

Based on chemical depth profiles, accumulation of iodine species on the surface of Cu electrodes is a major contributor to its poorer thermal resistance compared to Au and underlines its inherent reactivity with iodine.

J-V characteristics of Au and CrAu-based devices showed the presence of an *s-shape* curve which is indicative of an interfacial dipole. XPS measurements on the underside of these electrodes (by physically separating them using carbon tape) were performed showed different oxidation states of $I3d_{3/2}$. Additionally, $I3d_{3/2}$ core-level acquisition of Cu electrodes showed that concentration of iodine within a stored sample of Cu-based device was negligible compared to one that was thermally aged; where both Au-based devices that were stored and thermally aged showed the same core-level spectra. These data are in support of the obtained chemical depth profiles where interfacial features of I^- ($m/z = 126.92$) and AuI_2^- ($m/z = 450.73$) were detected in both reference and thermally aged samples. This may point to the low voltage threshold of underpotential deposition mechanisms (as described in ref. [132]) for Au/MAPbI₃ interfaces and may have occurred during current-voltage measurements.

Using a monoatomic Ar sputter beam, Au_x^- ions were detected within the organometallic halide layer. The discrepancy between observed metal diffusion in this case (Au) compared to that concluded from MPP-tracking and lightsoaking ageing conditions (Cu, Ag) may be due to the different reactivity of the beams used: Ar^+ vs. O_2^+ , respectively. In fact, depth profiles of Au^- showed no diffusion when using O_2^+ . Further confirmation is required by using monoatomic Ar sputter beam on all aged devices. However, noting that Au concentration remained the same regardless if the sample was thermally aged or if a Cr-blocking layer was used suggests that degradation of devices employing Au electrodes was not caused by Au diffusion. Additionally, different oxidation states of iodine was not observed for CrAu

electrodes. The presence of AuI_2^- ($m/z = 450.73$) is also visibly suppressed. Thus, the improvements seen in adding Cr to Au-based devices are likely to arise from the suppression of interfacial iodine species.

As before, to deconvolve any matrix effects, depth-resolved XPS and cross-section STEM/SEM with elemental analysis should be performed on these samples. Additionally, the discrepancy between reported improvements by adding a Cr-blocking layer [166] may be related to the different device architectures and interlayers used. Performing scattering experiments on areas underlying the electrodes can also prove insightful. Additionally, the thermal resistance(s) of the individual layers should also be considered.

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Appendices

Appendix A

Rights and Permissions

Figure 2.4: Copyright Clearance Center RightsLink Order Number: 4724370378392 **Figure 2.5:** Open access. **Figure 2.11 (2):** Copyright Clearance Center RightsLink Order Number: 1008045-1 **Figure 2.11 (3):** Copyright Clearance Center RightsLink Order Number: 4726440708661 **Figure 2.11 (4):** Copyright Clearance Center RightsLink Order Number: 1008561-1 **Figure 2.11 (5):** No order number given. **Figure 2.11 (1):** Copyright Clearance Center RightsLink Order Number: 1007950 **Figure 2.10:** Copyright Clearance Center RightsLink Order Number: 4724850822022 **Figure 6.9:** Copyright Clearance Center RightsLink Order Number: 4694760039340 **Figure 2.13:** Copyright Clearance Center RightsLink: No order number given.

Appendix B

Supplementary Figures

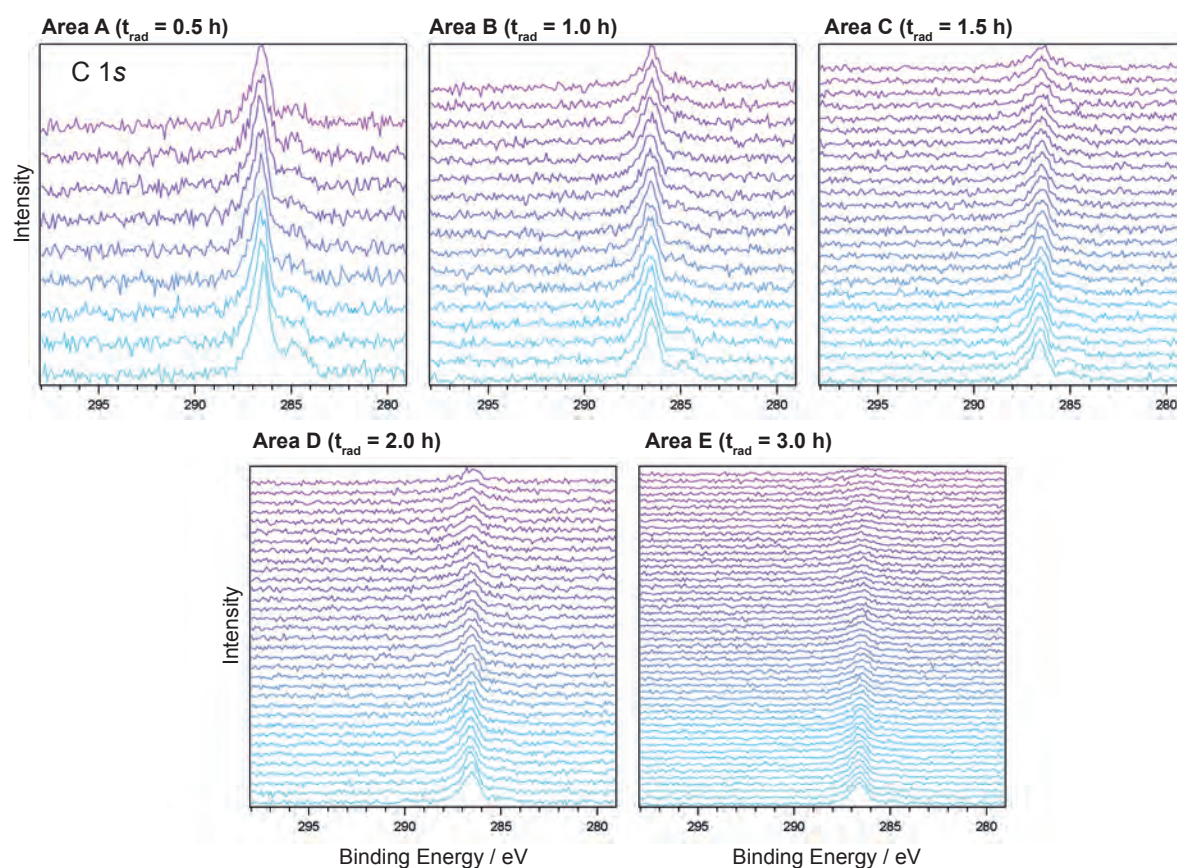


Figure B.1 Chapter 4, XPS: Core-level spectra of C 1s core-level from all analysis areas (A, B, C, D, E). Each spectrum is obtained from a single iteration loop $t_{\text{acq}} = 57.3$ s. Attenuation of signal is most apparent in $t_{\text{rad}} = 3.0$ h, related to removal of organic component in MAPbI₃.

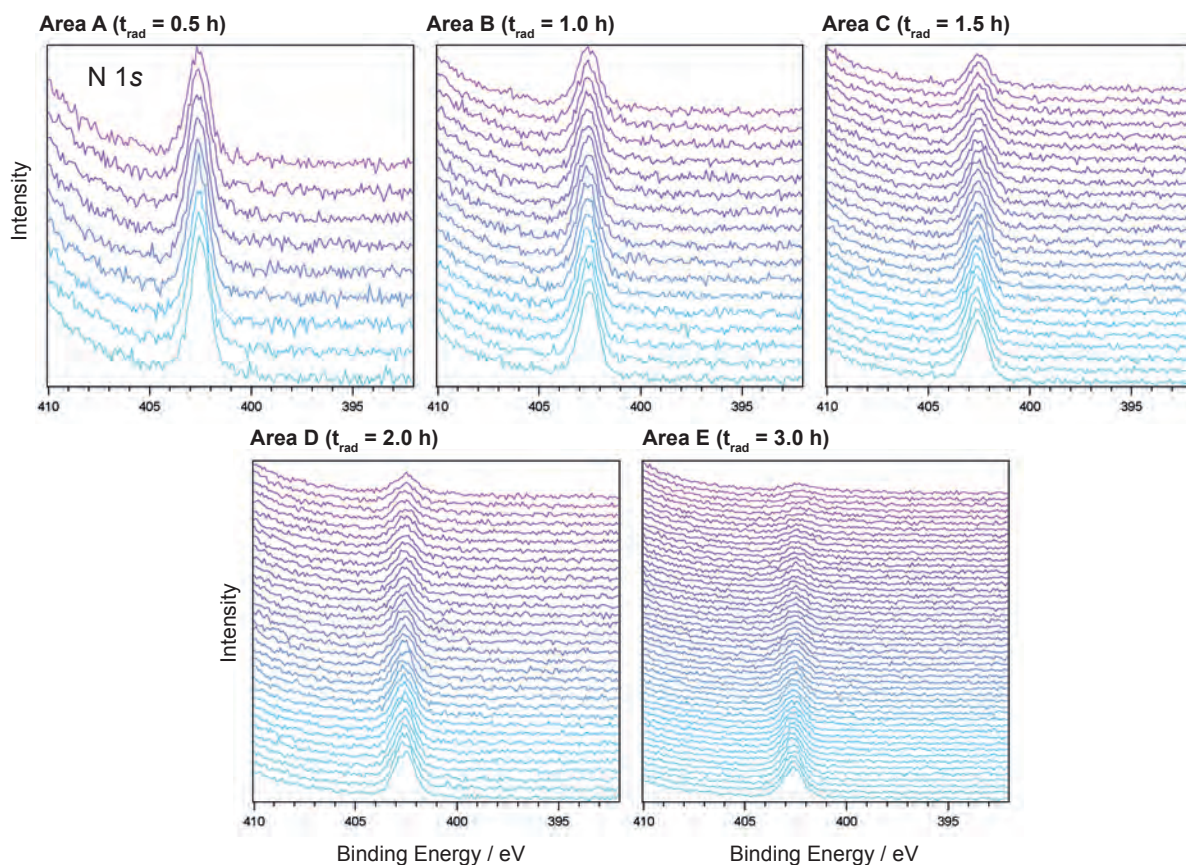


Figure B.2 Chapter 4, XPS: Core-level spectra of N 1s core-level from all analysis areas (A, B, C, D, E). Each spectrum is obtained from a single iteration loop $t_{\text{acq}} = 54.3$ s. Attenuation of signal is most apparent in $t_{\text{rad}} = 3.0 \text{ h}$, related to removal of organic component in MAPbI₃.

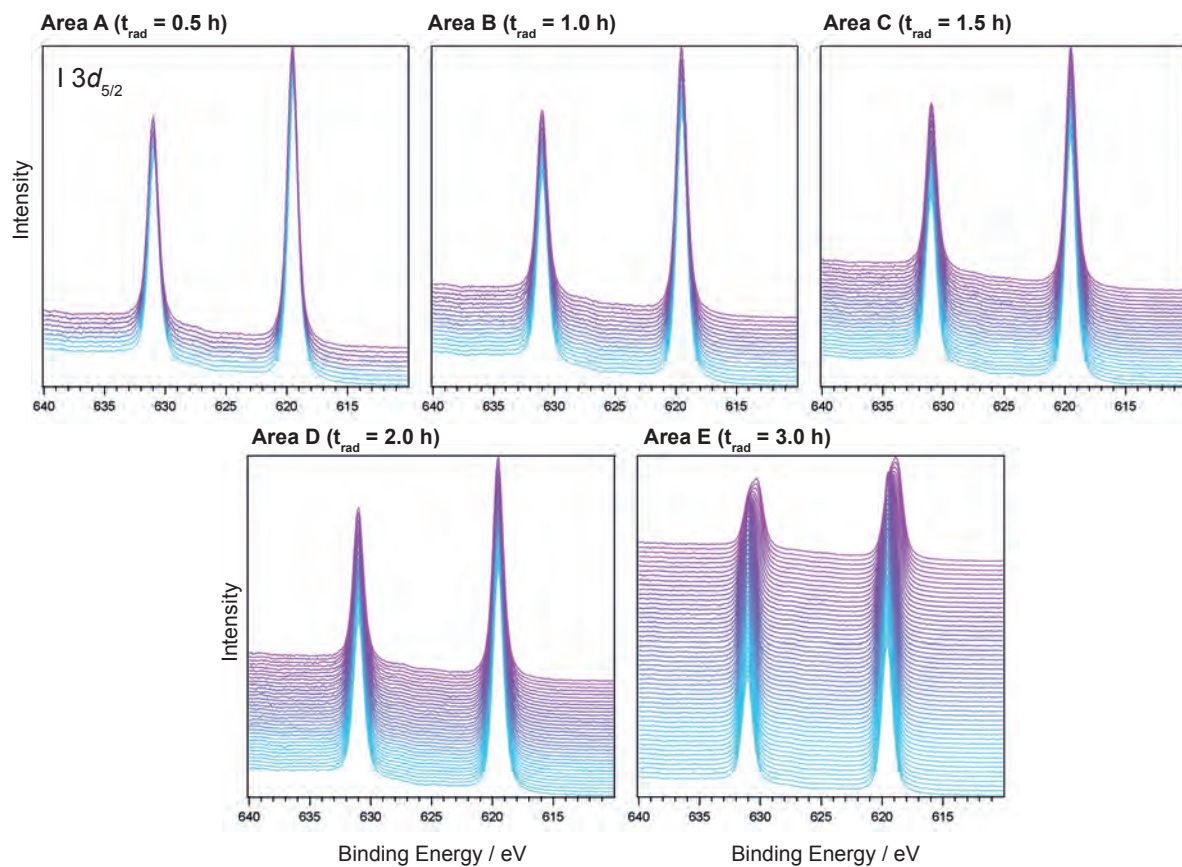


Figure B.3 Chapter 4, XPS: Core-level spectra of I $3d$ core-level from all analysis areas (A, B, C, D, E). Each spectrum is obtained from a single iteration loop $t_{acq} = 45.2$ s. Presence of secondary features at lower binding energies from the main peak at $t_{rad} = 3.0$ h.

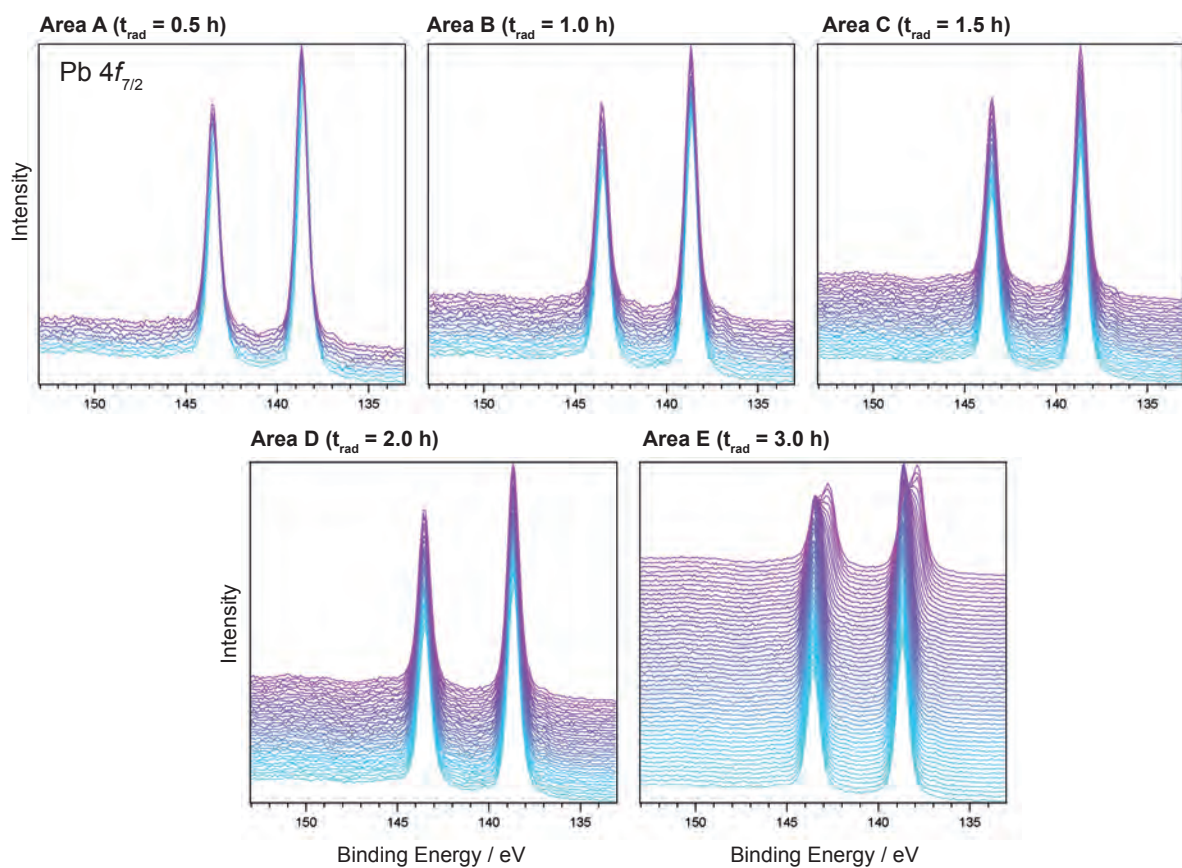


Figure B.4 Chapter 4, XPS: Core-level spectra of Pb 4f core-level from all analysis areas (A, B, C, D, E). Each spectrum is obtained from a single iteration loop $t_{acq} = 30.2$ s. Presence of secondary features at lower binding energies from the main peak at $t_{rad} = 3.0$ h.

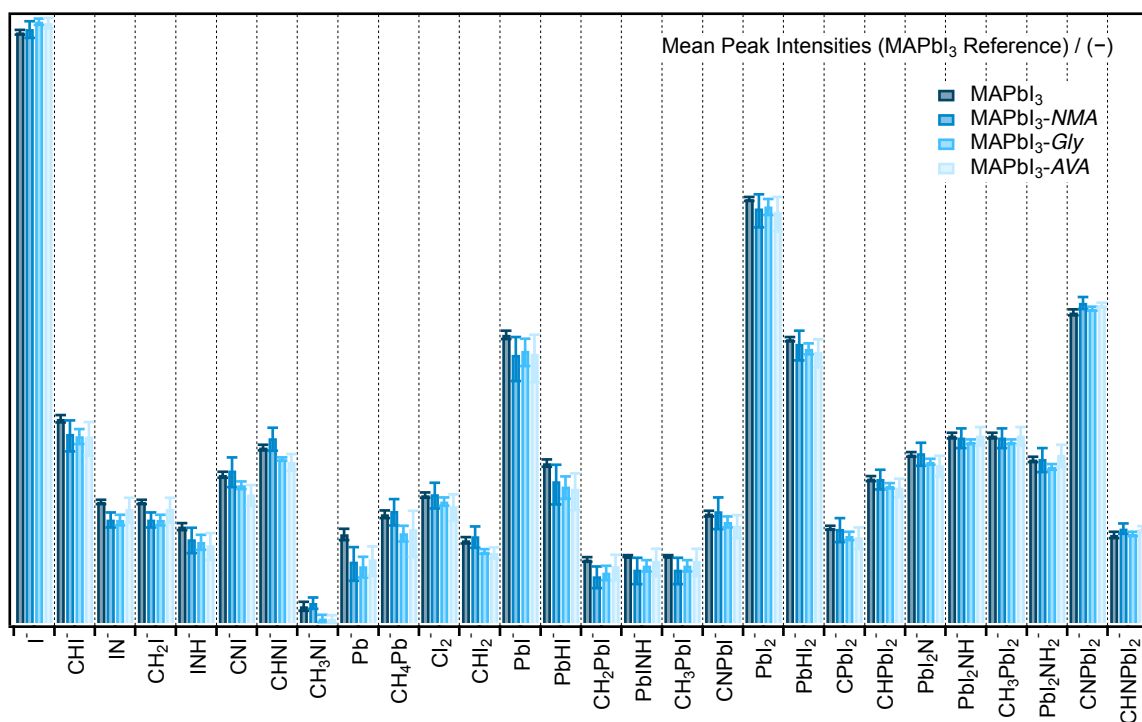


Figure B.5 Chapter 5, Static ToF-SIMS: (-) Mean peak intensities obtained from all samples by using MAPbI₃ as reference.

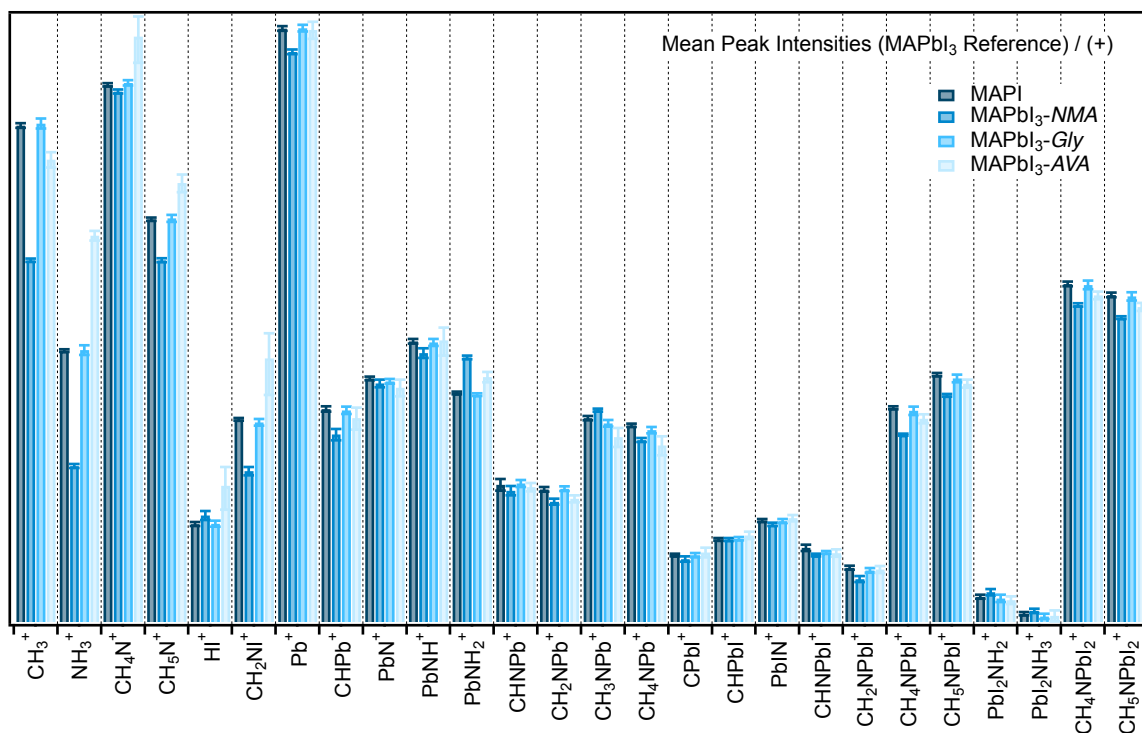


Figure B.6 Chapter 5, Static ToF-SIMS: (+) Mean peak intensities obtained from all samples by using MAPbI₃ as a reference.

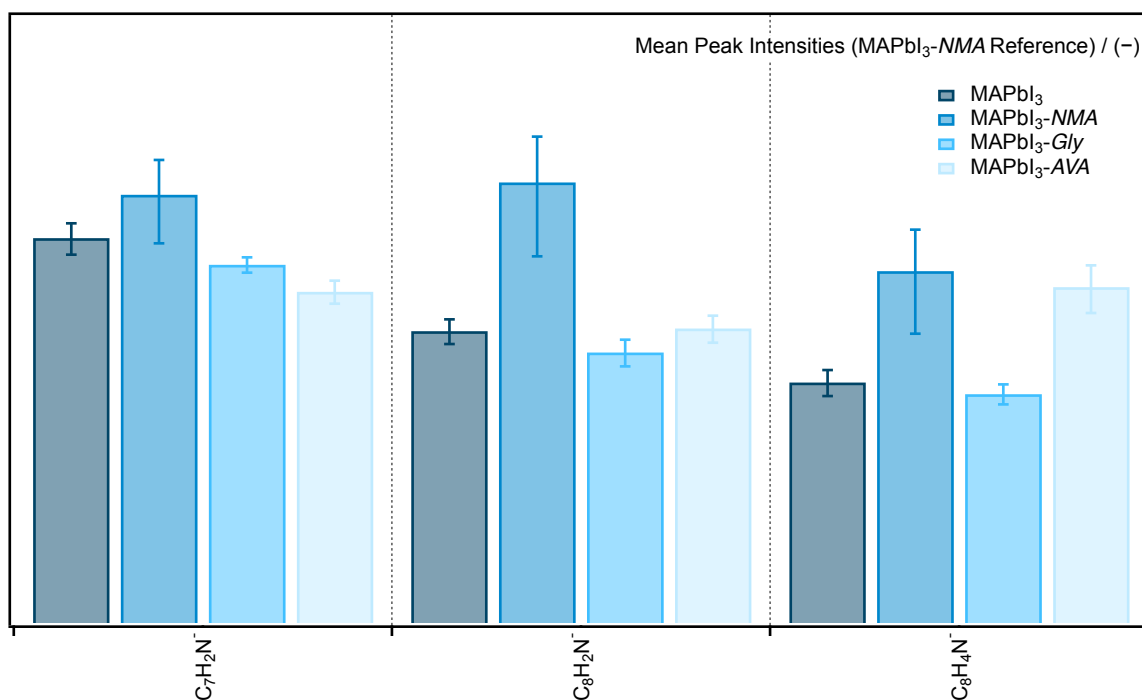


Figure B.7 Chapter 5, Static ToF-SIMS: (-) Mean peak intensities obtained from all samples by using MAPbI₃-NMA as a reference.

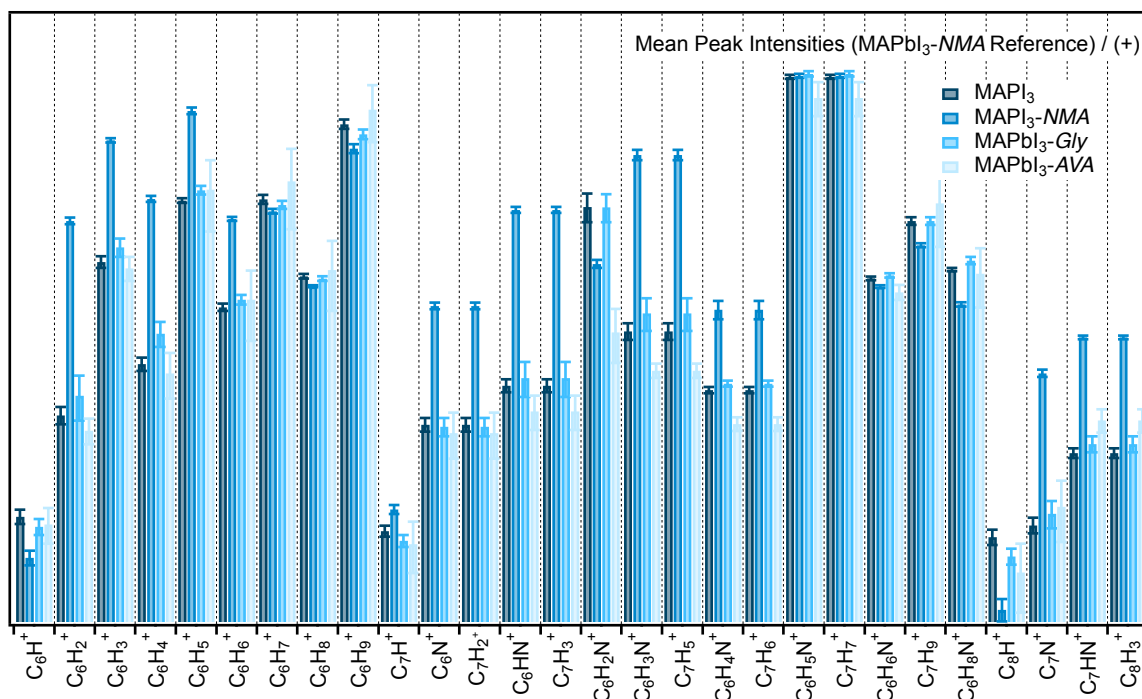


Figure B.8 Chapter 5, Static ToF-SIMS: (+) Mean peak intensities obtained from all samples by using MAPbI₃-NMA as a reference.

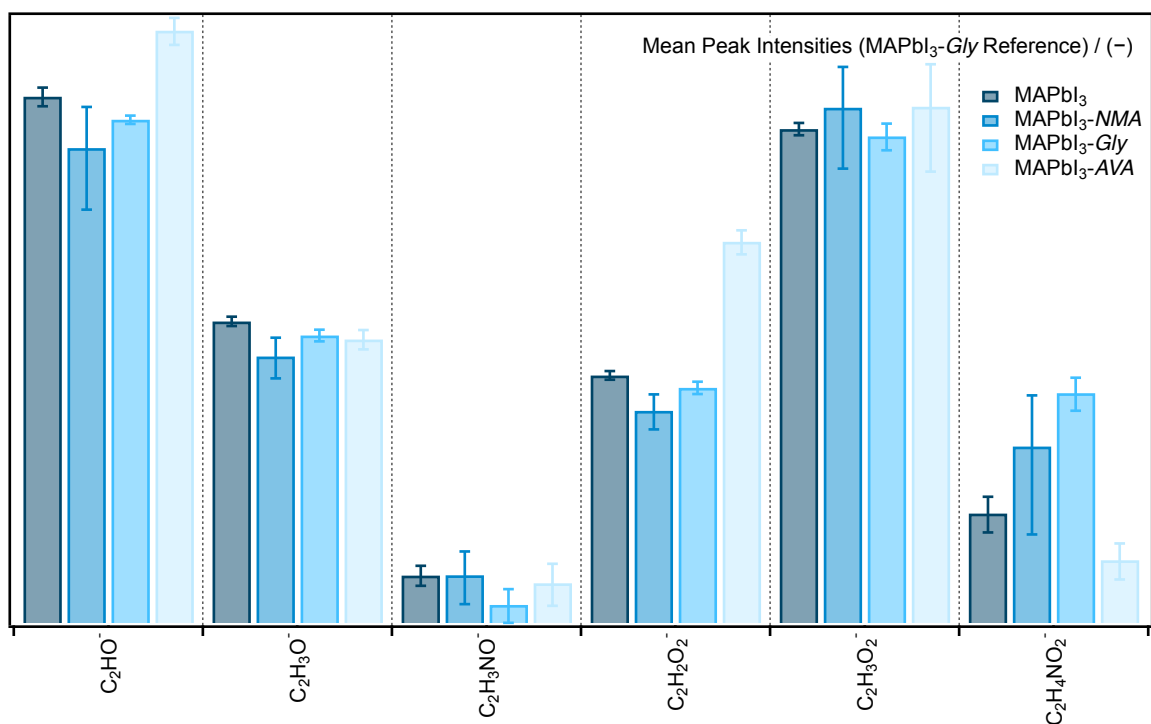


Figure B.9 Chapter 5, Static ToF-SIMS: (-) Mean peak intensities obtained from all samples by using MAPbI₃-Gly as a reference.

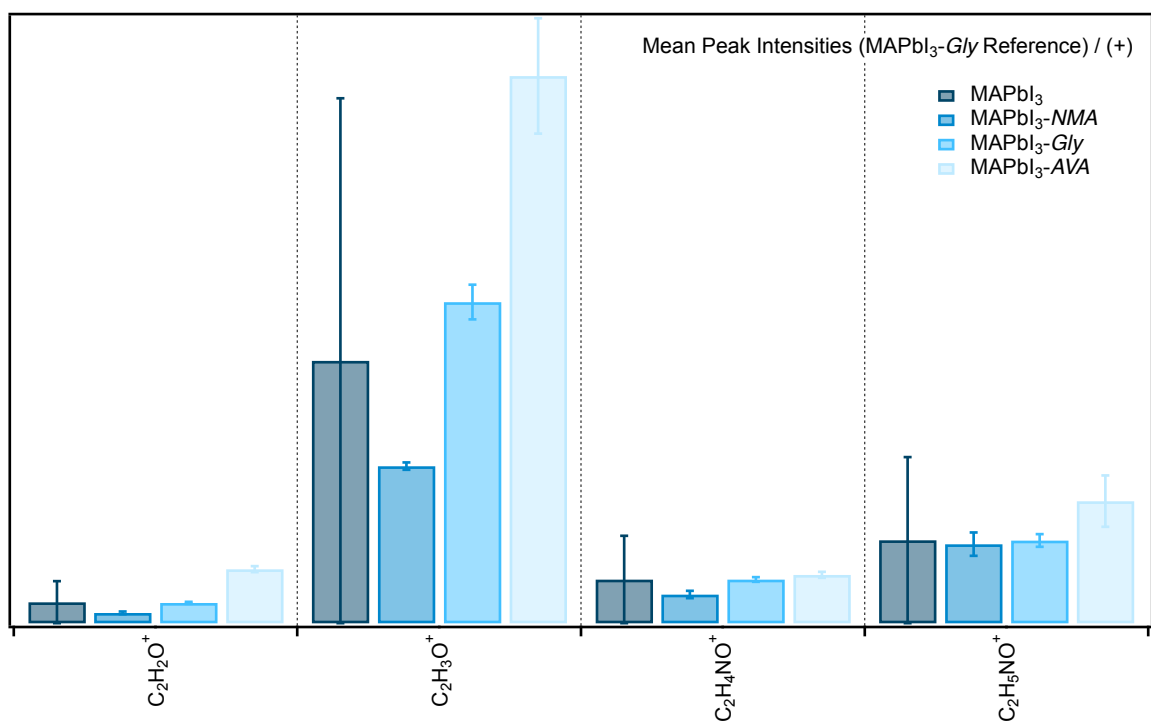


Figure B.10 Chapter 5, Static ToF-SIMS: (+) Mean peak intensities obtained from all samples by using MAPbI₃-Gly as a reference.

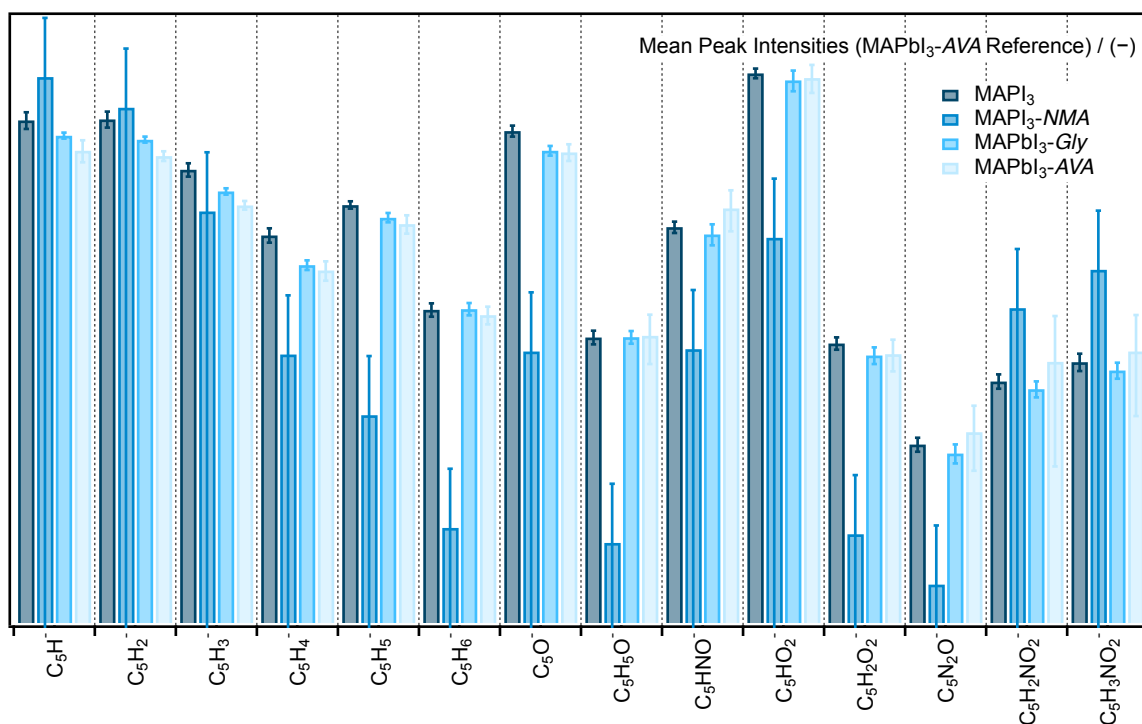


Figure B.11 Chapter 5, Static ToF-SIMS: (-) Mean peak intensities obtained from all samples by using MAPbI₃-AVA as a reference.

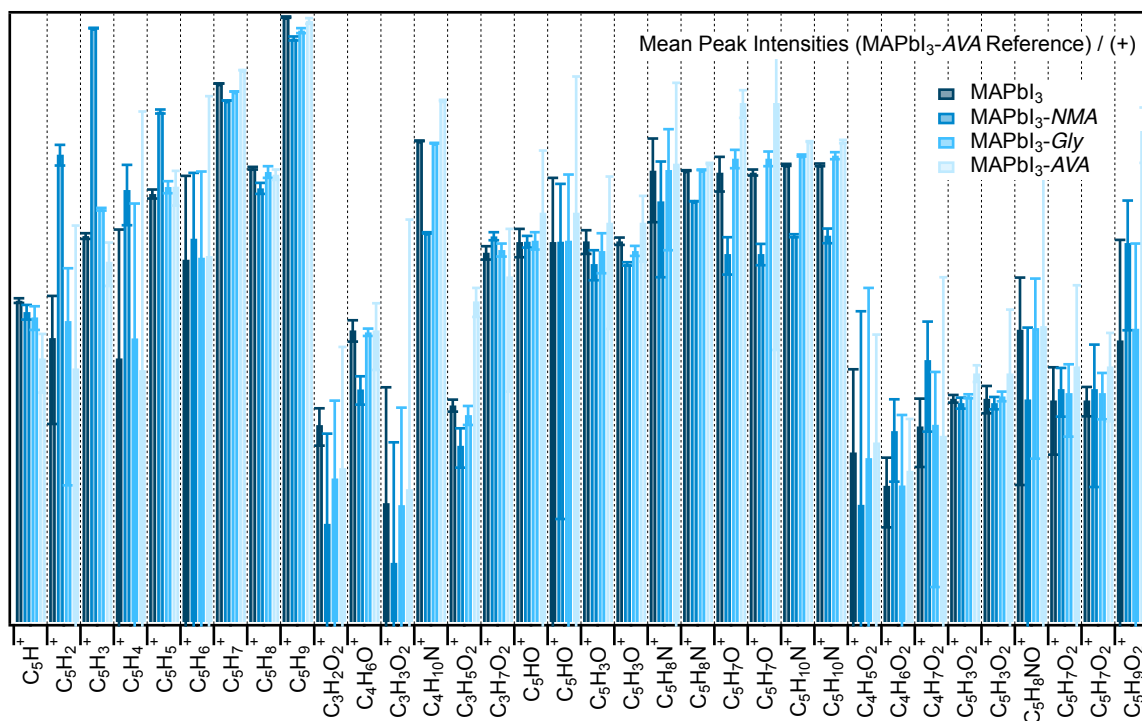


Figure B.12 Chapter 5, Static ToF-SIMS: (+) Mean peak intensities obtained from all samples by using MAPbI₃-AVA as a reference.

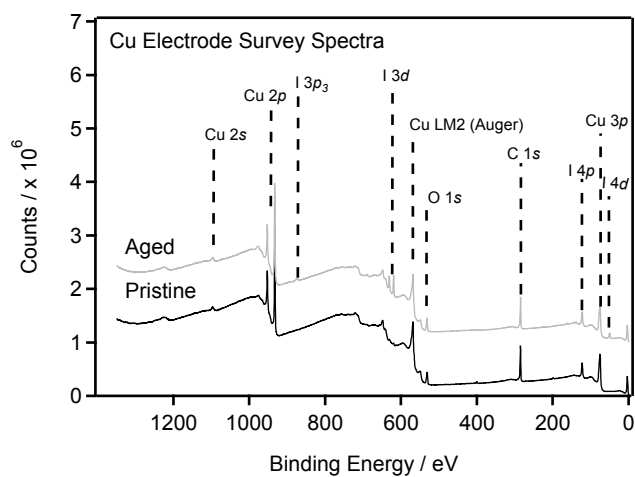


Figure B.13 Chapter 6, XPS: Survey spectra of peeled Cu electrodes for pristine and thermally aged devices.

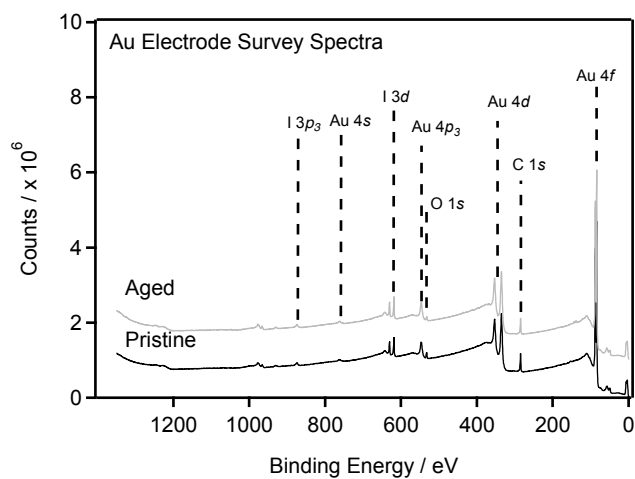


Figure B.14 Chapter 6, XPS: Survey spectra of peeled Au electrodes for pristine and thermally aged devices.

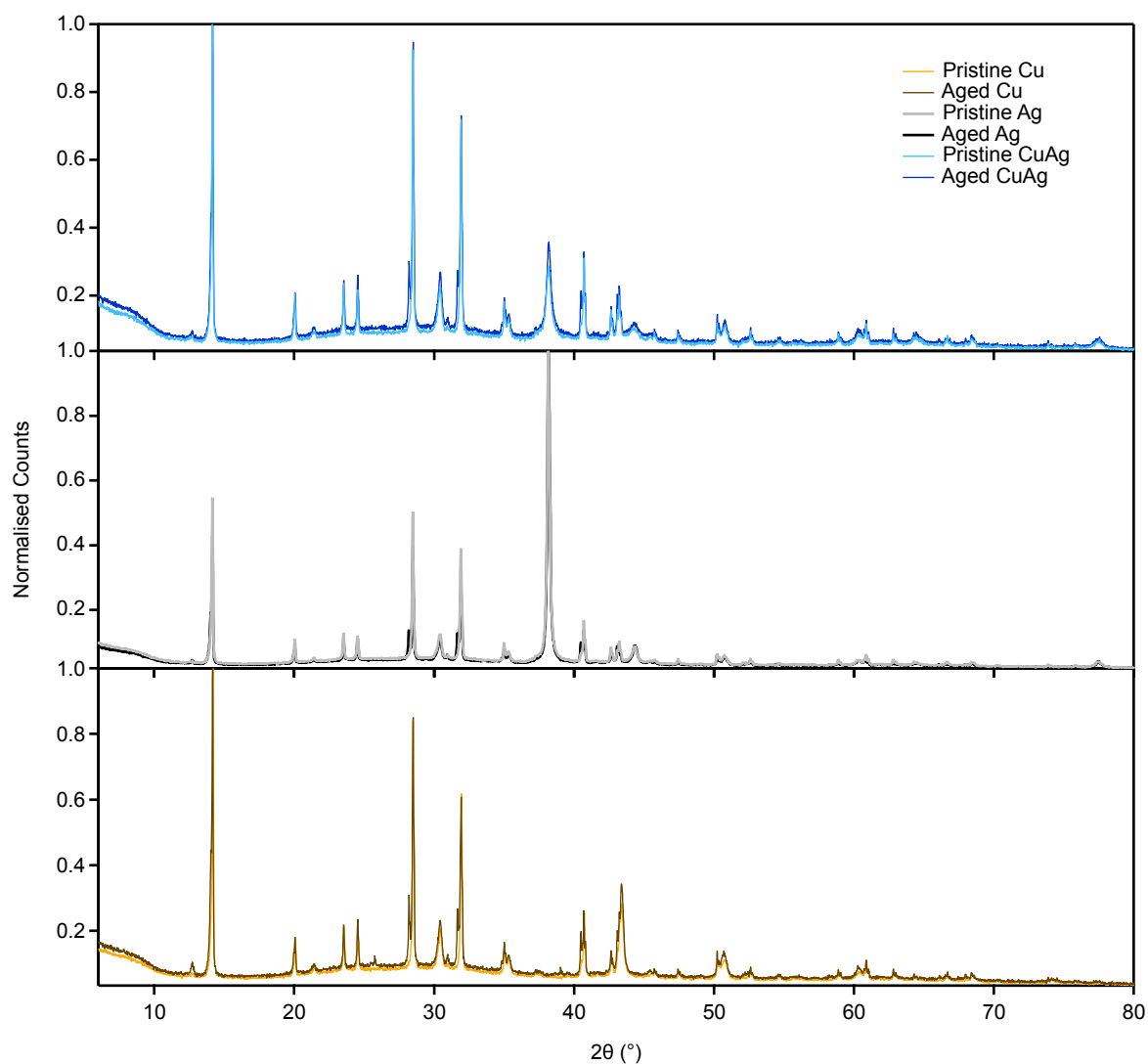


Figure B.15 Chapter 6, XRD: Diffraction data of aged (by MPP-tracking and LED illumination) and pristine samples of Cu, Ag, CuAg-based devices.

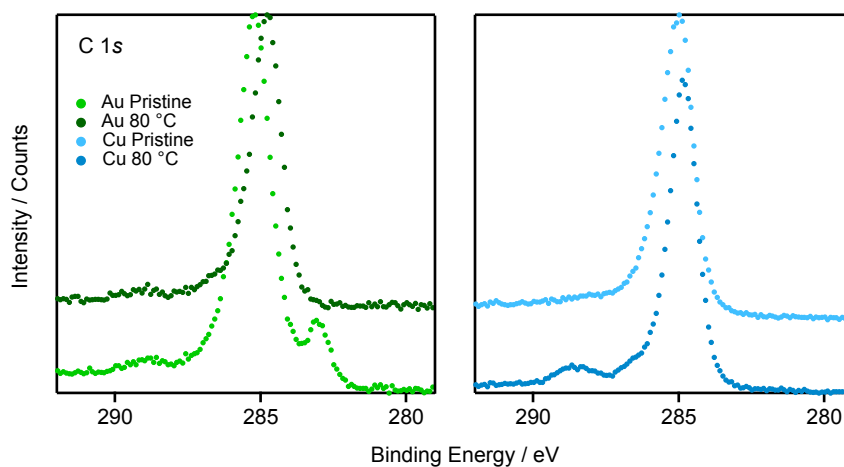


Figure B.16 Chapter 6, XPS: C 1s core-level spectra of pristine and thermally aged Au and Cu-based devices.