Exploring the Structural and Optical Response of Halide Perovskites Using High-Energy Electrons
"Seeing with electrons"

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This work has been submitted as a
Doctoral Thesis

Trinity Hall
April 2023
I would like to dedicate this thesis to my family, in particular to my dad, Jordi, who enabled me to study abroad, taught me the value of effort and dedication, and supported me at all times, especially in times of hardship.
Declaration

This thesis is the result of my own work and includes nothing which is the outcome of work done in collaboration except as declared in the Preface and specified in the text. I further state that no substantial part of my thesis has already been submitted, or, is being concurrently submitted for any such degree, diploma or other qualification at the University of Cambridge or any other University or similar institution except as declared in the Preface and specified in the text. It does not exceed the prescribed word limit for the relevant Degree Committee.

Jordi Ferrer Orri
April 2023
Abstract

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This thesis aims to investigate the nanoscale morphology, crystallography, composition, and optoelectronic structure of halide perovskites, a promising candidate for next-generation optoelectronic materials, using high-energy electron-beam microscopy techniques. This work addresses the stability challenge of PSCs from a material science perspective by understanding and controlling their complicated nanostructure. The unique macroscopic properties of lead halide perovskites are dictated by their nanostructure, which has direct ramifications on device performance and operational stability.

The thesis starts by reviewing hybrid halide perovskites and their heterogeneity at multiple length scales, and the different electron microscopy techniques used and developed in this work. It then reports in three experimental chapters the study of degradation mechanisms under an electron and X-ray beam using 4D-scanning transmission microscopy (4D-STEM), the development of cathodoluminescence (CL-SEM) to probe the optical properties of halide perovskites at the nanoscale, and the development of strategies to push the limits of 4D-STEM towards in-situ and operando conditions. The study demonstrates that high-energy electron probes are a powerful tool for studying perovskites at the nanoscale, and each experimental chapter addresses a specific technique development to enable new modalities of electron microscopy on halide perovskites. With these developments, this thesis yields valuable fundamental insights into the phase and operational stability of the beam-sensitive hybrid lead perovskites at the nanoscale.

Keywords: hybrid lead halide perovskites, solar cell, SEM, TEM, 4D-STEM, nano-diffraction, nanoscale, cathodoluminescence, beam damage, in-situ, operando

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• 1 paper in pre-submission stage

Contributing author

• 4 papers in pre-submission stage
List of abbreviations

- **AFM** - Atomic force microscopy
- **AM 1.5G** - Global horizontal irradiance spectrum (air mass) standard
- **BSE** - Back-scattered electrons
- **CCD** - Charged-coupled device
- **CL** - Cathodoluminescence
- **COD** - Crystallography open database
- **CW** - Continuous wave mode
- **DC** - Double-cation (double-halide perovskite) composition
- **DMF** - Dimethylformamide
- **DMSO** - Dimethyl sulfoxide
- **EBIC** - Electron-beam induced current
- **EDX** - Energy-dispersive X-ray spectroscopy
- **EL** - Electroluminescence
- **EELS** - Electron-energy loss spectroscopy
- **EM** - Electron microscopy
- **ETL** - Electron transport layer
- **FA** - Formamidinium ion cell
- **FIB** -Focused ion beam
- **FOV** - Field of view
- **FTIR** - Fourier-transform infrared spectroscopy
- **FWHM** - Full-width half-maximum
- **HOMO/VB** - Highest-occupied molecular orbital / Valence band
- **HTL** - Hole transport layer
- **ITO** - Indium tin oxide contact
- **I_{sc}** - Short-circuit current
- **KO** - Kanaya-Okayama (penetration depth)
- **LED** - Light emitting diode
- **LUMO/CB** - Lowest-unoccupied molecular orbital / Conduction band
• (L)HAADF - (Low) High-angle annular dark field
• MA - Methylammonium ion
• MEMS - Micro-electromechanical system
• NFM - Non-negative matrix factorisation
• PC - Principal component
• PCA - Principal component analysis
• PCBM - [6,6]-phenyl-C61-butyric acid methyl ester
• PEDOT:PSS - Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate
• PL - Photoluminescence
• PM - Pulsed mode
• PV - Photovoltaic cell
• PTAA - Poly(triaryl amine)
• PSC - Perovskite solar cell
• SEM - Scanning electron microscopy
• SED - Scanning electron diffraction
• SE - Secondary electrons
• SEM - Scanning electron microscopy
• SVD - Single value decomposition
• SNR - Signal-to-noise ratio
• STEM - Scanning transmission electron microscopy
• 4D-STEM - 4-dimensional STEM
• SiN - Silicon nitride
• (n)XRD - (nano) X-ray diffraction
• TC - Triple-cation (double-halide perovskite) composition
• TCSPC - Time-correlated single photon
• TEM - Transmission electron microscopy
• TRCL - Time-resolved cathodoluminescence
• UV - Ultraviolet
• VOC - Open-circuit voltage
• XRF - X-ray fluorescence
• eV - electron volt
• Eg - Band gap
• (v)BF - (Virtual) Bright field
• (v)DF - (Virtual) Dark field
Chapter 1

Introduction and Motivation

Photovoltaic technologies (PV) are key in the quest towards a low-carbon future, with the International Energy Agency predicting that by 2050, PV will become the leading source of energy.\(^1\)

Solar PV has been the fastest renewable technology annual growth in the last decade among all. This is attributed to the sharp decline in the cost of solar energy. PV is currently dominated by silicon technology, accounting for 95% of installed PV systems at the time of writing. The price of utility-scale PV installation costs fell by 81%, from US$ 4.73 / W in 2010 to sub-dollar US$ 0.88 / W values in 2020 (adjusted for inflation), mainly driven by the reduction in costs of the solar module itself and the inverter.\(^2\) However, cost reductions have slowed down in the last few years for silicon-based modules, as module prices are coming down to as low as they can be. Now, solar is dominated by other costs of the balance of the system that are harder to reduce, reaching a plateau soon as shown in Figure 1.1.\(^2\)

Therefore, despite its proven efficiency, long operating lifetime and reduced costs, silicon PV by itself is not enough to meet the ambitious deployment of PV at rates approaching 1 TW/year, unless new PV technologies with higher efficiency or cheaper production costs enter the market.\(^1\)

Halide perovskite PV technologies are promising candidates to support the deployment boost and clean energy security globally. Just after the 10\(^{th}\) anniversary of the first reported perovskite-sensitised solar cell by Miyasaka and co-workers,\(^3\) organometallic lead halide perovskite solar cells (PSCs) have become one of the most promising developments in optoelectronics as high-performance, inexpensively produced semiconductors.\(^4\)

The technical feasibility of commercializing any PV technology can be evaluated based on the golden triangle formed by the vertices of efficiency, lifetime, and cost, as shown in Figure 1.2.\(^5\) Silicon PV offers a good balance between module efficiency (champion
Introduction and Motivation

Figure 1.1: The rapid reduction of the cost of solar in the last decade. Reported in terms of total installed PV system costs, weighted by the scale of the capacity of the systems installed in each respective year. Adapted from [2].

lab cell value close to 27 %), long lifetime (over 25 years), and low cost (<$0.3 / W for the panel only). PSCs have potential due to their high efficiency in the same range as silicon (champion value of 25.7 %), and low manufacturing cost, which is estimated to potentially be lower than that of crystalline silicon, due to the use of earth-abundant precursor materials and lower temperature fabrication methods. [5] However, the main obstacle to their commercialization is their problematic stability. The lifetimes of PSCs are normally reported in the days, although the best cells in literature reports can be on the order of a year, partly limited by how long it takes to test stability. Industry claims even better lifespans. [6] This contrasts with the 20-25 years industry-standard lifetime of their silicon analogues. Such lifetime limitations can be tackled from a device engineering point of view by encapsulation of modules, which stops efficiency losses and lead leakage. [7] Proving the long lifetime is thus the primary challenge, which encompasses both the materials challenge as well as testing, overall hindering the commercialization of perovskite solar cells.

Besides the application of perovskites for solar cell devices, their bandgap tunability and low-temperature processing also opens up new applications in other optoelectronic device applications such as light-emitting diodes (LEDs), lasers, photodetectors or transistors. [8]
Figure 1.2: The golden triangle for PV commerciality analysis. The comparison of silicon and perovskite solar cells (PVSK denotes perovskite solar cell). Note the reported values in the figures are from 2018. As of the writing of this, the champion efficiency of silicon single crystal is 26.1% and 25.7% for PSCs.\textsuperscript{[9]} Adapted from \textsuperscript{[5]}.

Many of the unique macroscopic properties of lead halide perovskites are dictated by a complicated nanostructure, which has direct ramifications on device performance and operational stability.\textsuperscript{[10]} Therefore, some of the challenges posed by PSCs can be tackled by understanding its nanostructure and controlling it, namely by a material science approach.

Numerous methodologies exist to correlate the micro- and nanoscale structure of halide perovskites with their properties. Optical and atomic force microscopy techniques, as well as X-ray-based methods, have been useful for studying their composition and structure. This thesis focuses on using high-energy electron-beam microscopy (EM) techniques, to investigate the nanoscale morphology, crystallography, composition, and electronic structure of perovskites.\textsuperscript{[11]} These techniques, combined with advanced microscope components and multimodal detectors, make high-energy electron probes a powerful tool for studying perovskites at the nanoscale. Each of the experimental chapters addresses a specific technique development to enable new modalities of electron microscopy on halide perovskites.
Chapter 2 provides a review of hybrid halide perovskites, their heterogeneity at multiple length scales, their fundamental unique properties as optoelectronic materials, and the key concepts towards their application as PSCs. The current state-of-the-art microscopy studies and their limitations are also reviewed.

Chapter 3 reviews the key EM techniques used in this thesis. It also contains a description of electron-matter interaction and the consequent electron beam-induced specimen damage and how to measure it.

Chapter 4 reports the study on the degradation mechanisms under an electron beam, elucidating the limits of using 4D-scanning transmission electron microscopy (4D-STEM) on hybrid halide perovskites.

Chapter 5 focuses on the development of cathodoluminescence (CL-SEM) to probe the optical properties of halide perovskites on the nanoscale. The beneficial use of a pulsed, rather than continuous, electron beam is demonstrated through a series of examples of high-resolution optical characterization of model hybrid perovskites. A discussion of the importance of software technique development for data analysis, particularly for the efficient mining of physically significant information from noisy datasets and the use of multivariate statistical analysis algorithms is also discussed.

Chapter 6 discusses two strategies to push the limits of 4D-STEM towards in-situ and operando conditions, to make EM studies closer to the working conditions of optoelectronic devices. It includes the report of in-situ lateral biasing study, whereby the stoichiometry of perovskite films is found to play a crucial role in dynamic redox processes mediated by electrons and holes at different contacts at the nanoscale. It concludes with a discussion of the results and challenges of the fabrication of perovskite devices (moving beyond simply bare films) on electron-transparent substrates.

Overall, this thesis sheds light on the possibilities and limitations of electron microscopy techniques to understand the role of nanoscale structure in the behaviour of hybrid halide perovskites. It offers general guidelines for acquiring and critically interpreting data for beam-sensitive materials. The study provides experimental evidence of nanoscale phenomena that affect the performance and stability of these active materials in devices in both ground state and under external stressors. This work opens up new avenues for investigating the properties of these materials and for developing more efficient optoelectronic devices with the aid of this new advanced electron-based toolset with two main "big wins": (i) to expand developing techniques that can access the nanoscale both structurally (4D-STEM) and optically (CL), and (ii) to study perovskites in-situ under biasing, a step closer to operational conditions.
Chapter 2

Background

2.1 Lead halide perovskites

Perovskite is a crystal structure that follows the ABX$_3$ structure. This crystal structure was first described by Gustavus Rose in 1839 to refer to the mineral CaTiO$_3$.[12] It was named after the Russian mineralogist Lev Perovski and was normally used to describe almost exclusively oxide-based structures. Halide-based perovskites crystallise from halide salts to form crystals with the general formula ABX$_3$. While they became a widely-research topic only about 10 years ago due to their application as perovskite-sensitised solar cells by Kojima and co-workers,[3] early investigations of the then-named "double halides" go back to works published in 1827.[13] Yet, their potential use as semiconductors only started to be explored in the 1990s.[14]

The use of halide perovskites has exploded as a research field on its own in the last decade, due to their applicability as optoelectronic devices such as solar cells, light-emitting diodes (LEDs), photodetectors or transistors. The bandgap of halide perovskites can be finely tuned via chemistry, and films can be grown in low-temperature processing, virtually in any laboratory space worldwide.[15,16] From this point onwards, whenever the term perovskite is used, it will specifically refer to hybrid halide lead perovskites unless stated otherwise.

Halide perovskites also follow the ABX$_3$ structure, being A a monovalent cation (normally methylammonium (MA$^+$, [$\text{CH}_3\text{NH}_3]^+$), formamidinium (FA$^+$, [$\text{NH}_2\text{CH}=\text{NH}]^+$), caesium (Cs$^+$), or a mix of them), B a divalent cation (lead (Pb$^{2+}$) or tin (Sn$^{2+}$), or a mix of them), and X a halide anion (bromide (Br$^-$), iodide (I$^-$), chloride (Cl$^-$), or a mix of them, depending on the desired bandgap). Such chemical complexity can be further increased by alloying stochiometric ratios of these ions. Common device-relevant examples include the simple pure FAPbI$_3$ composition, the double-halide double-cation composition (FA,
CS and I, Br, here used during thermal evaporation of films), or triple-cation double-halide films (a highly reproducible recipe, established as the workhorse in many labs via solution-processing). While the aforementioned cations yield 3-dimensional crystals, the A-site cation can be replaced by longer organic cations, which force lead halide sheets to form, yielding quasi-2D, 2D or 1D perovskite analogues.

This thesis limits the scope of such chemical complexity and focuses on 3D FA-rich lead absorbers mainly. The reasons are outlined as follows: (i) FA-rich compositions show the most promising stability, as they avoid the use of volatile MA$^+$ or additional phase complications due to excessive Cs$^+$. (ii) Lead-based compositions show by far the best efficiency potential, as opposed to other lead-free compositions such as tin, which show indirect bandgaps or enormous stability issues. This, of course, has an implication on the plausible lead toxicity leaking to nature, especially in its metalorganic form. (iii) 3D absorbers show strong absorption and improved charge transport characteristics over other 2D systems. (iv) For the halides, the pure iodide and a mix of iodine-bromine systems are the main focus, as these compositions alone can realise bandgaps of from 1.5-1.6 eV (I only), 1.6-1.75 eV (with the addition of small fractions of Cs and Br), to >2 eV (Br only).

### 2.1.1 The connection between structure and property

The chemical diversity in the perovskite composition is further complicated by the structural heterogeneity of polycrystalline films both laterally (in-plane to the film) and vertically (across a film, through interfaces in devices) at multiple length scales. Structural features both in the atomic (nanometer scale) to the macroscopic (centimetre scale) can strongly affect the optoelectronic properties of perovskite films and devices, making a detailed understanding of the underlying relationships between the nanoscale structure and the properties that govern performance crucially.

A photon (or any high-energy particle like an electron) can excite the electronic states of a semiconductor material with the creation of charge carriers in the form of electron-hole pairs ($e^-$-$h^+$ pairs). The amount of charge carriers produced depends on the energy of the excitation, and the band-gap of the material, besides other parameters. Due to their excited energy state, the number of free carriers in a semiconductor will be reduced via an electronic relaxation event, either by (a) releasing a photon (radiative recombination), (b) via kinetic energy transfer to another charge carrier (Auger non-radiative recombination), or (c) via heat dissipation mediated by phonon emission (non-radiative recombination, thermalisation), as shown in figure 2.1.
2.1 Lead halide perovskites

Figure 2.1: Recombination of charge carriers. Schematic of the main recombination processes that occur in semiconductors: (a) radiative, (b) Auger, and (c) non-radiative (trap-assisted) recombination. The arrows on the diagram indicate the direction of electron transitions.

In traditional semiconductor physics, trap-assisted recombination emerges from the presence of atomic-scale defects in the material, such as vacancies or interstitials, creating traps for electrons (near the conduction band) or holes (near the valence band).\textsuperscript{29} Depending on the nature of the trap state, two scenarios are possible: shallow traps (only a few $k_B T$ away from a band edge, with $k_B$ being the Boltzmann constant and $T$ temperature, approximately 25 meV at room temperature),\textsuperscript{30,31} which are benign, and deep trap states, which can be detrimental to performance.\textsuperscript{32} Shallow traps only slow down the carrier transport through a trapping and de-trapping process but do not necessarily remove excited charge carriers. In contrast, deep traps can cause non-radiative recombination and cause energetic carriers to lose their energy via thermalisation, which can harm device performance, ultimately decreasing the open-circuit voltage, which is a critical metric for the electrical power delivered by photovoltaic devices.\textsuperscript{29,33}

Recent studies highlight the importance of studying the nanoscale of halide perovskites. Traps and defect states of halide perovskites, in addition to heterogeneous elemental composition, sometimes form secondary phases.\textsuperscript{34} These nanoscale features can impact the electronic and ionic diffusion pathways. Moreover, deep traps were found to appear at the interfaces between crystallographically and compositionally distinct grains, stemming as a source of non-radiative recombination.\textsuperscript{35} The presence of such defects, in combination with other phases, can not only reduce efficiency but can enhance degradation, which limits their durability.\textsuperscript{33} In the topic of durability, phase stability plays a key role.

Phase stability refers to the ability of a material to maintain its structural and compositional integrity under specific conditions of stress. A material can exist in different phases,
which are distinct arrangements of atoms or molecules with different properties, such as density, or electronic structure. The canonical ideal ABX₃ perovskite crystal structure is normally represented by the cubic \( Pm\bar{3}m \) group (also called alpha or photoactive phase), which contains corner-sharing \( BX_6 \) octahedra, with the A-cation located at the centre of the cube formed by eight adjacent octahedra.\(^{[36]} \) Many modifications to this structure are possible, but not any combination will result in the perovskite phase. This is because different ions lead to different ionic radii mismatches which can destabilise the crystal structure. Such a phenomenon can be described with the Goldschmidt tolerance factor \( t \), a parameter used to understand and predict the stability and structural properties of a given halide perovskite composition:\(^{[37]} \)

\[
t = \frac{(R_A + R_X)}{\sqrt{2}(R_B + R_X)}
\]

with \( R_A \), \( R_B \) and \( R_X \) are the radii of the \( A \), \( B \) and \( X \) site ions, respectively. It is a dimensionless quantity introduced by Goldsmith to determine the degree of distortion that occurs in the perovskite crystal lattice due to the size and charge of the constituent ions.\(^{[38]} \) This factor limits the pool of possible organic cations that can form the photoactive phase, within a tolerance of 0.8-1.0 to \( MA^+ \), \( FA^+ \) and \( Cs^+ \) (if only using Pb/Sn and halides), though it is challenging to come up with a general range due to the large range of stoichiometries halide perovskites can form.\(^{[39–41]} \) For larger bulkier ions, the mismatch is too large so other non-ABX₃ structures form, which is still considered part of the perovskite family (e.g. anti-perovskites, or low-dimensional perovskites).\(^{[42,43]} \)

Even when the tolerance factor is within range, the ionic mismatch forces the octahedral cages to become distorted and tilted, which leads to a lowering of symmetry from the cubic to lower-symmetry systems such as tetragonal, or orthorhombic types. Such octahedral tilting for the perovskite structure was systematically studied by Glazer, whereby tilting was decoupled in terms of component tilts about the pseudo-cubic axes \( (Pm\bar{3}m) \).\(^{[44]} \) Experimentally, octahedral tilting can be observed through the appearance of additional Bragg reflections compared to the ones obtained from the ideal cubic structure \( (Pm\bar{3}m) \), during diffraction experiments. Such additional reflections are normally called superstructure reflections, and they originate from the lower symmetry space group formed after octahedral tilting.\(^{[45]} \) For the specific case of halide perovskites, such superstructure reflections are harder to see due to the lighter nature of halides concerning Pb, yet work pioneered by Doherty managed to report the link of octahedral tilting with additives using electron diffraction techniques.\(^{[46]} \)

For the case of FA-pure perovskites (FAPbI₃), despite its nearly ideal bandgap, its photoactive phase (cubic, assuming rapid reorientation of the organic cation effectively
forming a sphere) is only stable above 150°C. In fact, at room temperature, the edge-sharing octahedra collapse into a face-sharing phase that is not photoactive (hexagonal type, $P6_3mc$). One can imagine all the intermediate phases which combine sequences of hexagonal and cubic closed-packed $AX_3$ stacks that result in a framework of face-sharing and corner-sharing $BX_6$ octahedra. These intermediate phases are called polytypes and are shown in figure 2.2. Polytypes are polymorphs which have identical close-packed planes, but their stacking sequence differs. They can be classified by the Ramsdell notation, where the letter denotes the crystal system of the compound (C for cubic, H for hexagonal) and the number denotes the total number of layers contained in a unit cell.\cite{47} For the case of FA-based perovskites, such polytypes interface between the photoactive (alpha, black) phase (3R in Ramsdell notation) with the non-photoactive (delta, yellow) phase (2H in Ramsdell notation).\cite{48} These phases form as a sequence from 2H to 4H, 6H, and eventually the 3R black phase during crystallisation. Only slight variations in free energy affect the different phases, making the formation and transformation between phases favourable.\cite{49} Moreover, efficiency losses and degradation weakness may arise from such polytypism, which can be inhibited by, for instance, alloying Cs$^+$ cations into the lattice.\cite{49}

Finally, precursors such as lead halide salts ($\text{PbI}_2$, $\text{PbBr}_2$) can remain unreacted in a film due to uncompleted conversion to perovskite structure.\cite{50} In fact, the best-performing cells have a few per cent excess $\text{PbI}_2$, as a slight excess of $\text{PbI}_2$ in the perovskite film has been observed to be beneficial by improving carrier lifetime, eliminating hysteresis effects, and increasing stability.\cite{51,52} The excess of $\text{PbI}_2$ is a double edge sword. On the one side, it can be beneficial as $\text{PbI}_2$ energy level alignment can be beneficial to match the hole transport layer and the perovskite layer. Moreover, $\text{PbI}_2$ can act as a passivation layer of grain boundaries, as the perovskite can grow epitaxially from the $\text{PbI}_2$ excess (see atomic electron micrographs in \cite{53}). On the other side, $\text{PbI}_2$ can have detrimental effects. Layers of $\text{PbI}_2$ that are too thick will act as an insulator, blocking charge transfer.\cite{54} Moreover, $\text{PbI}_2$ is prone to photolysis under light illumination, which inevitably leads to instability and hysteresis.\cite{55} Therefore, such chemical species need to be considered when studying the microstructure too, as have important ramifications for the properties of the perovskite films and devices. In short, the key candidates when trying to identify crystalline phases in the nanoscale can be (i) perovskite structure in its many flavours, (ii) perovskite hexagonal polytype phases that are not photoactive and (iii) unreacted salts, which are often added in intentionally to empirically optimise performance.\cite{55}
2.1.2 Defects and passivation

Due to the ionic nature of the perovskite structure and its solution processing manufacturing, halide perovskite films contain large densities of defects. Defects usually occur as dangling bonds and charged states from the B-cations or X-anions. These dangling bonds act as Lewis acids and can be fixed by Lewis bases that contain atoms which donate electrons, or by an excess of halides. On the other hand, X-anions act as Lewis bases which can be counterbalanced by additives that accept electrons or metal cations. Since undercoordinated cations and anions are typically found together, zwitterions, with charged ends, have been used as an effective way to passivate both defects with a single additive.

Defects do not simply come in the form of point defects, such as dangling bonds. Any real crystal must be imperfect due to entropy constraints. For solid-state crystallography, defects can range from point defects, and line defects to plane defects (0D, 1D and 2D, respectively). Examples of point defects include vacancies, interstitials, antisites and...
2.1 Lead halide perovskites

![Figure 2.3: Grain boundaries](image)

Different types of grain boundaries can be formed: (a) low-angle boundaries, (b) high-angle boundaries, (c) non-equilibrium grain boundaries containing a high density of defects and (d) amorphous grain boundaries. Adapted from [59].

Impurities. If these point defects are not charged (for example a pair of cation and anion vacancies) they are called Schottky defects, and if the pair results in a net charge, they are named Frenkel defects. Examples of line defects include dislocation, and plane defects include stacking faults, grain boundaries, surfaces and interfaces. [56] For grain boundaries, in particular, different types of grain boundaries can form during crystallisation (figure 2.3). Compared to atoms in the bulk phase, where the crystal lattice can form equilibrium at the minimum free energy of an infinite crystal, atoms at grain boundaries are arranged in a more disordered manner. This disorder is imposed by arrangement restrictions from the adjacent crystal lattices. Therefore, different types of grain boundaries can be formed: (a) low-angle boundaries, (b) high-angle boundaries, (c) non-equilibrium grain boundaries containing a high density of defects and (d) amorphous grain boundaries. [59]

Even a low to moderate concentration of defects can significantly have detrimental effects on the performance of well-established PV technologies like Si and III-V solar cells, namely they are defect intolerant. [60] This is attributed to defects tending to produce deep trap states. This susceptibility makes it necessary to use extremely pure raw materials and maintain very clean fabrication conditions, raising the fabrication energy and manufacturing costs. In contrast, perovskite films are described as "defect tolerant". This is exemplified by the production of high-performing films using simple fabrication methods which yield films with a large concentration of defects (density of point defects alone is estimated to be \(\sim 10^{14-17} \text{ cm}^{-3}\)). [61] Defect tolerance emerges from three key properties of perovskites. (i) Defect levels from the inorganic framework are likely to be located near (or even inside) the valance or conduction band. This is due to the higher-energy antibonding nature of the orbitals that form the valence band edge (Pb(6s) with I(5p) orbitals). Moreover, strong spin-orbit coupling lowers the conduction band edge, making defect levels more likely to be near these energy band edges. [62] (ii) While deep states are possible, their formation energy is higher than shallow trap states, making them less
Defects can be passivated. More generally, passivation strategies can be designed based on molecular chemistry from first principles (see Figure 2.4). However, for halide perovskites, alloying of different ions can also help with passivation. As described before, FAPbI$_3$ pure composition has a nearly ideal bandgap but the photoactive phase is unstable at room temperature. Partial substitution of FA$^+$ with MA$^+$ and/or Cs$^+$ can form mixed-cation perovskites with superior optoelectronic properties. Other monovalent alkali cations, such as potassium (K) and rubidium (Rb) have been widely used as effective additives in order to achieve superior optoelectronic properties. However, the trend of alloying FA-based perovskites with additional ions is currently being challenged by the recent trend towards simpler perovskite compositions (illustrated in Figure 2.5). Particularly, stabilisation of FAPbI$_3$ can be achieved through more subtle means than direct A-site cation and halide allowing. Such methods still involve the addition of small amounts of MA and other alloying cations such as caesium (Cs), methylammonium chloride (MACl) or formamidinium formate (FAFa), to name a few. Recently, a new strategy has been proposed that does not use MA or any other cations, in which ethylenediaminetetra-

Figure 2.4: Simpler or alloyed halide perovskites. Illustration of how the imperfections in halide perovskite films can be passivated by ionic bonding or coordinate bonding. Reproduced with permission from [58]. Copyright 2019 American Chemical Society.
2.1 Lead halide perovskites

Figure 2.5: Simpler or alloyed halide perovskites? Illustration portraying the race between complex multiple alloyed cation/anion compositions running against the stabilisation of FAPbI$_3$ for halide perovskite solar cells. Reproduced from the cover page of Journal of Materials Chemistry C $^{[67]}$. Copyright 2023 Royal Society of Chemistry.

traacetic acid (EDTA) stabilised the black perovskite phase by directing its growth from the solution in a manner that produces a small tilting of octahedral shape.$^{[46]}

These recent approaches to the passivation and stabilisation of perovskite films raise the question of whether using complex multiple cation/anion compositions is truly necessary for achieving high-performance and stable photovoltaic devices.

2.1.3 Beyond a bare film: perovskite devices

In a perovskite solar cell (PSC), the perovskite layer acts as the absorber, where photons irradiating the material are harvested into excitons (electron and hole pairs) which readily and spontaneously separate into free electrons and holes due to low exciton binding energy of 3D perovskite systems (lower than $k_BT$). In principle, the intrinsic ambipolar charge transport nature of halide perovskites can create an electrical and chemical gradient that separates these charge carriers from the absorber layer towards metal contacts, where photovoltaic electricity can be harvested. Carrier separation is dominated by diffusion as the carrier diffusion lengths in perovskites ($\sim 1\mu m$) tend to be greater than the thin-film absorber thickness, $^{[68]}$ on the order of $0.5 - 1\mu m$. In practice, the perovskite and the metal contacts are interfaced by an electron or hole transport layer (ETL, HTL, respec-
tively), which are tailored to have matching energy levels to enhance charge extraction. These transport layers can conduct electrons or holes solely, which then diffuse through until they reach the metal contacts, and thus result in higher device efficiencies. Finally, one of the contacts needs to be optically transparent, while the opposite acts as a back contact metallic mirror.

A plethora of device structures can be fabricated. The first optoelectronic device application using halide perovskites was the dye-sensitized architecture, where a thick mesoporous layer of TiO2 was used. This was quickly replaced by bi-layer devices, where the thickness of the mesoporous TiO2 was reduced, and a thicker perovskite layer was deposited for greater absorption of light and longer crystalline order. Planar architectures followed, with either an \textit{n-i-p} or \textit{p-i-n} configuration. Planar architectures eliminate the need for mesoporous TiO2, making the fabrication process less complex and less expensive. The development of planar devices would have not been possible without the rise of a plethora of organic polymer semiconductors with hole- and electron-specific conductivities. In this way, halide perovskite optoelectronics goes hand in hand with the organic semiconductors field.

Other applications for perovskite-based optoelectronic devices such as light-emitting diodes (LEDs), detectors, or transistors use very similar device architectures stemming from the planar one, with the special tuning of the hole and electron transport layers. More recently, significant interest has risen in controlling the surfaces and interfaces between the contact layers and the perovskite films with complex strategies such as self-assembled monolayers and surface treatments, the use of 2D-3D perovskite phases, or single crystals usage (as opposed to polycrystalline films) for devices. For example, the optoelectronic properties can significantly vary when films are grown on device contacts or other substrates, attributed to the inference of the different surface morphology, ion composition or strain at the interfaces.

Finally, perovskite films have a huge potential in tandem architecture, either as a silicon-perovskite tandem or an all-perovskite tandem, which enables to further push the solar cell efficiency beyond the single-junction Schottky-Queisser limit. An interesting use case is the use of PSCs for space photovoltaics. This is because hybrid halide perovskites are uniquely lightweight due to their thin-film nature compared to heavier silicon-based PVs or thicker III-V PVs. Moreover, they show excellent radiation hardness (resistance to degradation) under extreme space conditions of proton and electron exposure. This is important for space-PV as large fluxes of high-energy particles, such as trapped electrons in orbit extending up to 1 MeV energies, can trigger defect generation and degradation of these materials.
2.1 Lead halide perovskites

2.1.4 Soft material nature

Perovskites are not simply electronic semiconductors, but also ionic semiconductors. Due to their mixed ionic-electronic mobilities, it is important to assess the distribution of mobile ions and their effect on the band diagram. Although PSC band diagrams are difficult to model and compute, they can be rationalised. For instance, in FA-based compositions, ionic motion can result from vacancies or interstitials within the crystal structure. Overall, halide species are the most mobile species, with halide vacancies being more mobile than halide interstitials, and iodine-based defects being more mobile than bromine-based ones.\cite{82,83} Other reports also exalt the mobility of the organic cation species. Lead-based defects are normally stated as immobile.\cite{84,85}

One way to visualise how the energy bands are set up is determined by how the vacancies accumulate near the hole transport layer (HTL), and by how the immobile anions are distributed in the region depleted of vacancies near the electron transport layer (ETL). Figure 2.6 shows how the energy band align in the process of forming a device: (a) When the film is contactless, the mobile halide vacancies and the respective compensating anions are distributed uniformly. (b) When the ETL and HTL are stacked on opposite sides of the film, a built-in potential is created, which decreases linearly within the film, leading to the migration of mobile ions towards the contacts. (c) In a scenario where both cations and anions are mobile, then the charged defects would be symmetrically distributed near the contacts (forming layers following Debye theory). (d) In a more realistic case, where halide vacancies are mobile while anions are immobile, an asymmetrical ion distribution is produced. These ionic motions result in PSCs having analogous band diagrams to \( p-n \) junctions, in which the band structure is determined by the distribution of fixed ionized donors and acceptors in the \( n \) and \( p \) semiconductors, respectively.\cite{86} Attempts to experimentally determine the nature of these interfaces, mainly to forge connections between loss and performance at the interfaces, have involved the use of electron-beam-induced current (EBIC). Experiments on half-device or full-device structures revealed that a \( p-i-n \) junction is formed between the HTL-perovskite-ETL, with the interface between the perovskite and the transport layers being locations with the highest efficiency.\cite{87–89}

Oftentimes, a perovskite film can be directly contacted with a metal, as explored in Chapter 6. In traditional semiconductor physics, the type of contact that forms between the metal and the semiconductor can be either Ohmic or Schottky, depending on the relative work functions of the two materials. For an Ohmic contact, electrons flow from the metal into the semiconductor conduction band to lower their energy and a linear relationship between the voltage applied and the current that flows across the junction can be measured.\cite{90} In the case of a Schottky contact, a rectifying behaviour can be
Background

Figure 2.6: Energy diagrams of an intrinsic perovskite film in a device structure. Schematics for the band alignment for a perovskite film (a) with on contacts, (b) after the contact of ETL and HTL before any ionic motion, (c) after both action and anion motion or (d) in the case where halide motion if the only allowed ionic motion. (e) The band alignment is similar to that of a traditional p-n junction, where the donors and acceptors are fixed. Adapted from [86]. Copyright 2020 Cell Press.

observed, akin to a diode. [91] However, halide perovskites are ionic semiconductors and their device physics cannot be fully explained by such a traditional model. Factors like defects and ion migration can complicate the electrical nature of the junction. Literature has partial disagreements over their nature, with observations suggesting simple constant electric fields across the bulk [92] to more complex models, determined by the ionic density of the material, such as ionic diffusion models or capacitance models. In these complex models, the electric field does not extend across the contacts but may only be localized at the metal-perovskite interface. [93]

The implications of the soft material nature of perovskites are important to understand perovskite-based devices. For example, the biasing of perovskite devices can have a significant impact on their performance and stability, leading to the creation of hysteresis.
Hysteresis in an electric device can be defined as the observation of differences between forward and reversed current-voltage sweeps. While hysteresis can be useful in certain applications, such as memristor technology, it often hinders device performance. Biasing can be externally applied (e.g. for LED application), or be inherent to a device due to built-in fields in the device geometry (e.g. when PSC are connected in series). Hysteresis is thought to be attributed to ion migration. Ion mobility can not only mainly happen in-plane, across the film, but also laterally, out-of-plane. Both migrations are possible and have important effects on device behaviour and stability. In particular, the effect that lateral migration has on macroscopic properties has been studied with a lateral biasing geometry (metal-perovskite-metal). For FA-based compositions, preferential degradation has been reported in regions of positive internal potential, with the accumulation of anions (namely an anionic model). However, the presence of other factors, such as intrinsic defects, oxygen, or precursor residue can also play a role. Iodine, iodine interstitials, or iodine vacancies, as the most mobile species under lateral electrodes, can lead to the modification of the electronic properties via the accumulation of excessive vacancies, which in turn, can induce defects and quench photoluminescence (PL). The mobility of the organic cation species has also been measured. Moreover, ion migration in polycrystalline perovskites dominates through grain boundaries, as revealed by atomic force microscopy (AFM), where stronger hysteresis was observed at the grain boundaries than on the grain interiors. These findings were attributed to faster ion migration due to the aid of defects, which are more present in grain boundaries, similar to a diffusion process.

Finally, a solid-state electrochemical cell can be observed when lateral bias is applied, mediated by reduction potentials (see Table 2.1). For example, when multiple halides are alloyed, selective halide oxidation is mediated by holes preferring to oxidise $I^-$ to $I_2$ over $Br^-$. These redox reactions lead to Br-rich regions near the anode, where holes are mainly present, and create an unbalanced halogen transport flux across the contacts. These findings are explained by the higher electronegativity of bromine, as it forms a stronger hydrogen bond with the cation and a stronger ionic bond with the Pb than iodine does. This means that bromine has a lower tendency for oxidation and lower ionic mobilities than iodine. For the halide perovskite-specific elements, $Pb^{2+}$ is prone to reduction by the gain of 2 electrons, to form $Pb^0$. $I^-$ is prone to reduction by the loss of electrons (same as saying by the gain of holes) to form $I_2$ gas, more than $Br^-$. 
Table 2.1: List of reduction potentials for halide perovskite-specific elements. Reduction potential is a synonym for reductant strength (high = reductant, low = oxidant). Extracted from [99].

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Products</th>
<th>Standard Reduction Potential $E^0$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs$^+$ + e$^-$</td>
<td>Cs</td>
<td>-2.92</td>
</tr>
<tr>
<td>Pb$^{2+}$ + 2e$^-$</td>
<td>Pb</td>
<td>-0.126</td>
</tr>
<tr>
<td>I$_2$ + 2e$^-$</td>
<td>2I$^-$</td>
<td>0.5355</td>
</tr>
<tr>
<td>Br$_2$ + 2e$^-$</td>
<td>2Br$^-$</td>
<td>1.087</td>
</tr>
<tr>
<td>PbO$_2$ + 4H$^+$ + 2e$^-$</td>
<td>Pb$^{2+}$ + H$_2$O</td>
<td>1.46</td>
</tr>
<tr>
<td>BrO$^{2-}$ + 6H$^+$ + 5e$^-$</td>
<td>½Br$_2$ + 3H$_2$O</td>
<td>1.478</td>
</tr>
</tbody>
</table>

2.2 The importance of microscopy

A plethora of characterisation methodologies exists, attempting to correlate structure and properties at the micro- and nanoscale, in order to shed light upon questions related to a fundamental understanding of stability, performance and photophysics. Structural features ranging from the atomic (nanometer) to the macroscopic (centimetre) scale can strongly affect the optoelectronic properties of perovskite films and devices. [23,24] Therefore, the study of halide perovskites cover a large range of length scales: long-range (>10 $\mu$m), grain (100 nm to 10 $\mu$m) and sub-grain (<100 nm). [10,100] Long-range disorder is a result of both the polycrystalline structure at the nanoscale and hard-to-control fabrication procedures, which can induce wrinkling, strain, and device hysteresis. [101–103] At the grain scale, grain boundaries affect the optoelectronic properties of perovskites, causing non-radiative recombination sites, infiltration of species, and ion migration. [104] At the sub-grain level, crystallographic defects such as twins are observed. [53,105]

Significant progress has been made using a series of characterisation techniques that can access different length scales. To name a few, optical characterisation techniques like photoluminescence microscopy (PL) or transient optical microscopy are optical-diffraction limited. Scanning probe techniques such as atomic force microscopy (AFM) can access smaller length scales, such as morphology and electrical properties in the nanoscale but can only probe the surface. [10] Other techniques using X-rays (both lab-scale or synchrotron-based) have been found useful to study the structure and composition of thin films with a resolution of the order of tens of nanometers. [106] This Section will now focus on how high-energy electron-beam techniques have been used as a characterisation toolkit to probe the nanoscale morphology, crystallography, composition and electronic structure of halide perovskites using in-situ techniques. Techniques that can probe halide perovskites in-situ are powerful to accelerate fundamental understanding in
conditions closer to real applications. The theoretical background of these microscopies is described in Chapter 3.

### 2.2.1 *In-situ* and *Operando* Microscopy

The development of new sample holders for TEM which enable characterisation under external stimuli is moving the field from static vacuum experiments to *in-situ* experiments. A TEM with appropriate sample holders can now become a nano-laboratory on its own, as various stimuli can be applied to the specimen inside the column. Some commercial products include *in-situ* heating, electrical biasing and control of the atmosphere, while a few reports have also added light and mechanical stress inside the column. These new holders and micro-electromechanical systems (MEMS) chips, coupled with the recent development of improved microscope components, such as aberration correctors and direct electron detectors, enable *in-situ* data acquisition at low electron dosage.

Hybrid perovskites tend to also be sensitive to external stressors, so *in-situ* electron microscopy can be of prime interest. For example, halide perovskite *in-situ* studies involve the application of an electric bias, environmental conditions, temperature, light illumination, or electron illumination. It is fundamental to understand how local variations in the structure and composition affect the response of the devices to external stimuli, such as under working conditions, as well as how such properties evolve with time, and what causes loss of performance and device instability. Many *in-situ* TEM works have studied the atomic sub-grain structure, crystallisation and degradation of perovskite films in isolation.

It is important to not only consider the perovskite absorber layer in isolation but the whole device structure, as interfaces and contacts may create pathways unrelated to the perovskite itself, which can affect the cell instability, the evolution of traps, defects, or degradation seeds upon stimuli. In particular, the effect of biasing a perovskite film is extensively explored in this thesis. A limited number of *in-situ* studies on devices exist, summarised in Table 2.2. These studies try to understand the evolution of the structure and composition of the PSCs, as a complete device stack, under different stimuli such as heat, electrical bias, or atmospheric environment. These studies aim at understanding the break-down pathways in devices, both the perovskite film layer and also in the interfaces between device layers.
Table 2.2: List of *in-situ* electron microscopy studies on perovskite devices only (more studies exist on bare films).

<table>
<thead>
<tr>
<th>Stimuli</th>
<th>Sample</th>
<th>EM specs</th>
<th>Observations</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat</td>
<td>FTO</td>
<td>TiO(_2)(m)</td>
<td>MAPbI(_3)</td>
<td>spiro-OMeTAD</td>
</tr>
<tr>
<td>Heat</td>
<td>ITO</td>
<td>NiO(m)</td>
<td>MAPbI(_3) or Cs(^+)FA(^+)MA(^-) - I+Br</td>
<td>PCBM</td>
</tr>
<tr>
<td>Bias</td>
<td>ITO</td>
<td>PCB/PEI</td>
<td>MAPbI(_3)</td>
<td>spiro-OMeTAD</td>
</tr>
<tr>
<td>Air</td>
<td>ITO</td>
<td>TiO(_2)</td>
<td>MAPbI(_3)</td>
<td>spiro-OMeTAD</td>
</tr>
<tr>
<td>Bias</td>
<td>FTO</td>
<td>TiO(_2) (m)</td>
<td>MAPbI(_3)</td>
<td>spiro-OMeTAD</td>
</tr>
<tr>
<td>Bias +</td>
<td>FTO</td>
<td>SnO(_2)</td>
<td>FAMAPbI(_3)</td>
<td>spiro-OMeTAD</td>
</tr>
<tr>
<td>Heat</td>
<td>Light,</td>
<td>bias</td>
<td>FTO</td>
<td>TiO(_2)</td>
</tr>
</tbody>
</table>

2.2.2 Beam damage

There is no such thing as a free lunch. A key limitation hindering the study of perovskite samples using high-energy electron probes is beam damage. When an energetic electron beam interacts with the perovskite structure, different mechanisms can alter the pristine structure: heating of the sample as a raise in the local temperature,\(^{[136]}\) knock-on damage causing displacement of atoms and defect formation from elastic scattering, electrostatic charging, and radiolysis causing the breakage of chemical bonds by inelastic scattering.\(^{[137]}\) A theoretical description of these phenomena is described in Chapter 3. Understanding these processes is not trivial, especially for hybrid beam-sensitive materials like halide perovskites. A fundamental basis of this thesis therefore critically explores the limitation threshold of these techniques using empirical approaches.

The majority of the work related to beam damage in perovskites has focused on MAPbI\(_3\) and was recently reviewed\(^{[138–140]}\). The interaction of focused electron beams with halide perovskites can be quantified with critical radiation values, defined as particle fluences (in units of particles Å\(^{-2}\)) representing the rate of characteristic irreversible structural...
2.2 The importance of microscopy

changes under particle exposure. Rothmann et al.\textsuperscript{[141]} observed structure degradation of MAPbI\textsubscript{3} films after the extremely-small total electron dose of \(<100\ e^-\ \text{Å}^{-2}\) in the TEM at 200 keV. The beam damage mechanism for MAPbI\textsubscript{3} involves the loss of the organic moieties, which results in a lattice contraction and the formation of a supercell, ultimately degrading into PbI\textsubscript{2}. The supercell formation was later described as MAPbI\textsubscript{2.5}.\textsuperscript{[140,142]} Other studies report the detrimental effect of having excess Pb-related defects during fabrication, which aggregate and feed degradation at grain boundaries upon electron irradiation.\textsuperscript{[143]} However, Pb formation is usually observed as a degradation product of fully-inorganic compositions, such as CsPbI\textsubscript{3}, upon electron irradiation. This is because the inorganic cation is less prone to be reduced than its organic counterparts or than the Pb cation.\textsuperscript{[48,144]}

The appearance of an intermediate phase of degradation agrees with similar studies by scanning electron microscopy (SEM) techniques. Most SEM-based studies of perovskites operate between 1 and 30 keV and most TEM studies operate between 100 and 300 keV. However, lower energy electrons, in the range of 10 eV, are generated during SEM and TEM characterisation as scattering. Even these lower energy electrons (10 eV) can substantially alter the perovskite crystal structure.\textsuperscript{[145]} As the degradation progresses, significant changes in the sample morphology were observed due to the appearance of pores and cracks. Moreover, chemical spectroscopy suggested a decrease in nitrogen and iodine relative to the lead.\textsuperscript{[145]} Given the low energy of the electrons, heat-induced or knock-on damage is unlikely. However, the binding energy of MA\textsuperscript{+} in defect-free perovskites is similar to the electron energy, hence degradation is triggered by the ionisation of organic cation, leading to the formation of PbI\textsubscript{2}.\textsuperscript{[145]} Gaseous species like NH\textsubscript{3} and HI are likely to escape from the sample to vacuum.\textsuperscript{[146]}

Cathodoluminescence (CL) spectroscopy from an SEM has proven useful to study the effects of high-energy electrons on MAPbI\textsubscript{3}, FAPbI\textsubscript{3}, and CsPbI\textsubscript{3} perovskite thin films. Various experimental operating conditions, altering the voltage and current from 2 to 10 keV and from 0.2 to 14 nA, respectively, can induce changes in the CL spectrum.\textsuperscript{[147]} The results showed that the optical signal of the perovskite materials was inherently modified even at relatively low radiation doses. At lower probe currents and accelerating voltages, they observed excitonic peak broadening and a decrease in the CL signal. At higher electron energies, apart from the peak broadening, new higher energy photon peaks appeared in the CL spectrum, which was attributed to heat-induced damage from the electron beam that led to the formation of intermediary phases with larger bandgaps. Heating of the MAPbI\textsubscript{3} film prior to CL measurements also resulted in the appearance of higher energy peaks. At low-temperature CL measurements, the higher energy photon peaks were not
observed, but the damage-induced CL broadening effect was still observed. Beam damage on MAPbI₃ single crystals, a crystal with lower defect densities, degraded slower due to defect densities being inherently more unstable. Similar results were observed in FAPbI₃, and CsPbI₃ was more stable than perovskites with organic components. It is important to note that, due to the capability of CL to resolve higher spatial resolutions, compared to PL, CL has also been used to study the photo-physics of perovskites beyond pure beam damage, reviewed by Guthrey and Moseley. Examples include the study of asymmetric MA-based perovskite nanocrystal emission at different temperatures. CL can also compare the emission generated from a perovskite at the surface from the emission from the bulk, by changing the excitation depth with the acceleration voltage. Finally, CL can also be used to spatially map different phases of a semiconductor, given they emit at different energies. Tracing of the non-emissive to emissive phase-transition during nucleation of CsPbBr₃ nanowires was resolved during in-situ heating using CL, or the effect of photo-induced phase segregation was resolved in a single MA-based perovskite grain basis. Different 2-dimensional perovskite phases were spatially mapped on the nanoscale. They identified heterogeneity of the self-assembled 2D/3D phases, and transient CL was used to elucidate the different recombination dynamics for each of these heterogeneous low-dimensionality phases individually. The dynamics exhibited both Auger ultrafast recombination in the range of picoseconds and slower traces matching the time-resolved photoluminescence dynamics. CL has also been used to study the effect that different additive engineering strategies have on the improvements in luminescence efficiency and uniformity and on the lifetime of mixed-dimensional perovskite films.

Electron beam-induced current (EBIC) has also been used to study the effect of electron beam irradiation on MAPbI₃. They observed damage after the sixth scan (4.5 e⁻ Å⁻² per scan), which manifested as a decrease in EBIC signal and a decrease in diffusion length, proposing that the mechanism of damage was heating and that the improved stability of CsPbBr₃ was due to its higher thermal stability. With this technique, whole device architectures can be proved. Not only did the perovskite layer degrade but several pathways were also observed, that can lead to cell instability and beam damage, unrelated to the perovskite itself. For example, TiO₂ mesoporous layers were found to degrade but at higher electron fluences than the perovskite layer. EBIC has also been used to map the efficiency of charge extraction across PSC cross-sections under the effect of biasing and illumination.

Moving beyond the workhorse hybrid MAPbI₃ composition, Rothmann et al. reported high-resolution scanning transmission electron microscopy (STEM) images of evaporated
FAPbI₃ thin films, reporting the appearance of additional reflections at low fluences of 200 e⁻ Å⁻², the loss of the perovskite phase at 600 e⁻ Å⁻², and the eventual formation of PbI₂ grown on the lattice-expanded degraded phase of FAPbI₃ after 1,000 e⁻ Å⁻². In the presence of humid air, other mechanisms can involve the formation of hexagonal polytype intermediate phases, ultimately converting the photoactive α-phase to the yellow δ-phase (2H). These low electron beam radiation thresholds suggest that high-dose techniques such as EDX, EELS, EBSD, CL, and FIB sample preparation are non-representative to probing the pristine structure of MAPbI₃. This argument will be further discussed in detail in several chapters of this thesis, especially on the limits of CL and FIB.

Different approaches can reduce beam damage, such as cooling the beam-sensitive specimen or reducing the acceleration voltage and/or the electron dosage. The reduction of one beam damage mechanism often counterbalances the effects by increasing another. A lower acceleration voltage can reduce knock-on damage but reduces resolution and can increase radiolysis. For the specific case of halide perovskites, with a hybrid nature of both organic and inorganic components, cooling a MAPbI₃ thin film to cryogenic temperatures did not reduce damage. Cryogenic electron microscopy is normally beneficial for organic materials, but for the case of MAPbI₃, a much lower threshold of 12 e⁻ Å⁻² was reported (as opposed to 100 e⁻ Å⁻²). Reducing the electron dosage is always beneficial for beam damage reduction, being unavoidable and necessary for perovskite characterisation. Low-dose experiments result in a decrease in the signal-to-noise ratio.

In a similar way to electron probes, scanning X-ray probes can be used to study the nanoscale of halide perovskites. Such focused X-rays can also alter the pristine structure of halide perovskites, yet its effects have been less studied than for electron microscopy. The critical fluences for MAPbI₃/MAPbBr₃ derivatives vary for different microscopy techniques. The nano X-ray beam-induced current signal is highly sensitive to defects and was rapidly affected at the lowest fluences of 103 photons Å⁻². Nano X-ray diffraction (nXRD) and fluorescence (nXRF) were found to withstand 10x higher exposures since these signals are more intense, generated by larger volumes, and easier to record. Similar reported critical fluences of 102 and 104 photons Å⁻² for MAPbBr₃ and CsPbBr₃ single crystals were reported, respectively, yet the appearance of additional phases was not reported at these fluences. Other studies have reported comparable XRD signal decays due to loss of crystallinity after long X-ray exposures. These studies, specifically identifying the effect of synchrotron scanning probes on the material, are not to be confused with the plethora of laboratory XRD reports elucidating the degradation products of
halide perovskites at millimetre scale due to external factors such as light, air, temperature or passivating agents.\cite{48,49,156}

### 2.2.3 Summary and Outlook

Based on the material challenges and techniques presented in this Chapter, there are three prominent trends in the characterisation of perovskite PV looking ahead. The first trend is the use of correlative multimodal characterisation, where multiple spatially resolved techniques are applied to the same area of interest. Different maps of properties are then overlaid on each other to determine spatial correlations. This has already led to important discoveries such as the relationship between Br inhomogeneity and trap sites, phase impurities and degradation starting points, and local strain and nonradiative recombination.\cite{10,100,162,163} The second trend is \textit{in-situ} characterisation, where perovskite samples are probed in real time during specific processes. As described above, this method can reveal the processes as they happen, as opposed to \textit{post hoc} characterisation that only shows the result. Apart from electron microscopy, \textit{in-situ} characterisation can be performed using other instruments such as laboratory and synchrotron X-ray beamlines, PL, or AFM.\cite{164,165} The third trend is high-throughput characterisation assisted by robots and machine learning algorithms. This method allows for a large number of perovskite compositions and variables to be assessed quickly, enabling faster learning and future device improvements. Examples of applications include the search for new potential stoichiometries, crystallisation dynamics, antisolvent suitability, and stability studies.\cite{166–168}
Chapter 3

Experimental Methods

In this Chapter, the fundamental theory behind the different characterisation methodologies used throughout this thesis is described, outlining their possibilities and limitations. Each of these techniques aims to probe the structure and properties at the nano-, micro- and mesoscale of perovskite films and devices (Figure 3.1). Since this thesis primarily focuses on using high-energy electron-beam techniques as a characterisation toolkit to probe perovskites, a description of scanning electron microscopies is first described. Other characterisation techniques based on photon probes (like PL or X-ray diffraction techniques) are described concisely. Finally, the importance of appropriate sample preparation on relevant substrates is covered at the end of the Chapter.

Note that all the mentioned characterisation techniques in this Chapter benefit from post-processing analysis using statistics and machine learning. The most common non-supervised technique for microscopy and spectroscopy dimensionality reduction when dealing with multidimensional datasets (such as 4D-STEM, CL, PL, EDX) is principal component analysis (PCA), and its physically-constrained variant called non-negative matrix factorisation (NMF).\textsuperscript{[169]} PCA transforms multidimensional datasets into sorted orthogonal components by the decreasing order of variance. High-variance components account for primary features and explain most of the variations. NMF expands on PCA but constrains the components to be non-negative, easing the physical interpretation. The use of these techniques, limitations and future alternatives are described in Chapter 5 and in Chapter 7.

3.1 Electron Microscopy (EM)

Techniques in this realm include scanning electron microscopy (SEM), transmission electron microscopy (TEM) and scanning TEM (STEM). All these techniques can be
coupled to multimodal detectors capturing signals emerging from scattered electrons, emitted X-rays or cathodoluminescent photons, to name a few. Such techniques, coupled with the recent development of improved microscope components, such as correctors, direct electron detectors and new sample holders enabling in-situ experimentation, make the use of high-energy electron probes, now more than ever, a relevant powerful toolkit to study halide perovskites at the nanoscale.\textsuperscript{[110,111]}

All EM techniques stem from the different mechanisms electrons can interact with matter, as shown in Figure 3.2. Electrons can scatter elastically or inelastically, due to the electrostatic interaction of the incoming electrons with the Coulomb field of each atomic nucleus or with the electrons that surround each nucleus, respectively. Note that, technically, inelastic scattering can also happen due to interactions with quasiparticles like plasmons and phonons.\textsuperscript{[171]} The kinetic energy loss of elastically scattered electrons is negligible. In inelastic scattering, there is a significant transfer of energy to the specimen, which is then re-emitted as an X-ray, photon, secondary electrons, Auger electrons, plasmons, and phonons. Such loss of energy can also be in the form of a

\textbf{Figure 3.1: The link between microstructure and properties in crystals.} Schematic showing the different layers of complexity in the nano-, micro- and mesostructure of crystal systems. Such structures and defects often control the properties of the material. Adapted from\textsuperscript{[170]}. Copyright 2017 D. Raabe.
3.1 Electron Microscopy (EM)

Figure 3.2: Electron-matter interactions. Schematic of the different elastic and inelastic interactions of an electron beam with the specimen. Adapted from [174].

momentum transfer. Both processes are useful as elastic scattering results in diffraction information and inelastic scattering is key for analytical microscopy. [172]

Another way to categorise scattering is according to coherence. Electrons that retain their phase relationship after passing through the specimen are considered coherently scattered, while those that lose their phase relationship are incoherently scattered. Elastic scattering is normally coherent for small deflection angles, and it loses coherence at higher angles. Inelastic scattering is generally incoherent. [173] Coherent and incoherent scattering are both used in TEM mode, while only incoherent scattering is relevant in SEM mode. In TEM, while coherence and elasticity of scattering are not the same concepts, they are strongly linked to each other and elastic is commonly used to refer to coherent scattering and vice-versa. Although this Chapter focuses on scattering and diffraction from electrons, the key concepts presented are also relevant to the X-ray scattering techniques.

3.1.1 Theory of inelastic scattering

Any scattering event in particle physics can be described by a cross-section (\( \sigma \)) and a mean free path (\( \lambda \)). [175] In electron microscopy, the cross-section is the likelihood of a
certain type of scattering occurring, linked to many factors such as sample thickness and composition, beam energy or incidence angle. The mean free path describes the average distance that a particle can travel between two scattering events, and it is indirectly proportional to $\sigma$. For high-energy electrons, such as in TEM, $\lambda$ is in the order of 10s of nanometers but depends on the specimen. An estimation of the inelastic mean free path, based on the dipole formula derived from Egerton\textsuperscript{175} can be found:

$$\lambda = \frac{106F\left(\frac{E_0}{E_m}\right)}{\ln\left(\frac{2\alpha E_0}{E_m}\right)}$$

(3.1)

with $F$ the relativistic factor at 200 keV, $E_0$ the band gap, $\alpha$ the convergence angle, and $E_m$ the mean energy loss energy per scattering.

To estimate the mean energy loss per inelastic scattering in Equation 3.1, the effective atomic mass number ($Z_{\text{eff}}$) needs to be calculated. For specimens that are not made of single elements, the effective $Z$ can be estimated as follows:

$$Z_{\text{eff}} \approx \frac{\sum_i f_i Z_i^{1.3}}{\sum_i f_i Z_i^{0.3}}, E_m \approx 1.6Z_{\text{eff}}^{0.36} (eV)$$

(3.2)

with $f$ the atomic molar fraction (not mass).

For the FA-based perovskite compositions (containing FA, MA, Cs, I and Br atoms), $Z_{\text{eff}}$ is estimated to range between ~36-39 atomic units. For small convergence angles of $\alpha=1$ mrad at 200 keV, the mean free path $\lambda$ is estimated to be ~ 175-180 nm.

Since the samples imaged in TEM are normally thicker than, or similar to, the calculated $\lambda$, many electrons are likely to scatter more than once before transmitting through the sample. Since every scattering event is independent of the next, a Poisson model can be used to calculate the probabilities of no inelastic scattering, single scattering, and multiple scattering as follows:\textsuperscript{175}

$$P_n = \frac{1}{n!} \frac{t^n}{\lambda} \exp^{-t}$$

(3.3)

where $n$ is the number of scattering events (0, 1, or more for multiple scattering), $t$ is the sample thickness and $\lambda$ is the mean free path calculated in Equation 3.1.

For a sample with a thickness of 200 nm, a normal thickness for electron diffraction experiments, the possibility of inelastic scattering can be estimated using Poisson law in Equation 3.3, yielding an estimation of inelastic scattering listed in Table 3.1 and plotted in Figure 3.3. Upon electron-sample interactions and during elastic scattering events, a considerable proportion of electrons undergo multiple inelastic scatterings, leading to the transfer of energy and momentum to the sample.
3.1 Electron Microscopy (EM)

Table 3.1: Probability ($P_n$) of no, single, and multiple (n) inelastic scattering events in an FA-based perovskite film of 200 nm thickness for 200 kV electrons.

<table>
<thead>
<tr>
<th>Event Type</th>
<th>Probability ($P_n$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No inelastic scattering</td>
<td>$P_0 = 32%$</td>
</tr>
<tr>
<td>Single scattering</td>
<td>$P_1 = 37%$</td>
</tr>
<tr>
<td>Double scattering</td>
<td>$P_2 = 21%$</td>
</tr>
<tr>
<td>Triple scattering</td>
<td>$P_3 = 8%$</td>
</tr>
</tbody>
</table>

Figure 3.3: Probability of multiple inelastic scattering events against sample thickness. The probability ($P_n$) of no scattering, single scattering, and multiple (n) inelastic scattering events in an FA-based perovskite film to sample thickness. Calculated using Equation 3.3 for an electron energy of 200 keV with a sample of $Z_{eff} = 36$ a.u. (Atomic fractions: Cs: 0.0052, Pb: 0.3368, Br: 0.0584, I: 0.5260, C: 0.0183, N: 0.0394, and H: 0.0079).

3.1.2 Theory of elastic scattering

The simplest model for elastic scattering is based on the early model described by Rutherford, where an electron is attracted by a nucleus, changing the direction of the electron movement and creating a hyperbolic trajectory. The Rutherford model assumes that the cross section for scattering can be calculated by assuming that $Z$ atomic electrons are stationary free particles. Egerton$^{175}$ in Chapter 3.1.2 derives an estimation of the elastic cross section for an electron from integrating the differential cross section using the Rutherford and the Lenz model as follows:

$$
\sigma_e = \int_{0}^{\pi} \frac{d\sigma}{d\Omega} 2\pi \sin \theta d\theta = 1.87 \times 10^{-24} m^2 Z^{4/3} \frac{\nu^2}{c} \quad (3.4)
$$
with $d\sigma$ the differential scattering cross section integrated through $d\Omega$ the differential solid angle, $Z$ the effective atomic number, $v$ the relativistic velocity of the incident electron, and $c$ the speed of light in vacuum.

Elastic cross sections thus depend on the incident acceleration voltage and the sample composition. Equation 3.4 is too simple to describe heavier elements, such as lead, and more complex models using Hartree-Fock wavefunctions need to be used.

However, in a crystalline solid, it is difficult to apply the concept of the elastic cross-section for elastic scattering, as the regularity of the atomic ordering in a crystalline material affects the phase of the electron waves being scattered. Therefore, the magnitude of the cross-section depends on the crystal orientation relative to the incident beam mainly.

Such a complex phenomenon can be described by Bragg’s law and Laue’s theory, based on the periodicity of a crystal and the interference between consecutive scattered waves. Constructive interference occurs when two waves with phases that differ by an integer multiple of wavelengths combine to create a stronger wave, described by $n\lambda = 2d_{hkl}\sin\theta$ ($n$ an integer, $\lambda$ the wavelength, $d_{hkl}$ the interplanar spacing and $\theta$ the scattering angle) or, in vector form, which provides a framework for 3-dimensional crystals, represented by $\vec{K}_{in}$ and $\vec{K}_{out}$ respectively as:\[176\]

$$\vec{G} = \vec{K}_{out} - \vec{K}_{in}$$

$$\therefore |\vec{K}_{out}| = |\vec{K}_{in}| = 1/\lambda$$

$$\therefore 2\sin\theta/\lambda = |\vec{G}| = 1/d$$

where $\vec{G}$ is a vector with the direction along the lattice plane normal and length equal to the reciprocal of the interplanar spacing, $1/d$. In more mathematical terms, Laue's theory describes the electron wave as a complex exponential phase ($\vec{K}_{out} = Ae^{i(\vec{k}+\alpha)}$) wave and states that for diffraction, the difference in the 2 wavevectors must be equal to a reciprocal lattice vector.

Finally, the concept of the Ewald sphere is also important to describe diffraction in a crystalline system. A sphere with a radius equal to the incident electron beam $\vec{K}_{in}$ can be formed in the reciprocal lattice of a crystal. When waves are elastically scattered, they have the same wavelength and are located on the Ewald sphere. Any reciprocal lattice point that intersects the Ewald sphere satisfies the Laue diffraction condition and, consequently, Bragg’s law for the crystal being studied. Therefore, the diffraction pattern obtained will be a projection of the Ewald sphere intersecting the reciprocal space (see Figure 3.4b-c with two projected 2-dimensional diffraction patterns acquired by slightly rotating the Ewald
Figure 3.4: Ewald sphere. (a) Schematic showing the construction of the Ewald sphere for a transmission electron diffraction experiment. The scheme shows reciprocal space lattice rods, instead of points, because the sample for TEM is thin. (b-c) The resulting 2-dimensional diffraction patterns are obtained by projecting the points the Ewald sphere crosses to the detector plane. A slight rotation in the Ewald sphere (or in the reciprocal space) can move some diffraction spots, from b, away from the diffraction condition and not show in the diffraction projection, in c. (d-e) Effect of incomplete disc filling during diffraction, which is observed when the Ewald sphere is near, but not perfectly, the diffraction condition. Panel (a) adapted from [177].

Note that incomplete disc filling can happen when the Ewald sphere is near, but not perfectly at, the diffraction condition, which leads to spots that are not brighter at the centre of the diffraction spots but show a gradient (Figure 3.4d-e). Particularly for electron diffraction in TEM, electron-transparent samples that are very thin must be used. This leads to a reciprocal space lattice formed by elongated rods, rather than points, due to the inverse relationship between length from real to reciprocal space, which makes incomplete disc filling more likely.

This Section has now introduced the basis for diffraction formation during electron microscopy. However, a more detailed discussion on diffraction, including the derivation of kinematical and dynamical theories of electron scattering can be found in [171,178].

Finally, a comparison of elastic and inelastic scattering is insightful to make. A modification of Equation 3.4 can be made to calculate the inelastic differential cross section, by adding the Schatterly inelastic form factor (see Equation 3.16 in Egerton [175]). Integrating
over all scattering angles, the total inelastic cross-section can be estimated as:

\[ \sigma_i \approx (8\pi \gamma^2 Z^{1/3} k_0^{-2}) \ln(2/\bar{\theta}_E) \] (3.6)

with \( \gamma^2 = (1 - v^2/c^2)^{-1} \) the relativistic factor, \( Z \) the effective atomic number, \( k_0 = \frac{2\pi}{\lambda} = \frac{\gamma m_0 v}{\hbar} \) the magnitude of the incident electron wavevector with mass \( m_0 \) and velocity \( v \), and \( \bar{\theta}_E = \frac{\bar{E}}{(\gamma m_0 v^2)} \) the characteristic scattering angle corresponding to an arbitrary average energy loss \( \bar{E} \).

Comparison of Equation 3.4 and 3.6 yields Equation 3.7. The relationship between the inelastic and elastic scattering is thus only dependent on the atomic number \( Z \) in a linear manner.

\[ \frac{\sigma_i}{\sigma_e} \approx \frac{2 \ln(2/\bar{\theta}_E)}{Z} = C Z^{-1} \] (3.7)

Atomic calculations estimate the linear constant \( C \) to be around 17-18 for 50 and 100 keV electrons.[175,179] A plot of this ratio for different electron energies can be seen in Chapter 4 in Figure 4.3.

3.1.3 Transmission Electron Microscopy (TEM, STEM): 4D-STEM and SED

Being the characterisation tool par excellence for nanomaterials, TEM offers structural and chemical characterisation in the (sub-)nanometer scale. In a TEM, electrons are first generated from an electron gun, either from the older thermionic electron sources or the newer field-emission (FE) electron guns with a triode system, which offers higher current density, brightness, and monochromaticity. Electrons are then controlled through a set of electromagnetic lenses, namely condenser, objective, and projector lenses, which (de)magnify, collect, and control the electron beam.[180] Other components such as stigmators, scanning coils, aberration correctors, and drift correctors aid in the imaging process, which ultimately finalises with the projection of the image or diffraction pattern onto a screen or camera.

In general, TEMs can work in two modes: with the electron beam as a planar wavefront to image the specimen in parallel (similar to an optical microscope, depicted in Figure 3.2 in light green), or in scanning mode (STEM) with the electron beam being converged into a small nano-probe and scanning coils deflecting the probe in a raster manner (Figure 3.2 in dark green). In TEM mode, the contrast is a convolution of different factors: (i) mass-thickness contrast, denser and thick samples scatter more electrons, (ii) diffraction
3.1 Electron Microscopy (EM)

![Figure 3.5](image)

**Figure 3.5: Effect of convergence angle on the probe size.** (a) Calculated relationship between the diffraction-limited resolution (determined by the probe diameter $d_d$) for a given acceleration voltage (or relativistic electron wavelength) and a given convergence angle $\alpha$. (b) Mean diffraction images for STEM probes defined by 0.86, 3.4 and 12 mrad semiangle apertures. (c) A more general description of the probe size in terms of convergence angle, also taking into account lens aberrations, which dominate at large $\alpha$. Panel b reproduced from [181].

contrast, caused by Bragg’s diffraction of crystalline regions, (iii) composition contrast, the number of deflected electrons is proportional to the atomic number ($Z$), especially for high-angle diffraction, and (iv) phase contrast, from the interference between the deflected and the directly transmitted beam, which alters the phase of the electron wave and allows for high-resolution (HR)TEM. In this thesis, TEM imaging is only used as a rapid imaging method to check for electron transparency of the thickness of the specimens prepared.

From now on, all TEM techniques described are in STEM mode. In STEM, the electron beam is focused and scanned across an area. The signal generated at each position is then captured by a detector over a dwell time, resulting in a pixelated image of the measured property pixel-wise. Depending on which detector is used, multiple images can be formed. But before talking about detection, let’s discuss how the focused electron beam can be generated.
Electron beam formation

In this thesis, STEM is normally performed under the so-called "pencil-beam" alignment. Such configuration differs from the more conventional STEM alignment because the beam is set at very small convergence angles (1 mrad). At such small convergence angles, the spatial resolution the electron probe can measure is heavily limited by diffraction: \[ d_d \approx \frac{1200\Lambda}{\alpha} \] (3.8)

with \( d_d \) the diffraction-limited probe diameter (in nm), \( \Lambda \) the relativistic electron wavelength from the acceleration voltage (in nm), and \( \alpha \) the convergence angle (in mrad).

When the pencil beam alignment is used at normal TEM acceleration voltages (as shown in Figure 3.5a for 60 to 300 keV), the spatial resolution is limited in the order of 1-10 nm. However, the small convergence angle avoids the overlap between the central beam and diffracted spots, making the nanoscale diffraction easier to interpret, illustrated in the series of nano-diffraction acquired at different convergence angles in Figure 3.5b.\[181\] The scanning step size during STEM in pencil-beam alignment is set to match, or undersample, that of the diffraction-limited probe size (~5 nm for our experimental conditions). This ensures no overexposure of the electron beam on the beam-sensitive samples is done, thus getting as much information as possible without oversampling.

More generally, the probe size determines the spatial resolution in STEM mode, limited by the probe setup, chromatic and spherical aberration and diffraction. These can be described as: \[ d_{tot} = \sqrt{d_0^2 + d_c^2 + d_s^2 + d_d^2} \]

\[ = \sqrt{\frac{4I}{\pi^2 B\alpha^2} + \left(\frac{\Delta E}{E_0} C_c \alpha\right)^2 + \left(\frac{1}{2} C_s \alpha^3\right)^2 + \left(\frac{1200\Lambda}{\alpha}\right)^2} \] (3.9)

with \( d_{tot} \) the probe size, \( d_0 \) the probe setup size, \( d_c \) the chromatic aberration-limited probe size, \( d_s \) the spherical aberration-limited probe size and \( d_d \) the diffraction-limited probe size. These sizes depend on \( I \) the electron current, \( B \) the electron probe brightness, \( \alpha \) the convergence angle, \( \Delta E \) the energy spread of the electron probe to its acceleration voltage \( E_0 \), \( C_c \) the chromatic aberration coefficient in nanometers, and \( C_s \) the spherical aberration coefficient in nanometers. \[172\]

It is good to distinguish the pencil-beam alignment from the normal STEM alignment used for high-resolution (HR-STEM). In the pencil-beam alignment, the probe size is mainly limited by diffraction contrast \( d_d \). For normal STEM imaging mode, larger con-
3.1 Electron Microscopy (EM)

Figure 3.6: Schematics showing the effects of changing the convergence angle in STEM. (a) Comparison between pencil-beam (small convergence angle $\alpha$) and normal STEM (large convergence angle) STEM alignment. (b) The introduction of an aberration corrector, which controls the formation of the Ronchigram, allows for high-resolution imaging. (c) The relation between camera length and imaging mode in annular dark field imaging, linked to the semi-angle of detection ($\theta$). Ronchigram image reproduced from [182]. Copyright Microscopy Society of America 2019.

Convergence angles need to be used so the spatial resolution is not diffraction-limited, and thus angstrom and sub-angstrom spatial resolutions can be achieved (see Figure 3.5c). However, the use of larger convergence angles introduces other problems, such as lens aberrations. Since the beam is further away from the centre of the lenses when larger convergence angles are used, the STEM probe size is mainly limited by spherical aberrations. These aberrations, in turn, limit spatial resolution (see Figure 3.6a) by creating a circle of least confusion where the focal point is spread, no longer being a 0-dimensional point. In turn, the focal point is spread creating an offset and spread between the electron optics and the position of the sample. [172]

For these two reasons, STEM for high-resolution imaging needs the use of aberration correction, which (i) corrects for aberrations caused by the lens and (ii) moves the focal plane further down in the column (see Figure 3.6b). The inspection of the Ronchigram is a visual aid to understand aberrations and ensure both conditions are satisfied. Its key features include magnification and symmetry. The presence of aberrations affects the symmetry of the Ronchigram, and to optimize microscope imaging conditions, the aperture size must be balanced against the inclusion of aberrations, which gives the highest spatial resolution possible. [182]

Image formation

If the high-angle annular dark field (HAADF) detector is used, an image with high Z-contrast sensitivity is obtained (high semi-angle of detection $\theta$). HAADF images are simpler to interpret than (HR)TEM photographs, as they solely depend on chemical composition and specimen thickness. Depending on the length at which the annular
detector is positioned to the specimen (the camera length) other imaging modes can be achieved, such as atomic bright field imaging or low-angle annular dark field imaging (see Figure 3.6c and Table 3.2).

Alternatively, other detectors can be below the specimen, near the unscattered beam. These detectors can be segmented, which allows for the creation of simultaneous images for each division. Advanced STEM methods such as differential phase contrast use segmented detectors to understand how the electron beam is bent or deflected due to the electron-sample interaction. There is no limit to how many segmentations one could divide a detector into. Ultimately, an $m \times n$ pixelated detector can be created as an array. This is analogous to a camera. \cite{173}

If a camera is placed at the transmitted beam after the specimen, an image of the scanning probe can be recorded for every position. Such a technique is called 4-dimensional STEM (4D-STEM). \cite{183} A subset technique within the 4D-STEM umbrella is when the electron microscope configuration is set such that the diffraction space is imaged when the transmitted electron beam reaches the camera placed after the specimen. This mode also requires the use of very small convergence angles (pencil beam alignment) in order to avoid the overlap between diffraction conditions (see Figure 3.5b). Small convergence angles result in spatially-limited resolution, limited by diffraction as described in Equation 3.8. In such a setup, an electron diffraction pattern can be recorded at each scanned position, named scanning electron diffraction (SED). Each diffraction pattern corresponds to the local nano-structure from the position of the probe, normally limited at $\sim 5$ nm spatial resolution at 200 keV and 1 mrad convergence angle. SED is highly sensitive to crystal structure and strain. \cite{184} In this thesis, the name 4D-STEM is used to refer to SED, although the author notes that 4D-STEM can be used for a myriad of other modes.

The single incident angle nature in SED results in only a few diffraction spots satisfying the Bragg condition and hinders its interpretation. It is important to exercise caution when using electron diffraction, as it is not a kinematical process, like X-ray diffraction, and can involve multiple scattering events, especially for thicker samples. These dynamic effects can influence the interpretation of diffracted intensities and result in the appearance of forbidden reflections. More advanced techniques such as precession SED have been developed to overcome such limitations at the expense of more electron radiation exposure. Precession SED uses beam rocking to integrate through the Bragg condition, resulting in fully integrated electron diffraction patterns, resulting in patterns which are "more kinematical" and thus easier to interpret. \cite{185} While the precession-based technique was not used in this thesis, it has the potential to extend and improve the results reported here with the simpler SED method.
Table 3.2: Angles of collection for different detectors (real and virtual) during STEM data acquisition.

<table>
<thead>
<tr>
<th>STEM detector</th>
<th>Solid angle of collection ($\beta$, mrad)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABF (annular bright field)</td>
<td>6.2 to 12.6</td>
</tr>
<tr>
<td>(L)HAADF (low/high-angle annular dark field)</td>
<td>74.3± 0.3 to 233.3± 1.5</td>
</tr>
<tr>
<td>vBF (virtual bright field)</td>
<td>0 to 2</td>
</tr>
<tr>
<td>vDF (virtual dark field)</td>
<td>2 to 70</td>
</tr>
</tbody>
</table>

Data acquisition

Experimentally for all 4D-STEM data acquisition, data were acquired on the JEOL ARM300 CF E02 instrument at ePSIC (Diamond Light Source, Didcot-Oxford, UK). A monolithic Merlin-Medipix direct electron detector with 4 back contacts was used to acquire fast low-dose 4D datasets. These direct electron detectors allow for better signal-to-noise ratios (SNR) under lower doses due to the superior quantum efficiency compared to traditional CCD systems. The detector was set to 6-bit, to maintain the targeted electron fluence and fast acquisition readout rate. An acceleration voltage of 200 keV, nanobeam alignment (convergence semi-angle $\sim$1 mrad), electron probe $\sim$5 nm, probe current $\sim$3.54 to 3.59 pA, scan dwell time 1 ms, and camera length 20 cm

Each 4D-STEM dataset acquired consists of a 4-dimensional datacube, where each scan contains 256 x 256-pixel positions, with a diffraction pattern of 515 x 515 pixels within each. In the HyperSpy notation, which describes datacubes in terms of navigation and signal axes, these datasets are defined with 2 navigation axes and 2 diffraction signal axes ($<x, y|k_x, k_y>$). At 150 kX magnification for the JEOL setup, each scan covers a real space area of $\sim$1.3 $\mu$m (each pixel is $\sim$5 nm). The magnification can be increased to 200 kX or decreased to 100 kX, slightly changing the field of view probed to <1 or 2 $\mu$m, respectively. Each scan takes $\sim$17 GB of memory. For example, for the dataset in Chapter 4, a series of 75 4D-STEM datasets were acquired for a given region, resulting in a 5-dimensional datacube of 1.27 TB of diffraction data. In order to manage such large amounts of data (given that most desk computers in 2023 have RAMs of 16 to 32 GB), different strategies can be followed. Data rebinning, the process of clustering neighbouring pixels together to change the bin size and shape of the array (e.g. rebinning a diffraction pattern from 515 x 515 pixels to 257 x 257 px can reduce the data size by 4-fold). Data can be loaded in memory "lazily", an approach of deferring the actual loading of data from disk or memory until it is necessary for computation, enabling efficient handling of large datasets that do not fit in memory. This is done through the Python package dask. Finally, data processing can be parallelised, so the data processing workload is distributed among multiple processors or computing nodes to reduce the overall processing time and increase computational
efficiency. This can be done natively through the built-in package *multiprocessing* in Python.

All 4D-STEM datasets must be post-processed to correct for distortions and calibrated. The standard processing pipeline was done using *pyXem 0.14.2* (an open-source Python library based on HyperSpy-based for crystallographic electron microscopy) and *py4dstem 0.13.6*. All diffraction patterns were distortion corrected and calibrated with a gold cross grating using the standard *pyXem* calibration pipeline. The drift in the beam position of the non-scattered beam was corrected and centred, first using the centre-of-mass method from *py4dstem*, followed by a linear cross-correlation with a subpixel factor of 4 pixels. Dead pixels and detector junctions were masked. Beam centring is the process of ensuring that the diffraction pattern at every probe position is exactly at the centre of the origin of the dataset so at pixel 257.5 x 257.5 for a 515 x 515 pattern. Conveniently, all diffraction vector lengths can then be measured from the origin after centring. Often, sample drift in the navigation axis happens, which needs to be corrected by using linear cross-correlation with a subpixel factor of 100 pixels. Sometimes, diffraction patterns shown in the figures are scaled by a power law of 0.33 (power-law using the cube root, as shown in Figure 3.7), which was empirically found to achieve appropriate contrast between the weak diffraction patterns and the saturated central beam when using a 6-bit depth acquisition mode (1-10 counts versus 63 counts). This is because when we tune the power intensity ($I^{pow}$) the extremely weak features, such as detector dark current, are typically not that interesting and the brightest features are dominated by the central beam.

Note that all diffraction patterns in this work are reported in “ordinary” wavevectors ($k = \frac{1}{d}$). Note that these units differed from the “angular” wavevectors definition ($q = \frac{2\pi}{d}$) by a factor of $2\pi$, which is often used in X-ray crystallography literature.

One of the advantages of 4D-STEM data acquisition is the numerous processing methods that can be done post-data acquisition (as opposed to living imaging modes

**Figure 3.7: Power law on diffraction patterns.** Effect of power-law scaling in diffraction patterns (corresponding to a tetragonal perovskite FA-based structure). Weak features are easier to detect at higher scalings (cube root or biquadratic) compared to $I^1$. 


3.1 Electron Microscopy (EM)

Figure 3.8: Digital apertures for virtual imaging. Depending on which regions in the diffraction space are taken post-data acquisition, (a) virtual bright field (vBF), (b) virtual dark field (vDF) and (c) total scattering images can be created. (d) Schematic of the acquisition setup for the SED. The semi-convergence angle $\alpha$ and the semi-angle of detection $\theta$ are labelled.

During data acquisition.\cite{189} This is because 4D-STEM datasets acquire all datasets and data is only reduced to interpretable datasets in the post-processing stages. The key 4D-STEM post-processing and analytical methods particular to SED are described below.

**Virtual imaging**

We refer to virtual bright-field images (vBF) as the images reconstructed from taking the intensity integrated solely from the direct beam as a function of probe position, thus only containing information from the electrons recorded at zero scattering angle. By contrast, virtual dark-field images (vDF) are reconstructed by only taking the intensity from a Bragg-diffracted spot from the 2D diffraction pattern as a function of probe position, thus containing information solely on electrons scattered to specific Bragg angles (Figure 3.8).

For SED, the semi-convergence angle is set to 1 mrad. The range of the semi-angle of detection varies and can be selected digitally post-acquisition (during the formation of virtual images). It can be estimated as:

$$\theta = \tan^{-1}\left(\frac{|\vec{k}|}{CL}\right) \quad (3.10)$$

with $\theta$ as the semi-angle of detection, $|\vec{k}|$ as the reciprocal space vector length in detector pixel units (pixel range $\times$ pixel size), and $CL$ as the camera length.
Based on Figure 3.8a-c, $\theta$ can be estimated using Equation 3.10. A camera length of $2e - 1$ m and a pixel radius ranging from 0.04 (9 pixels in the detector) to 1.2-1.3 $\text{Å}^{-1}$ (256 pixels in the detector) for the vBF and vDF images, respectively, are used for all SED experiments reported in this thesis. The pixel size in the Merlin/Medipix detector is 55 $\mu\text{m}$. Therefore, vBF mapping is set to up to $\sim 2$ mrad (0.04 $\text{Å}^{-1}$) of semi-angle of detection, and for vDF is set from 2 to 70 mrad (up to 1.3 $\text{Å}^{-1}$). See Table 3.2 on how these virtual detectors compare to the real ones.

**Indexing of diffraction patterns**

Indexing a diffraction pattern to a zone axis (normally in the z-axis, in/out of plane) is the process of determining the Miller indices of the set of lattice planes that generate the observed diffraction spots. It is used to identify the crystallographic orientation of a given crystal and, therefore, identify the crystal structure.$^{[171]}$

Mathematically, the orientation of a crystal can be uniquely defined by a $3 \times 3$ matrix $M_{\text{\rightarrow}}$, such that:

$$d = M_{\text{\rightarrow}}d_0$$

$$\begin{bmatrix} d_x \\ d_y \\ d_z \end{bmatrix} = \begin{bmatrix} u_x & v_x & w_x \\ u_y & v_y & w_y \\ u_z & v_z & w_z \end{bmatrix} \begin{bmatrix} d_{x0} \\ d_{y0} \\ d_{z0} \end{bmatrix}$$

where $M_{\text{\rightarrow}}$ rotates vectors $d_0$ in the sample coordinate system to vectors $d$ in the parent crystal coordinate system. These rotations can also be described with a set of Euler angles, which describe a set of 3 chained angle rotations to the sample Z direction.$^{[190]}$

The simulation diffraction package PyXem uses Euler angles to describe any arbitrary orientation of a given crystal.$^{[191]}$

In practice, the indexing of a diffraction pattern can be done manually from the measurement of two diffraction vectors as follows. This method is commonly used and designed by Paul Midgley and his group members.

1. Ensure the diffraction pattern has been centred, calibrated and distortion-corrected.
2. Measure the reciprocal space length of two distinct Bragg diffraction spots (normally in $\text{Å}^{-1}$) and the inter-vector angle formed between the two spots and the origin.
3. Compare the vector lengths against a list of simulated vector lengths for the different plausible crystal structures of interest (see Section 3.1.3). All diffraction patterns can only be compared within the reciprocal-space resolution of the 4D-STEM tech-
nique. Normally, under the acquisition conditions described above, one pixel in the
detector can resolve 0.005 Å\(^{-1}\). This step results in a list of possible crystal planes
for each considered crystal phase for each diffraction spot.

4. For each distinct crystal plane, the cross product is calculated, as it returns a vector
in the \(z\)-direction zone axis, namely the crystal plane perpendicular to the electron
beam direction (see Equation (3.13)).

5. From the 2-dimensional simulation of the diffraction pattern for a given crystal at a
given zone axis, the experimental inter-vector angle is compared to the respective
simulated inter-vector angle. If the difference deviates by several degrees, the zone
axis related to that vector pair is rejected and the process is repeated for the next
potential vector pair.

\[
\mathbf{c}_z = \mathbf{g}_1 \times \mathbf{g}_2 = \det \begin{bmatrix}
h_{g1} & k_{g1} & l_{g1} \\
h_{g2} & k_{g2} & l_{g2} \\
h & k & l
\end{bmatrix} = u\mathbf{i} + v\mathbf{j} + w\mathbf{k}
\]

with \(\mathbf{c}_z\) the zone axis vector (in the \(z\)-direction, with Miller indices \(u, v, w\)), \(\mathbf{g}_1\) and \(\mathbf{g}_2\) the
measured diffraction peaks with \(h_i, k_i, l_i\) Miller indices.

This results in only one or a few possible zone axis indexings across all structures.
Oftentimes, dynamical scattering effects are visible, such as the appearance of forbidden
reflections or double scattering. Moreover, it is common to observe regions with multiple
grain overlaps near grain boundaries or in thicker films. It is also common to measure
diffraction patterns of grains far away from the zone axis. Finally, even near zone axes
with multiple bright diffraction spots visible, some crystal phases may result in diffraction
patterns that are too similar to differentiate. Indexing in all these mentioned cases is
normally inconclusive.

**Crystal Structure Library**

All diffraction patterns in this thesis could be closely indexed to a pseudo-cubic/tetragonal
perovskite unit cell (\(P, m\bar{3}m\)) with lattice parameters of \(a = b = 9.00\) and \(c = 6.36\,\text{Å}\).\(^{[163]}\) Despite the stoichiometry of the FA-based samples normally being more complex, involving
double/triple-cation double/single-halide compositions, this family of structures can be
approximated as a simpler unit cell made from the predominant ion at each site (C, Pb
and I).

Additional crystal structures are always also considered. In particular, for PbI\(_2\), which
can form in multiple polytype structures, the hexagonal 4H-PbI\(_2\) crystal phase (\(P6_3mc\),
lattice parameters of \(a = b = 4.56\) and \(c = 13.96\,\text{Å}\,\text{COD ID: 9009140}\) is used. However,
Experimental Methods

Figure 3.9: Crystal structures library. Schematics of common crystal structure files used for the simulation and indexing of experimental diffraction patterns in this thesis. (a) Schematic of how the tetragonal $P4/mbm$ perovskite unit cell is built from the $BX_6$ octahedra, showing a small tilt. (b) Histograms and (c) the unit cells at the a, b and c directions for the general perovskite, the $PbBr_2$ and the $4H-PbI_2$ phases. The histograms show how the Pb-Pb distances for the perovskite structure tend to be longer than for the lead halide structures. Other phases were also considered, such as the intermediate polytype phases.

since some ambiguity on the specific PbI$_2$ polytype across literature exists since different polytype phases are remarkably similar, other polytypes such as the 2H- or 6H-PbI$_2$ are sometimes also attempted to be indexed. Intermediate perovskite polytype phases could also be considered. Following Ramsdell notation, the three common polytypes of 2H, 4H and 6H are normally measured with diffraction lengths $<0.16 \, \text{Å}^{-1}$. Additional structures are also possible if none of the above match the diffraction pattern, such as various crystalline precursors, such as orthorhombic PbBr$_2$ crystal phase ($Pnam$, COD ID: 1530324, lattice parameters of $a = 80.6$, $b = 6.54$ and $c = 4.73$ Å), the cubic Pb crystal structure ($F\bar{m}3m$, COD ID: 20483), or the diverse family of tilted lower-
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symmetry perovskite structures (tetragonal or orthorhombic). The structure files were retrieved from the crystallography open database and the Material Project website.\textsuperscript{[193,194]}

All diffraction simulations are normally performed using the Crystal Maker suite (CrystalMaker Software Limited), using Crystal Diffract 6 for obtaining a list of simulated vector lengths, and Single Crystal 4 to simulate 2-dimensional diffraction patterns. Simulation parameters are adjusted to resemble the experimental data (200 keV, detector spot size $0.025\ \text{Å}^{-1}$, saturation 10, gamma 2).

3.1.4 TEM-based spectroscopy

Apart from a camera detector placed after the specimen, other detectors can be used to capture the energy of dispersed (scattered) particles. Such techniques can be used for analytical spectroscopy in EM. One of the most common EM spectroscopies is energy-dispersive X-ray (EDX). X-rays can be emitted from the energy lost via inelastic electron scattering during imaging in the EM. These X-rays can be collected and used for elemental mapping and quantification. A normal spectrum consists of a superposition of characteristic elemental peaks (unique to the transitions allowed transitions of electrons in the inner shells of atoms to the outer shells, named as $L\alpha, K\alpha$, with energies characteristic of the atoms present in the specimen), on a continuous bremsstrahlung background, the "breaking radiation" caused by the electrons slowing down through the specimen. Interpretation of EDX spectra is not trivial as some characteristic peaks may overlap with other elemental peaks, requiring the use of deconvolution or model fitting. Other peaks may be attributed to fluorescence and detector defects, spurious X-rays from unexamined parts of the sample, or system X-rays, resulting from the sample holder or microscope. For example, when a SiN grid is used, the most common system X-ray peaks are the $Si_{K\alpha}$ and $Si_{K\beta}$. Moreover, EDX cannot resolve light elements such as carbon or nitrogen well, which are relevant compositions in perovskites, since they have low X-ray fluorescence yields.\textsuperscript{[173]} Quantification of the elemental composition of a specimen in STEM-EDX in this thesis is achieved using the Cliff-Lorimer ratio method. This method involves calculating the ratio of characteristic X-ray intensities emitted by a material, using a calibration standard with a known binary composition. Then a linear relationship between the chemical composition of the material and the intensity of the emitted X-rays can be drawn. Normally, all elements are compared against the arbitrary Si peaks.\textsuperscript{[195]}

In parallel, the energy of the electrons in the transmitted electron probe can be collected to determine how much energy it lost after crossing the specimen, named electron energy-loss spectroscopy (EELS). EELS excels at locating lighter elements and can provide higher spatial resolution than EDX lacks and provide chemical information such
as oxidation states. Moreover, systems with monochromatic electron beams can even probe the electronic band gap states in the optical energy range (eV energies).\cite{175} This technique is mentioned for completeness but was not utilised in this thesis because it needs exceptionally thin specimens, of the order of <50 nm, which are hard to fabricate using conventional perovskite fabrication deposition methods. With the optimisation of thermal evaporation perovskite deposition, thin-enough films will likely be able to be imaged using advanced EELS.

In this thesis, compositional mapping using STEM-EDX was always acquired from an FEI Osiris FEG-(S)TEM. EDX spectra were obtained with Bruker Super-X SDDs with a total collection solid angle of $\sim 0.9$ sr, a spatial sampling of 10 nm per pixel, and a spectral resolution of 5 eV per channel. An electron beam current of 140 pA (less than 7,000 e$^{-} \cdot \text{Å}^{-2}$) and 50 ms dwell time was used (70 $\mu$m C2 aperture, spot size 6, and gun lens 5, 115 mm camera length). These conditions were reported by Felix Kosasih to be optimal.\cite{196} All EDX spectra were spectrally rebinned to 20 eV per channel, then denoised with PCA and NMF, and processed in \textit{HyperSpy 1.7}. Compositional maps were obtained using the integrated line intensities for $\text{Pb}_L\alpha$, $\text{I}_L\alpha$, and $\text{Br}_K\alpha$. For bromine, the $\text{Br}_L\alpha$ peak was not chosen since the tail overlaps with the dominating $\text{Si}_L\alpha$ peak. The Cliff-Lorimer method using the calibrated K and L-factors from Bruker was used when quantification of STEM-EDX is reported. HAADF images were acquired from a Fischione detector in parallel to the EDX acquisition, with a spatial sampling of 4 nm per pixel and a dwell time of 0.5 s.

### 3.1.5 Scanning Electron Microscopy (SEM) and Cathodoluminescence (CL)

SEM works on the same basic principles as STEM, where an electron beam is focused on a spot. The spot size is instrument dependent and ranges from 1 to 10 nm, yet some modern instruments can achieve sub-nanometer spot sizes on the sample surface. The beam is then moved in a raster pattern across the sample surface, interacting with its constituent atoms. One important distinction is that, unlike STEM, the sample in SEM does not need to be thin enough for electron transmission.

Figure 3.10a shows the beam-specimen interaction in the SEM, although the scheme is considered to be oversimplified. In general, two types of electron scattering can be distinguished in SEM: elastic and inelastic scattering. Elastic scattering results in backscattered electrons (BSE) with high energy, while inelastic scattering produces, among other signals, secondary electrons (SE) with low energy.
Detection of both types of electrons is facilitated by two detectors, which are commonly integrated into most SEM systems. BSEs are normally emitted from the sample in all available directions, with some preferential emission angles. A detector, usually mounted under the pole piece to maximise BSE yield for samples normal to the electron beam, can collect the electrons within a certain solid angle. The Everhart-Thornley detector (ET, phone home), equipped with a Faraday cage and some positive bias, is typically employed for signal acquisition dominated by SE. This imaging mode is the most common. However, it should be noted that the SE signal is not exclusively "pure", as it is a convolution of SE and BSE signals. Finally, while BSEs originate from the sample, SE can be formed indirectly from various sources. SEs can (i) directly originate from the surface, (ii) be produced when a BSE undergoes an inelastic scattering process close to the surface, in turn emitting a SE, or (iii) be generated by the interaction of BSEs with the SEM equipment walls. Due to their low energy, only surface-generated SEs can escape, so even minor alterations in the surface morphology can significantly impact the SE yield. In contrast, BSE can provide atomic and compositional contrast as the backscattering probability is proportional to the elemental composition. See Figure 3.10b and c for SE and BSE micrographs of the same region.

During the beam rastering across the sample, large amounts of electrons interact with the specimen. Each electron can be thought of as interacting with the specimen independently. Monte Carlo simulations are ideal to obtain an accurate depiction of the electron interaction volume, which refers to the region of the specimen where the electrons from
the beam penetrate and transfer their energy to. Figure 3.10d illustrates the simulation of 500 trajectories for carbon, silicon, copper, and gold at 0° tilt and acceleration voltage of 20 keV. These simulations provide a comprehensive view of the electron interaction volume, which is largely affected by the acceleration voltage and by the effective atomic number of the sample. While the electron probe size can be focused on the nanometer scale (~5 nm in the SEM systems used in this thesis), the interaction volumes for SEM are in the micrometre to nanometer length scales. A large number of electrons are required to produce a reasonable interaction volume.

Various software programs are readily accessible to conduct these simulations, with the most commonly utilized one being CASINO. This program is capable of simulating electron trajectories, computing BSE yield, displaying the regions of energy deposition by the electron beam, and demonstrating where visible cathodoluminescent photons and X-ray photons are produced in the specimen. The physical models implemented in CASINO can simulate from 0.1 to 30 keV, making it highly suitable for SEM. For example, it was used to estimate the electron penetration depth of MAPbBr₃ single crystals as 15 nm and a 1 µm for 2 and 30 keV, respectively.

Although the Monte Carlo simulation is a valuable tool, a simple approximation of the interaction depth can be described. Kanaya and Okayama (KO) developed a range equation that considers both inelastic and elastic scattering. It estimates the interaction volume as the radius of a hemisphere centred on the beam impact point that contains at least 95% of the trajectories. The penetration depth is proportional to:

\[
R_{KO}(nm) = \frac{27.6A}{\rho Z^{0.889}} E_0^{1.67}
\]  

with \(A\) the atomic weight (g/mol), \(\rho\) the density (g/cm³), \(Z\) the atomic number and \(E_0\) the beam energy (eV). Note that the KO penetration depth should only be taken as an approximation.

Similarly to a photon exciting the electronic states of an optoelectronic material with the creation of charge carriers as electron-hole pairs (\(e^- - h^+\) pairs), a high-energy electron beam can also excite the material and create large quantities of charge carriers. Note that this is a simplified statement, as many other electron-matter interactions such as near-band edge excitation, bulk plasmons, core-level excitations, or direct excitations can all lead to the emission of light in CL. Despite the disparities between optical and electronic excitation mechanisms, the emission spectra are nearly identical for both techniques. In this thesis, only CL from semiconductor materials is explored as incoherent CL emission. The number of electron-hole pairs produced (\(G\)) per electron can
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Figure 3.11: The Burstein-Moss effect. Schematic of the Burstein-Moss effect showing the effective increase in the original bandgap energy $E_g$ when high-fluence excitation leads to large charge carrier densities. Large charge carrier populations can saturate the band edge and populate higher vibrational energy states of the conduction band ($\Delta E_{BM}$). This results in blue-shifted emission. Adapted from [200]. Copyright Springer Nature 2014.

be estimated to depend on the energy of the electron beam ($E_0$) and the band gap of the material ($E_g$) mainly. It can be estimated by the relation described by Yacobi. [204]

$$G = \frac{E_0 I_b Q (1 - \gamma)}{e E_g} \approx \frac{E_0}{3E_g} I_b$$  \hspace{1cm} (3.15)

with $I_b$ the beam current (A), $E_g$ the band gap, $Q$ the quantum efficiency for charge carrier creation, and $\gamma$ the fractional energy loss due to backscattered electrons. Approximately, the number of charge carriers produced is proportional to the electron-beam energy over 3 times the band gap. [27] Equation 3.15 assumes that the ionisation energy to create an electron-hole pair $E_i = 2.8E_g + M$, with $M$ being a material-dependent factor ranging from 0 to 1. This phenomenon makes EM good to probe optoelectronic properties, with the advantage of higher spatial resolution of excitation than the photon-excited analogue techniques such as PL. Other advantages of CL over PL are the tuneable probing depth or the high excitation energy, which enables a more readily study of wide bandgap materials without the need for special lasers.

When large quantities of charge carriers are generated, quite common in CL, blue-shifted emission is expected due to the Burstein-Moss effect. When large charge carrier populations are generated, they can saturate the band edge, thus populating higher vibrational energy states of the conduction band (see Figure 3.11). [200]

The charge carriers produced by a scanning electron beam can be collected in the form of current, allowing the mapping of the electronically-excited carriers across a
device, called electron-beam-induced current (EBIC). Moreover, the charges can be left to diffuse and recombine by the emission of photons. A parabolic mirror or a reflective objective inside the microscope can direct the photons out of the vacuum chamber, to a spectrometer-charge-coupled device (CCD) system. The spectrometer can disperse the different energies of the emitted photons, and the CCD can be used to acquire the emission luminescence spectrum, called cathodoluminescence (CL). The intensity of the CL luminescence from SEM ($I_{CL-SEM}$) is proportional to:

$$I_{CL-SEM} \propto G_{Ib} \frac{Ib}{e} \eta F(\alpha, R)$$

(3.16)

with $G_{Ib}$ the generation rate of charge carrier pairs per second, $\eta$ the internal quantum efficiency (the radiative recombination efficiency), and $F(\alpha, R)$ the function to account for losses from absorption, reflection and non-radiative surface recombination. Here $\eta$ depends on the charge carrier lifetimes and can be calculated from $\eta = \frac{1}{1 + (\tau_{rr}/\tau_{nr})}$ with $\tau_{rr}, \tau_{nr}$ the radiative and non-radiative lifetimes.

CL spectroscopy can be measured by any (scanning) EM platform. While CL in an SEM is the most common technique and the one used in this thesis, other systems are also possible. For example, STEM-CL can potentially offer the highest resolutions.

The resolution in CL SEM-based techniques is not simple to determine. How close two areas with different luminescence properties can be measured by CL as two distinct signals is limited by the largest parameter of these three: (i) the electron probe size, (ii) the electron-beam penetration depth, proportional to the interaction volume, and (iii) the minority-carrier diffusion length. In general, in scanning-probe techniques, the electron
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probe size is small on the nanometer scale (∼5 nm in the CL-SEM system used in this project). The interaction volume for SEM can be estimated with Equation 3.1.14, normally in the order of hundreds of nanometers. Finally, the carrier diffusion length is sample dependent. It can be large, limiting the spatial resolution, or it can be small, such as in isolated nanostructures or under low-temperature experiments. Overall, the interaction volume is generally seen as the largest of the three parameters, limiting the spatial resolution of CL. For halide perovskite samples, the resolution can be limited by both the carrier diffusion length and the interaction volume. For MAPbBr₃ single crystals, for instance, the electron penetration depth was estimated to be 15 nm and 1 μm for 2 and 30 keV, respectively. [150]

As for the carrier diffusion lengths, certain perovskite compositions are known for their outstanding diffusion lengths in the micrometre range. [68] However, despite these large diffusion lengths, diffusion in polycrystalline films is limited by grain boundaries (reduced from 0.7 μm in single crystals to 0.05-0.17 μm for CsFA and CsMAFA alloyed systems, respectively). [205] In the case of single crystals, these lengths are also limited by the size of the nanostructures. Therefore, the CL-SEM resolution for each sample must be estimated independently.

CL has been used to characterize semiconductors at the nanoscale for many decades, yet only recently, transient CL, known as time-resolved CL (TRCL) has become accessible by adopting pulsed-mode electron beams (PM). To move beyond the well-established continuous wave (CW) electron beam (see Figure 3.12a-b), two main methods exist: (i) Beam blanking involving deflection plates to steer the electron beam away from the axis of the optical column. This method is simple but a minimum pulse duration of a few tens of nanoseconds can be achieved. [206] (ii) To use a pulsed laser to optically drive the generation of an electron pulse. The electron gun is set below its cathodic emission and UV-photon pulses of short time duration enter the vacuum chamber through a sapphire window and are focused on the cathode surface. An electron pulse of a short time duration of a picosecond or femtosecond is then generated, matching the laser pulse duration. The resulting photoelectrons are then directed and concentrated using an appropriate electron optical system. [207,208]

Since bright picosecond pulsed electron beams can be generated, it is now possible to measure TRCL to probe fast charge-carrier dynamics on the nanoscale. Extensive examples of this technique have been performed for III-V semiconductor nanostructures, [209,210] but only a couple of TRCL studies exist for halide perovskites, to my best knowledge. [153,154] In addition to enabling the acquisition of TRCL, the use of a pulsed beam can reduce the beam current to tens to hundreds of pA. [211] Low-injection conditions can be tuned to match *operando* conditions of optoelectronic devices, making this
technique interesting from a device characterization perspective. More importantly, low-current pulsed beams allow the material to relax electronically and thermally in between pulses, which can be beneficial to hinder beam damage.\cite{212,213} Chapter 5 discusses the novel use of PM as a beneficial tool to investigate the optical properties of perovskites using CL.

Experimentally for all CL-SEM data acquisition, data were acquired on the Attolight Allalin 4027 Chronos CL-SEM. The spectra were acquired with an iHR320 spectrometer (focal length of 320 mm, 150 gratings per mm blazed at 500 nm, 700 $\mu$m entrance slit) and an Andor 1024 pixel CCD with a 700-7,000 $\mu$m entrance slit. The readout rate frequency can be set to 3 MHz for short acquisition times, or to 50 kHz for long acquisition times. The CCD allows for horizontal binning, normally set to no binning or 2 binning, which combines the signal of two pixels into one digital value. However, it slows down acquisition time and makes the overall acquisition of a hyperspectral map x2 longer. The CCD also allows for signal amplification, normally set to x2 or x4, which amplifies the signal counts but also the background noise. All the measurements reported in this thesis were performed at room temperature under a high vacuum ($< 10^{-7}$ mbar). Samples must be electrically contacted to the metallic holder, using silver paint. When samples are prepared on top of insulating substrates such as glass, silver paint must also contact the top surface of the samples to stop sample charging. Painting the surface of the specimen should not have any impact on the active material, as imaging is done millimetres away from the edges.

Beam focusing before each CL map was always performed on regions of the sample at least 100 $\mu$m away from those used for the measurements, to avoid electron-induced damage prior to mapping. The highest resolution in the Attolight system is a 5 nm spot size on the sample surface. All beam currents were calibrated using a Faraday cup by Gunnar Kusch, at least every 6 months or when any maintenance of the microscope was done, whichever was shorter.

The electron pulsed gun, to activate PM, was obtained by pulsing an electron gun with the third harmonic of an Nd:YAG laser (355 nm) at a pulse width of 7 ps and a frequency of 80.6 MHz (12.41 ns). CL time decay curves were recorded with a time-correlated single photon counting (TCSPC, Becker & Hickl PMC-150-20) photodetector, with a temporal resolution of 80 ps and a spectral response from 450 nm, decreases at 750 nm and becomes ineffective beyond 850 nm. Only a spectral width of ±2 nm can be measured, given by the width of the optic fibre diameter connected to the TCSPC. Dwell times were normally extended until the TRCL signal was two orders of magnitude higher than the background. Spectrally and temporally resolved streak images can also be recorded in the same CL
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system, using a Horiba Streak camera (C10910-05): spectral width of ±40 nm, a temporal resolution of <2 ps, and spectral response from 200 nm, decreases at 850 nm, and becomes ineffective beyond 900 nm (Figure 3.12c).

CL hyperspectral maps (CL maps) consist of 3-dimensional datacubes, where each scan contains \( n \times n \)-pixel positions, with a spectrum of 1024 pixels within each. In the HyperSpy notation, which describes datacubes in terms of navigation and signal axes, these datasets are defined with 2 navigation axes and 1 signal axes (\( <x, y|E> \)). CL maps can be taken at various acquisition conditions, which are described for each experiment in this thesis. Such conditions include parameters such as (i) the acceleration voltage, normally using 1, 3, 5, 6 or 10 keV, (ii) the dwell time at each scanned pixel position, ranging from 22 to 502 ms, (iii) the field of view, proportional to the rastering pixel size or magnification, ranging from sub-micron to tens of micrometres, (iv) the electron beam current, normally ranging from as low as 14 pA to large values of 30 nA, and (v) the electron beam mode, either in CW or PM.

All CL datasets must be processed to correct for distortions and calibrated. A new standard processing pipeline was developed in this thesis, and it is described in Chapter 5 and published as an open-source Python package called LumiSpy.

Finally, SE imaging is also performed without CL. For that, a FEI Helios Nanolab Dualbeam FIB/SEM. A low acceleration voltage is used to better image surface morphology, normally at 2 keV. The lowest current possible, while still acquiring minimal SNR is used, normally at 200 pA. The working distance is \( \sim 4 \) mm, and an ET-detector is used (to mainly measure SEs) at varying magnifications ranging from 10 to 100 kx. The best image acquisition mode for the beam-sensitive samples, which can often also charge depending on the conductivity of the substrate, is the so-called TV mode. This mode allows for the acquisition of multiple frames at very short dwell times repetitively. The ideal conditions used for SE imaging are 1536 x1024 px, at 100 ns dwell time, 16-bit depth, integrating continuously over 64 frames. Sample drift must be corrected. Moreover, the scanning beam is set to skip 8 lines every time it rasters, and to average every 4 frames. Finally, samples must be electrically contacted to the metallic stub using carbon tape. Small strips of carbon tape that extend to the surface of the sample are also used, to avoid surface charging.

3.1.6 Beam damage theory

A key limitation of high-energy electron probes hindering the study of any sample, especially beam-sensitive ones, is beam damage. When an energetic electron beam interacts with the perovskite structure, different mechanisms can alter the pristine structure. Un-
derstanding these processes is not trivial, especially for hybrid beam-sensitive materials like halide perovskites. A fundamental basis of this thesis therefore critically explores the limitation threshold of these techniques using empirical approaches.

In order to quantify the amount of exposure from a beam (of electrons or any other particle), the concepts of flux, fluence and dose are useful.

- **Flux**: Number of particles per unit of time. It takes into account the beam source. E.g. $e^-$ per second, photons per second.
- **Fluence**: Number of particles per unit area. It takes into account the beam size as well. E.g. $e^-$ per Å$^2$, photons per m$^2$.
- **Dose**: Amount of energy absorbed per unit mass. It takes into account the sample-beam interaction as well. E.g. Joules per kg, Grays (Gy).

Most literature in the electron microscopy field misuses the term *dose*, as it does not adhere to the aforementioned standard particle-Physics definitions. The correct term when reporting $e^-$ per Å$^2$ is fluence. Calculating the dose for an electron microscopy experiment would require modelling the electron-beam-sample interaction, which is not trivial and requires many assumptions. In the X-ray microscopy field, the standard definitions are normally used and doses are always stated in Gray units. Note that sometimes *administered dose* is reported instead of the *absorbed dose*, a value which does not take into account the sample-beam interaction and is easier to calculate.

From a theoretical standpoint, beam damage can be classified depending on which electron scattering type it originates from, namely from elastic or inelastic scattering events. The rest of the Section is based on the description of damage from Egerton$^{[214]}$. From elastic scattering, atomic displacement and electron sputtering are possible. From inelastic scattering, heating, deposition, and radiolysis sample damage or mass loss is possible. moreover, electrostatic charging can happen due to both scatterings (see Figure 3.13a).

During an elastic scattering event, the energy of the electron does not change. However, the direction does, which results in a change of momentum through an angle $\theta$, which can transfer energy to the sample as follows:$^{[214]}$

$$E(eV) = E_{max} \sin^2(\theta/2) \approx C \frac{E_0(a + E_0)}{bA}$$  \hspace{1cm} (3.17)

with $E_0$ the incident electron acceleration voltage, $A$ the atomic mass number, and $C$, $a$, and $b$ constants. The angular dependence means that energy transfer is negligible (less than 1 eV) for small angles, but large energy transfer of several eV is expected for backscattered electrons ($\theta$) or when high $E_0$ are used in TEM. When the transferred energy surpasses that of the displacement energy ($E_d$) of the material being examined, which is
3.1 Electron Microscopy (EM)

Figure 3.13: Classification of beam damage. (a) Diagram classifying different mechanisms of electron beam damage based on elastic (green) or inelastic (orange) scattering. (b) The sputtering energy threshold for different elements, with $E_S$ as the sublimation energy per atom. Adapted from [214]. Copyright Elsevier 2004.

determined by its constituent atoms, atomic weight, bond strength, and crystal lattice, the atomic nuclei can be displaced to interstitial positions, leading to atomic displacement. For example, $E_d$ for graphite and diamond is 30 and 80 eV, respectively, values which are only surpassed when acceleration voltages of 100 keV or larger are used.

At the surface of the material, the displacement energy is lower ($E_s < E_d$) so atomic displacement is more likely to happen, with atoms leaving towards the vacuum. This process is known as sputtering. The sputtering rate is directly linked to the Rutherford cross section and the incident current density (in $e^{-}$ cm$^{-2}$s$^{-1}$). Figure 3.13b shows the threshold incident energy for each element, assuming that $E_s$ is the sublimation energy per atom. It shows that sputtering mainly concerns low-Z elements. Sputtering can be hindered by adding a thin layer of a heavy element to protect the surface, by adding a sacrificial layer, or by reducing electron exposure.

During inelastic scattering, incoming electrons collide with the electrons in the sample. Energy transfer to the sample during this process can lead to a local increase in temperature, known as electron-beam heating. For the case of thin specimens in TEM mode, heat generation can be described by the steady state equation that includes the contribution of the radial conduction of heat loss, in 2D, and the radiation heat loss from both sides of the specimen as follows: [214]

$$I \langle E(eV) \rangle (t/\lambda) = \frac{4 \pi \kappa I(T - T_0)}{0.58 + 2 \ln(2R_0/d)} + \frac{\pi (d^2/2) \epsilon \sigma (T^4 - T_0^4)}{0.58 + 2 \ln(2R_0/d)}$$

(3.18)

with $t$ the thin sample specimen, $\lambda$ the mean free path for inelastic scattering, $I$ the electron beam current, $d$ the incident beam diameter, $\kappa$ the thermal conductivity, $R_0$ the distance through the material in which the radial heat conduction happens, $\epsilon$ the emissivity of the sample, $\langle E \rangle$ the average energy loss per inelastic collision, $\langle E \rangle (t/\lambda)$ the
average energy per incident electron, \(\langle I/e \rangle \langle E(t/\lambda)\rangle\) the heat deposited per second (in Joules) and \(I\langle E(eV)\rangle(t/\lambda)\) the heat deposited per second (in eV). The second term of the sum is radiation heat loss.

If Equation 3.18 is used to calculate \(\Delta T = T - T_0\), it shows that the temperature rises \(\Delta T\) is independent of the sample thickness. The electron beam current \(I\) is the main factor attributed to heating. Changing the probe size \(d\) between TEM and STEM mode does not have a significant effect on heating, as \(d\) has a logarithmic dependence, due to the 2D radial heat flow model. The thermal conductivity \(\kappa\) is also important, as thermal degradation is expected for low \(\kappa\) while melting is likely to happen when \(\kappa\) is large. For perovskites, as \(\kappa\) is low,\(^{215}\) thermal degradation must be accounted for during electron microscopy.

In the SEM, since the sample is thicker, the heat flow model is radial in 3D. This results in lower \(\Delta T\), with the steady-state equation as follows:\(^{214}\)

\[
\Delta T = \frac{1.5}{\pi} \frac{I/V_0}{\kappa R}
\]  

(3.19)

with \(R\) the electron range. This equation yields \(\Delta T\) values of 0.1 and 10 °C for metals and polymers, respectively. For hybrid materials like halide perovskites, local heating is expected to be within this temperature range, but no experimental measurement exists to the author’s knowledge. Moreover, when the probe scans, the movement of the probe lowers this temperature rise by a factor of x10.

During inelastic scattering, radiolysis may also happen through the transfer of energy from the electron beam to atoms in the sample, leading to a momentum transfer to the nuclei of the atoms. The nature of the specimen affects radiolysis. Inorganic samples, like alkali halides or oxides, can suffer from ionisation during radiolysis. This can lead to halide condensation in clusters, which diffuse to the surface and result in a halide mass loss. This process is called electron-stimulated desorption. In parallel, vacancies can aggregate, forming voids. Organic samples can also suffer from radiolysis. In the case of molecules, chemical bonds are easily broken, resulting in a change in their electronic configuration and mass loss (particularly for volatile species such as H2, N2, or O2). If the organic is crystalised, loss of crystallinity also follows. Aromatic molecules are more stable as the energy deposition is delocalised by many electrons. Radiolysis can be reduced by: (i) cooling the specimen, which can reduce mass loss by x3-x100 due to reduced atomic mobility, (ii) coating the specimen, which reduces the escape rate for volatile species, thus making healing more likely, and (iii) increasing sample thickness, which can accept more electron exposure.
Radiolysis can be quantified using electron exposure quantities such as flux, fluence or dose. These are normally calculated by multiplying the incident current density by the exposure time. Oftentimes, a characteristic threshold for a given material and measurement can be set to the exposure at which the measurement decreased to $1/e \approx 37\%$ of the initial value.

In the SEM, radiolysis can only happen close to the surface, within electron range. When the acceleration voltage $E_0$ is reduced, the interaction volume is reduced according to Equation 3.14, and therefore the energy deposited per unit volume increases as follows:

$$R_{KO} \propto E_0^{1.67} \rightarrow V_{KO} \propto R_{KO}^3 \propto E_0^5$$

with $V_{KO}$ the estimated volume of interaction, and $\rho$ the energy deposited per unit volume.

Inelastic scattering of the electron beam can also result in deposition on the specimen. The hydrocarbon molecules in the chamber, from a non-perfect vacuum or emitted chemicals from sample damage, can be polymerised by the electron beam. Since the polymer has low mobility, it forms a layer that increases thickness rapidly.

When an insulating or semiconducting sample is probed with a negatively-charged electron beam, charging can occur from both elastic and inelastic scattering. By using the steady state equation for currents (current in must equal current out), the following can be derived:

$$\text{Current in} = \text{Current out}$$

(SEM) \quad I + \frac{V_S}{R_S} = I\eta + I\delta(V_S) = I\eta + \int_{eV_S}^{E_0 - eV_S} \left( \frac{d\delta}{de} \right) de$$

(TEM) \quad I - I_{\text{transmitted}} + \frac{V_S}{R_S} = I\eta(t) + I\delta(V_S)

The left-hand side of the equation (current in) contains $I$ the incident current, $V_S$ the surface potential developed in the beam, $R_S$ the effective electrical resistance between irradiated and surrounding regions of the specimen, and the leakage current through the grounded specimen (not included in Equation 3.21). The right-hand side of the equation (current out) includes the loss of electrons via BSEs and SEs with $\eta$ the backscattering coefficient, and $\delta(E)$ the SE yield. This yield is complex to calculate, as it depends on the surface potential $V_S$ and needs to be integrated over all the possible SE energy range $\epsilon$. 

\[\text{(3.20)}\]
(from $eV_S$ to $E_0 - eV_S$, as lower energies cannot escape into the vacuum and the highest energy must be $E_0 - eV_S$).

For TEM, the backscattered coefficient is reduced to $\eta(t)$ because of the thinner sample. The transmitted current $I_{\text{transmitted}}$ is also a current out. Such transmitted current approaches $I$ as thickness decreases or acceleration voltage increases. Therefore, since $I_{\text{transmitted}} \approx I$, then $V_S$ must be positive and large. If the voltage reaches large levels, while this voltage may not affect electron focusing, it creates an electric field (at the edges of the illuminated region) that may be high enough to cause an electrical breakdown, potentially lead to lateral ion migration or, ultimately, mechanical tear down of the thin specimen.

In short, sample damage caused by the interactions mentioned in this Section between the electron beam and the sample can heavily limit the use of electron microscopy. If radiolysis dominates, which is the main damage process for organics, the use of cryogenic temperatures or low acceleration voltages can help. If knock-on atomic displacement and sputtering are predominant, reducing the TEM accelerating voltage below some threshold value related to $E_d$ will largely eliminate the damage. If damaging effects arise from beam heating or electrostatic charging, reducing the incident-beam current or dwell time, as well as adding a thin conductive layer can be helpful. For the particular case of halide perovskites, which are hybrid mixing organics and inorganics, damage mechanisms will involve a convolution of all the mechanisms described. However, it has been experimentally found that lowering the temperature does not inhibit, or even slow, the beam-induced structural changes, but causes a rapid amorphization. At low temperatures, point defects caused by knock-on events are not mobile and therefore do not recombine, forming defect clusters and amorphous areas which are even more prone to degradation.\[141,157\]

### 3.2 Optical microscopy

Optical techniques like photoluminescence (PL) or its time-resolved analogue (TRPL) enable the mapping of light emission properties of perovskite thin films on the scale of micrometres, in the far field.\[31,216\] Atomic force microscopy (AFM) and its variants (such as Kelvin-probe force (KPFM), conductive AFM (cAFM), or scanning near-field optical microscopy (SNOM)) can probe the local morphology, the electrical response and the optics at the nanoscale in a non-invasive manner, respectively.\[217,218\] X-ray-based techniques, such as X-ray fluorescence (XRF) or (nano-focused) X-ray diffraction ((n)XRD) can measure the composition and structure of thin films with a resolution of the order
3.2 Optical microscopy

Figure 3.14: Hyperspectral PL mapping. The PL mapping is acquired by taking a series of energy-filtered PL images. Each image is sliced into uniform wavelength segments. These segments are shifted to bring together all segments of the same wavelength and then stitched together to form a hyperspectral dataset with respect to wavelength. Segments that cannot form a complete image are discarded. Retrieved from[219].

of ~50 nm if synchrotron radiation is used.[106] Despite none of these techniques being the focus of my PhD, the strong expertise on most of these tools from my research groups enables efficient collaboration to correlate the electron-beam characterisation with these other techniques.

Wide-field hyperspectral photoluminescence microscopy (PL) measurements were normally carried out to probe the optical signal before and after structural measurements using electron microscopies. Early measurements were carried out with the help of Elizabeth Tennyson, but most PL data was acquired by me unless stated otherwise. An optical microscope equipped with a Photon etc IMA system was used, with an x100 air, chromatic aberration corrected objective lens from Olympus. White light illumination was achieved with a 50-W halogen lamp. A 405-nm continuous wave laser, filtered by a dichroic mirror, was used for luminescence excitation. The emitted light from the sample was incident on a volume Bragg grating, which splits the light spectrally onto a CCD camera. The detector was a 1,040 x 1,392 resolution silicon CCD camera kept at 0 °C with a thermoelectric cooler and has an operational wavelength range of 400-1,000 nm. By scanning the angle of the grating relative to the incident light, the spectrum of light coming from each point on the sample could be obtained, as shown in Figure 3.14. This optical microscope was used in this thesis to acquire three types of datasets: (i) images using wide-field white light, (ii) panchromatic emission PL images, and (iii) hyperspectral 3-dimensional PL datacubes (PL maps). Normally, PL maps were acquired for 1-second exposure per angle, with a spectral resolution of at least 2 nm. The monochromatic excitation power was set to be equivalent to 1 sun (AM 1.5G spectrum). Calibrations followed as per the procedure previously reported[220] and designed by Kyle Frohna.
The data analysis of the hyperspectral PL datacubes is done in the same manner as for CL maps, described in Section 3.1.5, using LumiSpy.

In Chapter 4, synchrotron X-ray diffraction is used. Scanning nano-XRD (nXRD) data was acquired at the synchrotron beamline I14 of the Diamond Light Source (Didcot-Oxford, UK) by Tiarnan Doherty. 2D diffraction patterns were recorded at each stage position as the specimen was moved through the X-ray beam. An array of 3 Medipix 2048 x 512-pixel arrays in transmission mode (Excalibur 3M) was used to acquire diffraction data. To examine the effect of repeated maps on the same region of a film, a scan loop was measured within a 5 x 5 µm region until most of the diffraction spots were no longer visible. A 20 keV monochromatic X-ray beam (λ = 0.619 nm) was used, focused to ~150 nm. Samples were mounted onto the I14 standard sample holder and measured under a local flow of dry N2 to suppress perovskite degradation that is accelerated by moisture and oxygen. 2D sum patterns across the scanned region were used without processing. 1D patterns were radially integrated using the Data Analysis WorkbeNch (DAWN)\textsuperscript{221} with a CeO\textsubscript{2} calibration standard and a mask to remove dead pixels and detector edges. The 1D sum pattern for each frame was cropped from 0.6 Å\textsuperscript{-1} onwards and Origin Pro was used to subtract a baseline found from 20 baseline anchor points found via the 2nd derivatives and connected by line interpolation. Simultaneous X-ray fluorescence (nXRF) data was acquired with a 4-element Si drift detector. The nXRF maps were aligned using the Au\textsubscript{L\alpha} peaks and the summed signals across the scanned area were found for Pb\textsubscript{L\alpha}, I\textsubscript{L\alpha}, and Br\textsubscript{K\alpha}.

### 3.3 Sample preparation on electron-transparent substrates

All samples studied in this thesis were fabricated either through solution-processing or thermal evaporation. Moreover, for the TEM-based experiments in Chapters 4 and 6, the perovskite films were deposited on substrates compatible with TEM, limited by the electron transparency thickness constraint. The thickness constraint states that the specimen needs to be electron-transparent. For lead-based perovskites, such thickness is estimated to be below 200 nm (thickness at which, according to Equation 3.3 results in 32% of the electrons not elastically scattering).

Such small thicknesses are smaller than the common ones used for PSCs (~0.5- 1.0 µm).\textsuperscript{17,222} Two methods to obtain electron-transparent specimens exist:

1. Focused ion-beam (FIB) milling. It is a common method to prepare a specimen called lamella, which is a thin, electron-transparent slice of the bulk sample. Conventional FIB methods use gallium ions to mill specimens down to sub-200 nm
thicknesses, which can damage the pristine perovskite structure,\textsuperscript{[141]} and which is explored in Chapter 5. The use of FIB on halide perovskites in this thesis was developed and studied by Felix Kosasih.\textsuperscript{[196,223]}

2. Thin film deposition. Sub-200-nm thin perovskite films can be deposited using solution processing from diluted precursors, or thermal evaporation during shorter evaporation times. Especially for thin films, solution processing adds variability, often results in incomplete film coverage and is affected by the solubility limits of the reagents\textsuperscript{[224–226]} Evaporation offers excellent scalability and control, smoother morphology and film thickness detection, but has been studied less in literature.\textsuperscript{[227–234]}

While any perovskite stoichiometry combination is achieved using solution processing, thermal evaporation containing MA\textsuperscript{+} are hard to control due to the high volatility of methylammonium iodide (MAI).\textsuperscript{[235]} Thus, mainly FA-pure or FA-rich (with double cation double halide) formulations are common from evaporated samples. For completeness, the thickness constraint does not affect the best-performing perovskite LEDs, since they inherently conform to this thickness limitation (films are normally in the tens of nanometers). Perovskite LEDs are not studied in this thesis, but they are an interesting sample system for future TEM experiments.\textsuperscript{[236]}

Another constraint is the substrates need to be compatible with TEM. They need to be 3 mm diameter TEM grids with windows/holes that allow for the sample to be suspended on a thin amorphous layer or suspended in the vacuum, so the substrate does not add thickness. Different types of TEM grids exist, with varying surface roughness, surface chemistry and windows strengths. All TEM studies reported in this thesis use 30-nm silicon nitride grids (low-stress Si\textsubscript{3}N\textsubscript{4}, Norcada), from now on referred to as SiN. SiN grids mimic the surface properties of standard silicon substrates and offer smoother surfaces and higher robustness for fabrication than other TEM grids such as copper-carbon-meshes or ultrathin carbon. In Chapter 6 special biasing MEMS-based in-situ chips were used. Perovskite films were deposited on biasing chips designed by HennyZ (8 platinum electrodes deposited on a 50 nm low-stress amorphous SiN window, electrical noise: <4 pA).\textsuperscript{[237]} Moreover, during evaporation, the perovskite layer was set to \(\sim 100\) nm and edges of the grid were masked during evaporation, where the metallic contact connects to the TEM holder, to ensure a clean contact.

The optimisation for perovskite deposition on TEM-compatible SiN grids was initially developed by Tiarnan Doherty and proven to yield similar optical and structural films as the thicker analogues,\textsuperscript{[35,163]} methods which are further developed and used in this thesis. Sample preparation through solution processing was optimised by Yu-Hsien Chang and Satyawan Nagane, and sample preparation through thermal evaporation was optimised by
Yu-Hsien Chang and Terry Yang. These methods are described below. Moreover, to ensure that the electron-transparent substrates showed film quality consistent with standard substrates, PL, table-top XRD and SEM were performed as sample pre-checks before any further electron microscopy was performed. This is further described in Chapter 6 in Figure 6.9 and Figure 6.10.

The exact fabrication recipes used during this thesis are described below. In general, all procedures were followed inside an inert N₂-gas glovebox (O₂ and H₂O levels below 0.5 ppm). All chemicals used were purchased in the highest purity form commercially available. For the halide perovskite depositions, the organic salts (such as FAI and MAI) were supplied by GreatCell Solar, lead iodide from TCI with a >98% metal trace-based purity, and all other chemicals were purchased from Sigma Aldrich.

The samples measured in Chapter 4 were fabricated using solution processing. The perovskite precursors solutions were prepared by first dissolving FAI (1.0 M) and MABr (0.2 M), PbI₂ (1.1 M), and PbBr₂ (0.22 M) in a mixture of anhydrous dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) (4:1 v:v). A solution of CsI (1.5 M in DMSO) was then added to the precursor solution as 5% of the total volume, yielding a nominal \((\text{FA}_{0.79}\text{MA}_{0.16}\text{Cs}_{0.05})\text{Pb(I}_{0.83}\text{Br}_{0.17})_3\) perovskite precursor composition. Lead halide precursors were supplied by TCI, organic compounds were supplied by Greatcell Solar, CsI and solvents were supplied by Sigma. To fabricate thin electron-transparent specimens for SED, the perovskite solution was diluted in anhydrous DMF: DMSO 4:1 (v:v) in a 2:1 ratio of diluent to precursor solution, and spin-coated on SiN TEM grids with a 30-nm thick low-stress amorphous Si₃N₄ membrane window (NT025X, Norcada). Spin-coating was followed in two steps at 2,000 and 6,000 rpm for 10 s and 35 s respectively, with 20 µL of chlorobenzene added 30 s before the end of the second step. The films were then annealed at 100 °C for 1 h, yielding films of 200 nm. To fabricate thin films for the nXRD studies, the same protocol was used to prepare an almost nominally identical perovskite precursor solution of \((\text{FA}_{0.79}\text{MA}_{0.15}\text{Cs}_{0.06})\text{Pb(I}_{0.85}\text{Br}_{0.15})_3\). The precursor was then spin-coated on X-ray transparent windows (Norcada, NX7100C), following the same protocol as for the SED samples, and then annealed, yielding films of ~500-600 nm.

Due to the numerous samples described in Chapter 5, their fabrication methods are described within the Chapter itself.

The samples measured in Chapter 6 were deposited using a CreaPhys PEROvap evaporator inside an MBraun N₂ glovebox following the evaporation method reported. In short, the chamber was pumped down to a pressure lower than \(2 \times 10^{-6}\) mbar for the deposition and the evaporator walls, source shutters and shields were kept at -20 °C.
For the FA-pure composition (FAPbI$_3$), FA-rich composition (mixed cation lead mixed halide), FAI (GreatCell Solar, fresh powder for every deposition) and lead iodide (TCI, >98% metal-trace based purity) were filled into two different crucibles. Deposition rates for each source were set for FAI, and PbI$_2$ at 0.45 Å/s, and 0.90 Å/s, respectively, as measured with calibrated quartz crystal microbalances. For the FA-rich composition (mixed cation lead mixed halide), FAI, lead iodide and Cesium bromide (Sigma) were filled into three different crucibles. Deposition rates for each source were set for FAI, CsBr, and PbI$_2$ at 0.6 Å/s, 0.1 Å/s, and 1.20 Å/s, respectively, as measured with calibrated quartz crystal microbalances. The substrate temperature was 18 °C, and the sources-substrate distance was 35 cm.

For the FAPbI$_3$ film, a thin layer of the hole transport layer MeO-2PACz was spin-coated prior to evaporation, to ensure the optimal growth of the perovskite film, as the evaporation was optimized for devices. The MeO-2PACz powder (TCI >98.0%, molar weight 335.30 g/mol) was dissolved in anhydrous ethanol (Sigma) at a concentration of 0.34 mg/ml and stirred for >10 mins. For the spin-coating, 120 µL of MeO-2PACz solution was dropped onto the centre of the substrate, followed by a wait time of approximately 10 seconds (static method) before starting the spin-coating process. The spin speed was 4000 rpm (1000 rpm/s ramp) for 30 s with the spin-coater lid open. The substrates were then placed on a metal hotplate at 100 °C for 10 mins to evaporate the solvent. Immediately after, they were placed inside the evaporation chamber. The spin-coater and evaporator are both situated inside a N$_2$ glovebox. The addition of MeO-2PACz was not necessary for the FA-rich samples.

To ensure thin electron-transparent specimens for transmission electron microscopy (TEM), all perovskite films were deposited on MEMS-based biasing chips designed by HennyZ with 8 platinum electrodes (thick Pt with a sticking layer of Ta between the Pt and SiN, with Ta, diffused into the Pt with thermal annealing at about 800 °C during nanofabrication) deposited on a ∼200 nm low-stress amorphous silicon nitride window. The electrical noise from this design is below 4 pA, orders of magnitude higher than the measured currents. Moreover, during evaporation, the perovskite layer was set to be ∼90-100 nm, to ensure the overall specimen thickness did not surpass 300 nm, thus still being electron-transparent. The edges of the grid were masked during evaporation so that the metallic contact connecting the MEMS chip to the pins in the TEM holder was clean. To check the quality of the evaporated films, X-ray diffraction (XRD) and photoluminescence (PL) were measured compared to the optimal thicker perovskite film analogues.
Chapter 4

High-energy electron radiation effects on the structure: 4D-STEM

Text in this Chapter is adapted from Ferrer Orri, J. et al., Unveiling the Interaction Mechanisms of Electron and X-ray Radiation with Halide Perovskite Semiconductors using Scanning Nanoprobe Diffraction. Advanced Materials 34, 2200383 (2022).\(^{[238]}\) Sample preparation was performed by Tiarnan Doherty. SED data acquisition was performed by Tiarnan Doherty, with the aid of Duncan Johnstone and Sean Collins. XRD data acquisition was performed by Tiarnan Doherty with the assistance of Hugh Simons. All data processing, analysis and interpretation were completed by Jordi Ferrer Orri. Some of the interpretations received input from all authors in the publication above.

Chapter abstract: High-resolution microscopy using nano-probe diffraction reveals spatially-resolved changes in the local crystal structure of halide perovskite films upon irradiation with high-energy electrons and X-rays. High-angle defective grain boundaries trigger the formation of degradation phases, leading to changes in the crystal structure. Targeting high-angle grain boundaries is critical for film stability under high-energy radiation conditions, especially for space photovoltaic applications.

4.1 Introduction

As established in the previous Chapters, the interaction of high-energy electrons and X-ray photons with beam-sensitive semiconductors such as halide perovskites is essential for the characterisation and understanding of these optoelectronic materials. This Chapter uses nano-probe diffraction techniques to investigate structural properties on the nanoscale.
We perform studies of the interaction of electron and X-ray radiation with state-of-the-art triple-cation double-halide FA-rich perovskite films.

Understanding the interaction of the high-energy probe with the samples is critical for acquisition, data analysis, and detector applications. For example, the interaction of focused electron beams with halide perovskites has been reviewed and can be quantified with critical radiation values. These critical values are defined as particle fluences (in units of particles Å$^{-2}$) representing the rate of characteristic irreversible structural changes under particle exposure.\textsuperscript{[138,139]} For halide perovskites, for example, higher acceleration voltages increase these critical values by reducing the cross-section for beam-specimen interaction, while the use of cryogenic temperatures induces rapid amorphisation and reduces these values.\textsuperscript{[140,141]} Chapter 2.2.2 reviewed reports of the fluences that cause structural changes in MA and FA-based perovskites. In short, MA-based perovskites degrade at fluences as low as 100 e$^{-}$ Å$^{-2}$ by the loss of the organic moieties, resulting in lattice contraction and the formation of the supercell MAPbI$_{2.5}$, ultimately degrading into PbI$_2$.\textsuperscript{[140,141]} Excess Pb-related defects during fabrication can also aggregate and feed degradation at grain boundaries upon electron irradiation. However, Pb$^0$ formation is usually observed as a degradation product of fully-inorganic compositions, such as CsPbI$_3$, upon electron irradiation. This is because the inorganic cation is less prone to be reduced than its organic counterparts or than the Pb cation.\textsuperscript{[122,143,144]} Moving beyond the workhorse hybrid MA-based composition, FA-based thin films exhibit structural changes at fluences of 200 e$^{-}$ Å$^{-2}$, with the loss of the perovskite phase at 600 e$^{-}$ Å$^{-2}$, and the eventual formation of PbI$_2$ grown on the lattice-expanded degraded phase of FAPbI$_3$ after 1,000 e$^{-}$ Å$^{-2}$.\textsuperscript{[53]}

Chapter 2.2.2 also reviewed the effect that scanning X-ray probes have on halide perovskites, which has been less studied than for electron microscopy. In short, the critical fluences vary for different X-ray microscopy techniques. For MA-based and Cs-based compositions, changes in the electronic structure were measured at the lowest fluences of 103 photons Å$^{-2}$.\textsuperscript{[123,160,161,239]} No comprehensive studies on FA-based compositions have been reported to date. Rigorously establishing the radiation effects on these more complex compositions to allow elucidation of global mechanisms, as well as obtaining insight into the role of grain boundaries and complicated junctions, is of immense interest.

In this Chapter, we use two advanced nanoprobe diffraction techniques, SED and nXRD, to understand the respective interaction of 200 keV electrons and 20 keV X-rays with the local nanostructure of solution-processed halide perovskite films. By using low-dose diffraction microscopy, we can spatially resolve the diffraction information on the nanoscale as a function of radiation exposure (electron or X-ray fluence). The
use of finely tunable acquisition conditions allows us to track the compositional and structural evolution of degradation processes of hybrid perovskite films, as well as their spatial origin. We show that change is predominantly observed at specific sites in the polycrystalline film which are more defective and evolve towards new structures over time, such as PbI$_2$ and PbBr$_2$ formation. Specifically, high-angle grain boundaries in the polycrystalline structure trigger such changes to the nanostructure after fluences of $\sim 200$ e$^-$/Å$^2$. These changes are concomitant with the formation of pinholes and with a phase transition from tetragonal to cubic. A similar degradation pathway is caused by photon irradiation in nano-X-ray diffraction, suggesting common underlying mechanisms. These studies establish critical radiation values and interaction mechanisms of electron and X-ray radiation for mixed-cation mixed-halide perovskites, allowing the elucidation of global mechanisms for degradation, as well as stability windows in both measurement and application of these radiation types. This unique approach of using nano-probe diffraction to explore the radiation limits of these materials provides valuable information on the degradation pathways on the nanoscale.

4.2 Understanding electron-beam degradation using 4D-STEM

Thin films of a nominal (FA$_{0.79}$MA$_{0.16}$Cs$_{0.05}$)Pb(I$_{0.83}$Br$_{0.17}$)$_3$ stochiometry were solution-processed following optimized protocols for device fabrication compatible with SiN grids, ensuring reproducible and comparable results to high-performance devices prepared on standard substrates,\textsuperscript{[35]} while also enabling the use of transmission microscopy techniques. 5-dimensional datasets of the films were acquired by combining a time series ($t$) of 4D-STEM frames in SED mode. Each frame was acquired over the same region of the sample $(x, y)$ in SED mode, wherein each scanned position contains an electron diffraction pattern $(k_x, k_y)$. Between each frame, the electron beam was digitally driven to a controlled beam-parking position within the field of view before being blanked, labelled with a cross in Figure 4.1. Visible beam-induced accelerated changes are observed in the vicinity of the beam-parking position, within a radius of approximately $\sim 90$ nm, equivalent to the radius of the interaction volume (see Figure 4.2). The circular area around the beam parking position is disregarded, using the rest of the scan area for this study, only irradiated during beam rastering.

The rich diffraction-based multidimensional dataset enables the investigation of the effects of cumulative electron beam exposure on the nanoscale. Repeated scans were

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The rich diffraction-based multidimensional dataset enables the investigation of the effects of cumulative electron beam exposure on the nanoscale. Repeated scans were
High-energy electron radiation effects on the structure: 4D-STEM

Figure 4.1: Visualizing grain boundary types and their evolution under low electron exposure using SED on triple-cation double-halide FA-rich perovskite films. (a) Schematic of the perovskite grain showing the areas of interest from which diffraction patterns are extracted (in Arabic numerals), and three interfaces between crystallographic domains indicated by dashed lines (in Greek numerals): (i) grain bending across region 2 and 3, (ii) a twin grain boundary at (021) plane between region 3 and 4, and (iii) high-angle grain boundary interfacing two grains at different zone axes between region 1 and 3. The beam-parking position is labelled with a cross. (b) Evolution of vBF images of a perovskite film for up to 120 e− Å−2 fluence. (c) The resulting averaged diffraction pattern for four different areas at the 1st frame (12 e− Å−2) and (d) at the 10th frame (120 e− Å−2). Regions denoted with numerals in (a) correspond to the diffraction in (b) and (c). All intensity scale bars correspond to the normalized vBF and the diffraction intensity. Retrieved from [238].

acquired at total fluences from 12 e− Å−2 (1 frame) up to 900 e− Å−2 (75 frames), at which point the diffraction from the halide perovskite film had substantially degraded.

4.2.1 Calibration of flux and fluence for SED

Here, we report fluence in units of particles (electrons) per square ångström (Å). The fluence for the SED experiment was calculated from the measured probe current during data acquisition. A probe current of 3.59 pA is equivalent to a flux of 2 × 10^7 e− s−1. All
4.2 Understanding electron-beam degradation using 4D-STEM

Figure 4.2: Simulated electron beam trajectories of TEM sample. Simulated using CASINO v2.51\cite{199} at 200 keV for a layered sample containing FA-pure perovskite and a 30 nm SiN layer. A beam radius of 5 nm and 10^5 trajectories were simulated using the default simulation parameters. For the layered chemical composition, a 200 nm layer of density 4.16 g/cm^3 was used, using the triple-cation double halide perovskite composition (Atomic fractions: Cs: 0.0052, Pb: 0.3368, Br: 0.0584, I: 0.5260, C: 0.0183, N: 0.0394, and H: 0.0079). For SiN, a density of 3.17 g/cm^3 and a thickness of 30 nm was used.

SED maps were acquired at a 1 ms dwell time using a Gaussian-shaped beam which can be approximated to a circular beam of ~5 nm diameter, slightly overestimating the dose. These acquisition parameters result in a fluence of ~12 e^- Å^-2.

The simulation software CASINO v2.51, which simulates Monte Carlo electron trajectory in solids, was used to simulate the stochastic interaction volume for the electron beam.\cite{199} This model is used because of the polycrystalline orientation nature of perovskite samples, and the total sample thickness. In such samples, the electron beam is likely to spread more significantly than in a well-aligned single crystal, thus using the Monte Carlo method is more suitable and faster than multi-slice or Bloch-wave simulation methods. Figure 4.2 shows the trajectory of 10^5 electrons for a beam of radius 5 nm, for the default simulation parameters. The sample was modelled as 2 layers: a halide perovskite of 200 nm thickness and density 4.16 g/cm^3 (see the atomic composition of FAPbI_3 in the caption of Figure 4.2), and a 30 nm SiN layer. An interaction volume of ~90 nm radius contains the majority of the trajectories.

Conventional scan controls in STEM incorporate a left-to-right and row-by-row raster pattern requiring a "flyback" time for stabilizing, prior to sequential row scanning. Moreover, beam blanking typically has a finite rise time. Given these issues, unavoidable in common STEM setups, we specifically parked the beam in a controlled position within the field of view, labelled with a cross in Figure 4.1 in the main text. To understand the effect of beam parking, the excess irradiation fluence can be estimated. Beam blanking after
each scan was done manually. Based on Human Reaction Time studies, the average reaction time to click a button (task required to manually blank the beam at the end of a scan) is 273 ms, around 1/4 of a second. Assuming the reaction time during acquisition was no longer than 500 ms, the overexposure during the acquisition of the beam parking position is 500 ms per scan. Given the 1 ms dwell time during scanning, the overexposure at the parking position is x500 larger. Such overexposure is localised within the circular beam of ~5 nm diameter, yet its effects extend around the ~90 nm radius interaction volume.

4.2.2 Low fluence regime

Figure 4.1 shows the evolution of the local nanoscale diffraction of a representative perovskite grain at low electron exposure, up to a cumulative fluence of 120 e− Å−2 corresponding to the first 10 frames. The term grain is used here as the apparent area delimited by morphological grain boundary features observed in the electron microscope. For each diffraction pattern, electrons at a low scattering angle (the direct beam) are collected at the origin, which is surrounded by a series of diffraction peaks corresponding to scattering vectors near or at the Bragg condition. We create virtual bright-field images (vBF) of the scanned region by mapping the intensity of the direct beam below a virtual aperture of radius 4·10−3 Å−1 (semi-angle of the detector of 2.39 mrad), as a function of the probe position. Virtual dark-field images (vDF) can be created by mapping the intensity of selected scattered signals, corresponding to a fixed virtual aperture size and position in reciprocal space within 1.18 Å−1 range (70.3 mrad, see Chapter 3.1.3). The vBF images mostly contain information from the non-scattered beam and low-angle inelastic scattering, resulting in relatively lower intensities when the sample is at a strongly diffracting orientation or where it is thicker.

The grain labelled in Figure 4.1a exhibits intense diffraction as their orientations match a low-angle zone axis, and is thus selected for detailed study. The vBF images in Figure 4.1b reveal the polycrystalline nature of the perovskite film, as well as heterogeneity in the diffraction contrast within each grain. These variations in contrast are a result of chemical and structural heterogeneity on the nanoscale. To illustrate the difference between individual grains, diffraction patterns are obtained by summing pixels within the grain at the centre of the region of interest, denoted by Arabic numerals in Figure 4.1a. The diffraction patterns at the near-pristine state are shown in Figure 4.1c, acquired at the lowest electron fluence of 12 e− Å−2 (first frame).

All diffraction patterns can be indexed to a tetragonal perovskite structure in the P4/mbm space group with lattice parameters of a=b= 9.00 and c= 6.36 Å, each near the
[100] zone axis with slightly different crystal tilt relative to the electron beam. At least three different crystal orientations can be observed within this grain in this scattering geometry. The interfaces between crystallographic domains can be identified in the virtual images and labelled by dashed lines and Greek numerals in the schematic (also see Figure 2.3). Grain bending due to the soft perovskite lattice is observed in (i), across the upper and the lower parts of the central grain in Figure 4.1b (region 2 and 3, respectively). The difference between their diffraction patterns can be attributed to the small in-plane crystal tilt of \(\sim 2^\circ\) (see Equation 4.1). When sudden changes in crystal orientation are observed, different types of grain boundaries can be identified.\(^{[59]}\) In (ii) a twin boundary, a special case of a large angle grain boundary for which there is no atomic misfit, is observed between the regions 3 and 4 in Figure 4.1b. Detailed analysis of the diffraction pattern shows the lattice being mirrored across the \((02\bar{1})\) plane, marked with a dashed line. Distinctly, the grain boundaries around the central grain are (iii) high-angle, as inferred from orientation analysis on the adjacent grains being near the [111] zone axis instead (see Figure 4.1b-c region 1, for the diffraction pattern of an adjacent grain). The nature of these two types of grain boundaries is discussed in more detail later.

The evolution of the diffraction patterns in Figure 4.1, after 120 e\(^{-}\) Å\(^{-2}\) of accumulated fluence (10 frames), reveals that the strong diffraction contrast seen in the vBF images rapidly becomes more homogeneous. The diffraction patterns at the 1st and 10th frames show a small relative tilt of the order of a few degrees towards alignment to the [100] zone axis. We attribute these tilts to microstructural changes on the nanoscale, noting that bending of the support membrane cannot be excluded.

The degree of the grain tilting in-plane can be estimated by fitting an Ewald circle passing through the brightest diffraction reflections and using Bragg’s diffraction law:

\[
\theta \approx \sin^{-1}\left(\frac{\lambda}{2R}\right)
\]

with \(R\) as the radius of the fitted circle (in the same units as the wavelength) and \(\lambda = 2.5\) pm as the wavelength of the electron beam for 200 keV.

This tilting is visible in the regions labelled 3 and 4 in Figure 4.1c, showing more evenly distributed diffraction spots near the centre of the beam after 10 scans. These tilts are not observable in the region labelled 2, where the diffraction pattern, originally away from the zone axis by a larger tilt, would need to rotate by larger angles to get towards the zone axis. These observations suggest that changes in the perovskite microstructure may already start at extremely low electron exposure of tens of e\(^{-}\) Å\(^{-2}\). These fluences are sufficient to provide enough energy to modify the pristine grain orientation without measurable
Figure 4.3: Grain tilting. (a) In-plane grain tilting observed after little electron exposure, quantified based on Equation 4.1. (b) Map of the grain tilting across a scanned region, showing grains tilting towards the zone axis (white) and other grains staying off the zone axis (orange). Note that this SED crystallographic dataset was taken from a different halide perovskite film of the same composition grown on a SiN TEM grid. It was acquired at 300 keV using a JEOL ARM300F high-resolution STEM with a Merlin/Medipix direct detector with a single back contact (EM19793-2 session, ePSIC, Diamond Light Source, UK). (c) Compositional nXRF summed intensity over the scanned area against X-ray fluence for the Pb and halides. The nXRF spatially resolved map did not show any Cs or halide segregation. All peaks were normalised to the $PbL\alpha$ peak, and the $BrK\alpha$ peak was selected instead of the $La$ because the latter overlaps with the bright substrate Si peak. Adapted from [238].

lattice distortions. This tilting is very slight, from 1-5 degrees, sufficient to allow these grains to relax to the zone axis (see Figure 4.3a). The study of most of the indexable grains in the scanned region reveals that all grains show some degree of rotation if their initial state is not at the zone axis (Figure 4.3b). Similar changes in the tilt of grains, commonly seen in thin polycrystalline films deposited on TEM substrates, are observed from the diffraction patterns in most of the grains in the scanned region. Moreover, grain tilting was also observed in other SED experiments taken from other halide perovskite films of the same composition at other acceleration voltages of 300 keV (Figure 4.3).
4.2 Understanding electron-beam degradation using 4D-STEM

Figure 4.4: Probing the emergence of lead halide species on the nanostructure of FA-based perovskite films at high electron exposure using SED. (a) Schematic of the perovskite grain showing the areas of interest from which PbI$_2$ and PbBr$_2$ species is observed and from which diffraction patterns are extracted, labelled as 1 and 2, respectively. (b) The vBF images at the 20th and 40th frames. (c) For each frame, a normalized diffraction pattern from the labelled region is shown. Some additional diffraction spots, marked with white arrows, are observed: the extra reflections in region 1 can be indexed to PbBr$_2$ near the [111] zone axis, and the extra reflections in region 2 can be indexed to PbI$_2$ near the [100] zone axis. (d) Simulated patterns for the perovskite (Pvk), the PbBr$_2$ and the PbI$_2$ phases in white, green and red, respectively. The diffraction patterns computed using CrystalMaker match those seen experimentally. Retrieved from [238].

4.2.3 High fluence regime

We now consider further electron exposure by taking cumulative fluences up to 240 e$^{-}$ Å$^{-2}$, as shown in Figure 4.4a. The evolution of vBF contrast beyond 240 e$^{-}$ Å$^{-2}$ fluence suggests the formation of pinholes at the high-angle grain boundaries (Figure 4.4b). Degradation at the grain boundaries can be attributed to the loss of chemical species and lattice contraction due to the transformation from pristine perovskite to lead halide degradation products (see Figure 3.9 for the histograms of the Pb-Pb distances for the perovskite structure and some of the lead halide structures with shorter Pb-Pb distances). Similar observations have been reported in TEM mode. Overall, there is a constant decrease in the total intensity of the vBF images by $\sim$25% that occurs uniformly across the whole scanned area over 240 e$^{-}$ Å$^{-2}$ (20 frames), seen in Figure 4.1b. Further electron exposure results in roughening of the grain and a decrease of the total scattering intensity by $\sim$50% after 480 e$^{-}$ Å$^{-2}$ (40 scans), seen in Figure 4.4b. We note that such a large change in the
Figure 4.5: Mapping the evolution of the degradation species in an FA-rich film. (a) The diffraction patterns at the 40th frame, taken from region 1 in Figure 4.4 for the perovskite and PbBr$_2$ series, and from region 2 in Figure 4.4 for PbI$_2$. For each diffraction pattern, a dark-field virtual aperture is selected. (b) vDF images of the respective virtual apertures placed at: the (00$\bar{2}$) perovskite reflection (orange), the (221) PbBr$_2$ reflection observed within the grains (green), and the (011) PbI$_2$ reflection localized at the high-angle grain boundary (red). The colour scale range is set to 30% to better show the small changes in intensity. All vDF images are superimposed on top of the respective vBF images. (c) Intensity profiles taken from the perovskite (002), the PbBr$_2$ (221), and the PbI$_2$ (011) reflections. The 1/$e$ intensity threshold is shown with a dashed line. Retrieved from [238].

vBF intensity cannot be attributed to fluctuations of the electron emission gun alone. The loss of intensity of the direct beam could be attributed to the sample thickening by the deposition of an amorphous carbon layer on the surface and possible densification of the perovskite structure by amorphisation, the loss of the lighter elements such as the organic cations or redeposition of organics from a bad vacuum (see Chapter 3.1.6). These changes would increase scattering, as seen in the virtual images created from the annularly integrated vDF.
We now inspect how the diffraction patterns near the [100] zone axis, taken from the central grain, change in Figure 4.4c. Weak Bragg reflections emerge from region 1 in the grain in Figure 4.4a after 240 e\(^{-} \text{Å}^{-2}\) (20 frames). These additional reflections, marked with white arrows, cannot be indexed to the pristine perovskite structure at \(\tilde{k} = 0.23, 0.34\) and 0.47 Å\(^{-1}\). Close assessment reveals that the patterns from this region are indexable to PbBr\(_2\) at the [111] zone axis within a 0.01 Å\(^{-1}\) error, as shown in Figure 4.4d. This suggests the presence of these lead halide species epitaxially growing on the perovskite grain. We ruled out the possibility of this being due to superlattice reflections from the orthorhombic Pnma space group structure at the [001] zone axis since the reflections are not located at the expected \(\frac{1}{2}(hkl)\) positions.\(^{[44,140]}\)

In contrast, a diffraction pattern taken from region 2 in Figure 4.4a after 480 e\(^{-} \text{Å}^{-2}\) exposure (40 frames) shows diffuse diffraction, attributed to the amorphous SiN substrate or amorphisation of the perovskite crystal. Weak diffraction reflections at \(\tilde{k} = 0.26, 0.24\) and 0.26 Å\(^{-1}\) are also visible. These reflections are indexable to the 011, 010 and 01\(\bar{1}\) peaks of PbI\(_2\) at the [100] zone axis within 0.01 Å\(^{-1}\) error, as shown in Figure 4.4d. PbI\(_2\) can form by stacking PbI\(_2\) layers in many possible ways, resulting in different hexagonal polytypes.\(^{[192]}\) We note the reflections observed here suggest the formation of the 4H hexagonal polytype, in contrast to other hexagonal polytypes such as 2H or 6H reported in other studies.\(^{[53,143]}\) Despite some ambiguity in classifying the exact PbI\(_2\) hexagonal polytype in literature, these phases are remarkably similar and the formation of small precipitates of PbI\(_2\) is unambiguously observed.\(^{[243]}\)

To further understand the evolution of phases in Figure 4.4, we use SED to spatially map the crystallographic changes. Figure 4.5 shows the evolution of the vDF images created for the perovskite (00\(\bar{2}\)) reflection, the (211) PbBr\(_2\) reflection, and the (011) PbI\(_2\) reflection (Figure 4.5a). While the vDF image intensity for the perovskite diffraction peak fades upon exposure, the vDF images of the additional reflections can spatially pinpoint the origin of these changes (Figure 4.5b). The lead halides appear to be spatially anticorrelated: epitaxial 4H-PbI\(_2\) precipitates grow at the grain boundary and the PbBr\(_2\) reflections appear at the opposite side of the boundary within the perovskite grain. At extreme cumulative fluences of >480 e\(^{-} \text{Å}^{-2}\) (40 frames), most diffraction from crystalline species has faded, so the vDF images are dominated by diffuse scattering and noise, especially for diffraction spots near the direct beam. At these high fluences, the PbI\(_2\) diffraction features remain more visible than the PbBr\(_2\), possibly attributed to the bromine precipitates moving away from the zone axis. Some additional vDF images of PbI\(_2\) precipitates could be found in other regions, though we note that any PbI\(_2\) trace crystallites that are too small may be undetectable in SED. The PbI\(_2\) features are extremely local, only detectable across
a few scanned pixels (∼5-30 nm). Moreover, some PbI$_2$ features appear near diffraction spots attributed to the perovskite phase, creating noisy features in the vDF images at the early scans.

These changes are local to the bottom-left corner of the grain, suggesting that lead halides nucleate non-uniformly across the grain. Perovskite samples of similar compositions have been reported to show compositional heterogeneity across grains, with Br-rich clusters at the grain boundaries. Based on the homogeneity of the diffraction pattern across the grain in the pristine state of the film, chemical heterogeneity must be small, yet present enough to help drive the reported local changes. Distinctively, degradation does not appear to originate from the twin boundaries, consistent with theoretical predictions, whereby the octahedron face-sharing present at the twin boundary stabilizes the twins. Therefore, not all defects affect degradation in the same way.

Intensity profiles for the perovskite (00$\bar{2}$), the (211) PbBr$_2$, and the (011) PbI$_2$ reflections are plotted in Figure 4.5c. These profiles suggest that the critical fluence for this mixed cation composition, the fluence at which the original diffraction intensity has reached $\sim 1/e$ relative to its initial value, is $\sim$200 e$^{-} \text{Å}^{-2}$. At this critical fluence, the lead halide phases start to emerge. The critical fluence reported here is in close agreement with those by Rothmann et al. for the pure FAPbI$_3$ composition. We investigated other grains from adjacent regions, all of which exhibited similar progressive grain amorphisation with an equivalent critical fluence.

A grain near the [001] zone axis exhibits superlattice reflections attributed to the BX6 corner-sharing octahedra tilted away from perfect cubic symmetry towards the tetragonal perovskite phase. These superstructure reflections eventually disappear, as the sample is exposed to higher fluence and damaged (see white arrows in Figure 4.6b-c). The faster loss of superstructure reflections in comparison to the loss of the main bright reflections may suggest the loss of the tetragonal distortion trending towards a more cubic structure. Since the tetragonal distortion arises from cation alloying, the loss of the more volatile MA and or FA cations is likely to tend towards a cubic structure as it becomes to the single cation composition. These results are consistent with the reported degradation pathway described in this work. These results also offer more evidence that such a degradation pathway is also observed in regions away from where beam parking is happening.

### 4.3 Comparison to X-ray degradation

Finally, we perform analogous scanning probe synchrotron nXRD measurements to acquire a similar 5D dataset by combining a time series stack of multiple nXRD frames. Such
4.3 Comparison to X-ray degradation

Figure 4.6: Evolution of grain at the [001] zone axis of a halide perovskite film, showing super-lattice reflections. (a) The grain location is away from the beam-parking position, as shown in the vBF image at the 1st frame (left). The mean diffraction pattern from the orange circle region is shown at the centre and the simulated diffraction pattern at the [001] zone axis at the right, especially showing weak reflections in orange. (b) The evolution of the mean diffraction pattern over increased fluence. White arrows show the disappearance of the weak additional reflections due to octahedral tilt. (c) Comparison between intensity profiles taken from the (220) and the (320) tetragonal diffraction spots. Retrieved from [238].

an acquisition allows us to study the interaction of highly converged 20 keV X-rays on nominally equivalent triple cation composition perovskite films as previously presented for electrons. The use of nXRD allows for close comparison with SED because it similarly involves scanning over a localized region of interest. Unlike SED, this technique cannot access subgrain features under these conditions, as the X-ray beam diameter is $\sim 150$ nm.
High-energy electron radiation effects on the structure: 4D-STEM

Figure 4.7: Probing the evolution of the local structure of a region in an FA-rich halide perovskite film under X-ray exposure using nXRD. (a) Radially integrated nXRD evolution of a perovskite film over accumulated illumination over an area of 4 µm². Peaks are indexed to the $P4_{2}/mnb$ perovskite phase. The peak marked as (*) cannot be indexed to perovskite and corresponds mainly to the degradation phases. To analyze the weak reflections lost during radial integration, 2D nXRD diffraction patterns are shown in (b), with some areas of interest denoted by numerals. (c) The zoomed-in evolution of nXRD in 2D elucidates crystal tilting in region 1, the weak appearance of (002) 4H-PbI₂ in region 2, and the appearance of (211) PbBr₂ reflections in region 3. These findings are similar to the changes observed in SED. The use of Au fiducial markers results in the observation of Au diffraction. Retrieved from [238].

4.3.1 Calibration of flux and fluence for nXRD

Flux is defined as photons per second. In the nXRD experiment, flux was indirectly measured using a calibrator diode (Si). The diode outputs a flux value in Amperes (A) per second but has a responsibility factor. Taking as the diode responsibility conversion factor $0.108 \pm 0.0005$ A/W (from calibrations in the Diamond Light Source), the flux can be converted to photon power in Watts (W). The rate of photons at a particular wavelength
and power can be then calculated by using the equation for photon energy, \( E = \frac{hc}{\lambda} \) (where \( h \) is Planck's constant and \( \lambda = 0.619 \) nm from the beam energy of 20 keV), yielding a flux (photons per second).

However, the diode measurements will be slightly lower than the flux values on the sample, as the diode was placed within 200 mm away from the sample holder. X-ray attenuation by the air can be estimated using the mass attenuation coefficient \( (\mu / \rho) \) of dry air for a 20 keV beam from the NIST database, as \( \mu / \rho = 1.7 \times 10^{-2} \) cm\(^2\)/g, with \( \rho \) the density of the material. Assuming a mass density of air of approximately 1.2 kg/m\(^3\), an attenuation factor of \( 2 \times 10^{-5} \) cm\(^{-1}\) is found. The Beer-Lambert law describes an exponential decrease of the intensity with the distance travelled, such that \( I / I_0 = e^{-\mu x} \), with \( \mu \) the linear attenuation coefficient, \( x \) the depth of penetration and \( I_0 \) the initial beam intensity. Using the Beer-Lambert law, we can estimate the X-ray attenuation across the 200 mm to be 0.05%, therefore negligible.

The diode current measurement was \( 1.13 \times 10^{-7} \) A, which can be converted to a photon power of \( 1.1 \times 10^6 \) W. Without the need to account for the flux attenuation by the air, a final flux value of \( 3 \times 10^9 \) photons/s is calculated for each frame. Fluence (flux density) is defined as photons per unit area and can be calculated from the X-ray beam size (which matches the raster pixel size of the detector of 150 nm) and the dwell time per pixel (0.5 s), yielding a fluence of 775 photons Å\(^{-2}\) for each frame.

Figure 4.7a shows the spatially averaged 1D diffraction patterns across a scanned area of \( \sim 4 \mu \)m\(^2\) for X-ray photon fluences up to 7,750 photons Å\(^{-2}\). The main diffraction peaks are indexed to the same tetragonal \( P4/mmb \) perovskite phase as in SED. Some crystallographic plane reflections are more prevalent and decay more slowly. This information can be linked to the crystal structure, as the intensity of X-ray diffraction \( I_{hkl} \) is directly proportional to the square of the modulus of the structure factor, which, in turn, depends on the sum of the form factors for all atoms in the crystal unit cell. The form factor characterizes the scattering strength of individual atoms within the crystal lattice and is influenced by the electron density distribution around the atomic nucleus as such:

\[
I_{hkl} \propto |F_{hkl}|^2
\]
\[
F_{hkl} = \sum_n n \exp^{2\pi i(hx+kx+lx)}
\]

with \( I_{hkl} \) the diffraction intensity, \( F_{hkl} \) the structure factor, the resultant of all waves scattered in the direction of the \( hkl \) reflection by the \( n \) atoms contained in the unit cell,
and each of these waves shows an amplitude proportional to $f_n$ the atomic scattering factor.

For instance, the (110), (220), (130) and (222) planes are the brightest reflections. Diffraction intensity at these planes is strongly affected by the loss of the halogen atoms from the unit cell. In contrast, (111), (021) and (131) planes diffract less strongly, and their relative intensity is more affected by the loss of the organic cations since all contain A+X ion sublattices. In fact, the (220) and (130) planes exhibit the slowest decay rate, suggesting the rapid loss of the organic cation followed by the slower loss of the halides. The loss of I and Br can be further analyzed from the nXRF, acquired simultaneously with the nXRD data, in which the ILa signal systematically drops before the BrKa signal (see Figure 4.3c), suggesting I$_2$ being more volatile than Br$_2$. The (110), (220) and (130) plane reflections brighten after 2-4 frames ($\sim$1,400-2,800 photons Å$^{-2}$). A closer examination of these reflections in the 2D patterns (Figure 4.7c, region 1) reveals the appearance of additional Bragg reflections of the crystal planes, attributed to the crystals tilting closer to the zone axis, similar to the SED findings in Figure 4.1 albeit in nXRD we are sampling multiple grains.

Some weak and broad reflections appear after 5 frames (4,650 photons Å$^{-2}$) in the range $\sim$0.436± 0.003 Å$^{-1}$ (Figure 4.7a, marked with *). These reflections are not indexable to the perovskite structure and can be used to arbitrarily determine the X-ray critical exposure of hybrid perovskite systems. This critical exposure value is one order of magnitude higher than previously reported values for MAPbBr$_3$ single crystals (102 photons Å$^{-2}$), at which point the scattering image had changed by more than 10%, but it is lower than for CsPbBr$_3$ single crystals (104 photons Å$^{-2}$). The reflection at $\sim$0.436± 0.003 Å$^{-1}$ matches the (110) 4H-PbI$_2$ plane, but also matches phases like PbBr$_2$ or poly-phases. A closer examination of the 2D diffraction patterns reveals extremely weak additional reflections appearing, indexable to both (002) 4H-PbI$_2$ and (211) PbBr$_2$ (Figure 4.7c region 2 and 3, respectively). As these reflections are lost during radial integration, it is critical to analyze the full 2D data sets.

### 4.4 Theory of radiation-sample interaction

An estimation of the inelastic to the elastic mean free path for electrons can be found from the definitions from Egerton described in Equation 3.7 (Chapter 3.1.2). The following parameters were used: a collection angle of 10 mrad (does not affect the ratio between the cross sections), a $Z_{eff}$ of 36.4 atomic units, a mean energy loss of 27.2 eV, and an atomic density of $\sim$7 nm$^{-3}$. Figure 4.8a shows the log-log plot of the ratio between the inelastic to
4.4 Theory of radiation-sample interaction

Figure 4.8: Inelastic to elastic scattering cross section ratios. Ratio of inelastic to elastic scattering cross sections for (a) electrons and (b) photons at different energies. In blue, at the comparable energy of 80 keV. In orange, at the acceleration energies used for the data acquisition of the results presented in this Chapter. Retrieved from [238].

elastic scattering cross sections for electrons against the atomic number. The relation is linear in the log-log scale, not affected substantially by acceleration voltage from 80 to 200 keV.

For high-energy photons, the inelastic to the elastic mean free paths were retrieved from the XCOM Photon Cross Sections Database. [246] This web database provides calculated photon cross sections for scattering cross sections, as well as photoelectric absorption, pair production, and total attenuation coefficients. The database includes any element ($Z \leq 100$) at energies from 1 keV to 100 GeV. A custom-made script was used to retrieve all relevant data at the relevant energies used in this study. Coherent cross sections were used as elastic scattering cross sections and incoherent ones as inelastic ones. Figure 4.8b shows the log-log plot of the ratio between the incoherent to coherent (referred to as inelastic to elastic) scattering cross sections for photons against the atomic number. The relation is linear in the log-log scale.

From these approximations a relationship between the cross section ratios ($\frac{\sigma_i}{\sigma_e}$) and the atomic number ($Z$) can be found for both particles:

\[
(200 \text{ keV Electrons}) \quad \frac{\sigma_i}{\sigma_e} \approx 19 \times Z^{-1.0}
\]

\[
(20 \text{ keV Photons}) \quad \frac{\sigma_i}{\sigma_e} \approx 50 \times Z^{-1.7}
\]

(4.3)

The significance of these ratios on the perovskite compositions used here is discussed in the next section.
Figure 4.9: The grain boundaries in an FA-rich film affect the degradation pathway. (a) Evolution of vBF images of various grains and their surrounding grains after up to \(480 \text{ e}^{-} \text{Å}^{-2}\) fluence, showing stark changes in the morphology. (b) Schematic of multiple perovskite grains from which PbI\(_2\) and PbBr\(_2\) species are observed. The regions from which diffraction patterns are extracted are labelled as 1 and 2. (c) Diffraction patterns for two high-angle grain boundaries: in region 1 a grain boundary exhibiting the reflections only attributed to the perovskite phase of the grains at either side of the boundary, and in region 2 a grain boundary also exhibiting additional reflections and diffuse scattering, typical of amorphous defective phases. (d) Schematic of the degradation mechanisms and factors identified during degradation at high fluences, in cross-section view. Retrieved from \cite{238}.

4.5 Discussion

4.5.1 General degradation mechanism

The nature of the grain boundaries affects the degradation pathway. High-angle grain boundaries, labelled as 1 and 2 in Figure 4.9, are associated with the nucleation and growth of pinholes. Not all grain boundaries exhibit pinhole formation to the same extent, exemplified by region 2 being more altered than region 1 (Figure 4.9a). The initial diffraction pattern at this region reveals region 2 to show not only reflections attributed to the perovskite adjacent grains but also additional reflections and diffuse scattering. Although these additional reflections, already visible in the first frame, are difficult to index, they suggest the presence of defects. \cite{163} These defective high-angle boundaries can trigger faster degradation and larger morphological variations than less defective boundaries.
4.5 Discussion

In the schematic in Figure 4.9d, we propose a degradation mechanism whereby iodine segregation towards the grain boundary leaves bromine-rich areas within the perovskite grains, which form PbBr$_2$ at the surface to balance the iodine deficiency. Both PbI$_2$ and PbBr$_2$ are more thermodynamically stable and have higher thermal conductivity than the parent hybrid perovskite. The transformation dissipates energy and heats more effectively. These processes happen in conjunction with the loss of the more volatile I$_2$ and organic moieties. These changes result in a tetragonal to a cubic phase transition, the formation of small PbI$_2$ crystallites at the grain boundaries with pinholes, and the redeposition of some organics as a thin amorphous organic film on the surface of the specimen.

In this SED experiment the beam parking position was set at the centre of the image frame, as shown in Figure 4.5b, causing overexposure within the field of view. This may cause additional damage to the grain under beam parking and its boundaries, and trigger faster degradation. However, similar degradation pathways are observed in grains that are not adjacent to the beam parking position.

Our combined results offer an understanding of the changes induced by the interaction of electrons and X-rays with hybrid halide perovskite semiconductors. Each diffraction technique used offers some advantages over the other. nXRD provides excellent resolution in reciprocal space, but a lower resolution in real space. X-ray-based techniques are extremely useful to discern crystal structures with similar features. Since many of the degradation changes occur on the nanoscale, nXRD in general is unable to spatially resolve such changes. In contrast, SED offers excellent spatial resolution and allows the mapping of crystallographic changes at the nanometer scale. However, in SED, points in reciprocal space are broadened by a shape factor and spread out forming disks, due to the use of thin samples and a finite convergence semi-angle, respectively. In SED, the lower curvature of the Ewald sphere intersects multiple diffraction discs, which is not the case for X-rays. This limits the resolution in the reciprocal space of SED. Due to the similarity between pristine and intermediate perovskite degradation phases such as the 2H, 4H and 6H hexagonal polytypes, SED is not able to unambiguously assign similar structures. Moreover, due to the constrained acquisition geometry, not all grains produce interpretable SED patterns near a low-order zone axis. Further studies using precession electron diffraction, which offers a more complete integration of the diffraction space, could overcome the latter constraint if performed under low fluences.

The different natures of electrons and photons result in distinctive interactions with the specimen. For example, when electrons propagate through a material, they undergo elastic Bragg scattering and inelastic scattering. For a 200 keV beam, each inelastically
scattered electron transfers $\sim 27$ eV per scattering event to the specimen (see Table 3.1). This results in knock-on damage, radiolytic damage, and local heating.\cite{141} For a 200-nm thick film of the perovskite composition studied here at 200 keV, we estimate the probability of inelastic scattering to be twice that of no inelastic scattering (calculated with the Poisson model in the SI).\cite{175} The ratio of elastic versus inelastic cross-sections is inversely proportional to atomic number (proportional to $19Z^{-1}$ for electrons of hundreds of keV). For the triple cation perovskite composition, similar elastic and inelastic scattering probabilities are expected, based on the effective atomic number ($Z=36.4$). However, carbon atoms will contribute more to, and be more affected by, inelastic scattering than iodine or bromine, by a factor of 8 and 6, respectively. This is consistent with the damage mechanism proposed, in which the organic cations are the weaker species, and the halides restructure chemically to more stable intermediates. The effect of the inelastic cross-sections can be reduced by using thinner specimens or higher acceleration voltages, both of which will reduce the accessible diffraction information. A fine balance between these parameters is key. For the X-ray photons of tens of keV, the perovskite film is virtually transparent (see calculations in the SI). However, inelastic scattering is also always present in XRD, with a ratio of inelastic to elastic scattering cross-sections inversely proportional to atomic number by $50Z^{-1.7}$ for 20 keV photons. These ratios highlight the higher need to account for photon beam damage when X-rays are used on hybrid materials, especially for prolonged exposures (see estimations in the SI and Figure 4.8).

Similar mechanisms of interaction and damage can be seen with both electron and X-ray probes. Grains tend to tilt by a few degrees towards the zone axis after the first frames of acquisition ($\sim 100$ e $- A^{-2}$ and $\sim 1,400$-$2,800$ photons $A^{-2}$). We attribute these changes to non-destructive momentum-transfer processes on the nanoscale between the electrons and the specimen, yet beam-assisted annealing of the pre-strained films on the SiN support membrane cannot be excluded. These findings are important as they place constraints on the use of such techniques for elucidating the pristine microstructure of halide perovskites. Radiation exposure also leads to loss of crystallinity in the grains and degradation of the perovskite structure, with a critical fluence of $<200$ e $- A^{-2}$ and $<5,000$ photons $A^{-2}$ for SED and nXRD, respectively. The degradation mechanism proposed in this work is in agreement with the HR-STEM work on FAPbI$_3$ evaporated films by Rothmann et al., in which PbI$_2$ precipitates epitaxially growth from the perovskite.\cite{53} However, we observe crucial differences given by the more complex perovskite composition used in this study, in which simultaneous formation of PbBr$_2$ is also observed at the grains, potentially aided by the higher volatility of I$_2$ compared to Br$_2$, by the higher surface area present at the grain boundaries, and by small nanoscale chemical hetero-
4.5 Discussion

geneity at the grain boundaries.\textsuperscript{[220,243]} These findings can be extended to the radiation damage from a high-energy X-ray nanobeam, which also results in the emergence of lead halide species upon loss of the organic moieties across the whole scanned area (Figure 4.3c). The presence of the organic cation species at the A position has been proposed to trigger degradation processes towards PbI\textsubscript{2} as opposed to the Pb\textsuperscript{0}, mostly only seen from inorganic compositions, as the organics can undergo radiolysis more easily than the Pb\textsuperscript{2+} cation upon electron and X-ray illumination.\textsuperscript{[144,247]} Future work should focus on combining the microscopy techniques used here with the passivation strategies that have been successfully employed in halide perovskite semiconductors (passivation by coordinate bonding, ionic bonding, or chemical conversion),\textsuperscript{[58]} to gain a better understanding of the chemistry of passivation in hybrid halide perovskites. SED was recently used to understand the effect of surface-bound passivation agents on the crystallinity of halide perovskites through octahedral tilting stabilization.\textsuperscript{[46]}

4.5.2 Charge carrier concentration due to nano-probe excitation

The degradation mechanism proposed here contrasts with the degradation pathways observed from light-soaking. Photocarriers produced during light soaking can trigger the formation of I\textsubscript{2} via redox-mediated reactions, leaving metallic Pb\textsuperscript{0} and pinholes behind. Such changes are proposed to be seeded from crystallographic and compositional impurities.\textsuperscript{[163]} Light soaking can also trigger Cs segregation,\textsuperscript{[248]} but it was inconclusive whether this was observed in the nXRF mapping during the high-energy X-ray exposure study reported here (see Figure 4.3c). Cs mapping with nXRF was challenging due to its low stoichiometric concentration in the composition under investigation, and the energy of the peak overlapping with stronger signals from the I\textsubscript{L,β}, making it difficult to measure.

The use of high-energy beams results in faster degradation pathways of perovskites from the pristine state, compared to early-stage degradation from impurities caused by lower-fluence visible light irradiation. The illumination of any semiconductor with radiation can produce the excitation of charge carriers (electron and hole pairs) from the valence to the conduction band. These charge carriers can diffuse across the grains, of a mean size of around 100 nm. The carriers decay after a certain lifetime, shown to be of the order of hundreds of nanoseconds from photoluminescence studies of similar compositions,\textsuperscript{[25]} but much shorter lived (<1 nm) from comparable cathodoluminescence studies.\textsuperscript{[249]} Moreover, high-energy beams tend to induce high densities of charge carriers, triggering Auger processes which result in even shorter lifetimes.\textsuperscript{[25]} These findings suggest that the acquisition dwell time used here (1 ms and 0.5 s for SED and nXRD, respectively) is significantly longer than the charge carrier lifetimes, avoiding any accumulation of
High-energy electron radiation effects on the structure: 4D-STEM
carriers from pixel-to-pixel scanned. The charge carrier density produced by both the
electron and the X-ray beam can be estimated as follows.

For SED, the electron diffraction data were acquired at 200 keV and 12 \( e^{-} \text{Å}^{-2} \) per frame. Since the electron beam has significantly larger energy than the band gap of the material \( \sim 1.653 \text{eV} \), and since measurements are taken in transmittance mode, only the mean energy-loss energy from inelastic scattering is considered capable of creating charge carriers. For the acquisition conditions of the SED experiments (200 keV, 1 mrad collection angle, effective atomic mass effective \( Z_{\text{eff}} = 36.4 \), 200 nm sample thickness), the mean inelastic scattering energy loss is \( \sim 27.2 \text{eV} \) (refer to Equation 3.1). The inelastic scattering probability of single, double and triple scattering is of \( \sim 66\% \) (Table 3.1). Therefore, making the simplistic assumption that only \( 8 e^{-} \text{Å}^{-2} \) of the incoming fluence will scatter inelastically, each electron can approximately excite \( \approx E_{0}/3E_{g} \approx 6 e^{-}\text{-h}^+ \) pairs (see Equation 3.15). To estimate the lower and upper bounds of the charge carrier density, we assume a diffusion area ranging from the size of the beam \( \sim 5 \text{nm diameter} \) up to the size of the mean grain size \( \sim 100 \text{nm} \). Assuming also a mean interaction depth of 200 nm, due to the thin nature of the specimen for TEM studies, an interaction volume of \( ((5 to 100)/2)^{2}\pi \times 200 = 10^{-15} to 10^{-18} \text{cm}^{3} \) is estimated for each electron. Therefore, the charge carrier density of the localised excitation is \( 3 \times 10^{15} \) to \( 1 \times 10^{18} e^{-}\text{-h}^+\text{-pairs cm}^{-3} \) per incoming electron. This translates to a constant local excitation of \( 10^{16} \) to \( 10^{19} e^{-}\text{-h}^+\text{pairs cm}^{-3} \) per frame.

For nXRD, the diffraction data were acquired at 20 keV and 775 photons \( \text{Å}^{-2} \), as calibrated in the previous Section in the SI. In order to estimate the material transmittance at 20 keV, the pyMca 5.5.4 tool was used,\(^{[250]}\) assuming a density of 4.16 g \( \text{cm}^{-3} \),\(^{[251]}\) a film thickness of 600 nm and the film composition described in the methods. With an estimated transmittance coefficient of \( \mu = 0.984 \), a total fluence of 12.4 photons \( \text{Å}^{-2} \) will interact with the sample. We assume as an overestimation that each of the 20 keV photons can produce \( \sim E_{0}/E_{g} \approx 10^{4} e^{-}\text{-h}^+ \) pairs (see Equation 3.15). To estimate the lower and upper bounds of the charge carrier density, we assume a diffusion area ranging from the size of the beam (\( \sim 150 \text{nm diameter} \)) down to the size of the mean grain size (\( \sim 100 \text{nm} \)). From the interaction of 600 nm, the thickness of the specimen, an interaction volume of \( ((100 to 150)/2)^{2}\pi \times 600 = 10^{-14} to 10^{-15} \text{cm}^{3} \) is estimated for each photon, resulting in an overestimated localised excitation of \( 1 \) to \( 3 \times 10^{18} e^{-}\text{-h}^+\text{-pairs cm}^{-3} \) per photon, or \( 10^{19} e^{-}\text{-h}^+\text{pairs cm}^{-3} \) per frame. Again, these amount of charge carrier densities should be taken as over-simplistic overestimated approximations.

The charge carrier densities from the two different techniques are in a similar order of magnitude, higher than the charge carrier densities of these materials under 1 sun
4.5 Discussion

Figure 4.10: Fluence of high-energy electrons across the radiation spectrum in different orbits. The electron spectrum radiation fluence in orbits in the Earth (black) and in the harsher orbits near Jupiter (red), as simulated using SPENVIS. [252] This spectrum was used to relate the fluence from the experimental results of this work to space PV applications. Marked with a dashed vertical line, is the acceleration voltage used for the SED acquisition. Retrieved from [238].

illumination ($10^{14}$ to $10^{16}$ e$^-$-h$^+$-pairs cm$^{-3}$). Such large localized hot carriers can trigger radicals, multiparticle recombination and thermalisation processes on top of the knock-on damage, radiolytic damage, and local heating caused by the high-energy particle beam. Therefore, such high carrier concentrations can promote degradation of the perovskite in ways distinct from those encountered under illumination at 1 sun ($10^{14}$ to $10^{16}$ carriers cm$^{-3}$, mostly generated at band edge), likely aiding in the radiolysis of the organic cations in the perovskite. [247]

4.5.3 Implications for space PV

The state-of-the-art halide perovskites with FA-rich mixed-cation mixed-halide compositions are especially relevant for tandem and space photovoltaic applications. [18,253] Such compositions exhibit distinct chemical and structural degradation pathways. For the first time, we move beyond the better-studied MA systems and report degradation mechanisms in the nanoscale for these more complex materials. Reports have shown excellent radiation hardness under extreme space conditions of proton and electron exposure. [79–81] Large fluxes of high-energy particles, such as trapped electrons in orbit extending up to 1 MeV energies, can trigger defect generation and degradation of these materials, in similar
ways to the degradation induced during characterisation techniques.\cite{254,255} Moreover, radiation damage of hybrid perovskite is thought of being dependent on the total dose rather than on the dose rate.\cite{138,141}

Here we used microscopy techniques such as SED and nXRD may be used to mimic large total radiation exposures whilst characterizing defect generation and degradation in a vacuum. The radiation hardness described for electrons and X-rays supports the good resilience of these materials to degradation from electron radiation in space.

The electron spectra from the safer orbit near the planet Earth and the harsher orbit in Jupiter were simulated using SPENVIS.\cite{252} The fluence of the electron spectrum at 200 keV energy for both orbits was used as input to relate the fluence thresholds found in this study to space applications, as shown in Figure 4.10. The fluxes were calculated from the default orbits generated by SPENVIS for each planet and the default models for electrons for each planet (AE-8 MAX and D&G83 for the Earth and Jupiter, respectively). With a total flux of about $3 \times 10^{-9}$ e$^{-}$ Å$^{-2}$ s$^{-1}$ at 200 keV in the Earth orbit, a fluence of 200 e$^{-}$ Å$^{-2}$ would be accumulated after around $7 \times 10^{10}$ s $\approx$ 2,000 years. The same fluence threshold would be reached earlier at the harsher Jupiter orbit after only $\sim$200 years (with a total flux of $10^{-8}$ e$^{-}$ Å$^{-2}$ s$^{-1}$). These lifetimes are assuming radiation damage of hybrid perovskite is dependent on the total dose rather than on the dose rate.\cite{138,141} Despite the simplicity of these estimates, the resilience of these materials to degradation from electron radiation is promising for space PV applications as the radiation fluence used in microscopy are significantly larger than the radiation in space by several orders of magnitude. It is important to also note the differences between electron radiation in microscopes and space, such as the energy spectrum of space radiation extending up to 1 MeV energies, and the generally lower radiation fluxes in orbit.\cite{79,254} Combined with the reported excellent proton radiation hardness,\cite{79,81} this study once more places halide perovskites as promising candidates for space photovoltaic applications. Further studies should also include the effect of cryogenic temperatures on the degradation of halide perovskites.

### 4.6 Conclusion

Local changes in the nanostructure at extremely low radiation exposure have been identified, leading to changes in the orientation of the grains. At high radiation exposure, degradation of the perovskite phase involves iodine migration, producing decomposition to lead halide species. PbBr$_2$ reflections appear within perovskite grains that exhibit PbI$_2$
crystallites growing at their grain boundaries. Specifically, regions showing high-angle defective grain boundaries are important for degradation.

The findings reported in this Chapter provide a further understanding of the exposure limits of high-energy electron and photon beams, being $<200 \text{ e}^- \AA^{-2}$ at 200 keV and $<5,000$ photons $\AA^{-2}$ at 20 keV, respectively. These critical radiation exposure methodologies are crucial for any characterisation technique used to study the nanoscale of halide perovskites and, more generally, can be extended to any soft semiconductor, as well as to further understand the challenges that perovskite solar cells still face for space applications.

In the future, passivation and growth strategies targeting the removal of such high-angle defective grain boundaries will be critical for the further mitigation of halide perovskite instabilities, especially for applications vulnerable to high-energy radiation. Some examples where passivation can help with electron-beam stability are shown and discussed in Chapter 5. By combining known passivation strategies with novel microscopy techniques such as those described here, not only a better understanding of the chemistry of passivation in hybrid halide perovskites can be acquired, but it can also help extend the radiation that such materials can tolerate during electron microscopy.
Chapter 5

High-energy electron radiation effects on the optics: CL-SEM

Parts of this Chapter are adapted in part from Ferrer Orri, J. et al., Using pulsed mode scanning electron microscopy for cathodoluminescence studies on hybrid perovskite films. Nano Express 2, 024002 (2021),[249] and from Kosasih, F., Divitini, G., Ferrer Orri, J., et al., Optical emission from focused ion beam milled halide perovskite device cross-sections. Microscopy Research and Technique 85, 2351-2355 (2022).[256] CL-SEM data acquisition was performed by Jordi Ferrer Orri, with the constant aid of Gunnar Kusch and the early help of Elizabeth Tennyson.

Chapter abstract: Going beyond conventional high-current SEM-CL setups, used for traditional semiconductors, enables CL to start to play a role in resolving the complex heterogeneity of hybrid halide perovskites. The use of SEM-CL systems coupled with PM capabilities helps to probe the optical properties and degradation of these novel beam-sensitive semiconductors more robustly.

5.1 Introduction

As introduced in Chapter 3.1.5, cathodoluminescence (CL) in an SEM can investigate semiconductor materials by scanning an electron beam over a semiconductor. By collecting the optical properties of the material during scanning, CL-SEM can elucidate the structure-property relationship of halide perovskites at sub-micrometre spatial resolution.
While most CL studies on perovskites have focused on inorganic compositions, the characterization of hybrid halide perovskites, including the highest-performing compositions with organic and inorganic ions, is limited due to their lower stability under the electron beam.

This Chapter describes the technical development needed to adapt the standard CL-SEM technique to work for halide perovskites, from both a sample preparation and data acquisition standpoint, but also from a low SNR data processing and analysis standpoint. In order to reduce beam damage, an electron beam in pulsed mode (PM) is found to measure hyperspectral maps of hybrid perovskite compositions more robustly. Finally, a series of examples will be presented whereby PM and low-current CL have been proven useful to study the luminescence of several different perovskite compositions.

5.2 Technique development

5.2.1 Data acquisition

As described in Figure 3.12, CL is produced from the interaction of a scanning electron beam with the sample. Multiple parameters need to be accounted for in order to optimise and extract useful information from CL, especially in the case of beam-sensitive samples. Any organic-containing halide perovskite sample is difficult to image in CL mode. It is, therefore, primal to understand how a given set of acquisition conditions (e.g. a given acceleration voltage, beam current, dwell time, field-of-view (FOV), or beam scanning speed) affect the CL optical signal measured in the spectrometer.

Early on in the development of CL, a method to probe sample stability was designed. The CL emission intensity of a beam-sensitive sample always quenches due to electron-induced sample degradation. Acquiring a sequence of spectra from the same region over time is a useful metric to investigate the limited conditions for which a sample can be imaged. Figure 5.1 shows the CL intensity decay over exposing the same area with the electron beam over time. Such spectral evolution is best plotted as a 2-dimensional image (top), yet it can also be plotted as an overlay of spectra (bottom). When perovskites degrade through electron exposure, shifts in the emission are often also observed. These spectral stacks are always acquired at the start of any session, especially when new samples are imaged, in order to understand the limits of exposure a sample can tolerate. Once optimal conditions have been found (such as the left panel in Figure 5.1) where the spectral evolution does not shift and the sample is still emissive after the range of acquisition, then CL maps can start to be acquired.
5.2 Technique development

Figure 5.1: Understanding CL emission degradation. Evolution of a sequence of spectra over time, as a tool to investigate the limited conditions at which a sample can be imaged. Spectral stacks can be plotted as images (top) or as spectral overlays (bottom). Note that some beam-blanking behaviour, not physical, can be observed for the top panel as an oscillatory artefact. Sample: Top view LED semi-device on glass/ITO/ZnO/ethoxylated polyethyleneimine/perovskite (FAPbI$_3$, 30 nm) with passivation agent MSPE (from Yuqi Sun).\footnote{257} Spectral time evolution acquisition in CW, 5 keV, $\sim$625 pA, 20 ms per spectrum, 1000 reps, beam rastering at pseudo-spot mode (64 px, 15 x 15 $\mu$m$^2$, at 0.5 $\mu$s/ px).

Moreover, spectral stacks can also be used to compare the emission and stability between similar samples. For instance, Figure 5.1 was also used to compare the effect that the passivation agent MSPE (2-(4-(methylsulfonyl)phenyl)ethylamine) had on FAPbI$_3$ thin films for near-infrared LEDs.\footnote{257} Figure 5.1 shows the CL evolution for a sample without passivation (left panels) and after passivation (right panels), in which after passivation the CL emission is conserved at x5 brighter intensity for longer electron radiation exposure.

For some SEMs, electron optics work better at high-enough currents, such as between 1 to 30 nA. However, such currents are too high to image hybrid perovskites. The best strategy is not to lower the electron-gun emission current, but to make use of apertures to limit the electron current (or go to PM, as described in Section 5.3). In the particular case of the Attolight SEM-CL system in Cambridge, the current calibrated using the standard 100 $\mu$m-radius aperture is lowered by 1/4 or by 1/16 if the 50 or 25 $\mu$m-radius apertures
Figure 5.2: Effect of composition, FOV, and carbon coating on CL emission. Comparison of the effect of adding a thin carbon coating on different perovskite compositions (labelled as FA, TC and Cs). Bare means no additional carbon layer was added, and "Carbon" means a thin amorphous layer was added. In addition, the effect of the field-of-view (FOV) is shown column-wise. All spectral evolutions are plotted in the range of 0 to 150 counts. SE images of regions without and with carbon coating are shown on the right. Samples: (FA) ITO/FAPbI$_3$ with EDTA passivation (from Satyawan Nagane), (TC) ITO/perovskite triple-cation double-halide, (CS) ITO/CsPbBr$_3$ (from Zher Ying Ooi). Spectral time evolution acquisition in CW, 3 keV, ∼62.5 pA, beam rastering at pseudo-spot mode (64 px, at 0.1 μs/px). Dwell times were 250 reps x 100 ms, 750 reps x 25 ms, and 750 reps x 25 ms for large, medium, and small FOVs, respectively.

are used instead, respectively. Moreover, the SE image formation is enhanced due to the sharper focus of the electron beam.

5.2.2 Optimal sample preparation

In addition to optimising the microscopy parameters, proper sample preparation and stabilization can also lead to reduced beam damage and better acquisition of CL signal. Perovskite samples must be deposited on electrically conductive substrates and connected to the metallic sample holder, to avoid sample charging. Typically, ITO glass substrates are used, and it is important to ensure that all surfaces of the sample, including the bottom, top, and sides, are connected to a conductive element such as silver paint.
The addition of contact layers on perovskite films may also help dissipate charges and prevent volatile species from leaving the sample, shown for device cross-sections. However, adding contact layers on top of the perovskite film may not always be effective. It can result in more CL emission quenching than beam damage mitigation. This has been investigated for both the addition of an amorphous thin carbon layer as shown in Figure 5.2 and the addition of a hole transport layer as shown in Figure 5.3.

A series of perovskite samples with different compositions were prepared partially coated with a thin (nominal ~6 nm) layer of amorphous carbon using a carbon sputtering system, a common SEM sample preparation technique. A pure FAPbI$_3$ sample (FA), a triple-cation double-halide (TC) and a fully-inorganic CsPbBr$_3$ (Cs) composition was studied. Samples were provided by collaborators as stated in each of the captions. Figure 5.2 shows the spectral CL evolution, plotted at the same intensity range of 0 to 150 counts, for a continuous electron exposure on the same area for 15 seconds. The fully inorganic Cs composition shows the most stable CL emission, followed by the FA composition and the TC, both of which exhibit visible CL quenching and small blue shifts. In addition to
composition, the effect of the FOV used during CL mapping is also studied. Figure 5.2 shows, by different columns, that the smaller the FOV, the faster the CL is affected by electron exposure. At small FOVs, the electron flux is localised in smaller areas. Small FOVs can result in oversampling, especially when the resolution is limited in the order of 100s of nanometers, which can overexpose regions in the perovskite specimen, resulting in faster degradation.\[^{259}\] Figure 5.2 also shows that the addition of a thin amorphous carbon coating did not significantly change any of these trends. We expected the carbon coating to hinder degradation through (i) the encapsulation of the perovskite layer, slowing down the escape of volatile species to vacuum, and (ii) acting as a sacrificial layer for radicals to form and the surface from the accumulation of scattered electrons (see Chapter 3.1.6). However, the addition of a few nanometers of a layer resulted in the CL emission from the perovskite being absorbed or quenched by the carbon layer. The CL emission is estimated to be quenched by 1/2. For example, for the FA composition at a FOV of 1 µm, the maximum CL emission goes from 150 to 60 counts without and with the carbon layer, respectively. Such quenching made CL mapping not possible, as dwell times of >1 second per pixel were needed to get enough SNR.

Similar findings are observed in Figure 5.3, in which a thin film of the commonly used hole transport layer poly(triaryl amine) (PTAA), a p-type organic semiconductor, was added on top of a TC composition perovskite film.\[^{17}\] The comparison of the spectral CL evolution over continuous electron exposure on the same area for around 1 minute shows similar trends to those observed for carbon coating, with significant quenching when an extra layer is added. In addition to the spectral image, the absolute CL spectral evolution and the normalised CL emission are also shown in Figure 5.3a. They reveal some differences. At the start, the PTAA sample is x3 dimmer than when no transport layer is present (1,000 counts to 300 counts, respectively). However, after 10 seconds of exposure, both CL emissions are similar, in the 200 counts range. The presence of PTAA allows for the CL signal to slightly recover to 200 counts, after a small blue shift of ∼5 nm. The emission FWHM is also narrower after 10 seconds of exposure, compared to the bare perovskite film, which shows the appearance of a blue-shifted shoulder (marked with an arrow in the normalised CL emission panel). The chemical and structural interpretation for such changes is discussed later in this Chapter. However, the addition of hole and electron transport layers to a bare perovskite film is expected to quench emission due to the extraction of charge carriers.\[^{260–262}\] Finally, Figure 5.3b shows the same trends as observed in Figure 5.2, where the smaller the FOV, the faster the CL is affected by electron exposure, due to higher fluences.
5.2 Technique development

Figure 5.4: Common pre-processing steps for CL. The raw hyperspectral CL map contain common artefacts that need to be corrected. (a) The raw panchromatic CL image shows brighter emission at the edges, which dominate the dataset. (b) After edge cropping, cosmic ray peaks dominate the signal at some pixel positions, which can be deleted using a spike removal tool. The inset shows a spectrum corrupted by a cosmic ray. (c) The pre-processed dataset does not show artefacts. Sample: Top view PSC on glass/FTO/NiOx/perovskite (triple cation double halide) (from Felix Kosasih). [264] CL map acquisition in CW, 5 keV, ~1 nA, 10 ms dwell time.

In short, adding extra layers on top of the perovskite film has been discovered to impede the acquisition of CL data for halide perovskites rather than aiding it, as the signals are heavily quenched. As a result, no additional layers are used on top of the perovskite sample of interest from now on.

5.2.3 Data pre-processing

This Section covers a range of data processing and analysis techniques developed in this thesis for CL hyperspectral data.

When data is acquired from the Attolight CL-SEM it is saved in a .sur format. HyperSpy [263] can be used to load such file extension into a multidimensional 3-dimensional array. All CL maps contain artefacts that need to be corrected for before any data analysis is performed. This is called the pre-processing steps.

The pre-processing steps first involve a grating correction and spectral calibration, performed by the Attolight system and developed by Gunnar Kusch. Then, the raw CL maps normally show brighter emissions at the edges of the scanned region, which dominate the CL intensity in the dataset (see the histogram in Figure 5.4a). This can be attributed to an edge effect by which the pixels at the edges are surrounded by pixels that have not
High-energy electron radiation effects on the optics: CL-SEM

Figure 5.5: Common pre-processing steps for SE images in the SEM. The acquisition of SE images results in numerous artefacts, such as high-frequency electronic noise, low-frequency scanning artefacts, or intensity saturation. Raw SE images (in blue) are compared to processed SE images (in orange), where a fast-Fourier transform bandpass filter of 5-500 was applied, and the intensity histogram was adjusted to cover the full range, using ImageJ. The processing of the SE images is necessary as the detector readily saturates during data acquisition. Sample: Top view LED semi-device on glass/ITO/ZnO/ethoxylated polyethyleneimine/perovskite (FAPbI$_3$, 30 nm), (left) without and (right) with passivation agent MSPE (from Yuqi Sun). SE image acquisition in CW, 5 keV, ~625 pA, 10 s dwell time, and 2048 x 2048 px.

been exposed to electron radiation. Brighter edge emission is particularly observed for beam-sensitive materials like perovskites, but it is less pronounced for more beam-stable materials like inorganic perovskites or traditional semiconductors, and thus the edges are normally cropped out. After edge cropping, cosmic ray peaks dominate the signal at stochastic pixel positions. Since CL maps take minutes to hours to acquire, tens of spectra are convoluted with sharp spikes from terrestrial cosmic rays interacting with the CCD detector (see the histogram in Figure 5.4b). These spikes can be deleted using a spike removal tool by finding the first zero value in the histogram of CL intensities, as such:

\[
\text{threshold value} = \min_i : h_i = 0
\]

with \(h_i\) the height of the \(i\)th bin in the histogram and the \(\min\) function returns the smallest index \(i\) such that \(h_i = 0\). This equation finds the index of the first bin in the histogram that has a zero height, which is often used as a threshold value to filter out cosmic ray spikes. Then spikes are removed and interpolation between the signal just before and after the spike is done to synthetically stitch the signal. An example of the resulting pre-processed CL data is shown in Figure 5.4c.

Scanning defects are particular to rastering techniques like SEM. Such scanning artefacts can be corrected using Fast-Fourier transform filters, as shown in Figure 5.5. Such
filtering techniques can remove high-frequency electronic noise and low-frequency scanning artefacts.\cite{267} Moreover, a normalisation of the histogram of intensities for the SE image is also beneficial to better visualise surface morphology. These changes are shown from the raw SE images in blue to the filtered and normalised SE images in orange (Figure 5.5). Such processing is readily performed using ImageJ.\cite{266}

Finally, most luminescence data is acquired and stored using spectrometers and CCDs in wavelength units (nanometers). Spectra are often displayed using units of wavelength, but representing the data as a function of energy is more informative. For example, for quantitative analysis of photophysics, simply noting the intensity versus wavelength is insufficient and the transformation to the energy axis is required.\cite{269} Failure to do so can introduce inaccuracies during data analysis. For instance, trying to determine the true energy centre of a Gaussian emission band of a peak will yield different values if measured in units of wavelength or electron volts. These inaccuracies may be due to a failure to fully account for the sensitivity of the detection system, as well as the misuse of analytical techniques such as band de-convolution which are only appropriate for energy axes representations. These errors are not only scientifically incorrect but can also be misleading and introduce spurious features into the analysis.\cite{270} It is important to present spectral data accurately in order to properly understand and investigate scientific phenomena.

The transformation from wavelength scale to energy scale (in eV) results in an axis vector that is not uniformly spaced due to the nonlinearity defined by $E = \frac{hc}{\lambda}$, yielding the following relationship:

---

**Figure 5.6: The Jacobian transformation.** The conversion between wavelength and energy is non-linear. (a) A homogeneously distributed spectrum in the wavelength (in nm) transforms to (b) a non-linear distribution. (c) It is therefore important to remove the background from the raw signal (in red), or else the spectrum is dominated by the background after the Jacobian transform (see orange and blue). The Sample: Top view PSC on glass/FTO/NiOx/perovskite (triple cation double halide) (from Felix Kosasih).\cite{264} CL map acquisition in CW, 5 keV, \~1 nA, 10 ms dwell time. Panel a and b retrieved from the documentation of\cite{268}. 

\[ E = \frac{hc}{\lambda} \]
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\[ E = \frac{10^9 \frac{hc}{e}}{n_{\text{air}} \lambda} \]  

(5.2)

with \( \lambda \) the wavelength in nanometers, \( E \) the energy in eV, \( h \) the Planck constant, \( c \) the speed of light, \( e \) the elementary charge, and \( n_{\text{air}} \) the refractive index of air.\[271\] Note that the refractive index of air varies with wavelength, described by analytical formulations.\[272\] Despite CL being acquired in a vacuum inside the TEM, the coupled spectrometer and optics are in the air and such corrections are needed.

Finally, when only the wavelength axis is corrected in energy plots, distortions of the true spectra occur if only the axis of a signal is converted without adjusting the signal intensity. As illustrated in Figure 5.6a-b, when converting from wavelength to energy, the conversion formula must account for the fact that the integral of the signal should be equal for both units. Therefore, a renormalization factor that converts the signal intensity from counts/nm to counts/eV must be calculated. Given an energy axis, we require that \( I(E)dE = I(\lambda)d\lambda \) for energy conservation. Given \( E = \frac{hc}{\lambda} \), the Jacobian transform is derived as follows:\[269\]

\[ I(E) = I(\lambda)\frac{d\lambda}{dE} = I(\lambda)\frac{hc}{E}\]  

(5.3)

with \( I \) the intensity value per bin. The minus sign just reflects the different directions of integration in the wavelength and energy domains. It is also important to ensure background removal in the wavelength axis from the raw signal before the Jacobian transform is applied, or else the spectrum is dominated by the background (see Figure 5.6c).

In short, all these pre-processing steps are important to consider because failing to correct and adjust the signal properly can result in incorrect interpretations of the data.

5.2.4 Data analysis

Multiple analysis methods can be used to extract emission features from luminescence signals.

Gaussian fitting

Fitting the data is a common tool, as it enables the extraction of the emission shape parameters of the CL signal as model spectra. Multiple Gaussian distributions, with a
Table 5.1: Common reported PL peak energies for perovskite compositions and semiconductors linked to perovskite devices. Reported in nm and eV from selected literature.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Emission peak energy (PL), nm (eV)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsBr</td>
<td>291 nm (4.258 eV)</td>
<td>[273]</td>
</tr>
<tr>
<td>CsI</td>
<td>321 nm (3.857 eV)</td>
<td>[273]</td>
</tr>
<tr>
<td>PbI$_2$</td>
<td>515-540 nm (2.3-2.4 eV)</td>
<td>[274]</td>
</tr>
<tr>
<td>PbBr$_2$</td>
<td>396 nm (3.138 eV)</td>
<td>[275]</td>
</tr>
<tr>
<td>CsPbBr$_3$</td>
<td>520 nm (2.37 eV)</td>
<td>[276]</td>
</tr>
<tr>
<td>CsPbI$_3$</td>
<td>704 nm (1.76 eV)</td>
<td>[277]</td>
</tr>
<tr>
<td>MAPbBr$_3$</td>
<td>574 nm (2.16 eV)</td>
<td>[277]</td>
</tr>
<tr>
<td>MAPbI$_3$</td>
<td>780 nm (1.58 eV)</td>
<td>[278]</td>
</tr>
<tr>
<td>FAPbI$_3$</td>
<td>810 nm (1.53 eV)</td>
<td>[278]</td>
</tr>
<tr>
<td>Double cation double halide (FA, Cs, I, Br):</td>
<td>~765-775 nm (1.59-1.62 eV)</td>
<td>[254]</td>
</tr>
<tr>
<td>Triple cation double halide (FA, MA, Cs, I, Br):</td>
<td>~750-760 nm (1.63-1.65 eV)</td>
<td>[40]</td>
</tr>
<tr>
<td>ITO</td>
<td>300 350 nm (3.5-4.3 eV)</td>
<td>[279]</td>
</tr>
</tbody>
</table>

constant background offset, can be used to fit CL data, following Equation 5.4, where each Gaussian represents one of the emission peaks of interest.\cite{263}

\[
S(E) = C_{bkg} + \sum g_i(E) \exp \left( -\frac{4 \log(2)(E - E_{0,i})^2}{FWHM_i^2} \right)
\]  

(5.4)

with $C_{bkg}$ a constant background (yet background can also be fitted with any other line equation), $g_i(E)$ a Gaussian distribution for each emission phase $i$, written in the form defined by $E_0$ the central peak position, $I_{CL,i}$ the peak height at the central position, and FWHM the full-width half-maximum of the peak. Note that the same equation can be used to fit Gaussians in the wavelength dimension, by replacing $g_i(E)$ for $g_i(x)$, with $x$ the wavelength in nanometers. Each possible emission peak must be added to the model. Table 5.1 lists the most common emission peaks that need to be considered when analysing CL data from halide perovskites.

The fitting can be performed using different algorithms. The best fits were found when the least-squares loss optimization with the Levenberg-Marquardt algorithm was used, and a serpentine iteration path with bound parameters using the SciPy Python package.\cite{263} Compared to the other gradient-descent algorithms, the Levenberg-Marquardt algorithm is more resilient and can often obtain a solution even when its starting point is far from the final minimum at the expense of speed.\cite{280} It is important to set limited and correct boundary conditions for each Gaussian. It is also important to initialise all the boundary conditions for each scanned pixel prior to running the fitting. For example,
for the double-cation double-halide perovskite composition, the suggested boundary conditions when fitting in wavelength units are:

- $x_0$ initialised at 750 nm, ranging between 700-770 nm.
- $h$ initialised at 10, ranging between 0-500.
- FWHM initialised at 20, ranging between 0-200.

An example of the result of a good fit following these parameters is shown in Figure 5.7. The raw and the fitted data for four spectra are shown, with fitting three Gaussian peaks and the background offset, each shown in different colours.

An alternative to finding the position of the maximum intensity of a peak is the centroid analysis, particularly useful for non-symmetric peaks with pronounced shoulders. This method finds the centre-of-mass (COM) of an emission peak. It calculates it from the signal axis units and the intensity at each pixel value, as a weighted average of the peak as such:

$$\text{centroid} = \frac{\sum x_i I_i}{\sum I_i}$$

with $x_i$ the wavelength (or pixel number) at which the intensity of the spectrum $I_i$ is measured. This method is used for the analysis of PL data in Chapter 6.

**Spectral filters**

Emission images which spatially resolve different emission types can be formed post-acquisition from the hyperspectral CL dataset using spectral filtering. Panchromatic imaging can be formed by integrating the spectral intensity of the whole emission spec-
Figure 5.8: Types of hyperspectral filtering. Emission images can be formed post-acquisition from the hyperspectral CL dataset. (a) A panchromatic image is formed by integrating all the emission spectrum intensities for each pixel. (b) A band-pass filter can be used to crop the spectral dimension and form an image from a smaller spectral range, here 51±30 nm. (c) Machine learning techniques such as PCA + NMF can be used to denoise the CL dataset. Then emission images can be formed by selecting only components with physical features without noise (PC1 and PC3, marked with filled triangles). (d) To evaluate each component, the loadings and factors can be plotted. Sample: CsPbBr$_3$ quasi-2D LED film for LED application (from Miguel Anaya). CL map acquisition in CW, 6 keV, ∼10 nA, 50 ms dwell time.

Decomposition

More advanced analysis techniques involving statistics, probability and machine learning can also be used to denoise and deconvolve spectral signals, to form clearer spectral images. This can be done with dimensionality reduction algorithms as a means of better interpretability of experimental data, or for noise reduction. Principal component analysis (PCA) is, in particular, a widespread method to decompose complex data into smaller datasets. The rest of this subsection describes the mathematical foundations behind PCA adapted from\cite{281}, and its applications to CL data.

Linear algebra describes that any $m \times n$ matrix can be decomposed into the product of 3 matrices such that $X = U \Sigma V^T$. This is called singular value decomposition (SVD). This is analogous to understanding the effect that a linear transformation matrix $X$ has on a set of vectors $v$ as a decomposition of a rotation $V$, followed by a scaling transformation $\Sigma$, followed by a rotation transformation $U$. 
For a square symmetric matrix \( X \), such decomposition yields a very simple result: the singular values \( \sigma_i \) (the trace of \( \Sigma \)) correspond to the absolute values of the eigenvalues of \( A \) \( (\sigma_i = |\lambda_i|) \); and matrices \( U = V \) and their columns are the eigenvectors of \( A \). These eigenvectors are orthogonal to each other by definition.\(^{[281]}\)

However, most experimental datasets acquired are not square, let alone symmetric. For example, hyperspectral CL maps can be 128x128 pixels in the navigation axis, with 1024 px in the spectral axis. A way to explain any dataset as a square symmetric matrix is to create a covariance matrix such that:

\[
\text{2D: } \begin{bmatrix} \text{var}(x) & \text{cov}(x, y) \\ \text{cov}(x, y) & \text{var}(y) \end{bmatrix} \quad \text{3D: } \begin{bmatrix} \text{var}(x) & \text{cov}(x, y) & \text{cov}(x, z) \\ \text{cov}(x, y) & \text{var}(y) & \text{cov}(y, z) \\ \text{cov}(x, z) & \text{cov}(y, z) & \text{var}(z) \end{bmatrix} \ldots (5.6)
\]

Equation 5.6 shows how by using the variance and covariance descriptors of a dataset, a square symmetric matrix can be built. The variance (placed at the diagonal of the matrix) can be described as the mean squared difference between each data point and the centre of the distribution measured by the mean. The covariance (placed symmetrically at the upper and lower triangle) can be calculated as the product of taking the difference between each coordinate and their respective mean, separately.\(^{[281]}\)

Principal components analysis is the SVD of the covariance matrix. It returns a set of orthogonal vectors that explain most of the variance across a dataset. Each of these vectors or "directions" is called a principal component (PC). The first PC explains the maximum amount of variance in the data. The second PC explains the remaining variance in the data while being orthogonal to the first component. This process is repeated iteratively until the number of components is equal to the number of original variables or until a desired proportion of the variance in the dataset has been explained. A scree plot, which is a semi-logarithmic graph with variance on the y-axis and component index on the x-axis (shown in Figure 5.8c), is constructed to determine the number of principal components needed to explain most of the variance in the data.\(^{[282]}\) The scree plot typically shows a steep decline in variance for the first few components, followed by a plateau of low-variance components. Only selecting the first PCs results in a denoised signal \( S' \) and the remaining PCs correspond to noise \( N \). However, cropping right at the shoulder can lead to artifacts in the denoised signal and manual inspection is always necessary during processing.\(^{[283]}\)

Loadings and factors matrices can be obtained as the coefficients of the linear combination of the original variables from which the PCs are constructed.\(^{[284,285]}\) They offer a direct link between the decomposed PC dimensions and the original spectral dimensions, as shown in Figure 5.8d with the loadings as spectra and the factors as images. How-
ever, the loading and factor matrices may not be readily interpretable. For example, they can contain negative values, even though a spectrum cannot have a negative intensity count.\[282\] This unique property of PCA allows for the identification of physically significant information in terms of (anti)correlation of features. However, the components are determined solely based on statistical variance and cannot be interpreted directly as a physical signal. A non-linear variation of PCA is called non-negative matrix factorization (NMF). It aims to overcome this limitation by restricting the factor and loading matrices to only contain zero or positive numbers and requires convex optimisation to solve.\[286,287\] Moreover, NMF requires the user to specify the desired number of input components in advance, making it a less unsupervised method. In Figure 5.8c an emission image can be formed by selecting only components with physical features without noise, PC1 and PC3, which was evaluated for each component by manually inspecting its loadings and factors. PCA-NMF is a commonly used technique and is easily implemented using open-source software, as described in the next section.

### 5.2.5 LumiSpy: an open-source Python package

Dedicated proprietary software is commonly used for electron microscopy data analysis. These software programs usually come with a user-friendly graphical user interface for common data analysis tasks. However, their capabilities may be restricted compared to the potential of modern scientific programming languages for developing innovative data analysis methods. The popularity of HyperSpy,\[288\] a Python-based program used for scientific data processing, has demonstrated that developing microscopy software through open-source methods can lead to high-quality data analysis tools even when proprietary alternatives are available.

LumiSpy is a Python package extending the functionality for multi-dimensional data analysis provided by the HyperSpy library. It is aimed at helping with the analysis of luminescence spectroscopy data. While initial development has mainly focused on the analysis of cathodoluminescence data, it is aimed at other similar luminescence spectrosopies such as electroluminescence (EL), Raman, absorption, transmission or Fourier-transform infrared (FTIR) spectroscopy. It is open-source software that can be used on any computer running Python, the preferred language for scientific computing.

The first commit of the package was made on November 18, 2019, by me and has been under constant development ever since. It has a community of users and developers, mainly run by myself, Jonas Lähnemann, and Eric Prestat. LumiSpy offers an elegant yet powerful syntax for visualizing, analyzing, accessing, and storing multi-dimensional datasets and metadata of luminescent datasets, in particular spectrum images (one or
two-dimensional arrays of spectra). It simplifies the usage of external scientific libraries aimed at lowering the entry barrier to advanced interactive data analysis.

LumiSpy has been built as a robust and transparent framework, to ensure better reproducibility in the way luminescence data is interpreted. To achieve ease of use and transparency, it has been always built with rigorous clear documentation, metadata handling, and demonstration Jupyter notebooks (all accessible in https://lumispy.org). To ensure code robustness, continuous integration with rigorous code testing and coverage was set from the start. All code is peer-reviewed, which ensures that the package is always functional, and reliable, and bugs are controlled. Moreover, the package was published in the pypi and conda-forge libraries, so it can be installed easily from a single command. As a result, tens of users are using this package for their data analysis.

In particular, LumiSpy offers (i) additional Signal types, designed specifically for luminescence spectra and transients, (ii) transformation tools to switch from wavelength (nanometers) to non-uniform signal axes in common units such as eV (electron volt) or wavenumbers (Raman shift), (iii) a plethora of utility functions for luminescence spectroscopy, such as joining multiple spectra along the signal axis, unit conversion, centre-of-mass peak analysis, . . . , and (iv) signal tools to perform data normalization, data pre-processing such as spike removal, and scaling. Most of the data pre-processing and analysis functions described in this Chapter have been implemented into LumiSpy in the submission of this writing.
5.3 The use of an electron beam in pulsed mode (PM)

CL has been used to characterize semiconductors at the nanoscale for many decades. However, only recent innovations have allowed this technique to move beyond the well-established continuous wave (CW) electron beam CL imaging. Since the creation and application of an optically driven pulsed mode (PM) electron gun adapted to acquire CL, it is now possible to measure time-resolved cathodoluminescence (TRCL) using bright picosecond pulsed electron beams. In addition to enabling the acquisition of TRCL, the use of a pulsed beam can reduce the beam current to tens to hundreds of pA. While the electron beam interaction could be used as an accelerated platform to understand the material stability, electron beam damage is generally undesired for CL analysis. More importantly, low-current pulsed beams allow the material to relax electronically and thermally in between pulses, which can be beneficial to hinder beam damage. Optically driven pulsed electron beams have key advantages over beam deflection, including brighter and shorter pulses of electrons. However, there are also some limitations, the primary one being electron gun drift. Figure 5.10 demonstrates this limitation. In PM, the electron gun must be set below its cathodic emission and a UV-pulsed laser must be focused on its surface. To generate a bright electron pulse of short duration, the laser spot size (2.5 μm) must be perfectly aligned with the tip of the electron gun. Any drifts in this focal position due to hysteresis during electron emission or misalignment will result in a reduction of the electron emission and, consequently, the CL and SE signals.

Figure 5.10c illustrates such a phenomenon during the acquisition of a CL map, where the electron gun drifted only after 1/4 of the scan, resulting in the loss of most of the signal.
This issue can be mitigated by allowing the electron gun to relax for about 20-30 minutes after switching to PM from CW mode and realigning the laser positioning during this time. Additionally, it is crucial to continuously realign the laser after the end of each CL scan.

This Section describes how we exploit the use of a PM electron beam to characterise the triple-cation double-halide \((\text{FA}_{0.79}\text{MA}_{0.16}\text{Cs}_{0.05})\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3\). While the vast majority of historical CL work has been performed on traditional inorganic semiconductors, which show little to no beam damage, here we investigate how SEM acquisition parameters, especially beam current and beam mode (either CW or PM), affect the quality of the CL data for beam-sensitive perovskite thin films on glass substrates.

### 5.3.1 Sample preparation

Glass coverslips (18 mm x 18 mm, 0.13-0.17 mm thickness, Academy) were cleaned in acetone and isopropanol (10 minutes each) in an ultrasonic bath. The substrates were treated for 10 minutes in an oxygen plasma cleaner immediately before the spin-coating procedure. The perovskite precursors solutions were prepared by first dissolving \(\text{PbI}_2\) (1.1 M), \(\text{PbBr}_2\) (0.22 M), FAI (1.0 M) and MABr (0.2 M) in a mixture of anhydrous DMF and DMSO (4:1 v:v). CsI solution (1.5 M in DMSO) was then added to the precursor solution as 5% of the total volume. To form the \((\text{FA}_{0.79}\text{MA}_{0.16}\text{Cs}_{0.05})\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3\) thin films, 50 \(\mu\text{L}\) of precursor solution was deposited on each substrate. A two-step spin-coating procedure was used for the thin film formation: 10 seconds at 1000 rpm, and 20 seconds at 6000 rpm. Chlorobenzene (120 \(\mu\text{L}\)) was deposited onto the spinning substrate 10 seconds before the end of the procedure. Films were annealed at 100 °C for 1 hour. Lead halide precursors were supplied by TCI, organic compounds were supplied by Greatcell Solar, CsI and solvents were supplied by Sigma.

The film was fabricated at a small fraction of \(\text{PbI}_2\) excess (8 wt. %), as it is known to suppress non-radiative recombination for mixed halide mixed cation compositions.\(^{[40,51]}\) The sample had been exposed to ambient laboratory air for previous characterization measurements for ~10 hours and was consistently contained within a nitrogen box between measurements. The CL and PL emissions were checked to match the PL emission reported for similar compositions prior to the experiment.

### 5.3.2 Acquisition of CL data in PM

A series of 30 CL maps were acquired at different regions on the perovskite film. CL mapping was performed as described in Chapter 3.1.5, with a CCD readout rate of 3 MHz, horizontal binning of 2 and \(x2\) signal amplification. CL maps were taken at various
5.3 The use of an electron beam in pulsed mode (PM)  

**Figure 5.11: CASINO simulation of the CL intensity over depth in the hybrid perovskite composition.** CASINO v2.51 was used to simulate where the CL signal originates across a sample thickness for two acceleration voltages: 3 and 6 keV. A beam radius of 5 nm and $10^5$ trajectories were simulated using the default simulation parameters. For the layered chemical composition, a 1,000 nm layer of density 4.16 g/cm$^3$ was used, using the triple-cation double halide perovskite composition (Atomic fractions: Cs: 0.0052, Pb: 0.3368, Br: 0.0584, I: 0.5260, C: 0.0183, N: 0.0394, and H: 0.0079). The peak CL emission is simulated to be at a sample depth of 20-25 and 60-65 nm for a 3 and 6 keV electron beam, respectively, three times larger. These values are consistent with the differences observed in the CL emission spectra at different beam energies. Reproduced from [249].

![Figure 5.11: CASINO simulation of the CL intensity over depth in the hybrid perovskite composition.](image)

acquisition conditions, ranging between 3 or 6 keV acceleration voltage, at various dwell times from 22 to 502 ms, and different rastering pixel sizes ranging from 25 to 250 nm. The CL interaction depth at 3 and 6 keV is estimated to be $\sim 100$ and $\sim 250$ nm, respectively, as shown in Figure 5.11. The electron beam current was modified from 62.5 pA to 10 nA in CW beam mode, or from 14 to 115 pA in PM.

CL maps were analysed in LumiSpy 0.1, following the protocol described earlier in this Chapter, which includes background subtraction, cosmic-ray removal, edge cropping and spectral calibration. Fitting the data enables the extraction of the emission shape parameters of the CL signal. Three Gaussian distributions, with a constant background offset, were used to fit CL data, following Equation 5.4, where each Gaussian represents one of the three peaks of interest in this work (the perovskite, the intermediate degradation phase and the PbI$_2$ peaks, shown in Figure 5.7). This equation was fitted to the spatially averaged CL spectra for each map acquired to create Figure 5.12. Similarly, the Gaussians were fitted to the CL maps, resulting in spatially-resolved fitted hyperspectral maps, as shown in Figure 5.13.
Figure 5.12: Optimization of the CL acquisition conditions for halide perovskite thin films. (a) The spatially averaged CL spectra for a series of CL maps taken at different beam modes (continuous line in CW, dashed line in PM), at different beam currents (darker colours represent higher currents), keeping all other parameters unchanged and the CL intensity normalized to the pixel dwell time. The PbI$_2$ and the perovskite peaks are visible, as well as an intermediate degradation broad peak. (b,c) Normalized CL peaks for the (b) PbI$_2$ and (c) perovskite peaks, with visible peak position shifts. (d-i) Correlation of the beam current in nA, the beam mode (CW in blue, PM in orange), and dwell time (from 22 to 502 ms from smaller to larger dots) concerning different emission peak parameters are shown. (d,e) The fitted central peak position $x_0$ of the PbI$_2$ and the perovskite peak, respectively. (f,g) The CL intensity ($I_{CL}$) for the PbI$_2$ and the perovskite fitted peaks, respectively. (h) The perovskite to PbI$_2$ CL intensity ratio correlated to pixel dwell time. (i) The intermediate degradation peak to the perovskite CL intensity ratio correlated to beam current. The asterisk (*) shows scans with long dwell times of 502 ms. Reproduced from [249].
5.3.3 Optimization of the conditions for CL

A series of 30 CL maps were taken at different positions of a hybrid perovskite film under various acquisition conditions. For each map, the spatially averaged CL spectrum was reported. Figure 5.12 shows how the mean emission spectra are affected by various acquisition parameters. Figure 5.12a shows a subset of the mean spectra acquired at beam currents ranging from 14 pA to 10 nA, with darker colours representing higher beam currents; and acquired at two different electron beam modes, continuous line for CW, dashed line for PM. The absolute CL intensity values were normalized by the acquisition dwell time of each scan and all the spectra in Figure 5.12a were acquired at the same pixel size of ∼120 nm.

In Figure 5.12a, three main peaks are observed: the main perovskite peak at 740-760 nm (1.68-1.63 eV),[40] a peak corresponding to PbI$_2$ at 507-518 nm (2.39-2.45 eV),[289] and a broad intermediate peak ranging between 650 and 740 nm (1.68-1.90 eV). The PbI$_2$ peak is primarily ascribed to the small fraction of PbI$_2$ excess during the fabrication of the film. The broad intermediate peak is referred to as the intermediate degradation phase, as it only becomes prominent in conjunction with electron beam illumination. For each peak, the quality of the CL signal was determined from the parameterized variables of fitting the Gaussian models on the mean emission spectra for each map. More specifically, the fitted central peak position ($x_0$) and peak intensity ($I_{CL}$) of the different emission peaks were taken as indicators for signal quality. These indicators were then correlated with the respective acquisition parameters at which each CL map was taken, such as beam current, beam mode, acceleration voltage, rastering pixel size, or dwell time, to mention a few. Some parameters were found to have a bigger effect on the CL signal quality than others. These are discussed in depth below.

Figure 5.12b-i shows the effect of the electron beam current, beam mode (either CW or PM), and dwell time, on the fitted peaks for each map. The perovskite and PbI$_2$ emission peaks are analysed separately, as the perovskite peak appears to be more sensitive to electron irradiation, while the PbI$_2$ peak remains largely unaffected upon continuous electron beam exposure of up to 90 seconds. Figure 5.12c,e show that the perovskite peak position $x_0$ is dependent on the electron beam current (ranging between 14 pA to 10 nA) and the beam mode (blue for CW and orange for PM). Larger spreads of the values of the perovskite peak positions are observed under CW mode when other parameters such as pixel size or dwell time are changed. For example, marked in Figure 5.12e, we observe a spread of $x_0$ of 75± 10 nm (~50 meV) at 250 pA in CW, while at similarly low-current conditions of 115 pA in PM, a spread of $x_0$ shifts of 75± 3 nm (~10 meV) is measured.
At comparable currents, we find that PM allows for a more robust CL detection for the perovskite peak.

Figure 5.12c shows a small blue-shift of a few nanometers (∼10 meV) between the perovskite peak emission in CW and PM. Blue shifts at higher currents may be explained by the formation of beam-induced defects and by the Burstein-Moss effect, in which large charge carrier populations can saturate the band edge and populate higher vibrational energy states of the conduction band.\textsuperscript{[147,151,153,290]} At 115 pA and 6 keV, charge carrier concentrations in PM are estimated to reach concentrations as large as \( \sim 10^{18} \) e\(^-\)-h\(^+\)-pairs cm\(^-3\), assuming a cubic interaction volume of 200 nm depth (see Figure 5.11). The pulsed nature of the beam would allow carriers to relax, if the time delay between each electron pulse is larger than the charge-carrier relaxation time, resulting in lower blue shifts than in CW mode. Figure 5.13b, discussed later, is in agreement with this observation of blue shifts, with spatially averaged perovskite peak emission at 746-749 nm (1.66 eV) in CW compared to 752 nm (1.65 eV) in PM.

Figure 5.12g shows the effect of the perovskite peak intensity \( (I_{CL}) \) as a function of beam current and beam mode. For the perovskite peak, we find that PM acquisition can achieve CL intensities as large as those achieved in CW with twice the amount of current (250 pA in CW and 115 pA in PM). However, only low beam currents can be accessed in PM, which strongly limits the intensity of the CL signal.

The analysis of the PbI\(_2\) peak shows different trends, in which most of the observations seen for the beam-sensitive perovskite peak are not applicable. Figure 5.12b,d show a narrow spread of the peak position \( x_0 \) under both CW and PM, in the range of 3 nm (10 meV), when other parameters such as pixel size or dwell time are changed. A red shift of the PbI\(_2\) peak from 508-510 nm to 512-517 nm (2.43-2.44 to 2.40-2.42 eV) is observed when the largest beam current of 10 nA is used. This small red shift may be explained by the pre-existing PbI\(_2\) crystallites in the film growing thicker under excessive electron irradiation, as PbI\(_2\) single crystals show thickness-dependent photoluminescence.\textsuperscript{[289]} PbI\(_2\) degradation can also result in the creation of defects and peak shifts, consistent with these observations.\textsuperscript{[291,292]} For currents of 1 nA and lower, such red-shifted emission is not observed. Hence, PbI\(_2\) is a more stable phase and it is not as susceptible to beam damage as the perovskite phase. Figure 5.12f shows the peak intensity increasing proportionally to the used current. The PbI\(_2\) CL emission acquisition does not benefit from using PM in the same way the perovskite phase does.
5.3 The use of an electron beam in pulsed mode (PM)

5.3.4 Electron-beam induced degradation in PM

Given the relative stability of the PbI$_2$ peak, its intensity can be used as a reference from which to compare the perovskite peak intensity for each acquisition condition. In a pristine specimen, the ratio between the perovskite and the PbI$_2$ peak intensities (perovskite:PbI$_2$ ratio) is expected to be larger than 1 as the perovskite peak dominates. The ratio can decrease due to electron beam irradiation, and this can be taken as a measure of beam damage. Figure 5.12h shows that the perovskite:PbI$_2$ ratio is strongly related to the dwell time and the beam mode. At dwell times of 52 ms the perovskite:PbI$_2$ ratio is one order of magnitude larger for PM than for CW, and this suggests that PM is significantly better at preserving the pristine perovskite phase. However, at extremely low-current conditions, especially in PM, longer dwell times are required to acquire signal-to-noise ratios (SNR) sufficient to discern the background from the signal at each pixel. Longer beam exposures appear to enhance the degradation effect on the perovskite, as seen at larger dwell times of 102 or 502 ms in Figure 5.12h. A compromise between beam current and dwell time is thus needed to minimize the changes in the perovskite peak.

Another interesting feature is the intermediate degradation phase peak, which can be fitted with a broad Gaussian between 650 and 740 nm (1.68-1.90 eV). A ratio between the perovskite and the intermediate degradation peak intensities can be calculated (intermediate:perovskite ratio) as the former appears as the latter decays. The lower this ratio, the more pristine the perovskite. Figure 5.12i shows how the intermediate:perovskite ratio is affected as the beam current increases and as CW or PM is used. The degradation intermediate phase is more prominent when high beam currents above 1 nA are used in CW mode, as seen from the ratio increase by one to two orders of magnitude than when lower currents are used. Both for low CW currents of 62.5 and 250 pA, and PM, the degradation peak is low in intensity. Long dwell times in PM are correlated with the appearance of this degradation phase, marked with an asterisk on the figure. The combination of beam current and dwell time is thus affecting the appearance of the intermediate degradation phase.

The appearance of higher energy emission features than the perovskite phase is in agreement with other works studying electron beam damage.\[\text{[118,293,294]}\] While the nature of the intermediate degradation phase cannot be conclusively assigned from this CL analysis alone, it can be attributed to a series of factors:

- The low activation energy of halide-related defects enhances the vulnerability of these materials to beam-induced degradation,\[\text{[63,117]}\] which results in a broad distribution of trap states that can be optically active and detectable if present in large densities. However, defects can also lead to redshifts.
High-energy electron radiation effects on the optics: CL-SEM

- The loss of the more volatile iodine species due to electron beam irradiation could also result in the observed blue shifts. According to the experimental perovskite composition library explored by Bush et al. [101], the ratio of Br:I of 0.2:0.8 and 0.1:0.9 are reported to be at the wavelength range of 735-750 nm (1.65-1.68 eV) and 774-800 nm (1.55-1.60 eV), respectively, if the ratio of Cs:FA is kept constant at 0.2:0.8.
- Halide demixing across films has been reported after light soaking or device operation, showing facile halide redistribution between the surface and interface. [283,295,296]
- The formation of beam-induced small nanoscale crystallites could also result in a distribution of blue-shifted emission due to confinement effects. [297]
- Electron beam-driven amorphization of the perovskite phase can result in blue-shifted emission, with high-energy emission peaks observed from pressure-induced amorphization. [298]

Other acquisition parameters were found to have a smaller effect on the CL signal quality, such as electron beam energy. The effect of acceleration voltage is consistent with previous studies, [150,151,299,300] in which lower acceleration voltages probe the optical properties at the surface while at higher beam energies the bulk is probed, which can emit differently than the surface. Photons generated deeper in the bulk can also be absorbed by the perovskite layer and not contribute to the collected CL intensity. In general, beam damage is more sensitive to increasing beam current than to acceleration voltage at low and high voltage. [294] Finally, it is good to note that even though low electron-beam currents are used in these experiments (as low as 14 pA), the estimated electron fluence during CL scans can reach values of $10^{8-12}$ e$^{-}$ Å$^{-2}$ at the surface of the sample. These values only take into account the beam current $I$, the dwell time $t$, and the pixel area at the surface of the sample during beam rastering $S$, as:

$$\text{Fluence per pixel (e}^{-}\text{Å}^{-2}) = I(Cs^{-1}) \times 1C \times t(s) \times 1/S(Å^{-2}) \quad (5.7)$$

and ignore the fact that the radiation is then distributed throughout the much larger interaction volume of SEM (see Equation 3.14). These values, although not accurate, are orders of magnitude larger compared to the 10s to 100s e$^{-}$ Å$^{-2}$ in 4D-STEM methods and show the difficulties in comparing fluence and degradation mechanisms between SEM and TEM techniques.

5.3.5 **Spatially resolved CL in PM**

When PM is used, the beam current and dwell time need to be carefully adjusted in order to obtain sufficient SNR while maintaining the perovskite emission. We find that
5.3 The use of an electron beam in pulsed mode (PM)

Figure 5.13: Heterogeneity of CL emission of halide perovskite thin films under improving acquisition conditions. (a,b) The fitted Gaussian parameters for the perovskite peak from the CL maps, acquired from suboptimal at the top towards more optimized conditions at the bottom (the first three rows are taken in CW mode and the last row in PM). (c) The intermediate degradation phase peak to perovskite peak CL intensity ratio, a measure of beam damage, with (d) the histogram distribution. The mean values are reported on the top left for each map. Reproduced from [249].

>115 pA and < 50 ms, under the experimental conditions and samples reported here, gives the best results for the triple-cation double-halide composition. We now test how these parameters perform in spatially-resolved CL mapping. We use SEM CL to map the nanoscale heterogeneity of perovskite polycrystalline films. Figure 5.13 shows a series of CL maps for the fitted perovskite peak taken at different positions on the same perovskite film. The perovskite peak emission changes for spatially resolved CL maps as a function of acquisition conditions. We observe a gradual modification of the perovskite peak quality, measured in terms of the fitted Gaussian position $x_0$ (Figure 5.13a), and peak full-width half-maximum (FWHM, Figure 5.13b), as a function of beam current. In general, the CL maps acquired at higher currents show more heterogeneous distributions of the perovskite
peak features. Figure 5.13c shows a lower intermediate:perovskite intensity ratio for lower beam currents, suggesting a more pristine perovskite emission due to a reduction in beam damage and more homogeneous charge carrier recombination pathways. The least significant beam damage is recorded under PM, at a mean intermediate:perovskite ratio of 0.18. Figure 5.13d shows the histograms of the pixel distribution of this ratio. In PM, longer pixel dwell times, twice as long as in CW mode (from 22.28 ms in CW to 52.28 ms in PM), were used. These dwell times were short enough, within the threshold shown in Figure 5.12h, to result in no increment of beam damage. The use of even lower currents, such as 14 or 33 pA, resulted in reduced signal quality if dwell times of 52 ms were used, which complicated spectral fitting on a per-pixel basis.

The switch from CW to a PM electron beam under similar low-current conditions of 62.5 and 250 pA in CW and 115 pA in PM, reveals a further improvement in data acquisition in terms of peak consistency. Figure 5.13b shows a reduction in the FWHM magnitude and a more homogeneous distribution for the PM than in CW mode. Similarly, Figure 5.13a shows a more homogeneous peak position distribution for PM.

5.3.6 PL emission after PM CL

To investigate how the scanning beam in PM affected the perovskite films, correlative PL mapping was performed before and after CL. Figure 5.14a shows BF images taken before and after the CL maps, with no apparent surface morphology changes (in contrast to when CW mode is used, shown in Figure 5.17a,e). The PL panchromatic images, acquired under 10-sun equivalent laser illumination, show for the perovskite peak at ~780 nm that the sample after CL is as emissive as before CL mapping. The average PL spectra for the whole region are shown in Figure 5.17c in black, with a dashed line for the PL emission acquired before CL, and with a continuous line for the PL after CL. At closer inspection, three regions exhibit a blue-shifted shoulder in the PL emission, at ~740 nm (marked in red, green, and blue). These regions are where CL maps were acquired. In particular, here the CL maps were acquired in PM at 6 keV, 55 pA, 100 ms dwell time per pixel, and scanning 64x 64 and 128x 128 px at FOV of 10 and 15 µm, respectively. The blue-shifted shoulder is more prominent for the CL maps acquired at higher magnification (FOV of 10 µm). Figure 5.17d shows these regions as a superimposed bandpass-filtered PL image, containing bands for the blue-shifted shoulder (in blue) and the normal perovskite emission (in red). While perovskite emission is still present in the regions exposed to the electron beam during CL, the emission in such regions is dominated by the blue shoulder. These results are in agreement with the CL blue-shifted shoulder peak observed in Figure 5.12, attributed to halide redistribution or sample amorphisation.
5.3 The use of an electron beam in pulsed mode (PM)

Figure 5.14: PL emission after PM CL scans. Comparison of PL emission features before and after CL-SEM data acquisition in PM. (a) BF images of before (top) and after (bottom), taken with wide-field white illumination. (b) PL panchromatic image at 10-sun equivalent laser illumination before (top) and after (bottom). While the sample after CL is as emissive as before, 3 regions where CL maps were acquired are visible. (c) The average PL spectrum for the whole region is coloured in black (dashed for before CL acquisition, continuous for PL after CL acquisition). PL emission of the 3 regions, marked in red, green, and blue, exhibit degraded PL emission. (d) This is visible in the superimposed bandpass-filtered PL images for blue-shifted (in blue) and normal emission (in red). The CL maps, visible in the panchromatic PL images, were acquired at 6 keV, in PM at 55 pA, 100 ms dwell time per pixel, and 64x64 and 128x128 px at FOVs of 10 and 15 µm, respectively. Sample: Triple-cation double-halide solution-processed film (200 nm) on ITO (from Satyawan Nagane). PL maps acquired under 10-sun illumination, dwell time of 1 second, x100 objective.

It should be noted that when higher electron currents are used in similar compositions (double-cation as opposed to triple-cation) in CW mode, the PL emission after CL shows features that can be correlated with morphological changes at the surface, complete quenching of the perovskite emission, and red-shifted emission. This is discussed in a later Section in this Chapter (see Figure 5.17).

5.3.7 The potential of PM in CL-SEM

Figure 5.12 and Figure 5.13 show a more efficient data acquisition of the perovskite emission when a PM electron beam is implemented. Given a CW and a PM electron beam at
the same beam current, the PM beam produces short pulses of higher electron currents while the CW produces a constant flux of lower electron currents, both resulting in the same effective current. The higher excitation density in PM can produce larger densities of charge carriers which could saturate non-radiative recombination sites and lead to overall stronger emission. In CW mode, if currents are too low, the non-radiative recombination sites may never be saturated and a smaller fraction of recombination would be radiative. It is therefore the nature of a pulsed beam that allows for a more efficient CL acquisition. These mechanisms may not apply to materials with longer lifetimes, as charge carriers would remain excited for a longer time and the PM would give similar effects as the CW beam.

The use of PM unlocks the use of SEM CL on beam-sensitive hybrid perovskite materials and enables the acquisition of hyperspectral maps with high spatial resolution more robustly. CL can thus be used to explore the heterogeneity of optical properties at the nanoscale, at smaller length scales than photoluminescence. However, after scrupulous optimization of the acquisition conditions, CL still exhibits features related to beam damage. It must be noted that we have mainly analysed the effect of beam current, dwell time and beam mode, yet other parameters can be further investigated. For example, it was shown that temperatures as low as 80 K can hinder the formation of intermediate degradation high-energy peaks in mono-cation mono-halide perovskite compositions.\[147\] The modification of the pulse rate in PM electron beams may also further improve the CL acquisition for beam-sensitive materials, as longer separations between the pulses may allow the beam-sensitive material to fully relax electronically and thermally. These additional parameters should be further researched in future studies.

5.4 Applications of CL-SEM

This Section exemplifies how CL can probe optical properties that would be too difficult to study using optical microscopy.

5.4.1 Cross-sectional TEM samples of solar cell devices are emissive

The higher spatial resolution that CL can achieve compared to PL is used here to examine the structural quality of perovskite solar cell lamellae prepared by FIB milling via CL emission analysis (which could have not been spectrally resolved using optical microscopies). Cross-sectional transmission electron microscopy has been widely used to investigate organic-inorganic hybrid halide perovskite-based optoelectronic devices. Due to the
multi-layered nature of optoelectronic devices, electron-transparent specimens (lamellae) need to be prepared, often using Ga\(^+\) focused ion beam (FIB) milling.\(^{130,132,301}\) However, the suitability of FIB milling for specimen preparation of beam-sensitive halide perovskite has been questioned due to the expected Ga\(^+\) beam-induced heating and irreversible surface amorphisation through the accumulation of defects created by ion collision cascades.\(^{141,302,303}\) Therefore, FIB-induced modifications to halide perovskite lamellae need to be understood to guide future characterization work performed on them and determine the validity of those in the literature.

The structural integrity of perovskite in FIB milled lamellae can be probed by observing its radiative emission as the intensity and energy of perovskite luminescence are dependent on its crystal structure. Briefly, several groups have shown that applying compressive pressure to various halide perovskites induces gradual amorphisation. This causes a continuous reduction in photoluminescence and a band gap widening of \(\sim 0.2\) eV until emission is eventually eliminated by strong non-radiative recombination in the fully amorphous state.\(^{298,304,305}\) The band gap widening was found to be caused by suppression of atomic orbital overlap due to pressure-induced breaking of long-range order in the perovskite lattice.\(^{298}\) Interestingly, the original crystallinity and luminescence were largely recovered when the pressure was relaxed. The observed relationship between perovskite structure and luminescence means the latter can be used as a proxy to examine the former. This link between the two properties is valuable to assess the suitability of FIB milling since amorphisation is the primary form of damage suspected in FIB-milled perovskite lamellae due to ion collisions. A perovskite lamella producing an emission peak that is centred at the same energy as the emission of its parent device can be taken as a sign that the crystalline structure of the perovskites in the lamella is not amorphised by FIB milling. A lamella with a partially amorphised perovskite layer is expected to exhibit a broadened and blue-shifted luminescence peak relative to its parent device. Finally, an absence of emission is considered a manifestation of complete perovskite amorphisation.

A triple-cation, double-halide perovskite half-cell with a stack of glass/ITO/NiO/Cs\(_{0.05}\)FA\(_{0.81}\)MA\(_{0.14}\)Pb(I\(_{0.9}\)Br\(_{0.1}\))\(_3\) was fabricated. Top-view PL and CL data were acquired from the half-cell as reference points to evaluate the perovskite emission. A peak emission at 1.596\(\pm\) 0.002 eV (777 nm) and 1.612\(\pm\) 0.004 eV (769 nm) were observed for PL and CL, respectively (Figure 5.15a red and orange curves). The small blue shift from PL to CL and the high-energy tail seen in the CL spectrum are often observed in the literature, with both usually attributed to the filling of higher energy states by the higher concentration of excited carriers in CL.\(^{149,153,290}\) We fabricated a full-cell device with a PCBM/BCP electron transport layer and gold electrode, then cut a 200 nm-thick lamella using a Ga\(^+\)
Figure 5.15: Optical emission from a PSC cross-section. (a) Normalised perovskite emission spectra from (red) top-view PL, (orange) top-view CL, (green) first cross-sectional CL scan, and (blue) second cross-sectional CL scan. As the signal-to-noise ratio for the second cross-sectional CL scan is relatively low, normalization was performed on the Gaussian fit (blue line) rather than on the data points. The bottom panel shows the absolute CL signal for the two cross-sectional CL scans, the first being brighter than the second. (b) SE image of the PSC lamella. The perovskite emission characteristics (peak position $E_0$, and peak area $I_{CL}$) from the (c) first and (d) second cross-sectional CL scans of the PSC lamella. The PbI$_2$ emission characteristics ($E_0$ and $I_{CL}$) from the (e) first and (f) second cross-sectional CL scans of the PSC lamella. Dashed red lines mark the position of the perovskite layer. Reproduced from [256].

FIB. This lamella thickness has previously been identified as the ideal value for TEM characterisation of FIB milled perovskite device cross-sections by Jeangros et al. [132] This lamella was attached to a TEM grid and immediately transferred to the CL instrument, limiting air exposure to <5 minutes to prevent environmental degradation. The CL data was then post-processed and fitted with a Gaussian model in LumiSpy. Further details on the FIB milling procedure can be found in [256].

Figure 5.15b shows a secondary electron image of the lamella, acquired with a beam acceleration voltage of 5 keV. Figure 5.15c shows the fitted peak centre energy ($E_0$) and integrated peak area of the perovskite emission ($I_{CL}$) for the first CL scan. The interaction volume generated by the 5 keV electrons spans the entire 200 nm thickness of the lamella (Figure 5.11) This suggests that the CL emission emerges from the entire lamella thickness, with the top half contributing approximately two-thirds of the total intensity.
Figure 5.15a (green curve) and 5.15c show that the perovskite layer in the FIB milled lamella is luminescent, suggesting that the crystal structure is mostly preserved. Its emission is centred at $1.688 \pm 0.004 \text{ eV}$ (734 nm) with a full width at half maximum (FWHM) of $0.185 \pm 0.006 \text{ eV}$, blue-shifted by $0.076 \pm 0.006 \text{ eV}$ (35 nm) and broadened by $0.078 \pm 0.008 \text{ eV}$ compared to the top-view CL spectrum (FWHM = $0.107 \pm 0.006 \text{ eV}$, the orange curve in Figure 5.15a). The blue-shifted and broadened perovskite emission indicates that only a fraction of the perovskite, most likely the closest to the top and bottom surfaces of the lamella, is amorphised by the Ga$^+$ beam. While the emission data do not directly provide structural information, amorphisation is the most common type of specimen damage in Ga$^+$ FIB milling, especially for semiconductors,\textsuperscript{[306–309]} and it is also consistent with the observation of blue-shifted emission from amorphised perovskite as described above. This amorphisation is due to defect accumulation, thus it and the consequent emission blue-shift are irreversible, in contrast to the reversible pressure-induced amorphisation.\textsuperscript{[298,304,305]} In addition, a small extent of iodine volatilisation, which could be anticipated as it is more volatile than bromine, may also contribute to the blue-shift.\textsuperscript{[196]}

While it is established that a Ga$^+$ beam induces amorphisation, the low-keV electron beam can also cause specimen damage. Therefore, it is of interest to know whether the observed changes in emission are solely caused by the Ga$^+$ beam or by the CL electron beam as well. The effect of the CL electron beam on lamellae cannot be properly assessed by comparing the PL and top-view CL spectra because of the different nature of bulk specimens and thin lamellae. For example, the higher specific surface area of a lamella likely accelerates the loss of volatile molecules, a known beam damage mechanism in hybrid halide perovskites.\textsuperscript{[140,142]} To obtain an estimate of the effect of the CL electron beam on the lamella, we performed another CL scan on the same lamella and extracted its fitted emission parameters (Figure 5.15d) and average spectrum (Figure 5.15a blue dots). The perovskite layer was barely optically active after this second scan, with its emission weakened by a factor of eight, broadened (FWHM = $0.213 \pm 0.006 \text{ eV}$), and further blue-shifted by $0.110 \pm 0.006 \text{ eV}$ (44 nm) compared to the first scan. These results suggest that the CL electron beam contributes to perovskite amorphisation, in good agreement with previous studies which observed CL emission darkening and blue-shifting by 0.10-0.25 eV after exposure to an electron beam.\textsuperscript{[118,147,293]} Therefore, the $0.076 \pm 0.006 \text{ eV}$ blue-shift observed between the top-view CL and first cross-sectional CL spectra was likely caused by both the Ga$^+$ beam and the CL electron beam.

In addition, we observe PbI$_2$ emission (2.41-2.46 eV) only from a small number of isolated areas in the perovskite layer in both cross-sectional CL scans (Figure 5.15e$^-$f). PbI$_2$ has previously been identified as a product of beam damage-induced perovskite
decomposition,[147] and in Chapter 4. However, the perovskite films were deposited with a 4% excess of PbI$_2$, a more likely source of the PbI$_2$ emission observed, as opposed to Ga$^+$ beam-induced perovskite decomposition. Moreover, after the second CL scan, no additional PbI$_2$ is observed.

In conclusion, this subsection shows that a typical FIB-milled PSC lamella remains optically active, albeit with a slightly blue-shifted luminescence compared to its top-view CL emission. This blue shift supports the idea that PSC lamellae do not perfectly represent their parent device in terms of radiative emission. However, the extant luminescence and limited PbI$_2$ emission indicate that the perovskite structure and composition are in large part preserved. Hence, useful information can be obtained from electron microscopy studies of FIB-milled perovskite-based device lamellae as long as the electron dose is minimised and beam-induced damage is carefully considered. For example, investigations of device morphology, compositional heterogeneity, or comparative studies of multiple lamellae prepared with identical FIB milling parameters are fruitful methods of device characterization by transmission electron microscopy. These insights were only possible due to the higher spatial resolution of CL compared to other optical microscopies like PL.

### 5.4.2 Compositional mapping of optical phases

Another common application for CL is to spatially map different emissive (or lack of emissive) phases in a specimen. This is illustrated in Figure 5.16, where phase mapping was done on ∼120-nm-thick 3-dimensional triple-cation lead iodide perovskite films (Cs$_{0.05}$FA$_{0.17}$MA$_{0.78}$PbI$_3$ with 5% excess PbI$_2$) with an increasing amounts of surface additive. The additive, an iso-butylammonium iodide solution in IPA which contains a bulky organocation, can convert the surface of the 3D perovskite phase into a combination of 2D-Ruddlesden-Popper perovskite phases with varying emissions (see Table 5.2). The addition of these additives is known to achieve surface defect passivation, by reducing the defects at the surface and suppressing non-radiative recombination.\[310–312\] In particular, the open-circuit voltage of solar cells, which is strongly related to the recombination of defects in the surface of the perovskite layer, can be improved by the addition of a passivation layer at the surface.\[313\] While other surface passivation strategies exist, such as adding an excess PbI$_2$ or using molecular organic agents,\[55,58\] here we used CL to study the effect that the additive has on growing a thin layer of lower-dimensional perovskite from the 3-dimensional perovskite. CL maps were acquired at 3 keV, in PM, at a beam current 50-100 pA, and dwell time of 50 ms per pixel for 128x 128 scans at 56-μm FOV, a lower magnification than most other CL studies in this Chapter, due to the beam-sensitive nature of the sample.
5.4 Applications of CL-SEM

Figure 5.16: Phase mapping using CL. Phase mapping of a series of 3-dimensional triple-cation lead iodide perovskite films with an increasing amount of additive that convert it to 2D perovskite: (a) 1 mol% additive, (b) 5 mol% additive, and (c) 10 mol% additive. From left to right: mean CL emission spectra with the bandpass filter ranges in colour bands. The inset shows weak 2-dimensional emission at $\sim 570$ nm. SE images are shown together with 5 different bandpass-filtered images. Each colour corresponds to a perovskite phase, as listed in Table 5.2 Sample: Triple-cation lead iodine solution-processed film (120 nm) on glass/ITO with increasing isobutyl ammonium additive at the surface, which forms a 2D-Ruddlesden-Popper thin layer (from Amita Ummadisingu). CL maps were acquired at 3 keV, in PM, beam current 50-100 pA, and dwell time of 50 ms per pixel for 128x 128 scans at 56-$\mu$m FOV. SE images were acquired before each map at 1025 px and 10 $\mu$s dwell time.

SE images were acquired before each map at 1025 px and 10 $\mu$s dwell time. Figure 5.16a-c corresponds to 1 mol%, 5 mol%, and 10 mol% additive, respectively. Depending on the quantity of additive added, different phases are seen in the mean CL emission spectra. Bandpass filters are created for each possible phase, shown as colour bands. Some 2-dimensional phases are bright, while others are not present in large quantities and their emission is only observed in the inset (e.g. for 1 mol% weak 2-dimensional emission at $\sim 570$ nm is present). Due to the scanning nature of CL-SEM, spatially resolved information can also be obtained. SE images show roughening of the surface as more additive is added, creating 5-$\mu$m-sized star-shaped crystallites for the 10 mol% A series of 5 different bandpass-filtered images are also shown, each colour corresponding to a different lower-dimensional perovskite phase, listed in Table 5.2.

The more additives added, the bluer the CL emission becomes. The bandpass-filtered CL maps reveal some trends. At 1 mol% additive, most emission is still observed from the 3D phase (n= inf) at 750± 50 nm. However, some 2D phases are weakly emitting.
Table 5.2: Band gap energies for the different 2D perovskite phases, and for the 3D phase \((n = \text{inf})\), for triple-cation lead iodide compositions.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Energy (eV)</th>
<th>Wavelength (nm)</th>
<th>Bandpass filter colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{PbI}_2)</td>
<td>2.3-2.4</td>
<td>505</td>
<td>Purple</td>
</tr>
<tr>
<td>(n = 1)</td>
<td>2.36</td>
<td>525 (overlap with (\text{PbI}_2))</td>
<td>Purple</td>
</tr>
<tr>
<td>(n = 2)</td>
<td>2.15</td>
<td>576</td>
<td>Blue</td>
</tr>
<tr>
<td>(n = 3)</td>
<td>2</td>
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<td>(n = \text{inf})</td>
<td>1.58</td>
<td>755/760</td>
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</tbody>
</table>

The \(n = 3\) and \(n = 4\) phases (emitting at 653± 15 nm and 620± 20 nm, respectively) are heterogeneously distributed at the surface of the 3D phase, forming partial coverage and nano-sized granulates. When the additive is increased to 5 mol%, apart from the 3D phase, the emission is dominated by \(n = 4\) and \(n = 3\). Such phases now cover most of the surface and are more homogenous across the film. Some \(n = 2\) emission (at 576± 20 nm) is also observed at regions where the SE image shows a height contrast. Finally, when the 10 mol% additive is used, the 3D perovskite emission is not visible, possibly due to the transformation of the surface from 3D to 2D phases. At 3 keV, the interaction depth for CL is estimated to be <150 nm for 99% of emission, suggesting that the thickness of the 2D layer formed should be 150 nm or thicker. While weak emission is still observed for \(n = 3\) and \(n = 4\), the CL signal is dominated by the \(n = 2\) phase and a sharp peak at 510± 25 nm. Such two main phases are anti-correlated, with the 5-µm-sized star-shaped crystallites emitting at 510 nm. Such emission was first thought to be the \(n = 1\) phase (at 525 nm). However, the emission peak maximum is closer to the 505 nm \(\text{PbI}_2\) emission, suggesting that an excessive amount of additive may destabilize the perovskite phase and precipitate into the \(\text{PbI}_2\) precursor as crystallites, which form crystallites with sharp facets. \[55,224\] The insights provided by phase mapping using CL allow for a spatially-resolved understanding of the effects that the additive has on the growth and transformation from 3D to 2D perovskite phases. This is important for PSC passivation, as 2D layers at the surface can improve the efficiency of solar cells and extend the lifetime of perovskite-based devices. \[313\]

### 5.4.3 Correlation of CL with PL

In order to elucidate the effect of the scanning beam on the double-cation double-halide perovskite thin films, correlative hyperspectral CL and PL scans were acquired on perovskite films after both CW and PM. Results for the post-CL emission after PM was acquired using PL and already discussed in Section 5.3.6 and in Figure 5.14. After scanning in PM, the PL emission showed a blue-shifted emission shoulder apart from the bright
Figure 5.17: PL emission after CL scans. Comparison of PL emission features after CL-SEM data acquisition. (a) BF image was taken with wide-field white illumination. (b) PL panchromatic image at 1-sun equivalent laser illumination. The inset in panel a shows the average PL spectrum (black), and the emission from two regions of interest. These regions are marked as A (red) for the CL-scanned area, and roi B (blue) for a pristine region. (c-d) Spatially resolved maps (10 µm x 10 µm) for the Gaussian-fitted PL features for a region near the pristine and the CL beam-damaged region. (e) Comparison between the surface damage between a CL map after CW mode in red, and after PM in green. (f) CL spectrum of the same sample as in PL. (g) Spatially resolved maps for the Gaussian-fitted CL features for the same sample seen in PL. Sample: Double-cation double halide evaporated film (200 nm) on SiN TEM grid (from Yu-Hsien Chiang). PL maps acquired under 1 sun illumination, dwell time of 2 seconds, x100 objective. CL maps acquired at 6 keV in CW, 1 nA, 170 ms dwell time per pixel, 128x128 px.

perovskite emission. No surface morphology changes were reported. Now, we look at damages as seen from PL when more electron-scanning intensive conditions are used, namely in CW mode.

Hyperspectral PL scans were acquired from thermally-evaporated films on the SiN TEM grid after CL measurements in CW. Figure 5.17a shows the averaged intensity of the entire scanning area (2 µm x 3 µm) and the emission of two regions of interest (ROIs) A (in red), which comprises a region which had been scanned by the electron beam in CL measurements, and B (in blue), which is sampled from a pristine region which was never scanned by the electron beam. The pristine region B emits at wavelengths of 760-765
nm (1.62-1.63 eV), while the main peak at the beam-damaged region A is red-shifted at 780-785 nm (1.57-1.58 eV) and is three times less intense. The electron beam damage can cause elemental ion migration at the scanned region, modifying the stoichiometry and hence the band gap of the material due to halide segregation. Such ion migration leads to lower bandgap iodide-rich sites onto which carriers funnel. Damage to the organics can also result in a redshift.

It is important to note that, unlike in the PM study described in this Chapter (Figure 5.14), here significantly higher electron currents were used, to ensure degradation. The degradation was so extreme that the SE images after CL showed milling of the surface material, induced by the electron beam (Figure 5.17e, red square), suggesting that the original surface is no longer being probed. Such surface milling is not observed when PM is used, as shown in the green square and Figure 5.14a. Moreover, the post-CL emission from PL after PM did not show as much quenching of the main perovskite emission as when CW mode was used.

The PL panchromatic image, acquired under 1-sun equivalent laser illumination, in Figure 5.17b shows a less-emissive rectangular area at the centre, corresponding to the scanned region in CL. The spatially resolved maps in Figure 5.17c-d show the fitted Gaussian data for PL, for both a pristine region and a region partially damaged by the electron beam. The same fitting model was used and the spatially-resolved descriptors $x_0$ and $I_{CL}$ height are shown. For the region damaged by the electron beam, two areas can be delimited, with a boundary which gradually shifts the main peak wavelength from 760 to 785 nm (1.62 to 1.58 eV). The FWHM at the boundary is the largest, as a coexistence of both peaks exists. For the pristine region, despite a homogeneous single emission of $\sim$760 nm (1.63 eV) is observed, some highly-emissive grain-like regions of 1-2 $\mu$m size are found across the whole surface, emitting at 770 nm (1.61 eV). These grains are also observed in CL, as a result of some heterogeneity of evaporation. This heterogeneity could be caused by degradation from contact with air or from inhomogeneous evaporation during sample deposition.

The PL experimental results reported in Figure 5.17a are in agreement with the reported bandgaps. However, a mismatch in the central wavelength of emission between CL and PL is observed, shown in Figure 5.17f. A central peak emission of $x_0= 730$ nm (1.72 eV) is observed for CL, against the $x_0= 785$ nm (1.58 eV) for PL. Using the same fitting model as for PL, the spatially-resolved descriptors $x_0$ and $I_{CL}$ for the CL data in Figure 5.17g can resolve the small red-shifted grains to a higher extent than PL. This exemplifies the potential of CL, as an extension of PL.
Figure 5.18: PL and CL lengthscales. Comparison of the lengthscales that wide-field hyperspectral PL (simply referred to as PL in this thesis), confocal PL, and CL can probe. On the right, an overlay with all the PL maps and the CL maps. The respective mean CL spectra for each map are shown, each one acquired at different magnifications. CL can probe significantly larger lengthscales than PL while still obtaining large SNR. Sample: Triple-cation double halide solution-processed film (500 nm) on glass/ITO (from Satyawan Nagane). CL maps were acquired at 6 keV, in PM, beam current <115 pA, and dwell time of 94 or 174 ms per pixel for 128x 128 and 64x 64 px scans, respectively.

The mismatch between PL and CL emissions is commonly attributed to the blue shifts caused by the Burstein-Moss effect.\textsuperscript{[147,151,153,290]} At higher excitation currents, such as in CL, large charge carrier populations can saturate the band edge and populate higher vibrational energy states of the conduction band. This results in blue-shifted emission. Other factors like the interaction volume and certainly the more destructive nature of CL compared to PL, can also explain the mismatch between PL and CL emission.

Finally, Figure 5.18 shows the resolution (mis)match between the optical microscope techniques and CL. Wide-field hyperspectral PL can resolve FOVs in the order of \( \sim 60 \mu m \) when x100 objective is used. Confocal PL microscopy can push the magnification higher, to a FOV of \( \sim 30 \mu m \). CL can resolve a FOV of \( \sim 3 \mu m \) with good SNR. On the right of Figure 5.18, an overlay of all the PL maps and the CL maps is shown. The respective mean CL spectra for each map, each at different magnifications, show that CL can still probe significantly larger lengthscales than PL with good SNR luminescence signals. When both techniques are correlated, it is hard to locate common grains due to the mismatch of the pixel sizes between techniques.
Figure 5.19: CL-4D-STEM correlation. The CL maps were acquired in the same area as 4D-STEM. (a) SE image acquired during CL mapping. Although the perovskite emission in (c) had degraded (either due to exposure to air for 5 min (pre-STEM) + 5 min (post-STEM) + 5 min (pre-CL) or due to 4D-STEM electron exposure), the band-pass filtered emission in (b) for PbI$_2$ is visible. (d) Correlation with the diffraction data on the bright CL regions can be indexed to the [001] zone axis for PbI$_2$. Sample: Evaporated 100-nm perovskite double-cation double-halide (PbI$_2$ rich) on a 30-nm SiN grid (from Yu-Hsien Chiang). CL map acquisition in CW, 3 keV, $\sim$62.5 pA, 100 ms dwell time. 4D-STEM acquisition at normal SED conditions, described in Chapter 3.

5.4.4 Correlation of CL with TEM-based techniques

CL has a higher spatial resolution, thus it is better suited for comparisons with the length-scales that TEM-based techniques can probe. Figure 5.19 shows the correlation between a CL map and a 4D-STEM dataset in SED mode. SED was performed prior to CL mapping, and the perovskite emission (seen with a bandpass filter of 665±50 nm) was found to be relatively weak, particularly in the area where SED was scanned (Figure 5.19c). However, the sample is likely to have degraded (double-cation double-halide compositions emit at $\sim$760 nm), due to exposure to air during the one-day interval between the acquisition with the two techniques.

Despite the degraded perovskite phase, these perovskite films were deposited with an excess of PbI$_2$. PbI$_2$ cannot be resolved in PL mode, owing to the excitation laser wavelength being too close to the band edge. Conversely, it exhibits strong luminescence in CL and can be resolved (see Figure 5.19b with a bandpass filter of 510±50 nm). Therefore, the PbI$_2$ are a perfect example to demonstrate the resolution match between CL and SED. When both techniques are correlated, specific grains as seen in both SE images and SED virtual images exhibit nano-diffraction indexable to PbI$_2$ in the [001] zone axis. This short example underscores the synergy between these two main techniques, which should be explored further to better study structure-property relationships.
5.5 TRCL on perovskites: the challenges ahead

To date, a couple of papers have successfully reported the use of transient CL on hybrid beam-sensitive perovskites. Cortecchia et al.\textsuperscript{[153]} showcased the possibility of using such a PM system to probe the dynamics of 2D/3D perovskite nanocrystals. They identified heterogeneity of the self-assembled phases of different dimensionality, and probed the TRCL recombination dynamics for each phase, exhibiting both Auger ultrafast recombination in the range of picoseconds and slower TRCL traces matching the time-resolved photoluminescence dynamics. Zhao and Lian et al.\textsuperscript{[154]} used a PM system to study the improvements in luminescence efficiency, uniformity, and lifetime of mixed-dimensional perovskite films after layer and additive engineering.

5.5.1 TRCL on halide polycrystalline films

During this thesis, TRCL measurements were challenging to perform due to sample stability. They were recorded with a TCSPC photodetector at an acceleration voltage of 6 keV and beam current of $\sim 115$ pA. The resolution of the photodetector is 80 ps. Dwell times were extended until the TRCL signal was two orders of magnitude higher than the background, which varied from 60 to 400 seconds for each peak of interest. TRCL decays were normalized and smoothed using a 10-point mean filter before the $1/e$ values were found. Figure 5.20 shows the acquisition of spatially averaged TRCL decays on a hybrid perovskite polycrystalline film for the first time. Figure 5.20a shows the three peaks of interest selected for the TRCL signal at 507, 663 and 747 nm (2.45, 1.87 and 1.66 eV) for the PbI$_2$, intermediate degradation phase and perovskite phase, respectively. The PbI$_2$ and intermediate phases are shorter-lived than the perovskite phase, as shown in Figure 5.20b. The $1/e$ time decay value for the perovskite peak is found at $0.\pm 0.1$ ns. The lifetimes for the PbI$_2$ and intermediate phase TRCL decays could not be resolved as they are below the resolution limit of the detector (80 ps). The understanding of the dynamics and nature of these phases are beyond the aims of this work, hence we only present the $1/e$ value and no fitting models.

Despite the optimization of the experimental conditions used to acquire the TRCL data described in Section 5.3, the perovskite peak degraded continuously, as shown in the inset in Figure 5.20b. The inset shows the time evolution of the incoming photon counts to the time-correlated single photon counting photodetector for each peak over continuous beam exposure in PM. For the perovskite peak, the spikes in the photon count correspond to each of the 6 different regions of the sample that were scanned during TRCL acquisition. The perovskite emission completely degraded within 50-100 seconds of continuous beam
Figure 5.20: TRCL measurements on a halide perovskite thin film. TRCL spectra were measured at an acceleration voltage of 6 keV and beam current of ∼115 pA in PM. (a) The CL emission spectrum with the perovskite peak, the PbI$_2$ peak and a broad intermediate degradation phase. (b) TRCL spectra of the three peaks of interest (smoothed signal as a darker line). The inset shows the incoming photon counts per second. The 1/e intensity is shown as a dashed line on the y-axis. Reproduced from [249].

Rastering. In order to acquire SNR of two orders of magnitude, several different regions were scanned. For the PbI$_2$ and the degradation of higher energy peaks, only a single region was scanned to achieve the desired SNR. This is in contrast to Cortecchia et al. work, where they do not report any of these challenges, despite using the even more beam-sensitive MA-based perovskite composition. Moreover, they do not report the exact electron-beam current used during the TRCL measurements, which is estimated to be <30 pA at 6kV, based on the 7 nA reported for CW mode. After having measured several halide perovskites, this beam current seems rather small to produce enough CL signal for good SNR for TRCL studies.
5.5.2 Charge carrier concentration estimation

In Figure 5.20, the PbI$_2$ and the intermediate degradation phase exhibit extremely short-lived dynamics. These short TRCL curves may be attributed to the highly localized formation of these phases, in which charge carriers are produced in a confined volume at high densities, thus affecting lifetimes due to the nature of the bimolecular recombination. For the perovskite peak, the longer-lived carrier dynamics may be attributed to the large grains in the film, which can disperse the charge carriers, formed locally by the electron beam, across the grain. However, these lifetimes are significantly shorter than time-resolved photoluminescence measurements of similar compositions, in the order of hundreds of nanoseconds. [22] These shorter lifetimes may suggest degradation of the perovskite phase by the creation of beam-induced defects, which are visible in the broad intermediate degradation peak and act as charge carrier quenching pathways. Moreover, Auger processes may play a role due to the higher carrier densities produced in CL compared to PL. [25,314] Similar perovskite formulations, containing mixed iodide and bromide, are known to show higher Auger rates when the bromide fraction increases due to gradual changes in phase structure, which may here be caused by beam degradation. [22]

Charge carrier concentration produced during CL-SEM can be estimated to be in the order of $\sim 10^{18}$ e$^-$-h$^+$-pairs cm$^{-3}$ (see Section 4.5.2 on how to estimate it). TRCL curves were acquired at 6 keV and 115 pA, using a pulsed electron beam with a pulse frequency of 80.6 MHz (12.4 ns between each pulse). For a CW beam, 115 pA would correspond to $7.17 \times 10^8$ e$^-$ per second. If the beam is in PM, an estimation of 9 e$^-$ with an energy of 6 keV is present in each pulse. Since each electron has significantly larger energy than the band-gap of the material ($\sim 1.66$ eV), each electron can approximately excite $\sim 1,200$ e$^-$-h$^+$ pairs (see Equation 3.15). Assuming a mean excitation cubic volume of 200 nm$^3$ at 6 keV acceleration voltage, as shown in Figure 5.11, and assuming no diffusion, the charge carrier density of the localized CL excitation is $\sim 10^{17}$ e$^-$-h$^+$-pairs cm$^{-3}$ per incoming electron. Therefore, each beam pulse can excite up to $\sim 10^{18}$ e$^-$-h$^+$-pairs cm$^{-3}$. According to the findings in Figure 5.20, all these charge carriers are short-lived and relax within 2 ns, which is shorter than the pulse repetition rate. Therefore, the carrier concentration should not exceed the $10^{17}$ range at any point, since the time delay between each electron pulse is larger than the charge-carrier relaxation time. Such carrier densities are only of the order of defects in the perovskite crystalline structure (compared to the $\sim 10^{24}$ atoms per cm$^{-3}$). [28] They are enough to saturate the defects. These carrier densities are above the photovoltaic regime ($10^{14} - 10^{16}$ cm$^{-3}$) [315], close to the carrier densities at which Auger processes dominate for some perovskite compositions. Simulations for MAPbI$_3$ state that carrier densities $\geq 10^{18}$ cm$^{-3}$ are needed before Auger recombination dominates. [316]
Figure 5.21: Streak TRCL on CsPbBr$_3$ nanocrystals. Comparison of different acquisition conditions and processing methods for 2-dimensional TRCL data. (a) The raw streak images for CsPbBr$_3$ nanocrystals without and with manganese doping (125% wt.). Inset shows CL spectra acquired at beam currents of 10 nA (in CW, continuous line) and 0.1 nA (in PM, dash line). (b) Rebinning the signal axes by 10 results in a better SNR, yet it is still dominated by noise. (c) Streak image resulting from stacking multiple shorter-time acquisitions and then rebinning by 10. This approach results in the best SNR. Sample: CsPbBr$_3$ nanocrystals without and with 125% wt. Mn-doping on ITO (from Mahesh Gangishetty Lab). CL acquisition in PM at 5 keV, beam current <100 pA. During TRCL acquisition, the electron beam was scanned at 64x 64 px at a FOV of 2x 15 µm, and dwell time of 0.1 µs. The central wavelength was set to 478 nm. The streak camera was set to a time range of 4, normal gate mode, at the maximum MCP gain of 63, a focus time over 5, a calibrated delay time of 4,800, and an exposure time of 10ms. For panel a, an integration of 200,000 samples was set. For panel c, an integration of 1,500 was set but repeated 3 times, then all data were combined.

similar to the experimental results for MAPbBr$_3$ reporting third-order recombination at slightly higher carrier densities of >10$^{18}$ cm$^{-3}$.[317]

In CW mode, charge carrier concentration can be estimated in a slightly different way. A 250 pA and 6 keV electron beam corresponds to 1.56 × 10$^9$ e$^-$ per second. Given that each electron can approximately excite ∼1,200 e$^-$-h$^+$ pairs, the continuous beam can excite up to ∼10$^{26}$ e$^-$-h$^+$ pairs cm$^{-3}$ each second. Assuming the lifetime of the excitation is in the order of nanoseconds, the carrier density in CW mode is of the order of ∼10$^{17}$ e$^-$-h$^+$ pairs cm$^{-3}$, density values similar to the ones in PM.

5.5.3 TRCL on perovskite nanocrystals

Apart from TRCL decay curves acquired from a TCSPC detector, spectrally and temporally resolved TRCL can also be acquired using a streak camera. A spectral width of ±40 nm can be resolved with a temporal resolution of 10s of picoseconds within a 1 nanosecond range.
Figure 5.21 showcases the challenges involved in using such a system for the acquisition of TRCL data from halide perovskites. As a test study, we attempted to study the TRCL dynamics with the addition of manganese (Mn) on CsPbBr$_3$ nanocrystals, as it is known to result in passivated brighter and multi-peak emission.\textsuperscript{[318]} Note that the choice of a fully-inorganic perovskite composition is not coincidental, as the CL emission of hybrid compositions degrades too quickly for such studies.

The emission of CsPbBr$_3$ nanocrystals was observed at 478 nm, the wavelength at which the centre of the spectrometer was set, acquiring TRCL data from 478 ± 20 nm. A broad orange emission at 600 nm is normally observed in PL when Mn-doping is added.\textsuperscript{[318]} However, such emission was not visible during CL mapping, even when high currents of 10 nA were used. In Figure 5.21a, the raw streak images for CsPbBr$_3$ nanocrystals without and with Mn-doping (at 125% wt.) are shown. These images were acquired at an exposure time of 10ms per frame, integrated over 200,000 frames (>30 min continuous acquisition). Note that for other brighter semiconductors such as galium nitrides, acquisitions of seconds would yield the same SNR. At first, the images seem to be dominated by noise. However, these datasets can be rebinned in both the spectral and the temporal axes, yielding Figure 5.21b. After rebining by 10, a better SNR is observed, where some transient CL features can be resolved for the Mn-passivated sample. However, the signal is still dominated by noise. Alternatively, multiple shorter-time streak acquisitions can be acquired (10ms per frame, integrated over ~2,000 frames) and stacked together. Stacking three shorter-acquisition images and rebinning by 10, streak images with better SNR can be obtained (see Figure 5.21c). Using this method, a tail of ~1 nanosecond in the transient CL at 480 nm can be observed for the Mn-doped sample. The sample without passivation shows faster dynamics which cannot be resolved, shorter than the temporal measurement limit of ~50 picoseconds.

The use of additives like Mn in materials with narrow band gaps, like CsPbBr$_3$ nanocrystals, can be used to boost solar cell efficiencies by covering a broader spectral range.\textsuperscript{[318,319]} The mechanism by which the incorporation of Mn leads to dopant emission at ~600 nm involves the intra-d-shell transitions, which are normally forbidden. However, through the mediation of another absorbent like the perovskite nanocrystal, such dopant transition can be excited.\textsuperscript{[320]} For the case of nanocrystals, their quantum-confined nature and their high bandgap enhance the energy transfer to Mn d states, leading to intense Mn dopant emission.\textsuperscript{[321]} Therefore, Mn incorporation can lead to transfer dynamics between the host absorber and the dopant, which can in turn slow down the recombination dynamics. Such phenomenon is resolved in the TRCL trace in Figure 5.21c. The fact that the 600 nm emission from the dopant cannot be resolved in CL mode may be attributed to the differ-
ences between PL and CL, namely the charge carrier densities generated upon excitation, or the Mn excitation mechanism differing upon photon and electron excitation. The inset in Figure 5.21a shows two CL spectra acquired at extremely opposed beam currents of 10 nA (in CW) and 0.1 nA (in PM). Neither of the two conditions exhibits an Mn-derived emission at 600 nm. Note the broad peak from 300 to 600 nm can be attributed to the ITO substrate (see Table 5.1), which is not visible at the lower excitation densities in PM. The nature of excitation of the Mn-dopant in CL should be the subject of further studies, as it is possibly not linked to excitation density but to the nature of the excitation using electrons. However, it showcases the possibilities and large limitations of streak TRCL acquisition for halide perovskites, which are not as bright as other semiconductors and which suffer from electron-beam degradation.

5.6 Conclusion

This Chapter has studied the parameters affecting the acquisition of CL maps of halide perovskites, such as the effect of beam current, dwell time or beam mode, as well as the processing and analysis steps required for CL. PM electron beams are useful for the study of such films, yielding more robust results than CW mode. Using PM, the CL spectra strongly resemble those obtained from pristine perovskite emission in PL. Even in optimized conditions, some effect related to beam damage is observed in the form of an intermediate broad peak at higher energies, which limits the use of CL-SEM on perovskites. TRCL was proven to be challenging on polycrystalline films, due to electron-induced structural degradation, which affects the optical emission. The optimization described in this Chapter has helped to unlock the use of CL hyperspectral mapping on the more beam-sensitive hybrid perovskite compositions. As SEM-CL systems with PM capabilities become prevalent and equipped with more sensitive and faster detectors, we anticipate that CL will play a larger role in resolving the complex heterogeneity of the materials in the hybrid perovskite family, as well as other beam-sensitive semiconductors. Some examples have been shown in this Chapter, but that is just the start and we expect many more studies can be enabled from this understanding.
Chapter 6

Beyond static imaging: towards in-situ biasing STEM

Text in this Chapter has been submitted in part to peer review. All fabrication, technique development, data acquisition, and analysis were performed by Jordi Ferrer Orri unless stated otherwise. The lateral biasing setup (with the custom-made MEMS holder from Henny Zandbergen) was mainly developed by Chris Allen (ePSIC, Diamond Light Source).

Chapter abstract: The goal of this Chapter is to develop in-situ microscopy at the nanoscale, to probe perovskites under operational stressors. Due to the constraints of TEM specimens, mainly on thickness but also on the limited choice of substrates, fabrication is not trivial. Two device architectures are explored: (i) lateral horizontal devices and (ii) stacked vertical devices. The lateral architectures are better suited for TEM studies, but the stacked layers (“sandwich”) design closely matches state-of-the-art p-i-n devices.

6.1 Introduction

Critical gaps remain in identifying degradation pathways in single-cation and alloyed lead halide perovskites, and their dependence on composition, especially upon operation.\cite{67,322,323} In particular, ion mobility in perovskite devices can affect both the device’s performance and stability, and it can be accelerated during long periods of bias and even in the dark, shade or under reverse bias.\cite{93–95} Studies investigating the relationship between degradation, hysteresis, macroscopic properties, and ionic migration have produced mixed results.\cite{322} While preferential degradation has been observed in regions of positive
internal potential for MA$^+$ and FA$^+$-based compositions due to anion accumulation, intrinsic defects, oxygen, or precursor residue also play a role. Iodide and organic cation species are highly mobile and can induce defects and quench photoluminescence, and preferential oxidation of iodide ions over bromide ions is observed under lateral biasing.

The relationship between electron- and hole-driven reactions and their manifestation during composition modification need to be understood better to explore the relationship between ionic and electronic mobility. Macpherson et al. in our research group recently showed that degradation seeds on the nanoscale, and that hole trapping from photoexcitation drives perovskite phase instability, especially at defective non-perovskite phases such as hexagonal polytypes. They were unable to distinguish the contributions of electrons and holes to the degradation process because of the inherent nature of light soaking which produces both charge carriers.

This Chapter shows results that move a step further towards understanding how the nanoscale affects operation stability using a novel platform to monitor redox-related degradation reactions in-situ. The approaches shown in this Chapter help understand the degradation chemistry, help decouple the role of electrons from holes, and from the role of ionic migration. The new in-situ biasing platforms shown here stand out from other in-situ biasing electron microscopy experiments as it can image nanoscale features without sample preparations requiring radiation-intensive milling.

### 6.2 Horizontal biasing for TEM studies

Despite the majority of the PSC work has focused on vertical stack devices, horizontal (lateral) architectures are also possible and relevant. Tainter et al. demonstrated the use of a back-contact horizontal solar cell architecture that ensures all of the activity is lateral (the charge carrier transport is lateral, as well as the interfaces). Back-contact lateral architectures can also remove the need for a transparent top contact, which can be useful in TEM characterisation. Moreover, interfacial effects between different layers can be decoupled as the device layers are not superimposed. However, such device architectures normally require the use of photo- and electron-beam lithography and their compatibility with TEM-compatible SiN substrates remains to be studied.

In the first half of this Chapter, a simpler experimental design is used to study perovskite films under in-situ electrical bias stressors on the nanoscale.
6.2 Horizontal biasing for TEM studies

Figure 6.1: Lateral *in-situ* biasing MEMS-based system. (a) SE image of the MEMS-based grid with multiple Pt contacts on top of an electron-transparent SiN membrane, forming several windows to image from in TEM. The labels 5 to 10 correspond to the electric contacts in panels b and e. (b) Optical microscope image of the thin electron-transparent window with the metal contacts on top. (c) Custom-made TEM holder (JEOL type) with 9 metallic pins to contact the chip. (d) Adaptor connecting each pin of the holder with the adaptor box in (e) which transforms into a coaxial connector compatible with any power source. This design was custom-made by Henny Zandbergen for ePSIC, and *in-situ* lateral biasing was developed by Chris Allen (ePSIC, Diamond Light Source).

### 6.2.1 A MEMS-based TEM-compatible biasing platform

The effect of electrical biasing on the nanoscale of state-of-the-art FA-rich solar absorbers can be studied by employing a multimodal toolset of correlative *in-situ* low-dose electron and optical microscopy measurements. By applying a bias across FAPbI$_3$ films in a lateral geometry, we observe structural changes in the perovskite under operation that occur as a degradation front propagating from the positive contact across the film, corresponding to the hole-mediated oxidation of iodide. We concomitantly observe electron-mediated lead reduction throughout the film. Similarly, in alloyed FA$_{0.7}$Cs$_{0.3}$Pb(I$_{0.9}$Br$_{0.1}$)$_3$ films, which exhibit more compositional heterogeneity, localised morphological changes are observed throughout the film, particularly near initially defective sites. The lateral platform developed in this Chapter, utilising multimodal nanoscale techniques, decouples degradation mechanisms between those mediated by holes or electrons and those driven by ionic segregation, providing guidelines to stabilise absorber layers in optoelectronic devices.

A MEMS-based chip was developed by Henny Zandbergen (Delft University and HennyZ) and by Chris Allen (ePSIC, Diamond Light Source), as shown in Figure 6.1. [237,326] This MEMS-based chip enables *in-situ* lateral electrical biasing whilst imaging in a low-dose scanning transmission electron microscope (STEM), to visualise with high spatial
Figure 6.2: In-situ biasing across a FAPbI$_3$ absorber film. (a) Biasing chip with perovskite layer. (b) Current profile measured at 20 V over 90 min. (c) vBF images from 4D-STEM datasets after 0 to 90 min of biasing, with a white dashed line delineating the propagation contrast front. (d) Intensity profile of the vBF contrast, from summing the lateral regions in c. (e,f) 4D-STEM experimental diffraction patterns of perovskite grains from the marked regions in c. Red arrows indicate additional diffraction spots with spacings (<0.16 Å$^{-1}$). (g,h) HAADF images acquired post-biasing, with higher magnification images in g. (i) The vBF image near 0 V, with clusters forming and selected with red circles, used to form a mask for obtaining the (j) radial 1D-diffraction pattern showing the presence of Pb$^0$. (k) HAADF images after reversing the biasing polarity, showing the formation of a degradation front near both electrodes. (l) Top-view SEM image shows the metal contacts. (m-n) The degradation front linked to quenching of PL emission and bluer emission, also shown in (n) the absolute and normalized PL spectra.
resolution the evolution of the nanoscale properties of thin halide perovskite films under operation. Several contacts can be connected to apply electric fields between platinum contacts locally. Myself, with the help of Affan Iqbal and Tiarnan Doherty, used this platform to study how in-situ biasing affects high-quality hybrid perovskite thin films of 100-nm thickness and different compositions.

6.2.2 Visualising nanoscale bias-induced degradation in FAPbI$_3$

A FAPbI$_3$ composition thin film was thermally evaporated onto the MEMS-based biasing chip. Then, an electric field of 4 V$\mu$m$^{-1}$, 20 V across a separation of 5 $\mu$m, was applied in the microscope across two of the platinum contacts in the MEMS chip (Figure 6.2a) to match the same order of magnitude of fields solar cells experience under operational conditions.\[40\] Bias was applied for 90 min continuously and currents in the range of nano-amperes were measured (Figure 6.2b), resulting in an overall charge carrier density of 7($\pm4$)$\times10^4$ charge carriers nm$^{-3}$, and a current flux of 1000($\pm750$) mA cm$^{-2}$, about 50 times higher than the current density from a typical short-circuit current density in photovoltaics and light-emission diodes (in the order of 15-20 mA cm$^{-2}$).\[40,327\] In-situ 4-dimensional scanning TEM (4D-STEM) was used to acquire structural nanoscale diffraction data before, during, and after biasing for 0, 30, 60, and 90 min, with data recorded near the positive contact. The 4D-STEM datasets contain information on the nanoscale diffraction with a lateral spatial resolution of $\sim$5 nm and at minimal electron-beam-induced damage. Virtual bright field (vBF) images of the scanned region were created by mapping the intensity of the direct beam as a function of the probe position. A time series of sequential vBF images is shown in Figure 6.2c. From the 4D-STEM datasets, experimental nano-diffraction patterns from individual perovskite grains can be extracted by summing the data over a region of interest. Most grains show patterns that can be indexed to a tetragonal perovskite structure in the $P4/mbm$ space group, consistent with recent work on stabilised FA-rich systems.\[46\]

The vBF images reveal a net demarcation line of contrast change, that expands over time from the positive contact into the film. The evolution of this contrast “front” is observed in Figure 6.2d from the intensity profile of the vBF contrast, obtained by summing the pixel values in the horizontal axis over time. It shows a stronger drop in contrast near the positive contact, which can be attributed to the densification of the specimen and the deposition of degradation-induced amorphous carbon. High-angle annular dark field (HAADF) images acquired post-biasing show material loss at this front (Figure 6.2g), shown as a darker contrast near the positive contact, attributed to thinner or lower atomic number regions of the sample. Higher magnification HAADF images in Figure 6.2h show
that the majority of grains within the front are heavily damaged, showing beam-induced
stripes (see region i), when imaged post-biasing, using excessive electron irradiation in
HAADF imaging. In contrast, some of the grains remain unchanged (see region ii), as
do most grains far away from the front line (see region iii), under the same excessive
electron fluence, hinting at the grains modified during biasing being more susceptible to
electron-beam-induced degradation. Inspection of diffraction data from these two types
of grains, undamaged (far from the biasing front) and damaged (near the biasing front),
does not show any clear phase difference between the transformed and unmodified grains.
However, a qualitative analysis hints at degradation reactions being more prominent at
higher index zone axes than at lower index ones, which may be linked to the more reactive
faceted surfaces at higher index zone axes.\cite{328,329}

Regions near the 0 V contact on the opposite side of the channel do not exhibit the
formation of a front, but change through the creation of small 10-50 nm clusters at
the grain boundaries, in conjunction with the formation of pinholes, shown in Figure
6.2h. The radially-integrated 1D-diffraction pattern in Figure 6.2j, obtained from only
the masked clusters, suggests the presence of Pb\(^0\) in the vicinity of these pinhole sites.
A further inspection of the diffraction patterns at the start of the biasing experiment at
grain boundaries where pinholes form reveals that, apart from diffraction indexable to
the perovskite pristine phase at [011], and [001], zone axes, for Figure 6.2e and Figure
6.2f, respectively, additional spots are visible with spacings which are too small for the
pristine tetragonal phase. These can correspond to defective phases such as hexagonal
polytypes or PbI\(_2\) (with diffraction lengths <0.16 Å\(^{-1}\), marked with red arrows). This
process is reminiscent of the photoinduced degradation process observed by Macpherson
et al.\cite{163} on the nanoscale, where defective sites also result in the formation of local Pb\(^0\)
clusters through hole-mediated processes. The formation of such Pb\(^0\) clusters is primarily
observed near the 0 V contact, but they are also observed across the whole biased region
albeit to a lesser extent (see grain boundaries in Figure 6.2c).

Finally, the degradation from biasing the FAPbI\(_3\) film seems to be polarization depen-
dent. A series of additional studies, where the potential applied was reversed, are shown in
Figure 6.2k. After applying +20 V and then -20 V, a contrast front is observed on both sides.
Pb\(^0\) clusters are also found to form throughout the film. Control experiments without bias
allow us to exclude the impact of the electron beam on inducing these changes (see Figure
6.3), validating that these changes are due to the applied bias.

Compositional mapping using energy-dispersive X-ray spectroscopy (STEM-EDX)
taken across the metallic contacts after biasing contain iodine-poor lead-rich stoichiome-
tries overall. This is especially true near the positive electrode, correlated to the contrast
6.2 Horizontal biasing for TEM studies

Figure 6.3: Decoupling the effect of electron-beam induced changes. In order to understand if the morphological changes were caused by the electron beam exposure, a series of vBF images were taken only after biasing. These regions were never exposed to the electron beam before, nor during biasing, only post-biasing. The same morphological feature changes can be seen as the ones shown in the main text, suggesting the reported changes are not induced solely by the electron beam.

front formation, suggesting iodide reduction and outgassing, or iodine migration. Optical photoluminescence microscopy (PL) was performed on the same area post-biasing, measured 3 days after the biasing experiment and the specimens were always kept in inert-gas conditions, in the dark, and unbiased between measurements. The main PL emission peak is blue-shifted within the biased region compared to the emission from unbiased regions, and is most severe near the positive electrode, tapering off through that biased region (Figure 6.2m). This blue-shifted region tracks with quenched PL (Figure 6.2n), and correlates to the formation of the degradation front. It results in a high-energy shoulder in the emission at 1.62 eV (770 nm), consistent with smaller domains being generated during bias-driven degradation.\[330,331\]

6.2.3 Visualising nanoscale bias-induced degradation in FA-rich alloyed perovskites

We now turn to a stoichiometrically more complex FA-rich composition alloyed with small fractions of Cs in the A-site and Br in the X-site (nominal stoichiometry of FA$_{0.7}$Cs$_{0.3}$Pb(I$_{0.9}$Br$_{0.1}$)$_3$) again thermally evaporated to make a high-quality film that corresponds to strong devices with better phase stability than the FA-pure films.\[234\] Applying bias across this alloyed FA-rich film results in distinctly different phenomena compared to the FA-pure system, shown in Figure 6.4. Under the same conditions as above (Figure 6.4a), a series of
Figure 6.4: *In-situ* biasing in alloyed films reveal heterogeneous degradation. (a) Current profile measured at 20 V. (b) The vBF images generated from 0 to 90 min of biasing. (c) HAADF image acquired post-biasing, across the whole region between metallic contacts. A closer inspection of the vBF evolution from b is shown in (d), where degradation can be seen to seed at the grain marked in red. (e) The diffraction of the grain marked in red shows diffraction patterns with spacings below 0.12 Å\(^{-1}\). (f) Diffraction of 3 grains reveals they are aligned to the same [111] zone axis. (g) A comparison between the initial and final diffraction pattern of a grain not affected (in green) and affected (in orange) by the biasing. (h) Absolute PL intensity spectra for the pristine (in blue) and biased regions (in orange, dashed) and the normalised PL intensity spectra in the bottom panel.

vBF images near the 0 V metallic contact is shown generated from the *in-situ* 4D-STEM datasets when biasing for 0, 15, 25, 45, 70, and 90 min (Figure 6.4b). Clear morphological degradation in the form of contrast change is observed across grain boundaries. Unlike for the single-component FAPbI\(_3\) films, such changes are not localised near the positive contact in the form of a front but are observed throughout the whole biased area. This is further demonstrated by the HAADF image acquired after biasing (Figure 6.4c), where
6.2 Horizontal biasing for TEM studies

Figure 6.5: The effect of grain orientation during operational stability. The grains near the area in Figure 6.4b, where most degradation happens, show diffraction patterns indexable to high-angle grain boundaries to the [111] zone axis grains (numbered as 1, 2, 3). Degradation expands in this zone axis, leaving the grains at high-angle grain boundaries mostly unaffected.

degradation is seen across the whole region between metallic contacts, as thinner grains with darker contrast. The comparison between an unchanged and a damaged grain is shown in Figure 6.4g, in which the initial and final diffraction pattern during biasing is shown in green and orange, respectively. The degradation from biasing results in material loss and amorphisation of most of the crystalline phases, as seen from the almost complete fading of the diffraction from the pristine perovskite. Moreover, a diffuse scattering ring is also visible, which is mainly indexable to the amorphous SiN substrate and amorphous degraded product (an amorphous carbon layer from the re-deposited volatile organic cations). In addition to the degradation of the grain boundaries, there is also the formation of small Pb clusters throughout the film, particularly near the damaged areas.

A closer inspection of the in-situ vBF image evolution from Figure 6.4b shows degradation fronts stemming from localised positions in these alloyed FA-rich systems, in stark contrast to the unidirectional fronts in the single component FA systems following the field direction. One of these degradation seeds is shown at higher magnification in Figure 6.4d, as a grain marked in red. The mean diffraction pattern extracted from this grain contains diffraction spots with spacings below 0.12 Å⁻¹, attributed to defective hexagonal polytype phases (Figure 6.4e). The presence of such defects can trigger a degradation front extending through adjacent grains. Figure 6.4f shows the diffraction of three grains, which undergo severe consecutive degradation stemming from the phase impurity, as seen from the contrast in the vBF images. These three grains are strongly aligned and in approximately the same [111] zone axis. However, adjacent grains to the damaged ones which form a high-angle grain boundary, either by being at different zone axes or distinctively different orientations, are mostly unaffected by the degradation front (see Figure 6.5). These suggest that high-angle grain boundaries can hinder the degradation
Figure 6.6: Charge-carrier-mediated redox reactions dominate the nanoscale structure degradation of perovskite films under bias, driven by ions. (a) Iodide oxidation, which is hole mediated, is mainly localized near the positive contact where a large concentration of holes is injected from the electrode, leading to I$_2$ being expelled into the vacuum, resulting in the formation of a contrast front that moves (grey dashed lines evolve to darker continuous lines). (b) Heterogeneity at the nanoscale with defective phases conditions charge carrier funnelling and the same redox reactions are seeded from multiple places. Iodide oxidation is preferential over bromide due to its electronegativity.

front advancing, yet there could be other compositional factors too that might be difficult to understand. In addition to hexagonal polytypes, other biasing experiments with similar compositions but in initially more segregated films also show the presence of PbI$_2$ and CsPbI$_3$ phases as defective sites linked to degradation.

The main PL emission peak for the unbiased perovskite film is at 1.61 eV (770 nm). In the biased region, the emission peak is quenched by ~25% and red-shifts to 1.59 eV (790 nm, see Figure 6.4h). Effects are even more exaggerated in poor-quality films that are even more heterogeneous initially. In such samples, degradation during biasing was mainly observed in the vicinity of segregated chemical sites and the same trend in PL quenching and red-shifted emission was observed with larger shifts. Segregated chemical sites are expected to be quite defective, rich in iodide interstitials, and allow ions to move more easily. They can also funnel more current though, leading to faster degradation. [97]

6.2.4 Biasing-induced nanoscale degradation mechanism

Based on the above observations, in Figure 6.6 we propose a mechanism based on ionic and electronic conductivity, namely the interplay between charge-carrier-mediated redox reactions driven by the slower ion segregation under bias.
For the single component FAPbI$_3$ phase, the iodide ions ($I^-$, or iodide interstitials, $I^-_i$) are oxidised, driven by the lower standard reduction potential of Pb$^{2+}$ or Br$^-$ over I$_2$.\cite{95,99} Iodide oxidation, which is hole mediated, is mainly localized near the positive contact because these degradation reactions are limited by the supply of negatively-charged ions slowly diffusing in the direction of the electric field (Figure 6.6a). $I^-$ oxidation leads to I$_2$ gas being expelled into the vacuum, leading to material loss. In FA-based compositions, halide vacancies are more mobile but benign, while halide interstitials are less mobile and more harmful, which can speed up degradation and further cause damage to the perovskite.\cite{82}

In the alloyed system, due to the more complex composition, there are more clusters of defective phases and halide segregation dominates (Figure 6.6b). Moreover, bromide ions have a lower tendency for oxidation and lower ionic mobilities than iodide ions,\cite{98} so selective halide oxidation on iodide but not bromide is expected.\cite{95} This can lead to bromine-rich regions, defective but not leading to material loss, and iodine-rich regions due to their diffusion, also rich in defects but leading to severe material loss. Moreover, the degradation fronts occur at local sites across grain boundaries where halide defects are highest in density. Overall, all these local sites of degradation are sources of iodide and iodide interstitials ready to react, and these sites have higher ionic mobilities to keep the iodide supply and propagate the degradation.\cite{97} Interestingly, the structural observation of high-angle grain boundaries preventing the propagation of bias-induced degradation might not only be linked to hindered ionic migration across high-angle boundaries but also be linked to composition, because halide segregation may be physically inhibited at such grain boundaries. Similar facet-dependent mechanisms have been observed in which facets with the same orientation degrade under moisture, while such degradation does not propagate to other facets with different orientations in the vicinity.\cite{329}

Apart from ion migration, charge carrier mobility and funnelling are also key, as without bias no transient behaviour is observed (see completely different results from a similar experiment in Chapter 4).\cite{238} The large degradation fronts occur where hole trapping happens most prominently. For the single FAPbI$_3$ composition, most funnelling happened near the positive contact as a front. For the alloyed system, hole trapping predominantly occurred where halide defects were present, normally across boundaries, further exacerbating this mechanism.\cite{162,163} These two systems give a fundamental understanding of halide segregation, where hole trapping is also needed to drive segregation and degradation. For example, the FAPbI$_3$ film results in the formation of a front that moves slowly at a rate of $\sim$40 nm hour$^{-1}$ V$^{-1}$ ($\sim$0.5 $\mu$m after 60 min at 20 V, from Figure 6.2d). The front propagation rate is not linear, as it slows down after 30 min and almost stops after 60 min.
These observations, hard to explain from just ionic migration, suggest that the conduction of holes is also needed, which may become more inefficient across the degraded material front.

In parallel, electrons drive the reduction of \( \text{Pb}^{2+} \) to \( \text{Pb}^0 \), theoretically expected near the 0 V contact. However, in contrast to the directional front observed for the iodide oxidation, the lead reduction is not only observed near the 0 V contact but seen everywhere across the biased film. Such reduction is especially seen at grain boundaries, where electron accumulations have been reported to be due to downward band bending, and also near the presence of non-perovskite phases initially present before biasing, such as hexagonal polytypes, PbI2 or segregated Cs-rich phases. Moreover, holes can also migrate towards such defective sites and drive material loss in conjunction to lead reduction. This is suggested by the material loss at the grain boundaries seen in HAADF, from the EDX compositional maps not showing higher iodine-to-lead concentration where \( \text{Pb}^0 \) crystallites are formed.

While iodide-driven degradation is a reaction of holes, found everywhere, with iodide species, limited by ionic diffusion, in the \( \text{Pb}^{2+} \) case, the cations are more static and the reduction is driven by where the electrons are, hence happening everywhere but most significantly near the 0 V contact. Overall, the model proposed here assumes that both electron and hole charge carriers can move relatively freely, and the asymmetries and polarity-dependent observations result from halide migration which happens at much slower timescales.

All observations reported were made after applying a 20 V potential to the sample. When a smaller potential difference was applied (e.g. 30 min at 1 V or 20 min at 5 V), the measured currents were 1-2 orders of magnitude lower, and no discernable morphological changes were observed in vBF images acquired before and after biasing for comparable lengths of time. These findings may suggest the presence of an activation potential threshold for degradation, e.g. for ionic drift/diffusion, which is only overcome at electric fields of 4 V \( \mu \text{m}^{-1} \) or higher. However, the measured currents may suggest that faster degradation may also be linked to a higher current flowing at a given time (at 1 V: \( \sim 1 \times 10^{-11} \) A, at 5 V = \( \sim 1 \times 10^{-10} \) A, and 20 V: \( \sim 1 \times 10^{-8} \) to \( \sim 1 \times 10^{-9} \) A), and presumably also faster ion migration. Joule heating, especially near metal contacts, during biasing cannot be discarded. However, the better phase stability of the alloyed systems suggests that most grains near the contact can withstand the flow of charge carriers and are not heavily affected, allowing charge carriers to reach further degradation sites in the bulk. Therefore, Joule heating at the contacts is unlikely to be the main factor responsible for the observed
effects, as we would expect to see a degradation front near the contacts for the alloyed system if it were.

The proposed model does not consider the effect of the organic cations in the degradation pathway, since organic elements are too light to accurately be measured in STEM-EDX. Yet, these species can migrate at slower speeds and future studies should take advantage of this correlative nanoimaging platform to understand their role. We also show that the addition of compositional heterogeneity can introduce bandgap variation which can dominate both the ionic migration and the charge carrier flow, thus making biasing-induced degradation across the films more widespread. Moreover, the presence of defective and non-perovskite phases at nanometer length scales can act as seeds for degradation. These findings highlight the tradeoff between phase stability and operational stability, similar to how excess PbI\textsubscript{2} on FA-rich films is known to stabilise the perovskite phase,\textsuperscript{[234]} yet it can be a double-edged sword for the device, especially under light illumination owing to the susceptibility of PbI\textsubscript{2} to photolysis, which inevitably leads to operational instability and hysteresis.\textsuperscript{[55]}

The results shown here further elucidate the detrimental role that non-perovskite phases in the nanoscale have during electrical bias in the dark, with applied electric fields similar to solar cells at open circuit voltage,\textsuperscript{[40]} triggering degradation of the perovskite phase even without the presence of light.\textsuperscript{[95]} When bias is applied over fully non-perovskite films, such as PbI\textsubscript{2}-pure films, no structural changes are observed.

Metal-perovskite-metal contacts are theorized to form back-to-back Schottky metal-semiconductor junctions, but several works have proposed more complex models determined by capacitive and ionic diffusion models.\textsuperscript{[92,93]} Based on the redox reactions observed here on the nanoscale, we provide experimental evidence to show that the contact under positive bias is hole-rich and the 0 V contact is electron-rich.

This work has some inherent limitations that need to be considered. Some current leakage was observed across the edges of each metal contact, making the actual biased area hard to estimate. However, the changes are primarily in the region of bias. Moreover, the several connections required to drive a potential inside the electron microscope make it hard to also measure the actual voltage and current between the imaged windows, which could be accurately measured with a four-probe MEMS chip. Finally, all biasing was done \textit{in-situ} under a high vacuum, providing a maximum-stress environment. Such conditions will speed up the sublimation of species such as I\textsubscript{2} and will neglect side reactions triggered by the presence of oxygen, known to passivate some of the degradation pathways via PbO\textsubscript{2} formation.\textsuperscript{[163]} Further studies should explore the effect of other atmospheres under the presence of lateral bias, as well as the effect of passivation in not only phase but also operational stability. Finally, a better understanding of charge carrier mobility
between the different compositions using lateral transistor measurements may help further separate the role of ionic migration and charge carriers during biasing-induced degradation pathways.\textsuperscript{325,333}

### 6.2.5 Opportunities of this lateral biasing platform

We have used a combination of correlative and \emph{in-situ} low-dose electron and optical microscopy to study the impact of electrical biasing on state-of-the-art FA-rich solar absorbers at the nanoscale. We observe the interplay between charge-carrier-mediated redox reactions driven by the slow ion segregation under bias. For the FA-pure composition, hole-mediated oxidation of iodide causes a degradation front near the positive contact driven by iodide migration across the electric field, with the concomitant lead reduction throughout the film. The same mechanism is observed for alloyed double-cation double-halide compositions, in which nanoscale variations, halide heterogeneity, and more defective sites trigger widespread bias-induced degradation. Moreover, high-angle grain boundaries are shown to hinder this degradation front from advancing, suggesting that next-gen passivating agents should also optimise for operational stability by better grain orientation. The changes reported here are similar to those observed post-illumination,\textsuperscript{163} yet this platform enables the study of carrier injection through biasing rather than through optical excitation, meaning we can selectively decouple the hole- or electron-mediated processes.

We introduce a new approach using a nanoscale MEMS-based lateral biasing platform to study structure-property relationships of halide perovskites at the nanoscale without the need for cross-section samples. This approach brings nanoscale microscopy closer to \emph{operando} conditions and the study of operational stability, relevant for other compositions or passivation treatments. In the next Section, an attempt to move beyond bare perovskite films to full devices is discussed.

### 6.3 Towards full devices: vertical solar cells for TEM studies

The second half of the Chapter covers the attempt to extend technique development on fabricating and testing vertical devices (with a \emph{p-i-n} stacked architecture) on TEM-compatible substrates (SiN grids) and TEM-compatible thicknesses (below 200 nm for electron transparency), instead of lateral biasing. This is because most PSC devices are fabricated using the stack vertical architecture.
6.3 Towards full devices: vertical solar cells for TEM studies

Figure 6.7: The TEM-compatible SiN substrate and its shadow masks. (a) Dimensions of the SiN TEM-grids used as substrate (from Norcada). (b) SE images show the SiN grid surface being extremely smooth, hard to focus on, and rapidly charging at 1 keV and 10 µA. (c) To fabricate vertical devices, a sample holder for the SiN grids was designed to which a shadow mask can be attached. (d) A series of shadow mask designs can be manufactured following the mask template in (e). (f) In particular, 5 key mask designs were used to create vertical devices. These masks are shown from a top view and are used for the evaporation of metallic contacts or perovskite layers. (g) A picture of a SiN after all 5 layers have been deposited using the shadow masks in (f).

6.3.1 Fabrication

The most simple conventional PSC device comprises at least 5 layers: opaque contact, electron transport layer (ETL), perovskite absorber, hole transport layer (HTL) and a transparent contact. In the writing of this thesis, the best PSC devices can be fabricated from low-temperature solution-processed layers in full, except for the metallic contacts at the top and the bottom. However, as described below in detail, transferring such optimal fabrication methods to a TEM-compatible substrate is not trivial. The main takeaway of this Section is that fully-evaporated devices yield the most promising results when adapting optimal device fabrication protocols to thin PSC devices on SiN electron-transparent grids. Evaporation yields more reproducible results mainly because solution processing of several layers in a row, achieved using spin coating, proves to be challenging on the smaller SiN substrates. Factors such as surface uniformity and roughness, wettability of the substrate, or thickness control to achieve electron transparency are key and explored as follows.
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TEM-compatible substrates

While numerous types of commercial electron-transparent grids were considered, all attempts to fabricate vertical PSC devices for TEM studies were fabricated on 250 $\mu m^2$ single window SiN TEM grids (NT025X, Norcada) with a 30-nm thick low-stress amorphous SiN membrane windows on a 200-$\mu m$ thick, 3-mm diameter circular Si frame. Such SiN grids were originally found to be robust for solution processing and compatible with TEM sample holders by Tiarnan Doherty. The low-stress 30-nm SiN layer is designed to withstand most thermal processes up to 1000 °C and fabrication techniques such as spin-coating and thermal evaporation. However, the SiN window easily breaks under mechanical stress such as shock. Therefore, it is likely incompatible with common cleanroom processes such as photolithography, which require sonication or invasive mechanic stressors during lift-off. While photolithography was considered during the design of the fabrication of vertical PSC devices, it was never attempted due to practical difficulties: it is difficult to undergo mask alignment for such a small substrate (only 3 mm) and post-lithography steps usually involve sonication of mechanical stressors. Figure 6.7a depicts the dimensions of the SiN grids, putting these fabrication challenges in scale. Figure 6.7b shows an SE image of the SiN grids, as sold, with a smooth surface with poor electronic conductivity which rapidly charges.

In general, all substrates need to be cleaned and the surface chemistry must be compatible with the solvents used, to ensure optimal wettability and even coating. For that, UV-ozone treatment is used for 15 minutes. While this treatment is found to affect the quality of solution-processed films as it improves surface wetting of the organic solvents when films are evaporated, the UV treatment seems to have little effect on the grain size, smoothness or compositional distribution (see Figure 6.8e), as evaporation is less affected by substrate wettability. However, it is advised to follow initial cleaning to ensure complete dirt-free surfaces prior to device fabrication.

Stacked-device designs and masks

Each of the layers of a PSC needs to be deposited on top of an electron-transparent substrate, ensuring that the active area of the device (in which all 5 layers overlap) coincides with the SiN electron-transparent window. This is so the device itself can be imaged in TEM mode. In addition, ensuring that each layer does not expand through the whole substrate helps avoid short-circuiting with the opposite contact. All these requirements can be achieved with shadow masks during evaporation. Figure 6.7c shows the design and Figure 6.7d the vacuum-compatible stainless steel shadow masks. A compatible substrate
holder was also fabricated to ensure each of the SiN 3-mm grids was well aligned with the masks. After a few iterations on the design, the custom-made shadow masks were designed to sequentially evaporate each of the 5 layers. Figure 6.7e shows the mask design principle: the area of each SiN grid can be divided into 12x12 parts. Then, subdivisions can be cut off from a mask, allowing the evaporation of selective regions on the SiN grid. Figure 6.7f shows the 5 different designs needed to fabricate a full 5-layer stack with thick metallic contact pads at both edges. Figure 6.7g shows the resulting device on a SiN grid after using a such sequence of masks.

The main limitation of this approach is the edge sharpness one can obtain with shadow masks. Although the thickness of the masks was thinned down to 200 $\mu$m due to the limits of machining, the edges between each layer expanded 50-100 $\mu$m from the edge of the masks (see Figure 6.8g). This edge contrast is nowhere near what photolithography could achieve, and future work should focus on adopting non-invasive photolithography techniques on SiN grids.

### Evaporation of device layers

The viable PSC device structure compatible with SiN substrates is found to yield from fully evaporated devices. They can be fabricated using the masks described in the previous Section (see Figure 6.7f) using the following optimal protocol:

- **Pretreatment of SiN substrates (15 min UV-ozone treatment)**
- **Au evaporation (thick lateral metallic contact pads):**
  - Mask #1
  - Automatic evaporation - 90 nm
  - Rate of 0.1 Ås$^{-1}$ for the first 5 nm, then 0.5 Ås$^{-1}$ for the next 5 nm, then 1.0 Ås$^{-1}$ thereafter
- **Au evaporation (thin bottom contact)**
  - Mask #2
  - Automatic evaporation - 10 nm
  - Rate of 0.1 Ås$^{-1}$ for the first 5 nm, then 0.5 Ås$^{-1}$ thereafter
  - Note this layer is normally optically-transparent ITO in PSCs. Manual sputtering of ITO was attempted (see later discussion) but the large thickness required for good conductivity yielded samples which were too thick for transmission electron microscopy.
- **Spiro-TTB evaporation (HTL)**
  - Mask #3
  - Manual evaporation - 15 nm
- 0.1-0.2 Ås$^{-1}$ rate (e.g. $T = 170 \, ^\circ C$ at the beginning, $170 \, ^\circ C$ at the end)

**Perovskite evaporation (thin film)**
- Mask #3
- Double-cation double-halide or FAPbI$_3$ thermal evaporation following standard methods$^{[234]}$
- 100 nm thickness aimed

**C60 evaporation (ETL)**
- Mask #3
- Manual evaporation - 20 nm
- Rate 0.1-0.13 Ås$^{-1}$ (e.g. $T = 275 \, ^\circ C$ at the beginning, $300 \, ^\circ C$ at the end)

**Cu evaporation (thin top contact)**
- Mask #2, but rotated 180°
- Automatic evaporation - 10 nm
- Rate of 0.1 Ås$^{-1}$ for the first 5 nm, then 0.5 Ås$^{-1}$ thereafter

**Cu evaporation (thick lateral metallic contact pads)**
- Mask #1, but rotated 180°
- Automatic evaporation - 90 nm
- Rate of 0.1 Ås$^{-1}$ for the first 5 nm, then 0.5 Ås$^{-1}$ for the next 5 nm, then 1.0 Ås$^{-1}$ thereafter

Note that the evaporation temperature ranges described here are only relevant for the evaporation system in the laboratories in the Chemical Engineering and Biotechnology department. Evaporation in any other system should be adapted to match the slow evaporation rates. Evaporation optimisation of the materials and rates was developed with the help of Alessandro Mirabelli.

Figure 6.8 shows how thermal evaporation can be used to deposit any thin film layer covering virtually any substrate of any size or shape. For the perovskite absorber layer in particular, the morphology of the evaporated films is maintained from the centre of the SiN window to the edges of the substrate (Figure 6.8b,c). Evaporation also offers excellent control of film thickness, which is fundamental for creating electron-transparent devices on TEM grids. Figure 6.8d shows a cross-section of an evaporated film aimed at 120 nm (as measured with the *in-situ* Quartz-crystal microbalance inside the evaporator, tooled to calibrate), with an estimated measured thickness in the SEM of 123 ±27 nm (from $n=25$ measurements).

A limitation of thermal evaporation of perovskite absorbers is that the evaporation of some compositions is hard to control, such as MA-based compositions due to the volatility of MA-salts. Therefore, only FA-based absorbers are explored in this Chapter.
when evaporation is used, such as pure FAPbI$_3$ or double-cation (FA, Cs) double-halide compositions. Thermal evaporation was developed by Yu-Hsien Chiang and Terry Yang for the double-cation double-halide [234] and FAPbI$_3$ compositions, respectively.

Apart from the perovskite layer, transport layers and metallic layers are also evaporated to fabricate a PSC. Figure 6.8f shows a diagram illustrating the alignment of bands for $p-i-n$
PSCs. It displays the metal work functions and the bandgap of the semiconductor layers, which are approximate and taken from various sources.\cite{336-340} The choice of material for each layer was limited to those which can be fully evaporated and do not require solution processing. This is a compromise between efficiency and ease of evaporation. The final fully-evaporated PSC is shown in the mosaic of optical micrographs in Figure 6.8g, where the full-device stack layers are shown. This includes the Cu thin and thick layers, contact layers with the perovskites absorber, and Ag thin and thick layers from left to right. The length of the metallic thin contacts can be adjusted to overlap, more or less, on the electron-transparent SiN imaging window at the centre.

For the choice of transport layers which are compatible with thermal evaporation, spiro-TTB and C\textsubscript{60} were chosen for the HTL and the ETL, respectively.\cite{341,342} For the choice of the top and the bottom metal contacts, several materials were tried such as gold, copper, silver or aluminium, each with its advantages. Gold gives the best contacts but heavily affects electron transparency. Silver is known to diffuse through the contact layers and react with the halides, affecting device performance.\cite{343,344} Copper and aluminium form a thin oxide layer which is insulation and makes wire bonding and electrical contact from the surface to the contact pads harder. For all metals, achieving a continuous thin layer at 20 nm thickness is also challenging and requires slow evaporation rates and optimisation.

In highly-efficient PSCs, the device thickness is normally 500 nm or more, whereas here, the perovskite absorber layer is only evaporated to 100 nm thickness, to ensure electron transparency. To ensure the evaporated thin films are comparable to the thicker analogues, XRD and PL were acquired. Figure 6.9 and Figure 6.10 compare the film quality in terms of structure and optical properties between thin and thick evaporation films for the FAPbI\textsubscript{3} and the double-cation double-halide compositions, respectively. The XRD of 100 and 500-nm thick films for both compositions indicate that the thinner film has similar properties to the 500-nm films, although the SNR is lower due to the thinner nature of the film. Note that PbI\textsubscript{2} is normally present in excess during evaporation, especially for the double-cation double-halide composition.\cite{234} This is seen in the PbI\textsubscript{2} peak intensity variations from batch to batch, such as in Figure 6.9b between the samples evaporated on glass or ITO.

Thermal evaporation is normally optimised for device-relevant substrates, such as on ITO or transport layers. Here, perovskite is often directly evaporated on the SiN grids to reduce overall sample thickness, which can affect the quality of the perovskite films. Figure 6.9b-d explores the effect of substrate on the quality of the evaporated film. The XRD comparison of thin FAPbI\textsubscript{3} films on different substrates validates that good-quality
6.3 Towards full devices: vertical solar cells for TEM studies

Figure 6.9: Properties of FAPbI$_3$, thin, evaporated films (100 nm). (a) XRD comparison of 100 and 500-nm thick FAPbI$_3$ films, indicating that the thinner film has similar properties to the 500-nm film used in PSCs. Note these were evaporated on top of an ITO glass substrate with a thin spin-coated HTL layer of MeO-2PACz, an alternative to spiro-TTB. However, we extrapolate these results to be valid for other HTL materials. (b) XRD comparison of thin FAPbI$_3$ films on different substrates, where ITO and MeO-2PACz substrates yield better films due to optimized evaporation. All peaks are indexed to the cubic $P m\bar{3}m$ perovskite structure. (c) PL spectra comparison of the same films, showing similar emissions to thicker analogues. (d) Panchromatic PL images that yield the spatially-averaged spectra in panel c. The evaporation of thin FAPbI$_3$ films produces high-quality perovskite films similar to thicker analogues used for perovskite devices. The perovskite films were evaporated by Terry Yang.

perovskite films can be readily evaporated on all substrates. PL spectra comparison of the same films shows similar emissions to the thicker analogues in all substrates, including emission from the smaller electron-transparent SiN chips (Figure 6.10b).

In short, thermal evaporation has been identified as the most robust fabrication tool for the deposition of perovskite and all other layers for a PSC on SiN TEM grids.

Other conditions attempted

Other fabrication materials and techniques were also explored in order to fabricate devices with more optimal state-of-the-art materials or use the more widely-used solution-processing techniques.

For example, ITO films are the most widely used transparent conducting electrode for PSCs. Deposition of ITO on SiN using direct-current magnetron sputtering was found to be possible, but the standard thickness to yield a high-quality conductive film (~140 nm) $^{[345]}$ is too large to achieve electron transparency. Thinner homogenous thin films of ITO can be sputtered on the SiN grids without breaking the 30-nm window (Figure 6.11). The optimal sputtering conditions were found to be at $2.00 \pm 0.05$ Pa Ar-flow, $60 \, \text{W} \pm 0.5\%$
Figure 6.10: Properties of double-cation double-halide, thin, evaporated films (100 nm). Similar to Figure 6.9, the evaporation of thin FA-rich double-cation double-halide films produces high-quality perovskite films similar to thicker analogues used for perovskite devices. This is shown in (a) the XRD comparison of 100 and 500-nm thick films, and (b) in the PL spectrum of a 100-nm thin film on a SiN electron-transparent substrate resembling the emission of the thicker films. All XRD peaks are indexed to the cubic $Pm\overline{3}m$ perovskite structure. The perovskite films were evaporated by Terry Yang.

constant power, and 265 ± 5 V by Robert Zagt. Robert and I adapted these conditions to yield a ~20 nm ITO film with a sheet resistance of 30 $\Omega \square^{-1}$ (resistivity of $\rho \sim 60 \mu\Omega$ cm$^{-1}$) by only sputtering for 10 seconds. While thicker compositions yield better electrical properties, they are too thick for TEM due to the presence of the heavy elements indium and tin. It was therefore chosen to deposit a thin metallic layer instead of ITO, due to its better conductivity at electron-transparent thicknesses.

Solution processing using spin-coating techniques was also explored with three main limitations: dewetting of the solutions on the SiN grids, incomplete film coverage of the layer on the SiN, and the breakage of the thin SiN window during spin coating and annealing. Figure 6.12 shows how spin-coating can be a rapid fabrication process to deposit device layers but the quality of the deposited layers is highly conditioned by the substrate and the solution used.

Two main HTLs were explored: Poly[bis(4-phenyl) (2,4,6-trimethylphenyl) amine] (PTAA) and poly(3,4-ethylene dioxythiophene) polystyrene sulfonate (PEDOT:PSS). Both are electron-poor amorphous polymeric semiconductors with ideal HOMO-LUMO alignment with the perovskite band gap, similar to spiro-OMeTAD. Their polymeric nature enables quick solution processing via spin-coating, compared to more timely processes such as thermal annealing required for alternative transport layers such as TiO$_2$. However, solution processing on the smaller 3-mm diameter SiN substrates was challenging due to dewetting of the polymeric solution (Figure 6.12b). Even after optimisation of the substrate pre-treatment cleaning steps using UV ozone or O$_2$-plasma
6.3 Towards full devices: vertical solar cells for TEM studies

Figure 6.11: Thickness effect of ITO and evaporated perovskite. SEM and TEM images of a series of thermally-evaporated DCDH perovskite films on top of substrates containing 30 nm SiN thin film and a sputtered thin layer of ITO. The evaporated perovskite film is the same thickness throughout the series (~100 nm) while the ITO thickness varies from 0 to 70 nm. SEM images show the surface morphology (at 1 keV) while TEM images show the effect of the sample thickness on the electron transparency and contrast (at 200 keV acceleration voltage) for the different architectures. The inset in the top-right shows the electrical behaviour of a SiN substrate which contains a thin ITO layer of 20 nm between the SiN and the top Ag contact (black), compared to a substrate without an ITO layer (red). Due to the insulating nature of SiO2, the conductivity between the contacts is only high when a thin ITO layer is sputtered.

treatment (to improve wettability), the quality of the HTL films on the TEM grids was heterogeneous across the grid, especially at the SiN thin window as shown in Figure 6.12c, with numerous pinholes which lead to short-circuiting of the PSC (Figure 6.12d). The best protocol for depositing an HTL using solution processing was found using PEDOT:PSS for
Figure 6.12: Solution processing challenges on TEM grids. (a) Another common way to deposit the PSC layers is via solution processing using spin-coating. A key challenge during solution processing is the wettability of the SiN small substrates: (b) a droplet of PEDOT:PSS HTL solution is mostly non-wetting. Such non-wetting is also observed for the perovskite precursor solution. Non-wetting results in (c) inhomogeneous films across the SiN, especially at the electron-transparent window, and (d) incomplete coverage, seen as pinholes. (e) SE image showing bad crystallisation of the perovskite film near the edges of the substrate. (f) Mosaic of optical micrographs showing the incomplete coverage of the perovskite layer over the SiN grid, also seen with the naked eye in (g). All spin-coated perovskite films shown here are of the triple-cation double-halide composition.

30 seconds, 5000 rpm spin-coating, annealed at 145 °C for 20 min under N₂-gas flow, and then slowly cooled down to 80 °C. However, evaporation of spiroOMeTAD is preferred.

For the perovskite absorber, virtually any perovskite composition can be spin coated, including the MA-containing triple-cation double-halide state-of-the-art stoichiometries. While the spin coating of bare perovskite films on SiN is simple, the addition of the metallic contact and the previously deposited HTL modify the surface wetting and complicate the spin-coating of the perovskite layer further. On top of that, the precursor concentration needs to be diluted 2 to 3 times from the 1.2 M standard concentration,\textsuperscript{17} to obtain thin-enough films for TEM characterisation (∼150 and 200 nm, respectively). These two complications often result in heterogeneous film morphologies (Figure 6.12e), and incomplete film coverage of the SiN grid (Figure 6.12f, also visible with the naked eye in Figure 6.12g). Finally, for the ETLs, the polymeric version of C₆₀, phenyl-C₆₁-butyric acid methyl ester (PC₆₀BM or PCBM) can be spin-coated followed by bathocuproine (BCP) straightforwardly.

In short, most of the difficulties arising from solution processing due to the inherently different nature of the surface chemistry of SiN can be overcome by using thermal evaporation instead. Moreover, solution processing techniques do not offer spatial control over where each layer is deposited in contrast to masking during evaporation. Henceforth, if the fabrication of PSCs or perovskite devices is further explored in the future, thermal evaporation should be the best fabrication technique for SiN substrates.
6.3 Towards full devices: vertical solar cells for TEM studies

Figure 6.13: *JV*-curves for thin devices. The optoelectronic behaviour of PSCs fabricated on either standard ITO substrates (left) or on electron-transparent SiN grids (right) can be measured by sweeping a voltage and measuring the current (*JV*-curve). (a) The *JV* curve of a photovoltaic device, in which under bright illumination and positive potential, a photogenerated current is measured. (b) Failed PSC device showing a light dependence resistor behaviour. To measure the *JV*-curves of devices on small SiN substrates two contacting methods can be used: micromanipulators which result in (c) high-resistance contact between the tips and the contacts on the device, or wire bonding, which results in (d) cleaner contacts with low resistance. However, fabricating full devices on SiN substrates is non-optimal and numerous device failures can be recorded: (c,d) *JV*-curves without photovoltaic activity under the presence of light and with high resistivities, (e) *JV*-curve showing a diode behaviour without photovoltaic activity. Device architectures: (a) ITO| PEDOT:PSS (10 nm)| triple-cation double-halide perovskite (200 nm)| PCBM-BCP (20 nm)| Ag (35 nm), (b) ITO| Spiro (15 nm)| double-cation double-halide perovskite (70 nm)| C60 (20 nm)| Cu (15 nm), and (c,d,e) SiN (30 nm)| Au (10 nm)| Spiro (15 nm)| double-cation double-halide perovskite (100 nm)| C60 (20 nm)| Cu (10 nm).

6.3.2 Device testing

**Electrical contacts and *JV*-curves**

After the full vertical stack device fabrication, the quality of the PSC needs to be measured. For that, the relationship between the current and voltage can be studied using *JV* curves. To extract and measure *JV* curves from the small SiN substrates, two methods to electrically contact the devices were explored, illustrated on the right of Figure 6.13: (i) The use of a set of tungsten micro-probes attached to two micromanipulator arms under an optical, which enables the accurate contact of the probes with the thin PSC device metallic contacts. However, due to the thin nature of the metallic contacts and the sharpness of the tungsten tips, the contact normally resulted in scratches and peeling off of the metals resulting in bad electric contacts between the sample and the probes (see the visible scratches.
on the metal pads in Figure 6.8g). Alternatively, (ii) the use of wire bonding was found to yield better contacts. Wire bonding is a technique that connects the bond pads on a chip (the SiN grid) to the leads on a larger substrate using thin wires, in this case, made of aluminium. This technique is less invasive and is permanent, allowing testing devices also inside the TEM (see next Section).

$JV$ curves can determine the (opto)electronic properties of a device. If the sample behaves as a resistor, its $JV$ curve is represented by a straight line that intercepts the origin, making it a passive device, with the current proportional to the resistance at each voltage described by Ohm's law. A diode only permits current flow in one direction, which can be observed from the $JV$ curve (the current increases exponentially at positive voltages while it stays near zero at negative voltages). A solar cell functions similarly to a diode in the dark, but when illuminated, its $JV$ curve shifts downwards (into quadrant 4), making it an active device that provides electrical power to the connected circuit. Important properties such as open-circuit voltage ($V_{OC}$) and short-circuit current ($I_{SC}$) can be determined by analyzing its $JV$ curve as the intercepts of the x and y axes, respectively.[350] For example, Figure 6.13 compares the $JV$-curve of a working solar cell (Figure 6.13a), fabricated on a standard ITO substrate, with $JV$-curves from commonly seen device failures. Based on the $JV$-curve in Figure 6.13b, from a failed PSC device on a standard ITO substrate, the shape of the $JV$-curve crosses the intercept and shows a linear relationship, thus behaving as a resistor.

Changes in the illumination condition (from dark, to bright, to very bright as 1-sun equivalent illumination) changes the linear slope, thus behaving similarly to a light-dependent resistor. The failure of a PSC device is complex to pinpoint, however, two main parasitic resistive effects can dissipate the power generated by a solar cell: series and shunt resistance.

- **Series resistance** originates from the resistance that the current flowing through each material layer in a PSC encounters, such as the resistance of the metal contacts or the transport layers, or the resistance at the interfaces between layers. Series resistance mainly reduces the fill factor of a solar cell and is inherent to the material choice and the quality of the interfaces between layers.[351,352] In particular, since fully-evaporated devices were the only possible fabrication route on SiN substrates, the material choice here is not optimal, making series resistance higher than in optimal device architectures.

- **Shunt resistance** originates from manufacturing defects which provide alternative paths for the light-generated current to flow. Such current diversion reduces the amount of current through the absorber material and reduces the voltage from the solar cell. This effect is severe at low illuminations since less current is generated
Table 6.1: Measurements of the *in-situ* biasing holder and SiN chip, colour labelled in Figure 6.14a.

<table>
<thead>
<tr>
<th>Label</th>
<th>Description</th>
<th>Length (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Hole to pins</td>
<td>5.86 ± 0.06</td>
</tr>
<tr>
<td>2</td>
<td>Hole to edge</td>
<td>6.33 ± 0.05</td>
</tr>
<tr>
<td>3</td>
<td>Hole diameter</td>
<td>2.42 ± 0.01</td>
</tr>
<tr>
<td>4</td>
<td>Holder width</td>
<td>3.18 ± 0.01</td>
</tr>
<tr>
<td>5</td>
<td>Chip width</td>
<td>10.02 ± 0.01</td>
</tr>
<tr>
<td>6</td>
<td>Chip height</td>
<td>3.15 ± 0.01</td>
</tr>
<tr>
<td>7</td>
<td>Contacts to SiN window</td>
<td>4.97 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>Chip thickness</td>
<td>0.53 ± 0.01</td>
</tr>
</tbody>
</table>

from light.\[351,352\] In particular, the common presence of pinholes during the fabrication of electron-transparent devices (see, for example, Figure 6.12d-e), due to the need for unusually thin layers, is likely to result in high shunt resistances.

Figure 6.13c shows a PSC device with $I_{SC}$ at $\sim 0.1$ nA and $V_{OC}$ at $\sim 2$ V. However no light dependence is observed, attributed to the bad contacts between the micromanipulator and the top and bottom metal contacts. When wire bonding is used instead, better current readings are reported. Figure 6.13d shows a malfunctioning device in which dark currents are larger than under illumination, which may be attributed to shunt resistance from light-generated current ($V_{OC}$ decreases from $\sim 3.5$ to 2.5 V). Moreover, the fill factor shows clear signs of series resistance. Due to short-circuiting across the transport layers, these devices show light-dependent resistance behaviour instead of photovoltaic activity. Moreover, the main difference between panels d and e in Figure 6.13 is that in d the top and bottom metal contacts do not fully extend and overlap on the active area of the PSC, but a lateral voltage is thus applied. Panel e has fully overlapping metal contacts stacked between the active area of the solar cell. However, 6.13e does not show photovoltaic activity but just diode behaviour. This may be attributed to the bad quality of the perovskite film during thin evaporation, which resulted in unusual crystallisation.

Further attempts, following the optimal steps described in this Chapter, may eventually yield PSC with good JV curves. Figure 6.13e is the closest to achieving this milestone. Overall, these findings may suggest that thinning down the device architecture to 10-20 nm layers may unavoidably result in the formation of pinholes or low-quality films which inhibit charge extraction and have a detrimental effect on the PSC efficiency. However, the optimisation of each evaporated layer can result in lower series resistance and limited shunt resistance and, with the use of wire bonding, good electrical contacts can be made to the SiN electron-transparent PSCs.
**Figure 6.14: Self-made in-situ TEM biasing setup.** (a) Measurements of the in-situ biasing holder with 4 contact pins (adapted from the heating DENS solutions holder) and the respective SiN chip (inset). (b) The image on how the fabricated PSC on a SiN chip is wire bonded to the backbone Si chip and is electrically connected to the biasing holder. (c) Diagram of how the metallic pins on the holder relate to the biasing connector (circle with 5 cables), and to the coloured cables. (d) Setup for in-situ biasing in the TEM, where the power-source meter is connected to the biasing holder, which is then placed inside the vacuum chamber of the TEM. (e) Electron beam current was measured inside the TEM during 5 V biasing. Beam blanking can be measured.

**Electrical biasing inside the TEM**

Finally, the complete PSC devices can be wire bonded to substrates that are compatible with in-situ TEM holders, such as the commercial heating holder from DENS solutions (Figure 6.14a). The geometry inside a TEM is limited by the internal pole pieces and detectors. The exact measurement limitations of any sample that can fit inside the TEM using an FEI-based holder (from Thermo Fischer Scientific) are tabulated in Table 6.1. A key limitation is the height limitation a sample can have inside the TEM, estimated to be $\sim 350 \, \mu m$ for the FEI Tecnai model. Following such spatial limitations, the PSC device on the SiN grid can be placed on the in-situ holder, yet the wire bonding loop height must not surpass this limit. Moreover, simply stacking both DENS solutions (Figure 6.14a) with the SiN PSC sample results in samples that are too high for the TEM. Therefore, the DENS solutions chip had to be broken into 2 pieces and stitched to the SiN device with wire bonding (see right diagram in Figure 6.13).
6.3 Towards full devices: vertical solar cells for TEM studies

Figure 6.15: Alternative architectures. (a) STEM images of a perovskite LED device on a TEM grid (SiN| ITO| PEDOT:PSS| sPbBr$_3$ (quasi-2D nanocrystals in ligand solution)| TPBi) at 200 keV. Despite missing the top Ag contact, a very sharp contrast is observed due to the inherent thin nature of LEDs. However, the crystallisation of CsPbBr$_3$ was altered due to wettability issues of the SiN grid during solution processing. A continuous film should be observed instead. (b) Alternative design architectures were also explored during this thesis, which yielded worse results than the vertical architecture presented above. (c) A theoretical back-contact PSC design inspired from [325].

Figure 6.14b shows such a setup, in which 4 contact pins are accessible from the holder. Originally, the DENS solution holder is designed for heating experiments. However, here the heating holder is used for biasing by contacting two of the 4 accessible pins to the top and bottom contact of the device. Using a power-source meter, $J\!V$-curves and bias can be applied in-situ from the TEM holder (Figure 6.14c). The connection diagrams for how the metallic pins on the holder relate to the biasing connector (circular connector with 5 pins), and the colour-coded cables are shown in Figure 6.14d for future reference. It is important to ensure that the TEM holder is grounded, else the TEM software detects a pole touch error even though the sample is not hitting the components inside the TEM. Finally, such a setup can measure beam-induced current in TEM mode, as shown in Figure 6.14e where currents in the 10 nA range can be measured at 5 V bias when the electron beam is not blanked. Moreover, $J\!V$-curves could also be measured in-situ, as shown in Figure 6.13e.

6.3.3 Key challenges and opportunities

Fully evaporated devices have been identified as the most promising fabrication technique for electron-transparent PSC devices on SiN grids. Electrical contacts are better achieved using wire bonding, which is compatible with the TEM geometry constraints. Overall PSC device thickness remains the main challenge, as thinning down fabrication recipes from thicker optimal protocols results in defects and detrimental device performance. Perovskite LEDs are inherently thinner than PSCs, with emitter layers in the tens of nanometers, [236,257,261], especially for nanocrystal-based LEDs, [353] which is ideal for achieving full device thickness below 200 nm. Figure 6.15a shows STEM-HAADF micrographs of a complete state-of-the-art LED (SiN| ITO| PEDOT:PSS| sPbBr$_3$ (quasi-2D nanocrystals in ligand solution)| TPBi) without the top metallic contact. The sample
thickness is ideal for electron transparency, estimated here to be below 200 nm. However, such LEDs can only be fabricated using solution processing, which was not optimal and resulted in individual crystals instead of a continuous film. Further work should use the inherent thinner nature of perovskite LEDs to explore in-situ studies of such devices, yet the main limitation remaining is the optimisation of the solution processing on the SiN TEM grids. Finally, other device architectures were also considered, as illustrated in Figure 6.15b, in which the top metal contact is modified to a smaller area to reduce the short-circuiting likelihood. However, they yielded worse results than the final vertical structure presented above in this Chapter.

6.4 Conclusion

This Chapter has presented the key challenges of adapting state-of-the-art PSC device structures to TEM-compatible grids. A plethora of fabrication challenges exist, which can be solved by thermal evaporation. Lateral architectures are better suited for TEM studies. With these developments, we can now move a step further from studying phase stability towards understanding operational stability in the nanoscale of these FA-based perovskite solar cell absorbers. We present a novel platform to monitor redox-related degradation reactions in-situ, by employing a multimodal toolset of correlative low-dose electron and optical microscopy measurements. This approach helps understand the degradation chemistry and decouples the role of electrons from holes and the role of ionic migration. This platform stands out from other in-situ biasing electron microscopy experiments as it can image large fields of view at the nanoscale and does not require radiation-intensive milling, which could damage the specimen. In light of the continued drive of halide perovskites towards commercialisation, our study contributes to the nanoscale understanding of these complex materials under operational bias and offers insights into the development of more stable and efficient solar absorbers.
Chapter 7

Conclusions and Prospects

7.1 Conclusions

In this thesis, we developed a strong multimodal microscopy framework, centred around electron microscopy (EM), that is capable of probing the nanoscale of formamidinium (FA)-based halide perovskites, ultimately with electrical bias in-situ, which can probe the perovskite absorber under stress to better understand the operational stability and the structure-property relationship at the nanoscale. In particular, 4D-STEM and CL were identified as useful EM techniques to probe structure and optical properties, respectively. However, they both lead to electron-beam-induced damage to the beam-sensitive specimens. A significant portion of this thesis focuses on understanding structural and optical changes during electron (and, shortly, X-ray) nanoprobe radiation to understand the limitations of possibilities of these techniques, ultimately allowing for in-situ biasing of these films for the first time.

In Chapter 4, we identify that the nanostructure of FA-based perovskites can be affected by a low-dose electron beam (∼10 e− Å−2) in two phases: (i) at extremely low radiation exposure, changes in the orientation of the grains are seen, followed by (ii) at high radiation exposure, degradation of the perovskite phase is observed, involving iodine migration, producing decomposition to lead halide species such as PbBr2 concomitant with PbI2 crystallites. In particular, regions showing high-angle defective grain boundaries are hot spots for degradation. This further understanding of the exposure limits of high-energy electron and photon beams provided in Chapter 4, being <200 e− Å−2 at 200 keV and <5,000 photons Å−2 at 20 keV, is crucial knowledge prior to the in-situ measurements shown in Chapter 6.

In Chapter 5, we identify that the optical emission of FA-based perovskites can be also heavily affected by the electron beam scanning during CL. By studying the param-
eters affecting the emission quality from the perovskite upon changes of acquisition of CL maps, in particular the effect of the beam mode, namely continuous-wave (CW) or pulsed-mode (PM), we can yield more robust CL acquisition from these beam sensitive materials. Using a PM electron beam, the CL spectra strongly resemble those obtained from pristine perovskite emission in PL, yet, even in optimized conditions, some effect related to beam damage is observed in the form of an intermediate broad peak at higher energies (even for currents as low as <100 pA). Distinctively, when similar perovskite films are imaged in CW mode at higher electron-beam currents, the remaining emission post-CL is red-shifted and heavily quenched and the surface morphology is heavily milled away. While the exact degradation pathway differences between these two modes have not been fully elucidated, a PM electron beam can allow for the perovskite material to relax, cool down, and "self-heal" (in terms of ionic migration) between pulses, which can result in halide demixing [101, 283, 295, 296] or the formation of confined nanocrystallites.[297]

In CW, higher local temperatures may be reached leading to thermal degradation and damage to the organics. Note that the estimated electron fluence during CL scans can reach values of $10^{8-12}$ $e^- \text{Å}^{-2}$ at the surface of the sample, much larger than in 4D-STEM methods (without taking into account the radiation then distributes throughout the larger interaction volume of SEM). While further research should aim at understanding these two differences, and this thesis simply describes what causes could cause a red or a blue shift, these observations set clear limits on how to use CL-SEM on hybrid halide perovskites. However, it also unlocks the use of CL hyperspectral mapping on the more beam-sensitive hybrid perovskite compositions, supported by robust transparent processing and analysis methods as open-source software. Some examples have been shown in this Chapter, but that is just the start and we expect many more studies can be enabled from this understanding, especially as SEM-CL systems with PM capabilities become more prevalent and equipped with more sensitive and faster detectors.

In Chapter 6, we present a platform to monitor degradation reactions in-situ to understand the degradation chemistry and decouple the role of electrons from holes and the role of ionic migration. We decouple charge-carrier-mediated redox reactions driven by slow ion segregation under bias at the nanoscale. We compare the differences between FA-pure and alloyed device-relevant compositions during the hole-mediated oxidation of iodide diffusing through the electric field. An underlying mechanism is proposed, which causes a degradation front near the positive contact or defective sites, for the FAPbI$_3$ or the alloyed compositions, respectively. These findings are key for improving the operational stability of solar absorbers.
Overall, these observations, within the electron-beam-induced damage thresholds, showcase how useful low-dose 4D-STEM techniques are for advanced studies of the nanoscale of beam-sensitive materials, even enabling access to in-situ information.

This thesis describes two observations regarding high-angle grain boundaries in halide perovskites. In Chapter 4, high-angle defective grain boundaries were identified as a weak spot for electron-induced degradation, which has implications for perovskite phase stabilization. However, in Chapter 6, high-angle grain boundaries were observed to stop the propagation of degradation during in-situ biasing, which is related to operational stability. Although these observations may seem contradictory, they highlight the trade-off between phase stabilization and operational stability, similar to the case of PbI$_2$. Therefore, passivation and growth strategies targeting the removal of defects in high-angle grain boundaries will be critical for mitigating both phase and operational instabilities. Passivation strategies have been shown to help with electron-beam stability in Chapter 5, and combining these strategies with novel microscopy techniques can provide a better understanding of the chemistry of passivation in halide perovskites and extend the radiation tolerance of these materials during EM.

### 7.2 Prospects

#### 7.2.1 The future of halide perovskites

In the last decade, the relationship between the structure and properties of halide perovskite polycrystalline films has been a hot topic. Multimodal microscopy approaches have been instrumental in investigating these complex materials, leading to a new understanding of semiconductors, partially through seminal work by this group. We now have a better understanding of the origin of traps and the importance of multiple-length scales, including the nanoscale. However, questions about how much the findings from studying the perovskite absorber by itself relate to devices are still a work in progress. The nanoscale dynamics, namely the evolution of defects and their formation, as well as how they lead to the failure of a device, are not yet well understood. Therefore, microscopy and spectroscopy research is currently focused on developing operando and in-situ experimental setups to answer these questions. Advancements in technique development are starting to help elucidate the nanoscale evolution under stimuli. Early findings seem to suggest that the management of defects and stability through passivation and material phase control, or better-controlled crystal growth, is key to moving halide perovskites from the laboratory to the industry.
Another significant area of research that requires exploration is the impact of interfaces at the nanoscale. Of particular interest is the interface of perovskite with other materials in a tandem configuration, as it has the potential to boost and extend the efficiency of for examples commercial Si solar panels. Understanding the fundamentals between these two materials should be the primary focus of future research. While some questions have been answered to a certain extent through cross-sectional specimens, the advancement of fabrication tools (such as the ones presented in Chapter 6), and the advancement of better microscopy setups is starting to enables the study of full-stack devices from a top-view perspective too, providing a larger field of view and new insights into device operation.

I would like to add a final note on one key challenge in the PSC field that deserves more attention in the perovskite community, especially after spending years pushing the stability limits of these new materials with high-energy radiation: the issue of organometallic lead toxicity and its leakage to nature upon degradation. Rather than trying to cure toxicity issues after developing and deploying new materials, I believe that prevention should be a key focus during the development stage (see the case of the microplastics issue, only 70 years after the first commercial petrochemical polymers). Recent years have witnessed the rise and maturity of tools like life cycle assessments (LCA), which can help us evaluate the true impact of new technologies and materials. As such, I think it is important that the perovskite field and other academic disciplines, as well as funding bodies, take LCA evaluations more seriously and use them as a key metric to drive funding and scientific progress. While some people may argue that academic development should solely focus on generating knowledge and that practical concerns can be addressed at later commercial stages, it is becoming increasingly clear that the commercialization of academic research is closely tied to the commercialization of science. In fact, the gap between the two is narrowing more than ever before. Thus holistic evaluations of new materials should be leveraged to ensure that the environmental impact of new materials is properly assessed and addressed, especially for energy materials focused on sustainability, and even more for materials which can easily degrade.

7.2.2 The future of electron microscopy

This thesis takes steps in pushing the limits from static to dynamic EM on beam-sensitive materials with the development of in-situ techniques. I suspect more and more work will focus on making EM closer to real operando conditions, not only by adding external stimuli but also by adding atmosphere. A particular low-hanging fruit is the study of perovskite LEDs, as they are inherently thin and only electrical biasing is needed to
Figure 7.1: CL and 4D-STEM correlation for a non-perovskite solar cell material. A cross-section of an alloy of Cu, In, Ga disulfide (CIGS) used for next-generation solar cells. These devices are analogous to CIGSe₂ solar cell absorbers and show a notch-type bandgap emission with a red-shift followed by a blue-shift as you go deeper into the material. STEM techniques were used to (a) map the cross section in HAADF and in 4D-STEM. (b) Virtual dark field (vDF) images were stitched together, obtaining nanoscale diffraction across the grains in the cross-section, being able to resolve (c) high-angle grain boundaries and (d) the two Ga-rich/Ga-poor crystalline structures with distorted diffraction vector spacings. (d) These two diffraction features can be readily resolved in 4D-STEM and also in (f) CL panchromatic maps, acquired in the same area as 4D-STEM. The perfect pixel resolution match is exemplified with (g-h) the band-pass CL images for the Ga-rich and Ga-poor emission, respectively. The coloured boxes represent the scale of each of the 4D-STEM maps acquired previous to CL-SEM in STEM mode. Sample: CIGS with a 0.98 Cu:(In + Ga) ratio, and a 0.34 Ga:(In + Ga) ratio, fabricated by Rachel Oliver and her group and collaborators. 4D-STEM and CL-SED acquisition at normal SED conditions and CW mode, described in Chapter 3.

replicate operational conditions. How do the shape, size, ordering, composition and structure of the nanocrystal-based LEDs change under operation in terms of emission and structure, or where do the failure mechanisms of LEDs originate are questions which answers are ramified on the nanoscale.

For PSCs, apart from biasing, in-situ illumination using a custom-made holder can be also added. While such special holders have been proposed, their use is limited. While they could allow for in-situ light soaking experiments in the TEM, which combined with biasing would mimic operando conditions thus going beyond ex-situ characterisation experiments after light-soaking, the electron beam itself can also act as the excitation radiation, generating charge carrier densities larger than those generated under 1 sun (see Section 4.5.2).

In the field of halide perovskites, EM has not yet been explored to its full potential. Cathodoluminescence is an example where, in this thesis, we have shown it is particularly interesting to match the resolution mismatch between optical microscopies and electron microscopies when probing optical signals. In fact, attempts to correlate SED with CL-SED
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on other non-perovskite solar cell materials are also exciting, as shown in Figure 7.1, a cross-section of an alloy of Cu, In, Ga disulfide (CIGS), with at 0.98 Cu:(In + Ga) ratio, and a 0.34 Ga:(In + Ga) ratio. These devices are analogous to CIGSe$_2$ solar cell absorbers and are interesting because they show a notch-type bandgap emission with a red-shift followed by a blue-shift as you go deeper in the material. To explore that, cross-section lamella of CIGS absorbers were imaged using 4D-STEM first, in SED mode, followed by SEM-CL mapping on the same region. STEM techniques were used to map the nano-diffraction of the cross-section by stitching together several scans. The nanoscale diffraction across the grains can resolve, besides others, high-angle grain boundaries, and the region where the two Ga-rich/Ga-poor crystalline structures with distorted diffraction vector spacings are placed (Figure 7.1e). These structural features closely match the optical features resolved by panchromatic CL maps, acquired in the same area as 4D-STEM. Some of the structural features result in dark grain boundaries, while others do not. This example showcases the perfect synergy between STEM and CL-SEM in terms of pixel resolution. Both structural and optical methods can resolve the notch-type bandgap across the depth of the solar cell absorber. Future studies should expand on using time-resolved CL (TRCL) mapping on these regions, which just became possible due to hardware and software improvements, to include some correlative understanding of the transient emission across the cross-section, akin to confocal optical microscopy using TRPL.

The development of a pulsed beam was found beneficial, but more work should focus on understanding this process further and modifying the acquisition parameters further. What if the pulse mode is modulated by making pulse separation longer to let the relaxation of the semiconductor happen for longer? What is the effect of cryogenic temperatures in such relaxation, and can it help with retrieving the optical signal? Questions that once answered, will continue to expand on the usefulness of CL in probing beam-sensitive semiconductors, not only limited to halide perovskites but many other semiconductors. In particular, I expect TRCL to eventually be possible on dimmer beam-sensitive materials through the use of better detectors, optimal acquisition conditions and optimised chemical structures and surface chemistry.

Finally, I want to reiterate that in the field of halide perovskites, EM has not been yet explored to its full potential. With the recent advances and optimisation of thermally evaporated halide perovskite films, greater control of the thickness of films can be achieved. This means that high-quality thin-enough films can be fabricated for the first time, which can enable the use of techniques that normally require ultrathin specimens (below 50 nm), such as high-resolution (HR)-STEM$^{53}$ or even electron-energy loss spectroscopy (EELS). I believe that EELS, in particular, can offer invaluable information on the optical properties
of perovskites at the nanometer and sub-nanometer resolutions. Moreover, exceptional monochromated electron beams are becoming more prevalent, allowing to image of the optical bands of EELS at great spectral resolution.\textsuperscript{[361,361,362]} Interesting questions using this newly-accessible technique include: how does optical-EELS link to the defects and traps, to complement on the successful findings from photo-emission electron microscopy (PEEM)\textsuperscript{[162]}? What are the optics at the grain boundaries and transport-layer interfaces? How homogeneous are the optical and electronic properties across the nanoscale heterogeneities? How does HR-STEM correlate with the nanostructure as extensively seen, and studied, from 4D-STEM?

Note that the same multimodal microscopy approach to material understanding developed in the Stranks lab in recent years also has huge potential to be applied to other materials with critical questions on how the structure and optics are linked. An example, explored by me as a side project, tried to shed light on the nature of single-photon quantum emitters in colour centres (defects) in hexagonal 2D boron nitride, which proved all these techniques to be useful.

### 7.2.3 The future of material discovery

Detectors continuously get better in an exponential manner. In this thesis, we have used direct electron pixelated detectors (Medipix), which I believe are the current standard and make scintillators with CCDs obsolete. This development is not slowing down. For instance, as event-based detectors hit the market in the next years, they have the potential to get the time dimension into the acquisition data, allowing for a better understanding of how data acquisition changes at fraction of times. One can dream of being able to filter structural and spectral datasets based on cumulative fluence, making the understanding of damage-induced changes significantly easier. These significant developments in detectors finally give EM good direct detectors that enable us to "see" what was before impossible to see, namely at extremely low fluences and on beam-sensitive materials.

Only about a decade ago, most data processing was done live, by adding physical energy filters and apertures during data acquisition. Now, most data processing is done after the experimental acquisition, in the computer. While this thesis heavily makes use of virtual dark field images, I would personally struggle to generate dark field images using real apertures during TEM data acquisition. EM has shifted to a data driven direction. Data acquisition is not the limiting factor anymore. We now produce unprocessable amounts of data in minutes (an estimated overall data size analysed in this thesis surpasses the 20 TBs). Therefore, one of the key developments in EM is new ways to compress, process
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Figure 7.2: Towards more automated pipelines for material discovery. The rise of (a) high-throughput mapping of new materials at the nanoscale enables a better and more statistically-significant understanding of (b) the features of the nanoscale, such as structural phases and microstructure. These identified features can be linked to (c) other material properties such as compositional, optical or electronic. High-throughput correlation of features enables accurate (d) guided optimisation of the fabrication and optimisation of new materials, which could eventually become fully automated. With such a streamlined automated and quantitative pipeline, (e) rapid discovery, optimisation and deployment of new materials can be envisioned, revolutionising interdisciplinary sectors.

and analyse these large datasets, yet quite sparse, in a robust insightful and rapid, even real-time, manner.

A bigger key development in EM is the shift towards computational EM, and ultimately automated feature identification at the nanoscale together with artificial intelligence (AI)-driven material discovery (see Figure 7.2). With the rise of high-throughput mapping of new materials at the nanoscale, a better and more statistically-significant understanding can be gained of what features of the nanoscale matter. Moreover, combining structural data of the micro and nanostructure with other material features such as compositional, optical or electronic properties can lead to a more meaningful high-throughput correlation of features. This learning can be combined to guide material discovery and optimisation, and if combined with robotics, the whole process may eventually become fully automated. Streamlined automated and quantitative pipelines for material discovery can lead to better and more rapid discovery, optimisation, and deployment of new materials. These advancements have the potential to revolutionise many interdisciplinary sectors such as energy material, hardware, quantum materials, or even healthcare, and EM can be a critical enabler. The method proposed here is not impossible, especially if one takes
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Figure 7.3: Automated phase mapping for halide perovskites. (a) Supervised learning is an option to train a model (here a deep neural network using TensorFlow[^366]) based on the simulation of diffraction patterns using diffsims[^187] (an open-source Python package). Then, the trained model can be used to infer what is the most likely crystal phase present at each scanned pixel in a 4D-STEM dataset. (b) Unsupervised learning methods such as encoder-decoder neural networks can be used to transform a given diffraction pattern into a latent space, which can be clustered to identify known and unknown features between diffraction patterns. Once a cluster is selected, a phase map can be created and a mean diffraction pattern (here as an azimuthally integrated 2D pattern) can be plotted. The encoder-decoder was coded by Po-Yen Tung.

Inspiration from the biological cryo-EM field on structural biology in which automation has boomed and is enabling exponentially faster drug discovery.[^363–365] Why cannot material science do the same?

During the second and third years of my PhD, I explored the topic of automation for the analysis of large datasets of 4D-STEM of halide perovskites, in particular the problem of phase mapping of the different perovskite, impurity and precursor phases present in...
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polycrystalline films, as shown in Figure 7.3. Supervised learning, in which a model, here a deep neural network using TensorFlow,[366] was trained on the simulation of diffraction patterns of all the different possible known phases and orientations, using diffsims,[187] an open-source Python package. Once the model was trained, it could be used to infer (incorrectly) what the most likely crystal phase present at each scanned pixel in a 4D-STEM dataset was (Figure 7.3a). Many difficulties were found with this approach, with the main challenges being: the simulated data did not resemble the experimental data due to the use of too simple models to simulate diffraction without dynamic effects or multiple scattering. Moreover, experimental datasets on halide perovskites have inherently low signal-to-noise due to the low fluences used. Moreover, supervised models require the assumed knowledge of which phases are present. However, as shown throughout this thesis and in previous works, the nanoscale of halide perovskites is heterogeneous and very sensitive to compositional changes. Finally, such an attempt lacks generalisability to be applied to other material systems. However, similar supervised learning methodologies have been proposed with better generalisability.[181,190]

Alternatively, with the collaboration of Po-Yen Tung, unsupervised learning methods such as encoder-decoder neural networks were also explored (Figure 7.3b). These models can be used to transform a given diffraction pattern into a latent space, similar to previous work done with battery materials.[367] The latent space is a non-physical set of dimensions that contain the features learnt, and clustering of this space can lead to the identification of known and unknown features between diffraction patterns, without the need to input previous knowledge. A cluster can be selected and a phase map, corresponding to regions where a given feature in the latent space dominates, can be created. Similarly, a mean diffraction pattern from the phase map, here shown as an azimuthally integrated 2D pattern, can be plotted. This method also failed at identifying regions with phases of interest, such as the hexagonal perovskite polytypes, as the clustering of latent space was dominated by the bright grains, near the zone axis, and weaker features were not learnt.

However, these two approaches showcase the potential of both supervised and unsupervised methods as tools to explore these large datasets, as means of dimensionality reduction, and as methods to link the multidimensionality of spatially resolved spectra and images. Data science, a newly coined term for applied statistics and applied probability, has now fully encountered EM and is changing the way microscopists interact with the nano-world. It is an exciting time to explore, develop and use the tools provided by machine learning and AI, to support and boost the microscopy outputs. "What a time to be alive!"[368]
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7.2.4 The importance of open-source

To conclude, the importance of open-source software cannot be overstated. While the methods section of research papers is typically extremely explicit about the chemicals used and how the samples were made, as well as the data acquisition process, it often lacks transparency and reproducibility regarding the data processing and analysis. Even the preprocessing of data, including the specific version of a package used, can significantly impact the interpretation and claims of a study. I believe drawing inspiration and standards from computer science can help address this issue: the triangle connecting open-source code, with good readable documentation, and good demo notebooks. This triangle can help ensure transparency and reproducibility in data processing and analysis. Other tools like the use of docker files or dependency files, together with open data initiatives, are also important for ensuring reproducibility.

Going a step beyond, the future of research reporting and publication may benefit by evolving into something more similar to code development platforms (e.g. GitHub or GitLab). In such publication platforms, scientists could share methods, data, and analysis at much earlier stages than the interpretation stage and publication stage (see the recently published Octopus initiative as an example). This would allow for more collaborative, transparent, and merit-based data acquisition, data analysis, and data interpretation. This is crucial because research groups are often too small to be experts in all aspects of research such as sample fabrication, data acquisition, and data analysis. Collaboration, transparency, and reproducibility are key for advancing research.
Acknowledgements

Let me start by acknowledging my academic supervisors. The NanoDTC allowed me to have two project supervisors, which I am very grateful for. I would like to acknowledge Sam Stranks and Cate Ducati for supporting this project during the last 4 years, and for letting me grow, try, fail and succeed at understanding the art of academic research. Thank you for the financial and personal support given and for the many lessons, opinions and advice shared. Thank you for involving me in new projects and novel ideas, especially during times of hardship, covid and family illnesses. Thank you for the two wonderful groups you made me part of, from which I learnt from the best and brightest. In particular, thank you for the flexibility and understanding given to me during all these years so I could develop skills outside just academia such as in developing entrepreneurship, teaching and personal skills.

Most of this work was supported financially by the NanoDTC EPSRC grant (LJAG/ 790/ T4), the ERC HYPERION grant and several ePSIC (Diamond Light Source) sessions. Thank you to these funding bodies, in particular the NanoDTC. The NanoDTC has provided an invaluable platform to learn, connect and gain inspiration through Cambridge. In particular, Karishma Jain and Kim Cole for their constant support in times of doubt and for their investment and trust in me and my development. Without their career advice and support, Cambridge would have been much less valuable.

I would also like to acknowledge my college, Trinity Hall for their constant support during my years in Cambridge. Thank you for making me feel at home in college, for the generous financial support to travel and to develop entrepreneurship skills, and for the social support within the MCR (in particular Clare Kerr). I have made lifetime friendships in Trinity Hall and would like to specially mention Kelsey Granger, Ivona Bravic, Paraham Bournhoud and Ehsan Esadi, as they were always present in my personal life to support me during times of happiness (such as when winning blades during rowing) and times of hardship.

A PhD is not the easiest time as it is a continuous process of learning and challenges. The first year was the year to settle in, to me, a completely new field of sciences. The second year taught me how to start projects on my own and be creative. The third year
taught me the art of finishing projects. All these valuable project management skills would have not been possible without the plethora of people who have helped me, supported me and cheered me up when I needed them the most. In particular, thank you Affan Iqbal (Habibi), my office buddy. Affan has always been there during the days after lockdown, sharing our windowless office and always present there at 7 am when Kapitza was empty. Thank you Affan for all the discussions, the Diamond times together and, especially, the many hours spent in the office together writing both of our theses in parallel. With Affan comes all the Kapitza squad, including Dan Sowood, Darsy Unson, Alessandro Mirabelli, and Satya Nagane, the people with whom I have shared countless lunches, controversial debates and many 2x1 pizzas on Mondays. Thank you for making the work environment a fun and personal space to share science, but most of all, share our thoughts and personal worries about graduate life and the future. In Kapitza, Beth Tennyson and Tiarnan Doherty were also very important at the beginning of my PhD. They were whom I used to share my office with and they mentored me. Tiarnan taught me what makes a good or a bad scientific question, and Beth showed me how to be kind in such a competitive academic world.

Apart from the Cavendish (Kapitza), half of my PhD has been in the Materials Department (MSM). There, May Ching Lai has been a very important friend and support during the last years of PhD, a friend to share Jupyter notebooks, FIB lamellae, and much gossip. Thank you for keeping the social life of the EMG and making the work environment more fun and engaging. In the Microscopy group, I would also like to thank Giorgio Divitini, Felix Kosasih, and Duncan Johnstone, who were primordial in the first year of my PhD and who gave me dummy projects to get started, and shared all their expertise and experience in electron microscopy. In MSM, there is Gunnar Kusch, without whom I would have given up on CL much earlier on, and possibly also academia. Gunnar was the post-doc who invested the most time in helping me grow and develop academic skills: he thought me how to peer-review, how to do reproducible and robust science, and most importantly, how to supervise graduate students well. Thank you, Gunnar for all these years of collaboration and friendship (although remember that there are many other wonder materials apart from GaN). With Gunnar also comes a special thanks to Rachel Oliver for supervising all my CL work very closely and kindly.

I would like to quickly thank YuQi Sun, Hio-Ieng Un, Amita Ummadisingu, and Alessandro Caiazza (Eindhoven) besides many others, who trusted me in helping them understand their materials and samples with the skills and techniques developed during my PhD. Thank you for your trust, collaboration and interest in electron microscopy. In particular, I would like to thank Sasha Sneyd for the informative video we developed together, which
allowed me to share what my PhD research entails with the general public. I am sure I am
forgetting several people who should also be acknowledged here, as academia is truly a
social endeavour.

The last group of people I must acknowledge and thank deeply is my NanoDTC cohort,
the c2018: Alice, Eduardo, George, Elizabeth, Aoife, Giovanni, Kunal, Alice and Tobias.
They have been a constant support and group of friends to share our deepest struggles
and successes, to travel with, celebrate birthdays abroad, and most of all, to value each
other’s work and to understand how hard doing a PhD can be.

Last, but by no means least, thank you to my family. Especially my siblings, cousins
(including Ari), grandparents and parents. Us dedico aquest doctorat a tots vosaltres, en
particular al pare (ja que el teu accident va marcar un punt d’inflexió), i a tots els 4 avis,
els que hi són i els que ja han marxat durant aquests anys de doctorat. Vosaltres m’heu
ensenyat que és l’esforç i la dedicació.
References


References


1.1 The rapid reduction of the cost of solar in the last decade. Reported in terms of total installed PV system costs, weighted by the scale of the capacity of the systems installed in each respective year. Adapted from[2] 6

1.2 The golden triangle for PV commerciality analysis. The comparison of silicon and perovskite solar cells (PVSK denotes perovskite solar cell). Note the reported values in the figures are from 2018. As of the writing of this, the champion efficiency of silicon single crystal is 26.1 % and 25.7 % for PSCs. [9] Adapted from [5] 7

2.1 Recombination of charge carriers. Schematic of the main recombination processes that occur in semiconductors: (a) radiative, (b) Auger, and (c) non-radiative (trap-assisted) recombination. The arrows on the diagram indicate the direction of electron transitions. 11

2.2 Polytype transition between hexagonal 2H (delta, non-photoactive, yellow) phase to cubic 3R (alpha, photoactive, black) phase. Stacking sequence of AX3 (where A is lead and X is a halide) in three hexagonal lead halide perovskite polytypes (2H, 4H, and 6H) and two cubic or rhombohedral perovskite phases (3C and 3R). The hexagonal close-packed (h) arrangement is denoted by light blue circles, while the cubic close-packed (c) arrangement is denoted by dark blue circles. A refined unit cell structure is shown, displaying the various possible arrangements of the octahedra and their connectivity. When octahedra share faces, a 1D array (2H) is formed, whereas a 3D framework (4H and 6H) is formed when octahedra share corners or a combination of corners and faces. Adapted with permission from [49]. Copyright 2017 American Chemical Society. 14
2.3 Grain boundaries Different types of grain boundaries can be formed: (a) low-angle boundaries, (b) high-angle boundaries, (c) non-equilibrium grain boundaries containing a high density of defects and (d) amorphous grain boundaries. Adapted from [59].

2.4 Simpler or alloyed halide perovskites. Illustration of how the imperfections in halide perovskite films can be passivated by ionic bonding or coordinate bonding. Reproduced with permission from [58]. Copyright 2019 American Chemical Society.

2.5 Simpler or alloyed halide perovskites? Illustration portraying the race between complex multiple alloyed cation/anion compositions running against the stabilisation of FAPbI$_3$ for halide perovskite solar cells. Reproduced from the cover page of Journal of Materials Chemistry C [67]. Copyright 2023 Royal Society of Chemistry.

2.6 Energy diagrams of an intrinsic perovskite film in a device structure. Schematics for the band alignment for a perovskite film (a) with on contacts, (b) after the contact of ETL and HTL before any ionic motion, (c) after both action and anion motion or (d) in the case where halide motion if the only allowed ionic motion. (e) The band alignment is similar to that of a traditional $p$-$n$ junction, where the donors and acceptors are fixed. Adapted from [86]. Copyright 2020 Cell Press.

3.1 The link between microstructure and properties in crystals. Schematic showing the different layers of complexity in the nano-, micro- and mesostructure of crystal systems. Such structures and defects often control the properties of the material. Adapted from [170]. Copyright 2017 D. Raabe.

3.2 Electron-matter interactions. Schematic of the different elastic and inelastic interactions of an electron beam with the specimen. Adapted from [174].

3.3 Probability of multiple inelastic scattering events against sample thickness. The probability ($P_n$) of no scattering, single scattering, and multiple (n) inelastic scattering events in an FA-based perovskite film to sample thickness. Calculated using Equation 3.3 for an electron energy of 200 keV with a sample of $Z_{eff} = 36$ a.u. (Atomic fractions: Cs: 0.0052, Pb: 0.3368, Br: 0.0584, I: 0.5260, C: 0.0183, N: 0.0394, and H: 0.0079).
3.4 **Ewald sphere.** (a) Schematic showing the construction of the Ewald sphere for a transmission electron diffraction experiment. The scheme shows reciprocal space lattice rods, instead of points, because the sample for TEM is thin. (b–c) The resulting 2-dimensional diffraction patterns are obtained by projecting the points the Ewald sphere crosses to the detector plane. A slight rotation in the Ewald sphere (or in the reciprocal space) can move some diffraction spots, from b, away from the diffraction condition and not show in the diffraction projection, in c. (d–e) Effect of incomplete disc filling during diffraction, which is observed when the Ewald sphere is near, but not perfectly, the diffraction condition. Panel (a) adapted from [177].

3.5 **Effect of convergence angle on the probe size.** (a) Calculated relationship between the diffraction-limited resolution (determined by the probe diameter $d_d$) for a given acceleration voltage (or relativistic electron wavelength) and a given convergence angle $\alpha$. (b) Mean diffraction images for STEM probes defined by 0.86, 3.4 and 12 mrad semiangle apertures. (c) A more general description of the probe size in terms of convergence angle, also taking into account lens aberrations, which dominate at large $\alpha$. Panel b reproduced from [181].

3.6 **Schematics showing the effects of changing the convergence angle in STEM.** (a) Comparison between pencil-beam (small convergence angle $\alpha$) and normal STEM (large convergence angle) STEM alignment. (b) The introduction of an aberration corrector, which controls the formation of the Ronchigram, allows for high-resolution imaging. (c) The relation between camera length and imaging mode in annular dark field imaging, linked to the semi-angle of detection ($\theta$). Ronchigram image reproduced from [182].

3.7 **Power law on diffraction patterns.** Effect of power-law scaling in diffraction patterns (corresponding to a tetragonal perovskite FA-based structure). Weak features are easier to detect at higher scalings (cube root or biquadratic) compared to $I^1$.

3.8 **Digital apertures for virtual imaging.** Depending on which regions in the diffraction space are taken post-data acquisition, (a) virtual bright field (vBF), (b) virtual dark field (vDF) and (c) total scattering images can be created. (d) Schematic of the acquisition setup for the SED. The semi-convergence angle $\alpha$ and the semi-angle of detection $\theta$ are labelled.
3.9 **Crystal structures library.** Schematics of common crystal structure files used for the simulation and indexing of experimental diffraction patterns in this thesis. (a) Schematic of how the tetragonal $P4_1mbm$ perovskite unit cell is built from the $BX_6$ octahedra, showing a small tilt. (b) Histograms and (c) the unit cells at the a, b and c directions for the general perovskite, the $PbBr_2$ and the $4H-PbI_2$ phases. The histograms show how the Pb-Pb distances for the perovskite structure tend to be longer than for the lead halide structures. Other phases were also considered, such as the intermediate polytype phases.

3.10 **Signal formation in the SEM.** (a) The different scattering events during SEM and the respective detectors to acquire signal from such events. Comparison of two images taken from the same area, (b) formed with a BSE detector and (c) formed with the SE electrons. (d) A series of Monte Carlo simulations for 20 keV electrons across pure elemental samples of carbon, silicon, copper and gold. All length scales are comparable. Panel a is adapted from [197]. Other panels are adapted from [198]. Copyright Springer Science+Business Media LLC 2018.

3.11 **The Burstein-Moss effect.** Schematic of the Burstein-Moss effect showing the effective increase in the original bandgap energy $E_g^0$ when high-fluence excitation leads to large charge carrier densities. Large charge carrier populations can saturate the band edge and populate higher vibrational energy states of the conduction band ($\Delta E_{BM}$). This results in blue-shifted emission. Adapted from [200]. Copyright Springer Nature 2014.

3.12 **CL in the SEM.** Diagrams for a CL-SEM system working (a) in CW mode and (b) in pulsed mode. (c) Depending on the detector used at the spectrometer, (top) hyperspectral CL mapping, (middle) TRCL decay curves or (bottom) streak camera TRCL images can be acquired. All data in panel c is synthetic. Panel a is adapted from the Attolight website.

3.13 **Classification of beam damage.** (a) Diagram classifying different mechanisms of electron beam damage based on elastic (green) or inelastic (orange) scattering. (b) The sputtering energy threshold for different elements, with $E_S$ as the sublimation energy per atom. Adapted from [214]. Copyright Elsevier 2004.
3.14 **Hyperspectral PL mapping.** The PL mapping is acquired by taking a series of energy-filtered PL images. Each image is sliced into uniform wavelength segments. These segments are shifted to bring together all segments of the same wavelength and then stitched together to form a hyperspectral dataset with respect to wavelength. Segments that cannot form a complete image are discarded. Retrieved from [219].

4.1 **Visualizing grain boundary types and their evolution under low electron exposure using SED on triple-cation double-halide FA-rich perovskite films.** (a) Schematic of the perovskite grain showing the areas of interest from which diffraction patterns are extracted (in Arabic numerals), and three interfaces between crystallographic domains indicated by dashed lines (in Greek numerals): (i) grain bending across region 2 and 3, (ii) a twin grain boundary at (02\bar{1}) plane between region 3 and 4, and (iii) high-angle grain boundary interfacing two grains at different zone axes between region 1 and 3. The beam-parking position is labelled with a cross. (b) Evolution of vBF images of a perovskite film for up to 120 e Å⁻² fluence. (c) The resulting averaged diffraction pattern for four different areas at the 1st frame (12 e Å⁻²) and (d) at the 10th frame (120 e Å⁻²). Regions denoted with numerals in (a) correspond to the diffraction in (b) and (c). All intensity scale bars correspond to the normalized vBF and the diffraction intensity. Retrieved from [238].

4.2 **Simulated electron beam trajectories of TEM sample.** Simulated using CASINO v2.51 [199] at 200 keV for a layered sample containing FA-pure perovskite and a 30 nm SiN layer. A beam radius of 5 nm and 10⁵ trajectories were simulated using the default simulation parameters. For the layered chemical composition, a 200 nm layer of density 4.16 g/cm³ was used, using the triple-cation double halide perovskite composition (Atomic fractions: Cs: 0.0052, Pb: 0.3368, Br: 0.0584, I: 0.5260, C: 0.0183, N: 0.0394, and H: 0.0079). For SiN, a density of 3.17 g/cm³ and a thickness of 30 nm was used.
4.3 **Grain tilting.** (a) In-plane grain tilting observed after little electron exposure, quantified based on Equation 4.1. (b) Map of the grain tilting across a scanned region, showing grains tilting towards the zone axis (white) and other grains staying off the zone axis (orange). Note that this SED crystallographic dataset was taken from a different halide perovskite film of the same composition grown on a SiN TEM grid. It was acquired at 300 keV using a JEOL ARM300F high-resolution STEM with a Merlin/Medipix direct detector with a single back contact (EM19793-2 session, ePSIC, Diamond Light Source, UK). (c) Compositional nXRF summed intensity over the scanned area against X-ray fluence for the Pb and halides. The nXRF spatially resolved map did not show any Cs or halide segregation. All peaks were normalised to the $\text{Pb}^{\text{L}\alpha}$ peak, and the $\text{Br}^{\text{K}\alpha}$ peak was selected instead of the $\text{La}$ because the latter overlaps with the bright substrate Si peak. Adapted from [238].

4.4 **Probing the emergence of lead halide species on the nanostructure of FA-based perovskite films at high electron exposure using SED.** (a) Schematic of the perovskite grain showing the areas of interest from which PbI$_2$ and PbBr$_2$ species is observed and from which diffraction patterns are extracted, labelled as 1 and 2, respectively. (b) The vBF images at the 20th and 40th frames. (c) For each frame, a normalized diffraction pattern from the labelled region is shown. Some additional diffraction spots, marked with white arrows, are observed: the extra reflections in region 1 can be indexed to PbBr$_2$ near the [111] zone axis, and the extra reflections in region 2 can be indexed to PbI$_2$ near the [100] zone axis. (d) Simulated patterns for the perovskite (PvK), the PbBr$_2$ and the PbI$_2$ phases in white, green and red, respectively. The diffraction patterns computed using CrystalMaker match those seen experimentally. Retrieved from [238].
4.5 **Mapping the evolution of the degradation species in an FA-rich film.** (a) The diffraction patterns at the 40th frame, taken from region 1 in Figure 4.4 for the perovskite and PbBr$_2$ series, and from region 2 in Figure 4.4 for PbI$_2$. For each diffraction pattern, a dark-field virtual aperture is selected. (b) vDF images of the respective virtual apertures placed at: the (00$\bar{2}$) perovskite reflection (orange), the (221) PbBr$_2$ reflection observed within the grains (green), and the (011) PbI$_2$ reflection localized at the high-angle grain boundary (red). The colour scale range is set to 30% to better show the small changes in intensity. All vDF images are superimposed on top of the respective vBF images. (c) Intensity profiles taken from the perovskite (00$\bar{2}$), the PbBr$_2$ (221), and the PbI$_2$ (011) reflections. The 1/e intensity threshold is shown with a dashed line. Retrieved from [238].

4.6 **Evolution of grain at the [001] zone axis of a halide perovskite film, showing superlattice reflections.** (a) The grain location is away from the beam-parking position, as shown in the vBF image at the 1st frame (left). The mean diffraction pattern from the orange circle region is shown at the centre and the simulated diffraction pattern at the [001] zone axis at the right, especially showing weak reflections in orange. (b) The evolution of the mean diffraction pattern over increased fluence. White arrows show the disappearance of the weak additional reflections due to octahedral tilt. (c) Comparison between intensity profiles taken from the (220) and the (320) tetragonal diffraction spots. Retrieved from [238].

4.7 **Probing the evolution of the local structure of a region in an FA-rich halide perovskite film under X-ray exposure using nXRD.** (a) Radially integrated nXRD evolution of a perovskite film over accumulated illumination over an area of 4 $\mu$m$^2$. Peaks are indexed to the $P4/mbm$ perovskite phase. The peak marked as (*) cannot be indexed to perovskite and corresponds mainly to the degradation phases. To analyze the weak reflections lost during radial integration, 2D nXRD diffraction patterns are shown in (b), with some areas of interest denoted by numerals. (c) The zoomed-in evolution of nXRD in 2D elucidates crystal tilting in region 1, the weak appearance of (002) 4H-PbI$_2$ in region 2, and the appearance of (211) PbBr$_2$ reflections in region 3. These findings are similar to the changes observed in SED. The use of Au fiducial markers results in the observation of Au diffraction. Retrieved from [238].
4.8 **Inelastic to elastic scattering cross section ratios.** Ratio of inelastic to elastic scattering cross sections for (a) electrons and (b) photons at different energies. In blue, at the comparable energy of 80 keV. In orange, at the acceleration energies used for the data acquisition of the results presented in this Chapter. Retrieved from[238].

4.9 **The grain boundaries in an FA-rich film affect the degradation pathway.**
(a) Evolution of vBF images of various grains and their surrounding grains after up to 480 e⁻ Å⁻² fluence, showing stark changes in the morphology. (b) Schematic of multiple perovskite grains from which PbI₂ and PbBr₂ species are observed. The regions from which diffraction patterns are extracted are labelled as 1 and 2. (c) Diffraction patterns for two high-angle grain boundaries: in region 1 a grain boundary exhibiting the reflections only attributed to the perovskite phase of the grains at either side of the boundary, and in region 2 a grain boundary also exhibiting additional reflections and diffuse scattering, typical of amorphous defective phases. (d) Schematic of the degradation mechanisms and factors identified during degradation at high fluences, in cross-section view. Retrieved from[238].

4.10 **Fluence of high-energy electrons across the radiation spectrum in different orbits.** The electron spectrum radiation fluence in orbits in the Earth (black) and in the harsher orbits near Jupiter (red), as simulated using SPENVIS. [252] This spectrum was used to relate the fluence from the experimental results of this work to space PV applications. Marked with a dashed vertical line, is the acceleration voltage used for the SED acquisition. Retrieved from[238].

5.1 **Understanding CL emission degradation.** Evolution of a sequence of spectra over time, as a tool to investigate the limited conditions at which a sample can be imaged. Spectral stacks can be plotted as images (top) or as spectral overlays (bottom). Note that some beam-blanking behaviour, not physical, can be observed for the top panel as an oscillatory artefact. Sample: Top view LED semi-device on glass/ITO/ZnO/ethoxylated polyethyleneimine/perovskite (FAPbI₃, 30 nm) with passivation agent MSPE (from Yuqi Sun). [257] Spectral time evolution acquisition in CW, 5 keV, ~625 pA, 20 ms per spectrum, 1000 reps, beam rastering at pseudo-spot mode (64 px, 15 x 15 μm², at 0.5 μs/ px).
5.2 **Effect of composition, FOV, and carbon coating on CL emission.** Comparison of the effect of adding a thin carbon coating on different perovskite compositions (labelled as FA, TC and Cs). Bare means no additional carbon layer was added, and "Carbon" means a thin amorphous layer was added. In addition, the effect of the field-of-view (FOV) is shown column-wise. All spectral evolutions are plotted in the range of 0 to 150 counts. SE images of regions without and with carbon coating are shown on the right. Samples: (FA) ITO/FAPbI$_3$ with EDTA passivation (from Satyawan Nagane), (TC) ITO/perovskite triple-cation double-halide, (CS) ITO/CsPbBr$_3$ (from Zher Ying Ooi). Spectral time evolution acquisition in CW, 3 keV, $\sim$62.5 pA, beam rastering at pseudo-spot mode (64 px, at 0.1 $\mu$s/ px). Dwell times were 250 reps x 100 ms, 750 reps x 25 ms, and 750 reps x 25 ms for large, medium, and small FOVs, respectively. 96

5.3 **Effect of PTAA layer on CL.** (a) Comparison of the CL evolution over electron exposure for around 1 minute on the same area without and with the added layer of PTAA. The spectral image is shown at the top, the absolute CL spectra evolution in the middle, and the normalised CL emission in the bottom. (b) Comparison of the effect of FOV in the spectral CL evolution. Samples: (TC) ITO/perovskite/(PTAA) triple-cation double-halide (from Satyawan Nagane). Au top contacts were also deposited, and CL mapping was done in the vicinity of the contacts. Spectral time evolution acquisition in PM, 6 keV, $\sim$55 pA, beam rastering at pseudo-spot mode (512 px, at 2 $\mu$s/ px). Dwell times were 100 reps x 500 ms. For panel a, a FOV of 13 $\mu$m was used, for panel b large and small FOVs of 430 and 7.5 $\mu$m were used. 97

5.4 **Common pre-processing steps for CL.** The raw hyperspectral CL map contain common artefacts that need to be corrected. (a) The raw panchromatic CL image shows brighter emission at the edges, which dominate the dataset. (b) After edge cropping, cosmic ray peaks dominate the signal at some pixel positions, which can be deleted using a spike removal tool. The inset shows a spectrum corrupted by a cosmic ray. (c) The pre-processed dataset does not show artefacts. Sample: Top view PSC on glass/FTO/NiO$_x$/perovskite (triple cation double halide) (from Felix Kosasih). CL map acquisition in CW, 5 keV, $\sim$1 nA, 10 ms dwell time. 99
5.5 **Common pre-processing steps for SE images in the SEM.** The acquisition of SE images results in numerous artefacts, such as high-frequency electronic noise, low-frequency scanning artefacts, or intensity saturation. Raw SE images (in blue) are compared to processed SE images (in orange), where a fast-Fourier transform bandpass filter of 5-500 was applied, and the intensity histogram was adjusted to cover the full range, using ImageJ.\[^{266}\]

The processing of the SE images is necessary as the detector readily saturates during data acquisition. Sample: Top view LED semi-device on glass/ITO/ZnO/ethoxylated polyethyleneimine/perovskite (FAPbI\textsubscript{3}, 30 nm), (left) without and (right) with passivation agent MSPE (from Yuqi Sun).\[^{257}\]

SE image acquisition in CW, 5 keV, \(\sim\)625 pA, 10 s dwell time, and 2048 x 2048 px. .......................................................... 100

5.6 **The Jacobian transformation.** The conversion between wavelength and energy is non-linear. (a) A homogeneously distributed spectrum in the wavelength (in nm) transforms to (b) a non-linear distribution. (c) It is therefore important to remove the background from the raw signal (in red), or else the spectrum is dominated by the background after the Jacobian transform (see orange and blue). The Sample: Top view PSC on glass/FTO/NiO\textsubscript{x}/perovskite (triple cation double halide) (from Felix Kosasih).\[^{264}\] CL map acquisition in CW, 5 keV, \(\sim\)1 nA, 10 ms dwell time. Panel a and b retrieved from the documentation of\[^{268}\] .......................................................... 101

5.7 **Gaussian fitting of CL data.** The raw and fitted data for two mean spectra were taken from two CL maps. The three Gaussian fits and the background offset are shown in different colours. Sample: triple-cation double-halide film (from Yu-Hsien Chang). CL map acquisition in CW, 6 keV, and (left) \(\sim\)250 pA, 22 ms dwell time, and (right) \(\sim\)62.5 pA, 52 ms dwell time. ........ 104
5.8 **Types of hyperspectral filtering.** Emission images can be formed post-acquisition from the hyperspectral CL dataset. (a) A panchromatic image is formed by integrating all the emission spectrum intensities for each pixel. (b) A band-pass filter can be used to crop the spectral dimension and form an image from a smaller spectral range, here $51 \pm 30$ nm. (c) Machine learning techniques such as PCA + NMF can be used to denoise the CL dataset. Then emission images can be formed by selecting only components with physical features without noise (PC1 and PC3, marked with filled triangles). (d) To evaluate each component, the loadings and factors can be plotted. Sample: CsPbBr$_3$ quasi-2D LED film for LED application (from Miguel Anaya). CL map acquisition in CW, 6 keV, $\sim 10$ nA, 50 ms dwell time. . . . . . . . . . . 105

5.9 **LumiSpy.** Snapshot of the documentation website of LumiSpy (https://lumispy.org).108

5.10 **Beam intensity drift in PM.** SE images of a perovskite film evaporated on a textured Si substrate. (a) SE image was acquired before a hyperspectral CL map was acquired. (b) Same SE as panel a, but with rebinning to match the pixel size of the CL map. (c) SE image acquired during the CL map, where the electron gun drifted after 1/4 of the scan. Sample: double-cation double-halide evaporated film on textured Si substrate (form Yu-Hsien Chiang). SE image acquisition in PM, 6 keV, $\sim 33$ pA, 10 $\mu$s dwell time for panel a, and 1 second dwell time for panel c. . . . . . . . . . . . . . . . 109

5.11 **CASINO simulation of the CL intensity over depth in the hybrid perovskite composition.** CASINO v2.51 [199] was used to simulate where the CL signal originates across a sample thickness for two acceleration voltages: 3 and 6 keV. A beam radius of 5 nm and $10^5$ trajectories were simulated using the default simulation parameters. For the layered chemical composition, a 1,000 nm layer of density 4.16g/cm$^3$ was used, using the triple-cation double halide perovskite composition (Atomic fractions: Cs: 0.0052, Pb: 0.3368, Br: 0.0584, I: 0.5260, C: 0.0183, N: 0.0394, and H: 0.0079). The peak CL emission is simulated to be at a sample depth of 20-25 and 60-65 nm for a 3 and 6 keV electron beam, respectively, three times larger. These values are consistent with the differences observed in the CL emission spectra at different beam energies. Reproduced from [249]. . . . . . . . . . . . . . . . . . . . . . . . . . . 111
5.12 **Optimization of the CL acquisition conditions for halide perovskite thin films.** (a) The spatially averaged CL spectra for a series of CL maps taken at different beam modes (continuous line in CW, dashed line in PM), at different beam currents (darker colours represent higher currents), keeping all other parameters unchanged and the CL intensity normalized to the pixel dwell time. The PbI$_2$ and the perovskite peaks are visible, as well as an intermediate degradation broad peak. (b,c) Normalized CL peaks for the (b) PbI$_2$ and (c) perovskite peaks, with visible peak position shifts. (d-i) Correlation of the beam current in nA, the beam mode (CW in blue, PM in orange), and dwell time (from 22 to 502 ms from smaller to larger dots) concerning different emission peak parameters are shown. (d,e) The fitted central peak position $x_0$ of the PbI$_2$ and the perovskite peak, respectively. (f,g) The CL intensity ($I_{CL}$) for the PbI$_2$ and the perovskite fitted peaks, respectively. (h) The perovskite to PbI$_2$ CL intensity ratio correlated to pixel dwell time. (i) The intermediate degradation peak to the perovskite CL intensity ratio correlated to beam current. The asterisk (*) shows scans with long dwell times of 502 ms. Reproduced from [249].

5.13 **Heterogeneity of CL emission of halide perovskite thin films under improving acquisition conditions.** (a,b) The fitted Gaussian parameters for the perovskite peak from the CL maps, acquired from suboptimal at the top towards more optimized conditions at the bottom (the first three rows are taken in CW mode and the last row in PM). (c) The intermediate degradation phase peak to perovskite peak CL intensity ratio, a measure of beam damage, with (d) the histogram distribution. The mean values are reported on the top left for each map. Reproduced from [249].
5.14 **PL emission after PM CL scans.** Comparison of PL emission features before and after CL-SEM data acquisition in PM. (a) BF images of before (top) and after (bottom), taken with wide-field white illumination. (b) PL panchromatic image at 10-sun equivalent laser illumination before (top) and after (bottom). While the sample after CI is as emissive as before, 3 regions where CL maps were acquired are visible. (c) The average PL spectrum for the whole region is coloured in black (dashed for before CL acquisition, continuous for PL after CL acquisition). PL emission of the 3 regions, marked in red, green, and blue, exhibit degraded PL emission. (d) This is visible in the superimposed bandpass-filtered PL images for blue-shifted (in blue) and normal emission (in red). The CL maps, visible in the panchromatic PL images, were acquired at 6 keV, in PM at 55 pA, 100 ms dwell time per pixel, and 64x 64 and 128x 128 px at FOVs of 10 and 15 µm, respectively. Sample: Triple-cation double-halide solution-processed film (200 nm) on ITO (from Satyawan Nagane). PL maps acquired under 10-sun illumination, dwell time of 1 second, x100 objective.

5.15 **Optical emission from a PSC cross-section.** (a) Normalised perovskite emission spectra from (red) top-view PL, (orange) top-view CL, (green) first cross-sectional CL scan, and (blue) second cross-sectional CL scan. As the signal-to-noise ratio for the second cross-sectional CL scan is relatively low, normalization was performed on the Gaussian fit (blue line) rather than on the data points. The bottom panel shows the absolute CL signal for the two cross-sectional CL scans, the first being brighter than the second. (b) SE image of the PSC lamella. The perovskite emission characteristics (peak position $E_0$, and peak area $I_{CL}$) from the (c) first and (d) second cross-sectional CL scans of the PSC lamella. The PbI$_2$ emission characteristics ($E_0$ and $I_{CL}$) from the (e) first and (f) second cross-sectional CL scans of the PSC lamella. Dashed red lines mark the position of the perovskite layer. Reproduced from [256].
5.16 Phase mapping using CL. Phase mapping of a series of 3-dimensional triple-cation lead iodide perovskite films with an increasing amount of additive that convert it to 2D perovskite: (a) 1 mol% additive, (b) 5 mol% additive, and (c) 10 mol% additive. From left to right: mean CL emission spectra with the bandpass filter ranges in colour bands. The inset shows weak 2-dimensional emission at $\sim 570$ nm. SE images are shown together with 5 different bandpass-filtered images. Each colour corresponds to a perovskite phase, as listed in Table 5.2 Sample: Triple-cation lead iodine solution-processed film (120 nm) on glass/ITO with increasing isobutyl ammonium additive at the surface, which forms a 2D-Ruddlesden-Popper thin layer (from Amita Ummadisingu). CL maps were acquired at 3 keV, in PM, beam current 50-100 pA, and dwell time of 50 ms per pixel for 128x 128 scans at 56-$\mu$m FOV. SE images were acquired before each map at 1025 px and 10 $\mu$s dwell time.

5.17 PL emission after CL scans. Comparison of PL emission features after CL-SEM data acquisition. (a) BF image was taken with wide-field white illumination. (b) PL panchromatic image at 1-sun equivalent laser illumination. The inset in panel a shows the average PL spectrum (black), and the emission from two regions of interest. These regions are marked as A (red) for the CL-scanned area, and roi B (blue) for a pristine region. (c-d) Spatially resolved maps (10 $\mu$m x 10 $\mu$m) for the Gaussian-fitted PL features for a region near the pristine and the CL beam-damaged region. (e) Comparison between the surface damage between a CL map after CW mode in red, and after PM in green. (f) CL spectrum of the same sample as in PL. (g) Spatially resolved maps for the Gaussian-fitted CL features for the same sample seen in PL. Sample: Double-cation double halide evaporated film (200 nm) on SiN TEM grid (from Yu-Hsien Chiang). PL maps acquired under 1 sun illumination, dwell time of 2 seconds, x100 objective. CL maps acquired at 6 keV in CW, 1 nA, 170 ms dwell time per pixel, 128x 128 px.
5.18 **PL and CL lengthscales.** Comparison of the lengthscales that wide-field hyperspectral PL (simply referred to as PL in this thesis), confocal PL, and CL can probe. On the right, an overlay with all the PL maps and the CL maps. The respective mean CL spectra for each map are shown, each one acquired at different magnifications. CL can probe significantly larger lengthscales than PL while still obtaining large SNR. Sample: Triple-cation double halide solution-processed film (500 nm) on glass/ITO (from Satyawan Nagane). CL maps were acquired at 6 keV, in PM, beam current <115 pA, and dwell time of 94 or 174 ms per pixel for 128x128 and 64x64 px scans, respectively. . . . 129

5.19 **CL-4D-STEM correlation.** The CL maps were acquired in the same area as 4D-STEM. (a) SE image acquired during CL mapping. Although the perovskite emission in (c) had degraded (either due to exposure to air for 5 min (pre-STEM) + 5 min (post-STEM) + 5 min (pre-CL) or due to 4D-STEM electron exposure), the band-pass filtered emission in (b) for PbI$_2$ is visible. (d) Correlation with the diffraction data on the bright CL regions can be indexed to the [001] zone axis for PbI$_2$. Sample: Evaporated 100-nm perovskite double-cation double-halide (PbI$_2$ rich) on a 30-nm SiN grid (from Yu-Hsien Chiang). CL map acquisition in CW, 3 keV, ~62.5 pA, 100 ms dwell time. 4D-STEM acquisition at normal SED conditions, described in Chapter 3. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 130

5.20 **TRCL measurements on a halide perovskite thin film.** TRCL spectra were measured at an acceleration voltage of 6 keV and beam current of ~115 pA in PM. (a) The CL emission spectrum with the perovskite peak, the PbI$_2$ peak and a broad intermediate degradation phase. (b) TRCL spectra of the three peaks of interest (smoothed signal as a darker line). The inset shows the incoming photon counts per second. The 1/e intensity is shown as a dashed line on the y-axis. Reproduced from [249]. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 132
5.21 **Streak TRCL on CsPbBr₃ nanocrystals.** Comparison of different acquisition conditions and processing methods for 2-dimensional TRCL data. (a) The raw streak images for CsPbBr₃ nanocrystals without and with manganese doping (125% wt.). Inset shows CL spectra acquired at beam currents of 10 nA (in CW, continuous line) and 0.1 nA (in PM, dash line). (b) Rebinning the signal axes by 10 results in a better SNR, yet it is still dominated by noise. (c) Streak image resulting from stacking multiple shorter-time acquisitions and then rebinning by 10. This approach results in the best SNR. Sample: CsPbBr₃ nanocrystals without and with 125% wt. Mn-doping on ITO (from Mahesh Gangishetty Lab). CL acquisition in PM at 5 keV, beam current <100 pA. During TRCL acquisition, the electron beam was scanned at 64x 64 px at a FOV of 2x 15 µm, and dwell time of 0.1 µs. The central wavelength was set to 478 nm. The streak camera was set to a time range of 4, normal gate mode, at the maximum MCP gain of 63, a focus time over 5, a calibrated delay time of 4,800, and an exposure time of 10ms. For panel a, an integration of 200,000 samples was set. For panel c, an integration of 1,500 was set but repeated 3 times, then all data were combined.

6.1 **Lateral in-situ biasing MEMS-based system.** (a) SE image of the MEMS-based grid with multiple Pt contacts on top of an electron-transparent SiN membrane, forming several windows to image from in TEM. The labels 5 to 10 correspond to the electric contacts in panels b and e. (b) Optical microscope image of the thin electron-transparent window with the metal contacts on top. (c) Custom-made TEM holder (JEOL type) with 9 metallic pins to contact the chip. (d) Adaptor connecting each pin of the holder with the adaptor box in (e) which transforms into a coaxial connector compatible with any power source. This design was custom-made by Henny Zandbergen for ePSIC, and in-situ lateral biasing was developed by Chris Allen (ePSIC, Diamond Light Source).
6.2 **In-situ biasing across a FAPbI$_3$ absorber film.** (a) Biasing chip with perovskite layer. (b) Current profile measured at 20 V over 90 min. (c) vBF images from 4D-STEM datasets after 0 to 90 min of biasing, with a white dashed line delineating the propagation contrast front. (d) Intensity profile of the vBF contrast, from summing the lateral regions in c. (e,f) 4D-STEM experimental diffraction patterns of perovskite grains from the marked regions in c. Red arrows indicate additional diffraction spots with spacings (<0.16 Å$^{-1}$). (g,h) HAADF images acquired post-biasing, with higher magnification images in g. (i) The vBF image near 0 V, with clusters forming and selected with red circles, used to form a mask for obtaining the (j) radial 1D-diffraction pattern showing the presence of Pb$^0$. (k) HAADF images after reversing the biasing polarity, showing the formation of a degradation front near both electrodes. (l) Top-view SEM image shows the metal contacts. (m-n) The degradation front linked to quenching of PL emission and bluer emission, also shown in (n) the absolute and normalized PL spectra.

6.3 **Decoupling the effect of electron-beam induced changes.** In order to understand if the morphological changes were caused by the electron beam exposure, a series of vBF images were taken only after biasing. These regions were never exposed to the electron beam before, nor during biasing, only post-biasing. The same morphological feature changes can be seen as the ones shown in the main text, suggesting the reported changes are not induced solely by the electron beam.

6.4 **In-situ biasing in alloyed films reveal heterogeneous degradation.** (a) Current profile measured at 20 V. (b) The vBF images generated from 0 to 90 min of biasing. (c) HAADF image acquired post-biasing, across the whole region between metallic contacts. A closer inspection of the vBF evolution from b is shown in (d), where degradation can be seen to seed at the grain marked in red. (e) The diffraction of the grain marked in red shows diffraction patterns with spacings below 0.12 Å$^{-1}$. (f) Diffraction of 3 grains reveals they are aligned to the same [111]$_t$ zone axis. (g) A comparison between the initial and final diffraction pattern of a grain not affected (in green) and affected (in orange) by the biasing. (h) Absolute PL intensity spectra for the pristine (in blue) and biased regions (in orange, dashed) and the normalised PL intensity spectra in the bottom panel.
6.5 **The effect of grain orientation during operational stability.** The grains near the area in Figure 6.4b, where most degradation happens, show diffraction patterns indexable to high-angle grain boundaries to the [111]_t zone axis grains (numbered as 1,2,3). Degradation expands in this zone axis, leaving the grains at high-angle grain boundaries mostly unaffected.

6.6 **Charge-carrier-mediated redox reactions dominate the nanoscale structure degradation of perovskite films under bias, driven by ions.** (a) Iodide oxidation, which is hole mediated, is mainly localized near the positive contact where a large concentration of holes is injected from the electrode, leading to I\(_2\) being expelled into the vacuum, resulting in the formation of a contrast front that moves (grey dashed lines evolve to darker continuous lines). (b) Heterogeneity at the nanoscale with defective phases conditions charge carrier funnelling and the same redox reactions are seeded from multiple places. Iodide oxidation is preferential over bromide due to its electronegativity.

6.7 **The TEM-compatible SiN substrate and its shadow masks.** (a) Dimensions of the SiN TEM-grids used as substrate (from Norcada). (b) SE images show the SiN grid surface being extremely smooth, hard to focus on, and rapidly charging at 1 keV and 10 \(\mu\)A. (c) To fabricate vertical devices, a sample holder for the SiN grids was designed to which a shadow mask can be attached. (d) A series of shadow mask designs can be manufactured following the mask template in (e). (f) In particular, 5 key mask designs were used to create vertical devices. These masks are shown from a top view and are used for the evaporation of metallic contacts or perovskite layers. (g) A picture of a SiN after all 5 layers have been deposited using the shadow masks in (f).
6.8 **Fully evaporated devices on TEM SiN grids.** (a) Multisource thermal evaporation of perovskite films can be used. Evaporation affords homogeneous coverage both at (b) the centre and at (c) the edges of the TEM grids. (d) SE image of a cross-section of an evaporated perovskite film on a 30 nm SiN grid, with a 10 nm layer of Cu. The average measured thickness for evaporation is $123 \pm 5.4$ nm while the targeted thickness for evaporation was 100 nm, as measured on the Quartz balances inside the evaporator. (e) Evaporation on SiN grids is not affected by the surface pre-treatment as UV cleaning for 15 minutes does not influence the film morphology. This is in contrast to solution-processing methods which are more affected by the wettability of the substrate and its pre-processing treatments. (f) Band alignment diagram for the $p$-$i$-$n$ PSCs. Note the metal work functions and the bandgaps of the semiconductor layers are approximate and taken from [336-340]. (g) Mosaic of optical micrographs showing the full-device stack layers: Cu thin, Cu thick, absorber and contact layers, Ag thin and Ag thick, from left to right. The length of the metallic thin contacts can be modified to overlap on the SiN imaging window. All evaporated films shown here are of the double-cation double-halide composition, evaporated by Yu-Hsien Chiang.

6.9 **Properties of FAPbI$_3$, thin, evaporated films (100 nm).** (a) XRD comparison of 100 and 500-nm thick FAPbI$_3$ films, indicating that the thinner film has similar properties to the 500-nm film used in PSCs. Note these were evaporated on top of an ITO glass substrate with a thin spin-coated HTL layer of MeO-2PACz, an alternative to spiro-TTB. However, we extrapolate these results to be valid for other HTL materials. (b) XRD comparison of thin FAPbI$_3$ films on different substrates, where ITO and MeO-2PACz substrates yield better films due to optimized evaporation. All peaks are indexed to the cubic $Pm\bar{3}m$ perovskite structure. (c) PL spectra comparison of the same films, showing similar emissions to thicker analogues. (d) Panchromatic PL images that yield the spatially-averaged spectra in panel c. The evaporation of thin FAPbI$_3$ films produces high-quality perovskite films similar to thicker analogues used for perovskite devices. The perovskite films were evaporated by Terry Yang.
6.10 Properties of double-cation double-halide, thin, evaporated films (100 nm). Similar to Figure 6.9, the evaporation of thin FA-rich double-cation double-halide films produces high-quality perovskite films similar to thicker analogues used for perovskite devices. This is shown in (a) the XRD comparison of 100 and 500-nm thick films, and (b) in the PL spectrum of a 100-nm thin film on a SiN electron-transparent substrate resembling the emission of the thicker films. All XRD peaks are indexed to the cubic \(Pm\bar{3}m\) perovskite structure. The perovskite films were evaporated by Terry Yang. . . . . . . . . 158

6.11 Thickness effect of ITO and evaporated perovskite. SEM and TEM images of a series of thermally-evaporated DCDH perovskite films on top of substrates containing 30 nm SiN thin film and a sputtered thin layer of ITO. The evaporated perovskite film is the same thickness throughout the series (~100 nm) while the ITO thickness varies from 0 to 70 nm. SEM images show the surface morphology (at 1 keV) while TEM images show the effect of the sample thickness on the electron transparency and contrast (at 200 keV acceleration voltage) for the different architectures. The inset in the top-right shows the electrical behaviour of a SiN substrate which contains a thin ITO layer of 20 nm between the SiN and the top Ag contact (black), compared to a substrate without an ITO layer (red). Due to the insulating nature of SiO2, the conductivity between the contacts is only high when a thin ITO layer is sputtered. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 159

6.12 Solution processing challenges on TEM grids. (a) Another common way to deposit the PSC layers is via solution processing using spin-coating. A key challenge during solution processing is the wettability of the SiN small substrates: (b) a droplet of PEDOT:PSS HTL solution is mostly non-wetting. Such non-wetting is also observed for the perovskite precursor solution. Non-wetting results in (c) inhomogeneous films across the SiN, especially at the electron-transparent window, and (d) incomplete coverage, seen as pinholes. (e) SE image showing bad crystallisation of the perovskite film near the edges of the substrate. (f) Mosaic of optical micrographs showing the incomplete coverage of the perovskite layer over the SiN grid, also seen with the naked eye in (g). All spin-coated perovskite films shown here are of the triple-cation double-halide composition. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 160
6.13 **JV-curves for thin devices.** The optoelectronic behaviour of PSCs fabricated on either standard ITO substrates (left) or on electron-transparent SiN grids (right) can be measured by sweeping a voltage and measuring the current (JV-curve). (a) The JV curve of a photovoltaic device, in which under bright illumination and positive potential, a photogenerated current is measured. (b) Failed PSC device showing a light dependence resistor behaviour. To measure the JV-curves of devices on small SiN substrates two contacting methods can be used: micromanipulators which result in (c) high-resistance contact between the tips and the contacts on the device, or wire bonding, which results in (d) cleaner contacts with low resistance. However, fabricating full devices on SiN substrates is non-optimal and numerous device failures can be recorded: (c,d) JV-curves without photovoltaic activity under the presence of light and with high resistivities, (e) JV-curve showing a diode behaviour without photovoltaic activity. Device architectures:
(a) ITO| PEDOT:PSS (10 nm)| triple-cation double-halide perovskite (200 nm)| PCBM-BCP (20 nm)| Ag (35 nm), (b) ITO| Spiro (15 nm)| double-cation double-halide perovskite (70 nm)| C60 (20 nm)| Cu (15 nm), and (c,d,e) SiN (30 nm)| Au (10 nm)| Spiro (15 nm)| double-cation double-halide perovskite (100 nm)| C60 (20 nm)| Cu (10 nm).

6.14 **Self-made in-situ TEM biasing setup.** (a) Measurements of the in-situ biasing holder with 4 contact pins (adapted from the heating DENS solutions holder) and the respective SiN chip (inset). (b) The image on how the fabricated PSC on a SiN chip is wire bonded to the backbone Si chip and is electrically connected to the biasing holder. (c) Diagram of how the metallic pins on the holder relate to the biasing connector (circle with 5 cables), and to the coloured cables. (d) Setup for in-situ biasing in the TEM, where the power-source meter is connected to the biasing holder, which is then placed inside the vacuum chamber of the TEM. (e) Electron beam current was measured inside the TEM during 5 V biasing. Beam blanking can be measured.
6.15 **Alternative architectures.** (a) STEM images of a perovskite LED device on a TEM grid (SiN| ITO| PEDOT:PSS| sPbBr$_3$ (quasi-2D nanocrystals in ligand solution)| TPBi) at 200 keV. Despite missing the top Ag contact, a very sharp contrast is observed due to the inherent thin nature of LEDs. However, the crystallisation of CsPbBr$_3$ was altered due to wettability issues of the SiN grid during solution processing. A continuous film should be observed instead. (b) Alternative design architectures were also explored during this thesis, which yielded worse results than the vertical architecture presented above. (c) A theoretical back-contact PSC design inspired from\textsuperscript{[325]}.

7.1 **CL and 4D-STEM correlation for a non-perovskite solar cell material.** A cross-section of an alloy of Cu, In, Ga disulfide (CIGS) used for next-generation solar cells. These devices are analogous to CIGSe$_2$ solar cell absorbers and show a notch-type bandgap emission with a red-shift followed by a blue-shift as you go deeper into the material. STEM techniques were used to (a) map the cross section in HAADF and in 4D-STEM. (b) Virtual dark field (vDF) images were stitched together, obtaining nanoscale diffraction across the grains in the cross-section, being able to resolve (c) high-angle grain boundaries and (d) the two Ga-rich/Ga-poor crystalline structures with distorted diffraction vector spacings. (d) These two diffraction features can be readily resolved in 4D-STEM and also in (f) CL panchromatic maps, acquired in the same area as 4D-STEM. The perfect pixel resolution match is exemplified with (g-h) the band-pass CL images for the Ga-rich and Ga-poor emission, respectively. The coloured boxes represent the scale of each of the 4D-STEM maps acquired previous to CL-SEM in STEM mode. Sample: CIGS with a 0.98 Cu:(In + Ga) ratio, and a 0.34 Ga:(In + Ga) ratio, fabricated by Rachel Oliver and her group and collaborators. 4D-STEM and CL-SED acquisition at normal SED conditions and CW mode, described in Chapter 3.171
7.2 **Towards more automated pipelines for material discovery.** The rise of (a) high-throughput mapping of new materials at the nanoscale enables a better and more statistically-significant understanding of (b) the features of the nanoscale, such as structural phases and microstructure. These identified features can be linked to (c) other material properties such as compositional, optical or electronic. High-throughput correlation of features enables accurate (d) guided optimisation of the fabrication and optimisation of new materials, which could eventually become fully automated. With such a streamlined automated and quantitative pipeline, (e) rapid discovery, optimisation and deployment of new materials can be envisioned, revolutionising interdisciplinary sectors. ................................................................. 174

7.3 **Automated phase mapping for halide perovskites.** (a) Supervised learning is an option to train a model (here a deep neural network using TensorFlow\(^{[366]}\)) based on the simulation of diffraction patterns using diffsims\(^{[187]}\) (an open-source Python package). Then, the trained model can be used to infer what is the most likely crystal phase present at each scanned pixel in a 4D-STEM dataset. (b) Unsupervised learning methods such as encoder-decoder neural networks can be used to transform a given diffraction pattern into a latent space, which can be clustered to identify known and unknown features between diffraction patterns. Once a cluster is selected, a phase map can be created and a mean diffraction pattern (here as an azimuthally integrated 2D pattern) can be plotted. The encoder-decoder was coded by Po-Yen Tung. ................................................................. 175
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