

Control of electronic properties of metal halide perovskites through vacuum co-deposition



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Abstract

As perovskite-based photovoltaic devices near commercialisation, it is imperative to develop thin-film deposition techniques that can be applied on an industrial scale. Vapor deposition is a solvent-free fabrication technique that is widely implemented in industry and can be used to fabricate metal halide perovskite thin-films. Understanding and controlling grain growth and structure of polycrystalline thin films of metal halide perovskite semiconductors is an important step in improving the performance of solar cells based on these materials, as it allows for the development of thin-film passivation techniques compatible with large-scale manufacturing.

I demonstrate that it is possible to accurately control the crystallite size of $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI_3) thin films by adjusting the substrate temperature during vacuum co-deposition of inorganic (PbI_2) and organic ($\text{CH}_3\text{NH}_3\text{I}$) (MAI) precursors. Films co-deposited onto a cold substrate temperatures (-2°C) had large, micrometer-sized crystal grains while films that formed on a room temperature (23°C) substrate produced grains of only 100 nm in average diameter. I was able to isolate the effects of substrate temperature on crystal growth by developing a new method to control sublimation of the organic precursor. Furthermore, I found substrate temperature directly affects the adsorption rate of MAI, which in turn affects crystal formation and solar cell device performance through changes to the conversion rate of PbI_2 to MAPbI_3 and stoichiometry.

Next, the passivating effect of using PbCl_2 as the inorganic precursor for vapor-deposited $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI_3) is demonstrated, as compared to films fabricated using PbI_2 as the inorganic precursor, which is the conventional approach. Furthermore, I find the partial substitution of PbI_2 for PbCl_2 in $[\text{CH}(\text{NH}_2)_2]_{0.83}\text{Cs}_{0.17}\text{PbI}_3$ films enhances photoluminescence lifetimes from 5.6 ns to over 100 ns, photoluminescence quantum yield by more than an order of magnitude, and charge carrier mobility from $46\text{ cm}^2/\text{Vs}$ to $56\text{ cm}^2/\text{Vs}$. This approach results in significantly improved solar cell power conversion efficiency, from 16.4% to 19.3% for the devices employing perovskite films deposited with 20% substitution of PbI_2 with PbCl_2 . This method presents a scalable, dry and solvent-free route to passivating non-radiative recombination centres and hence improving the performance of vapor-deposited metal halide solar cells.

This thesis combines an overview of the fundamentals of solar cells and the vapour co-evaporation technique with comprehensive studies of the impact of a range of parameters on the optoelectronic properties of the resulting metal-halide perovskite films, providing detailed understanding of the mechanisms that can be used to improve the performance of vacuum-deposited metal-halide perovskite solar cells.

List of Publications

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List of Abbreviations

AM	Air mass
BCP	Bathocuproine
CTL	Charge transport layer
CVD	Chemical vapour deposition
E_g	Bandgap energy
E_U	Urbach energy
EDX	Energy-dispersive X-ray spectroscopy
EQE	External quantum efficiency
ETL	Electron transport layer
FA	Formamidinium, $\text{CH}(\text{NH}_2)_2^+$
FF	Fill-factor
FTIR	Fourier transform infrared spectroscopy
FTO	Fluorine-doped tin oxide
FWHM	Full-width half-maximum
HTL	Hole transport layer
IQE	Internal quantum efficiency
ITO	Indium-doped tin oxide
J_{SC}	Short-circuit current
JV	Current-voltage
MA	Methylammonium, CH_3NH_3^+
MHP	Metal-halide perovskite
MPP	Maximum power point
OPTPS	Optical-pump terahertz-probe spectroscopy
PCE	Power conversion efficiency
PV	Photovoltaic
PL	Photoluminescence
PLQY	Photoluminescence quantum yield
QCM	Quartz-crystal microbalance
QFLS	Quasi-Fermi level splitting
SEM	Scanning electron microscopy
TCSPC	Time-correlated single photon counting
TRPL	Time-resolved photoluminescence

V_{OC}	Open-circuit voltage
XPS	X-ray photoemission spectroscopy
XRD	X-ray diffraction

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Chapter 1

Introduction

Every few hours, the Sun provides enough energy to power the entire world's needs for a whole year. In the face of man-made climate change, one of humanity's biggest challenges of the 21st century, solar energy presents one of the largest sources of renewable energy. Global warming and climate change have been driven by the unprecedented growth in greenhouse gas emissions and atmospheric CO₂ over the past few decades, in turn caused by the continued use of fossil fuels in industry and everyday life. In spite of wide-spread knowledge of the disastrous consequences climate change would have on our planet, in 2019 almost 85% of global energy consumption was still produced from fossil fuels [1]. Already, the reports from the Intergovernmental Panel on Climate Change (IPCC) paint a grim picture of future climate scenarios, with the 2015 Paris Agreement target of 1.5 °C [2] only achievable through significantly increased investment in all forms of renewable energy, and carbon capture [3] [4]. In all scenarios, solar energy plays a major role in future production of renewable energy, but further technological advancements are still needed to maximise its potential.

Solar energy plays a crucial role in achieving net-zero carbon emissions because it presents our planet's largest renewable energy reserve, dwarfing even the world's energy consumption as shown in Figure 1.1. In their 2015 review of the Earth's energy

supplies, Perez et al. estimate the solar energy potential to 23000 TWy/y [5], over a thousand times the total world’s energy use of 20.0 TWy in 2019 [6]. For comparison, the next largest renewable energy resource of wind is only estimated to provide up to 130 TWy/y [5]. While not being able to solely rely on solar power for intermittence reasons, it is no surprise that solar energy must hence play a significant role in any net-zero energy production scenario. Indeed, in his 2009 book “Sustainable Energy – without the Hot Air”, David MacKay explores what it would take to produce all our energy from renewable sources, with the clear conclusion that, with the exception of unprecedented growth in nuclear power, humanity must rely on solar power for a significant portion of its energy production [7]. However, challenges still remain in converting sunlight to useable energy as efficiently as possible. Indeed, the value quoted above from Perez et al. represents the maximum collectable potential reaching the Earth’s surface, at 100% power conversion efficiency (PCE) over all land-mass [5]. In reality, there is still room for significant improvements of the cost and efficiency of solar power conversion.

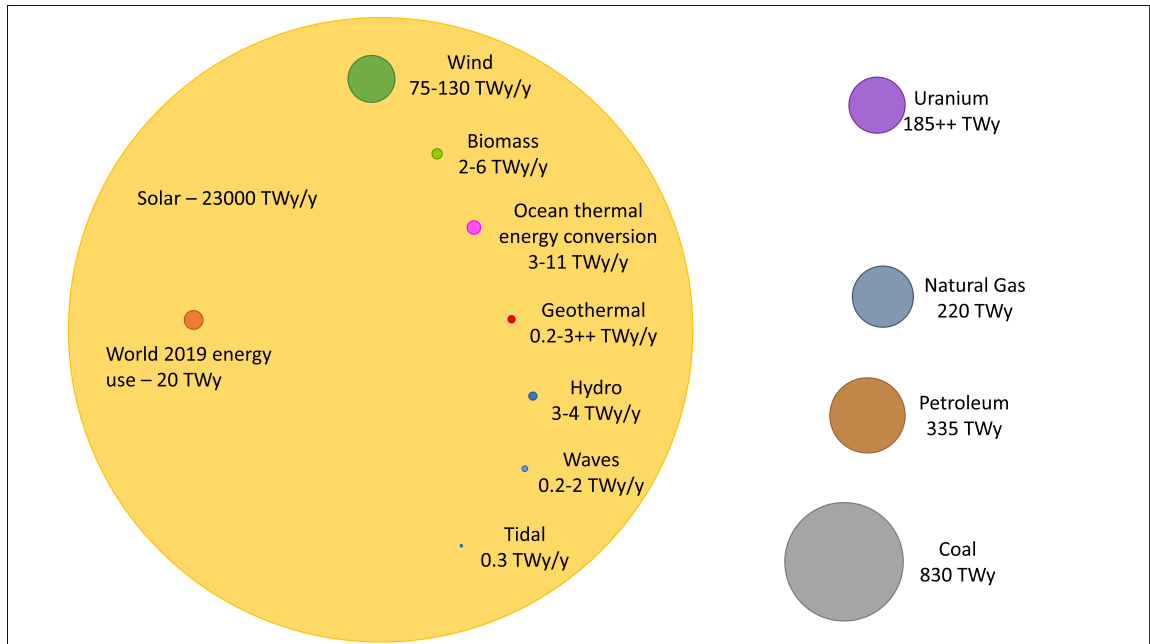


Figure 1.1: Estimate of the world’s energy reserves, drawn to scale, using the 2015 values from Perez et al. [5]. The 2019 global energy use comes from ref. [6].

On average, the Sun provides approximately 1361 W/m^2 of energy in electromagnetic radiation just outside of the Earth's atmosphere [8]. However, the actual power available on the surface of the Earth is less because of absorption through molecules in the atmosphere, as well as projection of the irradiance on the curved surface of the Earth. The former absorption also depends on the angle of incidence of the sunlight, as lower angle irradiance will need to traverse more atmosphere to reach the ground. This results in higher average insolation for lower latitudes. The effect of the Earth's atmosphere is accounted for using the air mass coefficient (AM) to describe the solar spectrum after a certain length of atmosphere [9]. For example, AM0 refers to the solar spectrum outside the atmosphere, while AM1 describes the solar spectrum at sea level with the sun directly overhead. However, because most developed countries implementing solar panels lie significantly off the equator, the AM1.5 solar spectrum is typically used as the standard for solar irradiance to characterise research solar cells. The AM1.5 spectrum corresponds to sunlight after traversing 1.5 lengths of atmosphere, at a solar zenith angle of 48.2° [10], and is compared to the AM0 spectrum in Figure 1.2. The corresponding 1 Sun illuminance is 1000 W/m^2 [11], meaning about 360 W/m^2 are absorbed in the atmosphere. The number quoted earlier from Perez et al. assumed an average 65% atmospheric absorption. In London, the yearly-averaged solar insolation is 109 W/m^2 , just under 3 times less than locations right at the equator [7].

The energy contained in sunlight then needs to be converted to a form useable by our society. The most direct way of collecting energy is to directly heat objects. For example, hot water panels use sunlight to heat water, while some power plants use mirrors to concentrate large amounts of sunlight to produce electricity from the generated heat [7, 12, 13]. Alternatively, sunlight can directly be converted into electricity through photovoltaic (PV) devices, allowing electricity generation on smaller scales [7]. PV materials operate by absorbing photons at or above the material's bandgap,

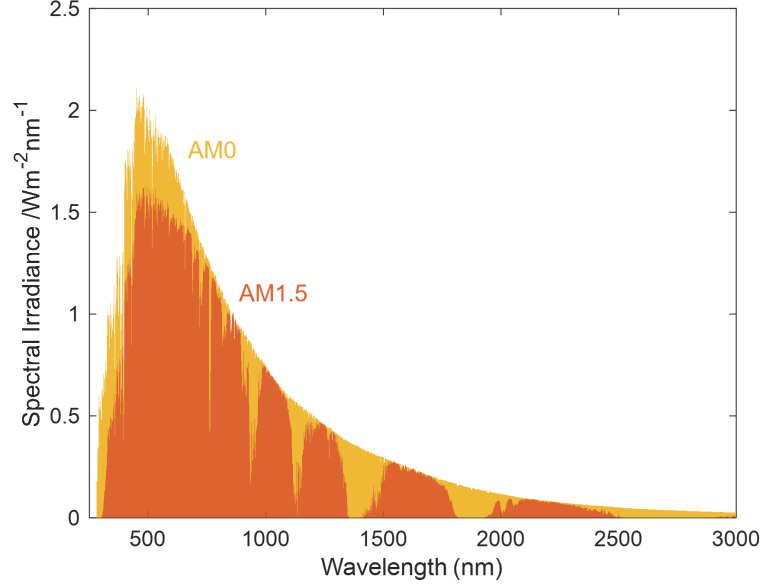


Figure 1.2: Solar irradiance just outside the Earth’s atmosphere (AM0, yellow) and after absorption through the atmosphere at solar zenith angle 48.2° (AM1.5, red). Reproduced using the ASTM G173-03 provided by the National Renewable Energy Laboratory (NREL) [11].

and converting them into electron-hole pairs at the bandgap energy [14]. While lower bandgap materials are able to absorb a larger subset of the solar spectrum, they also produce lower energy electron-hole pairs, limiting their overall efficiency, and vice-versa for high bandgap materials. This efficiency limit for single-junction PV cells is the Shockley-Queisser limit, described in 1961 [15]. At AM1.5, this gives a maximum theoretical efficiency of about 33% for a material with a 1.34 eV bandgap [16]. Currently, the most succesful way of getting around the Shockley-Queisser limit is to multiple PV materials of different bandgap into a so-called tandem cell. The theoretical efficiency limit for a cell with infinitely many layers then increases to 68% [17]. Succesfully implemented in a number of systems [18, 19], multi-junction tandem cells have proven to be a viable way of surpassing the Shockley-Queisser limit, and have become a prime focus of technological advancements in PV research.

The history of solar cells begins in 1883, when selenium was used by Charles Fritts to make the first working solar cells, albeit to low PCE $<1\%$ [20, 21]. It was in 1954

when Bell Labs demonstrated the first practical implementation, using silicon to reach around 6% PCE [22]. From that point on, silicon solar cells established themselves as the premier material for PV devices, largely dominating the market for rooftop and commercial solar cell applications [23]. While there exists viable competition since the mid-2000s in the form of CdTe [24] and copper-indium-gallium-selenide (CIGS) [25] solar cells, the high-efficiency, stability, and environmental safety ensure the continued domination of silicon-based solar cells on the PV market.

In general, there are two approaches to reducing the cost of photo-electricity generated per unit of energy: either reduce the cost of PV material, or improve its energy yield. While the former has been achieved through the aforementioned CdTe and CIGS, and notably organic-based solar cells [26], these alternative materials often have lower PCE [23]. Because ultimately the cost of the PV panel is only one part of the balance-of-system costs of the entire installation, reducing the cost of the PV material at the cost of efficiency is not always economically viable. Typically, the solar cell module comprises about 40% of the total balance-of-system costs [23]. Conversely, while more efficient PV devices exist in the form of III-V semiconductors such as GaAs, and multi-junction cells thereof, the fabrication cost of these materials is so high that they are only used in specialist applications, such as in space or with solar concentrators [27]. As such, there is yet room for PCE and cost improvements in the PV industry through improvements in the aforementioned technologies, or entirely new materials.

Organic-inorganic metal halide perovskites (MHPs) are a novel class of semiconductors that have leapt to the forefront of PV research following the unprecedented growth in their PCE [28, 29], which has now reached 25.7% in single junction devices [30]. First demonstrated in a solar cell in 2009 [28], MHPs are based on the chemical structure ABX_3 , where A is a cation, typically organic such as $CH_3NH_3^+$ (MA^+) or $CH(NH_2)_2^+$ (FA^+), B is a metal cation such as Pb^{2+} or Sn^{2+} , and X a halide anion

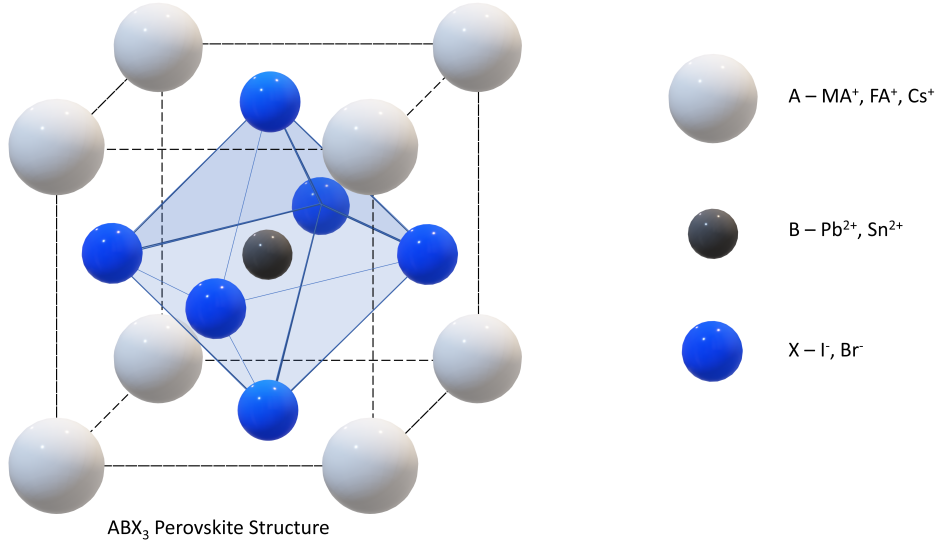


Figure 1.3: ABX₃ crystal structure of metal-halide perovskite, with examples of common materials for the A, B, and X site. MA, and FA are organic molecules, CH₃NH₃ and CH(NH₂)₂, respectively.

such as Br⁻ or I⁻ [31], as illustrated in Figure 1.3. In particular, this material has garnered interest because of its band-gap tunability [32–36] which is a result of the excellent solid-state mixing between different perovskite formulations. For example, excellent miscibility has been demonstrated between iodides and bromide-based perovskites, allowing continuous tuning of the bandgap between the pure iodide and bromide formulations [32, 34, 35]. Similarly, stability and performance improvements of MHP solar cells were achieved with the introduction of inorganic Cs⁺ at the A-site [34, 35], while low-bandgap (~ 1.2 eV) MHPs were demonstrated through Pb and Sn mixing at the B site [33]. Moreover, MHPs are compatible with a range of manufacturing approaches [31]. Together with their bandgap tunability, this makes them an ideal candidate for tandem applications, be it in all-perovskite configurations [37, 38] or in combination with established silicon technologies [19, 39, 40]. The latter is particularly relevant for the commercial feasibility of this new material, as MHPs can be deposited at relatively low cost on top of existing silicon wafers to improve

the PCE of existing market leader technology. With perovskite-on-silicon tandems recently reaching 29.8% certified PCE [30], MHP solar cell technology is poised to deliver the next major advancement in efficiency for the photovoltaics industry. Figure 1.4 illustrates the unprecedented growth of perovskite solar cell PCE, as compared to current market leading monocrystalline Si.

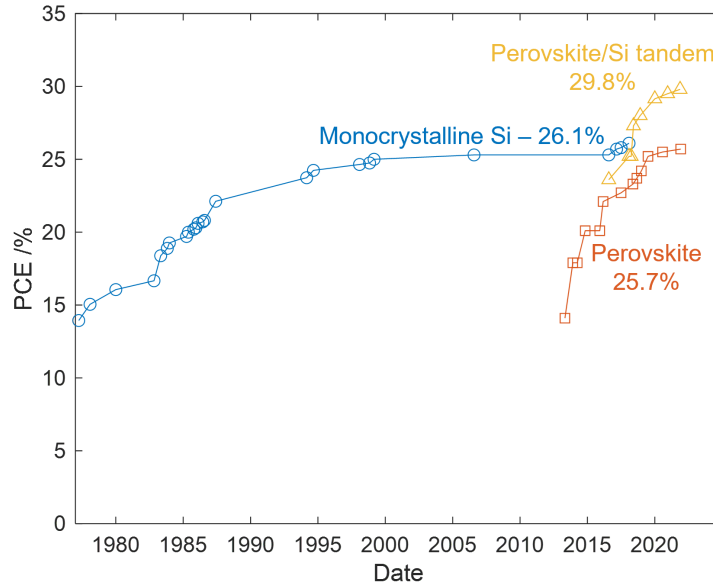


Figure 1.4: Certified best research solar cell efficiency for monocrystalline Si (blue), perovskite single-junctions (red), and monolithic perovskite/Si tandems (yellow). Data from the National Renewable Energy Laboratory (NREL) [30].

A significant challenge to the wide-scale adoption of MHP technology is developing an industrially scalable and compatible manufacturing technique. Vacuum deposition, where precursors are heated under vacuum to sublime and condense onto the desired substrate, is an ideal candidate, as it allows for conformal coating of large substrates [41], fine control over the thickness of the perovskite layer [42], and deposition in a highly controlled atmosphere. Therefore, while solution processing routes for MHPs may be more cost effective at small scale (particularly in terms of capital investment), at industrial scale vapour deposition offers significant cost advantages in terms of device yield as well as avoiding economic and environmental costs associated

solvent procurement and disposal [43]. Furthermore, vapour deposition has particular potential for the fabrication of multilayer devices, such as tandem and multijunction solar cells [44, 45] where layers of different material must be deposited sequentially and precise control over film thickness is critical. Indeed, vacuum deposition readily allows multiple layers to be deposited on top of each other without damaging the previous layers, and without solvent orthogonality constraints [43]. Having already been used in other commercial optoelectronic devices such as OLED displays [31, 44], and CIGS thin film PV modules [25], vacuum deposition is a proven technology readily applicable to upscale MHP solar cell production.

This thesis focuses on the vacuum deposition technique of co-evaporation, where the individual precursors of the MHP are sublimated simultaneously under vacuum. The aim is to better understand the crystallographic and optoelectronic properties of films made via this method, to allow improvements in the resulting solar cell. First, Chapter 2 provides a theoretical overview of the operation of solar cells, the process of co-evaporation, as well as a detailed literature overview of the state of vacuum-deposition. Chapter 3 then provides an overview of the experimental techniques used in this work. The experimental results start with Chapter 4, which investigates the effects of changing the substrate temperature during deposition on the crystallographic and optoelectronic properties of the MAPbI₃ films. Chapter 5 continues with an investigation of the passivation of MAPbI₃ films through the use of Cl in the precursors. Chapter 6 then details my research on co-evaporated MHPs with more than two sources, before concluding remarks and an outlook are provided in Chapter 7.

Chapter 2

Background

2.1 Photovoltaic Cells

2.1.1 Single Junction Solar Cell

The basic operation of a single junction solar cell is to produce a current through the absorption of photons. This process requires the use of a semiconductor, a material where the separation, known as the bandgap (E_g), between the valence and conduction band is low enough that these bands can be thermally populated by electrons. Photons with energy equal to or higher than the bandgap of a semiconductor material will be absorbed and excite an electron from the valence band to the conduction band, with the energy gained by the electron initially being equal to the energy of the photon. The electron rapidly thermalises to the bottom of the conduction band, such that the net energy gain can only ever be at best equal to the bandgap of the material. Phonons, i.e. vibrations of the crystal lattice, are produced as a result of this thermalisation process. A hole will be formed in the valence band, resulting overall in an electron-hole pair formation. A current will then be generated if the charges are separated and collected at different ends of the material [46].

There are multiple ways to ensure effective charge separation of electron-hole pairs.

First, the semiconductor must have a high enough dielectric constant to screen the relative charges of the electron and the hole, to reduce their coulombic binding energy. Then, in the presence of an electric field, charge carriers will drift in opposite directions, according to their charge. Finally, charge carriers can generally diffuse throughout the material, typically driven by a gradient in charge carrier-concentration. In order to generate a net electrical current, electrons and holes must also be preferentially collected at opposite ends of the material. This is achieved through a type of diode called a p-n junction. Here, p and n refer to p-type and n-type semiconductors, which are formed by doping an intrinsic semiconductor such that it either has an excess of holes (p-type) or electrons (n-type) at room temperature. A p-n junction then consists of the interface between a p- and n-type semiconductor. Close to the point of contact, electrons from the n-type material will move to the p-type material, forming a depletion region and resulting in an electric field. As a result, charge carriers can only flow through the junction in one direction, ensuring current generation [14].

MHP-based solar cells generally operate more akin to a p-i-n structure (Figure 2.1), which means that the p- and n-type materials are in contact with an intrinsic semiconductor rather than each other directly. The internal field is set up by the electron and hole transport layers (ETL and HTL) acting as the n- and p-type regions, while the perovskite acts as the intrinsic semiconductor. The ETL and HTL are called as such because they preferentially collect electrons or holes, respectively, providing an energy barrier to the opposite charge carrier. ETL and HTL operate by having a Fermi level that is slightly lower, in the case of ETL, or higher, for HTL, than the absorbing material. This results in an electron or hole affinity, respectively. Initially, the depletion region formed in the perovskite layer by contact with the ETL and HTL will traverse the entire perovskite layer. The mobile ions within the perovskite then move according to the generated electric field, with positive and negative ions moving towards the p- and n-type layer, respectively, resulting in the flat band structure

shown in Figure 2.1. Finally, electrodes are added to connect the ETL and HTL, forming a complete circuit and pinning the Fermi level [14].

What sets MHPs apart from many other semiconductors is their high defect tolerance, which is crucial for these materials as it allows the formulation of complex MHP compositions across a range of bandgaps. This defect tolerance originates from the fact that the band structure of MHPs is primarily determined by the interaction of the X-site halide and B-site lead molecular orbitals. This means that changes or vacancies in the A-site cation will have little to no effect on the band-structure of the MHP film, and not introduce additional defects. Furthermore, both the valence and conduction bands in MHPs exhibit antibonding character, which results in shallow defect formation. As such, most defects that do form tend to have only a minor impact on the charge-carrier dynamics, resulting in the observed defect-tolerance of MHP semiconductors [47].

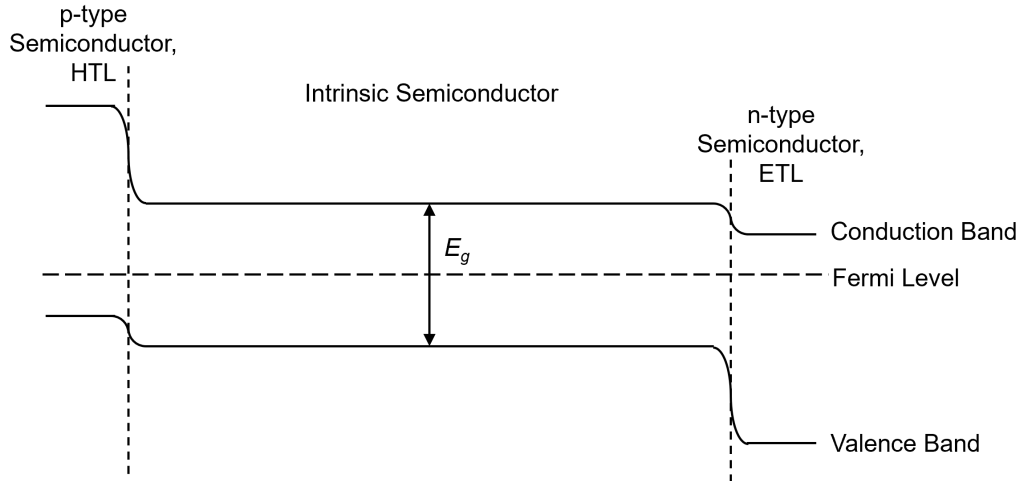


Figure 2.1: Diagram of a p-i-n junction. The intrinsic semiconductor has its conduction and valence band equidistant from its Fermi level. It absorbs the most photons, generating electron-hole pairs. The p-type semiconductor has its valence band closer to its Fermi level, and acts as a hole transport layer (HTL), allowing passage of holes but not electrons. The n-type semiconductor has its conduction band closer to its Fermi level, and acts as an electron transport layer (ETL), allowing passage of electrons but not holes.

2.1.2 Current-Voltage Curve

The operation of a solar cell is best described by its current-voltage (JV) curve, which represents the current flowing through the cell as a function of applied bias. In the dark, a solar cell operates like a diode, with a small negative saturation current J_0 . Under light, the photovoltaic device now produces a significant positive current, allowing power to be extracted if an external load is connected. The limits of the power-generation region are defined by the value of the photogenerated current in the absence of applied bias, called the short-circuit current (J_{SC}), and the maximum value of the applied bias that results in net 0 current, called the open-circuite voltage (V_{OC}). The J_{SC} represents the total amount of photons converted to current by the solar cell, and can be expressed as

$$J_{SC} = q \int_0^\infty \text{EQE}(\lambda) \phi(\lambda) d\lambda,$$

where q is the electric charge of an electron, EQE is the external quantum efficiency which represents the probability of a photon being converted into one electron in the external circuit, as a function of wavelength, and $\phi(\lambda)$ represents the incident photon flux. For an ideal solar cell, i.e. an ideal diode, the relationship between the current J and voltage V is given by

$$J = J_{SC} - J_0(e^{qV/k_B T} - 1),$$

where k_B is Boltzmann's constant, and T the temperature of the photovoltaic cell. This is represented graphically in Figure 2.3. Note that here the voltage is defined such that photovoltage and hence power is generated by the solar cell for $V > 0$. The V_{OC} can then be related to the J_{SC} by the following relation:

$$V_{OC} = \frac{k_B T}{q} \ln \left(\frac{J_{SC}}{J_0} - 1 \right).$$

The origin of this photovoltage comes from the Fermi levels of the photogenerated electrons and holes being different inside the semiconductor. Specifically, when a semiconducting layer is exposed to light at or above its bandgap, the conduction and valence band will be populated with electrons and holes, respectively. Because the intra-band recombination rate is significantly longer than the inter-band thermal relaxation time, the electrons in the conduction band and the holes in the valence band can be considered as isolated systems internally in equilibrium, with their own separate quasi-Fermi level. In theory, the extrinsic V_{OC} will be equal to the intrinsic quasi-Fermi level splitting (QFLS), though in practice, that is not always the case due to contact losses. Figure 2.2 shows a schematic of the QFLS and V_{OC} in a MHP solar cell operated at open-circuit.

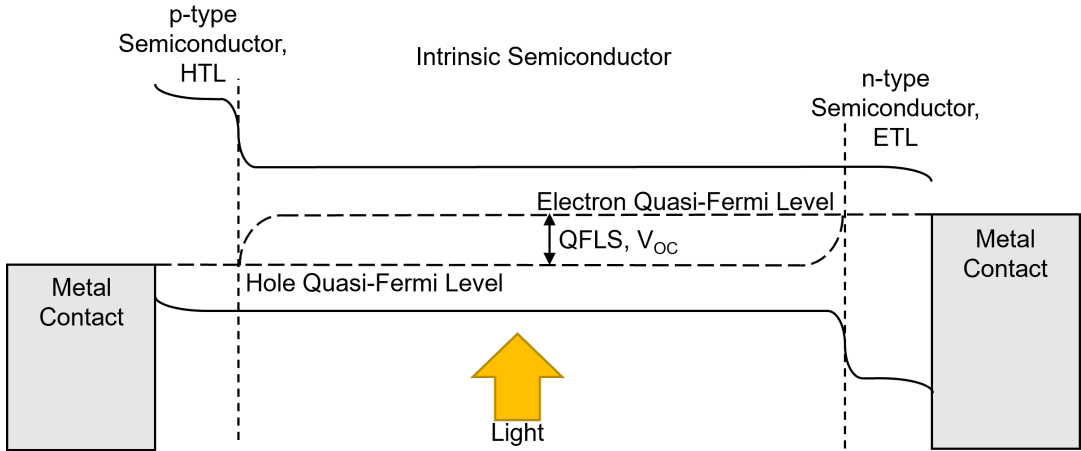


Figure 2.2: Diagram of a p-i-n device under open circuit and illumination. The holes in the valence band and the electrons in the conduction band now behave with distinct quasi-Fermi levels. The quasi-Fermi level splitting (QFLS) gives the V_{OC} of the device.

Within the power generation region, the power-density P generated by the solar cell is defined simply by $P = JV$, where J is the current-density and V the voltage provided by the cell. As a result, the power generated by the cell will vary as a function of the resistive load connected to it (Figure 2.3). In general, there will be a maximum power point (MPP), a value of J and V where maximum power is produced

by the cell. The PCE of the cell is then defined as the ratio of the maximum power (P_{MPP}) to the incident power (P_{in}), i.e.

$$\text{PCE} = \frac{P_{\text{MPP}}}{P_{\text{in}}}.$$

The MPP also allows the definition of the fill-factor (FF), which is a measure of how much the JV curve fills the square defined by the J_{SC} , V_{OC} , and the axes. Specifically, it is the ratio of P_{MPP} to the power generated if the JV curve was square, i.e.

$$\text{FF} = \frac{P_{\text{MPP}}}{J_{\text{SC}}V_{\text{OC}}}.$$

Together, PCE, J_{SC} , V_{OC} , and FF represent the JV figures of merit of a solar cell, and are used to determine the effectiveness of a solar cell at converting sunlight into electrical energy[14].

2.1.3 Shockley-Queisser Limit

The fundamental efficiency limits of a solar cell can be seen to arise from the fact that only photons with energy above the bandgap are absorbed, but that these photons only provide energy equal to the bandgap of the material. This means that, while a low-bandgap material will absorb many photons, each of those photons will only provide a small amount of energy. For a high-bandgap material, the opposite is true: few photons are absorbed, but they each provide much more energy. Another limiting factor is the loss of energy due to charge-carrier recombination, where an electron and a hole recombine to emit a photon. This recombination rate depends on the temperature of the cell through the so called thermal voltage of the cell:

$$V_T = \frac{k_{\text{B}}T}{q}$$

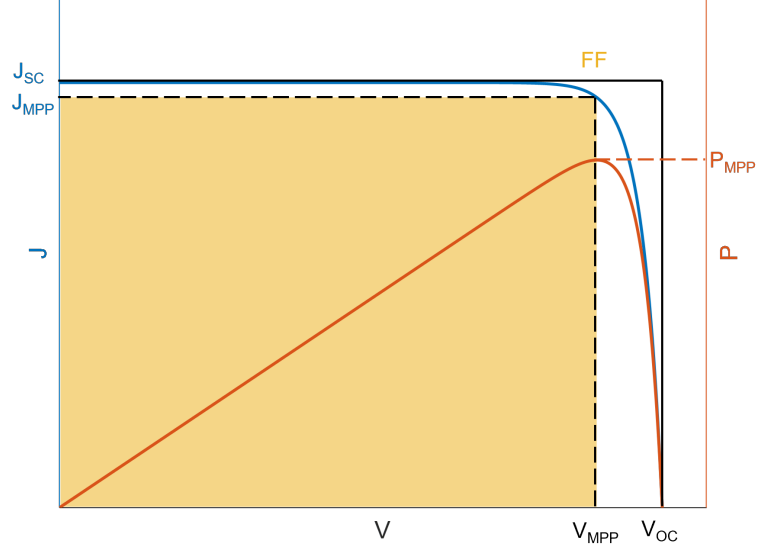


Figure 2.3: Current-voltage (JV) curve for a photovoltaic cell based on an ideal diode (blue) under illumination, with the corresponding power output P (red). The yellow rectangle is delimited by the voltage and current at max power point (J_{MPP} , V_{MPP} , and P_{max} respectively). The area of the yellow rectangle compared to the area delimited by the open-circuit voltage (V_{OC}) and the short-circuit current (J_{SC}) represents the fill factor (FF).

Indeed, the open-circuit voltage is determined by the relative thermal voltages of the cell and the Sun, with $V_{OC} = E_g$ if the Sun is infinitely hotter than the cell, and $V_{OC} = 0$ if they are at the same temperature. In real-world applications, this means that the open-circuit voltage is always lower than the bandgap of the material, reducing the maximum theoretical efficiency. Thermodynamically, this limit comes from the maximum amount of work that can be extracted from a system using the Sun as a heat source and the solar cell as a heat sink. The interplay between these two effects is the basis of the Shockley-Queisser limit, giving the maximum theoretical efficiency for a material of a particular bandgap exposed to the solar spectrum. In a real solar cell, there are additional further losses due to reflection, transmission, as well as not every photon resulting in an electron-hole pair, i.e. imperfect EQE [14].

2.1.4 Tandem Cells

One way to get around the Shockley-Queisser limit is to combine two materials of differing bandgaps, with light first being incident on the high-bandgap material. High energy photons will be absorbed by the high-bandgap material, resulting in high voltage electron hole pairs, while less energetic photons will be transmitted through to the lower-bandgap material. In this way, it is possible to absorb a high number of photons while avoiding large thermalisation losses associated with low-bandgap materials, as shown in Figure 2.4 [19].

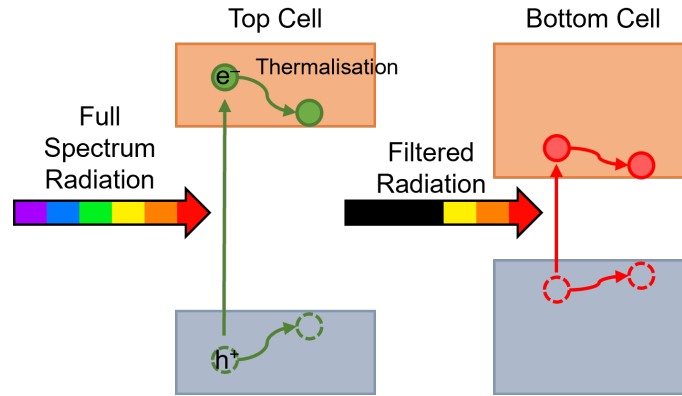


Figure 2.4: Working principle of a tandem solar cell: high energy photons are absorbed more efficiently with less thermalisation losses in the high-bandgap material, while low energy photons go through to the lower-bandgap bottom cell.

There are two ways to couple the different materials, the first being a 4-terminal tandem cell, where two individual cells are merely optically coupled, so that each cell outputs its current through 2 terminals. Since each cell is operating independently, there are no constraints on the electrical properties of each cell. A 4-terminal device can be either stacked mechanically, in which case the two cells are simply placed on top of each other (Figure 2.5a), or coupled optically, where the light is separated into short and long wavelength components, which are then transmitted to the appropriate cells (Figure 2.5b). Mechanically stacked 4-terminal devices suffer from higher parasitic absorption in the transparent conducting material, as well as requiring a

larger amount of transparent conduction material. In the other case, the main loss mechanism here is the optical coupling method, as the light above the bandgap of the high-bandgap material must be separated effectively from the rest. For this purpose, typically, a dichroic mirror is used [14, 19].

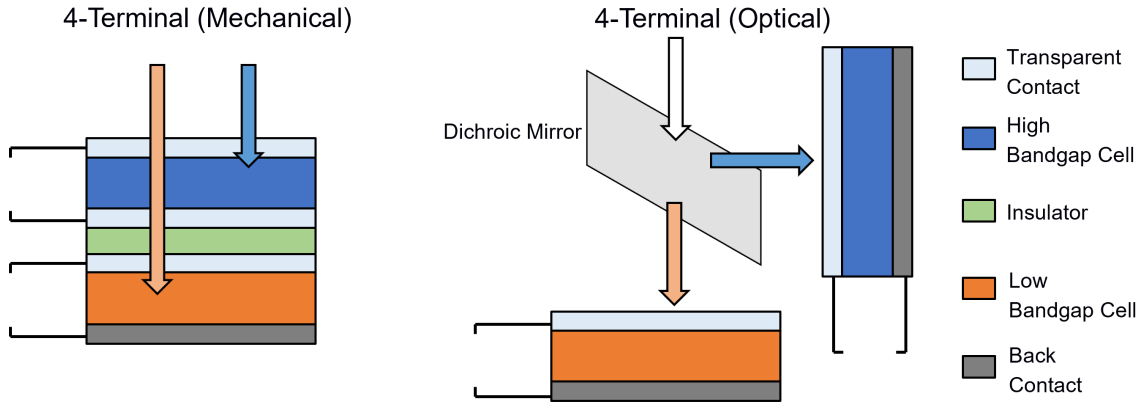


Figure 2.5: Diagram of possible 4-terminal tandem configurations. In a mechanically stacked 4-terminal cell (left), the top cell must have two transparent contacts, and the cells are separated by a semi-transparent insulating layer. In an optically coupled 4-terminal cell (right), the incident full spectrum is split by a dichroic mirror, and redirected to the appropriate bandgap cell.

The second way to couple the different materials is a 2 terminal tandem cell, also called a monolithic tandem. Here, the two materials are directly stacked on top of each other with a conducting buffer layer in between, such that all charge carriers of one type are collected at a single contact, resulting in only two terminals for the entire cell, as shown in Figure 2.6. Because the charge carriers generated in one material must pass through the other as well, the current flowing in each part must be the same, a condition called as current matching. The overall current flowing through the tandem will always be that of the lowest-current sub cell. [19].

2.1.5 Multi-Junction Cells

Further improvements can be made by adding additional materials, i.e. junctions, to the stack, forming so called multi-junction cells. This allows for even finer distribution

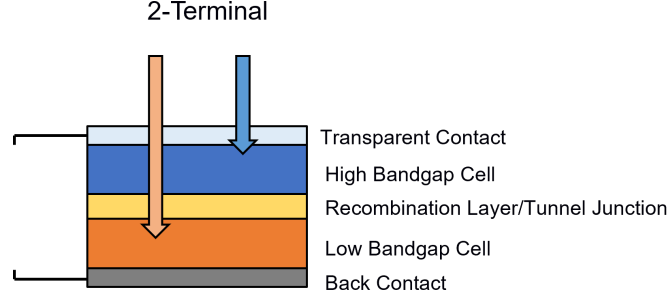


Figure 2.6: Diagram of a 2-terminal tandem cell. The top and bottom cell are electrically connected by a thin recombination layer.

of photons to particular bandgap materials, further reducing the amount of energy lost in the thermalisation of electrons excited above the bandgap of a material, though there are diminishing returns to adding junctions. The current best efficiency solar cells are made of group III-V semiconductor composites, reaching 44.7% efficiency under 297 suns using a GaInP/GaAs/GaInAsP/GaInAs quadruple junction solar cell [18].

2.2 Evaporated Perovskite Solar Cells

The recent growth of MHP solar cell PCE has primarily been through developments in lab-based solution processing deposition techniques. However, these methods are often less suitable for large-scale production of MHP solar cells. As a result, interest in vapour deposition for MHP layers has increased, as this method allows conformal deposition over large areas. Despite being highly compatible with large-scale manufacturing, the cost of research-scale equipment for vapour deposition is significantly higher than the cost of a spin-coater. This has led to a vast asymmetry in the amount of research effort undertaken on MHP vapor deposition, in comparison to solution processing. Nevertheless, a variety of methods have been developed to produce perovskite absorber layers through vapour and vapour-assisted deposition. Vacuum co-deposition, where individual precursors are sublimed simultaneously under vacuum

is the most common method, but other vapour deposition techniques have also been demonstrated successfully. In sequential deposition, the precursors are evaporated onto the substrate one at a time. In chemical vapour deposition (CVD), the precursors in gaseous form are transported to the substrate via an inert gas stream after sublimation. Finally, in single source deposition, the final material itself is ground into a crucible and then evaporated onto the substrate [44].

The most common type of perovskite absorber is an organic-inorganic hybrid, MAPbI₃. To form MAPbI₃ via co-evaporation, two sources are required, as illustrated in Figure 2.7. There are currently two ways to produce MAPbI₃ via vacuum co-deposition, called the PbI₂- and PbCl₂-routes. In the PbI₂-route, the organic component (MAI) and the inorganic component (PbI₂) are evaporated simultaneously, subliming into the perovskite phase directly. The resulting films have small grains, yet still display high performance, contrary to what is usually observed for spin-coated films. In the PbCl₂-route, the organic component evaporated is MAI while the inorganic component is PbCl₂. Upon mixing, perovskite MAPbI₃ will be formed as well as MACl. The latter leaves the material upon annealing, resulting in MAPbI₃ films with larger grain sizes than those from the iodide route. The PbI₂-route has the advantage of not requiring any annealing step, hence allowing deposition on temperature sensitive flexible substrates.

High-efficiency devices based on vapour deposited perovskite layers have been demonstrated, with efficiencies recently surpassing 20% [48]. Initially, work on evaporated perovskites focused on optimising the deposition conditions to form good MAPbI₃ solar cells, as well as developing contact layers for ideal PCE. The first report of a solar cell with a vapour deposited perovskite layer showed promising efficiencies of 15.4% [49]. Here, the HTL and ETL were planar TiO₂ and doped 2,2',7,7'-tetrakis-(N,N-di-p-methoxyphenylamine)9,9'-spirobifluorene (Spiro-OMeTAD), respectively, deposited via conventional spin-coating methods.

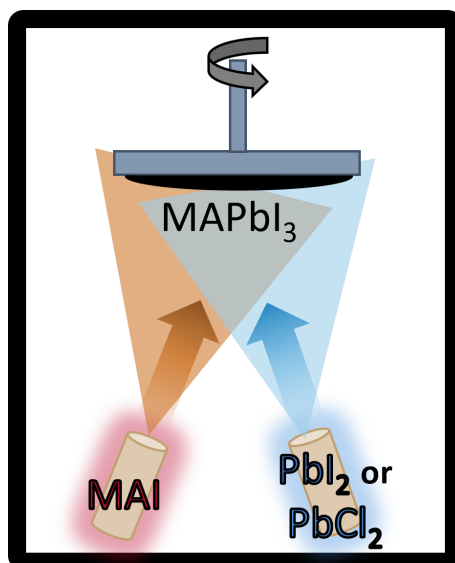


Figure 2.7: Diagram of the vacuum co-evaporation process to form MAPbI_3 , the most common material for MHP solar cells. MAPbI_3 can be formed co-deposition of MAI and either PbI_2 or PbCl_2 . For the latter, an excess of MAI is required.

The perovskite layer of average thickness 330 nm was deposited via the PbCl_2 -route, and this work demonstrated that continuous, uniform MAPbI_3 layers could be deposited using vacuum co-deposition [49]. Mid-2014, Lin et al. demonstrated that, unlike for solution-processed films at the time, it was not necessary to use the PbCl_2 -route to obtain high-quality MAPbI_3 films, and that the simpler PbI_2 -route results in efficiencies of 16.5% [50]. At this time, the preferred way to control the sublimation rate was still by keeping the precursor crucibles at a constant temperature rather than direct rate control. In addition, this work investigated more advanced CTLs, using ITO/PEDOT:PSS/PCDTBT/perovskite/ PC_{60}BM /LiF/Ag. The multiple n- and p-type layers resulted in improved FF, demonstrating the need for optimised CTLs to achieve the highest PCE in vapour-deposited MHP solar cells. From this point onward, the PbCl_2 -route was generally abandoned in favour of the PbI_2 -route, but a detailed comparison of the effects of both routes was never carried out, remaining an open question in the field.

The next step was achieved early 2016, when the previous way of controlling PbI_2

and MAI was first challenged. Indeed, Hsiao et al. used a quartz micro-balance to control the deposition rate of PbI_2 , while controlling the MAI deposition rate through the chamber pressure [51]. This method of depositing the precursors yielded higher efficiencies as compare to the previous method of constant source temperature, yielding efficiencies up to 17.6%. Furthermore, this work showed that it is not necessary to deposit the precursors together, and good films can be made by depositing PbI_2 and subsequently reacting it with the MAI vapour. The authors demonstrated the feasibility of using evaporated CTLs, resulting in fully-evaporated solar cells, an important step to proving the upscalability of the vapour deposition process. However, with this work it became clear that MAI does not sublime directionally, behaving rather as a gas and depositing throughout the chamber. From this point onward, controlling the MAI sublimation dynamics and finding the best way to reproducibly deposit MAI became a major focus of the MHP evaporation research community.

An alternative to direct sublimation of MAI was attempted by Yin et al., who used CVD to achieve 18.9% PCE MAPbI_3 solar cells [52]. Hot air containing MAI vapour is passed over PbI_2 films as they are annealed in situ, forming perovskite through a vapour-solid reaction. This method has the advantage of not requiring high vacuum, being able to run at atmospheric pressure, though again the film needs to be annealed at 150 °C, making this method incompatible with temperature sensitive flexible substrates. Ultimately this would work against CVD as a method, as Momblona et al. demonstrated that an annealing step is not required for high-performance MAPbI_3 films grown via the PbI_2 -route, demonstrating efficiencies as high as 20% in fully-vacuum processed solar cells [48]. Here, the authors used direct rate control of both MAI and PbI_2 , though note that this is particularly challenging for the MAI, which must first be carefully outgassed before a stable rate can be achieved. This work demonstrates the benefits of using direct rate control for sublimation of the precursors, as films could now be made thicker and maintain the correct stoichiometry, as

compared to the constant source temperature method used early on. As with previous works, careful optimisation of the CTLs proved key to enabling the high PCE shown in this work, but that the neat evaporated MAPbI₃ was otherwise sufficient. Figure 2.8 shows a schematic of this device architecture, as well as the JV curves for the champion devices, which remained the highest vapour-deposited solar cells for a number of years.

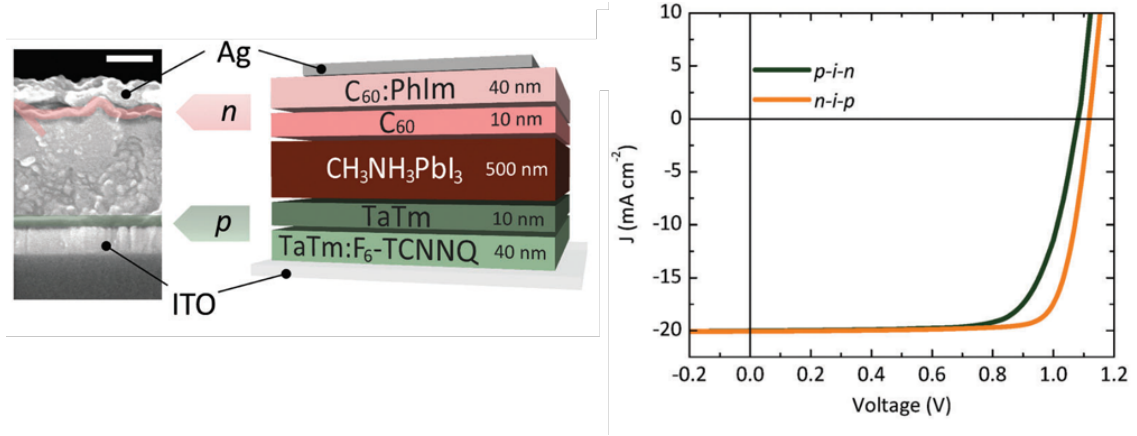


Figure 2.8: Schematic of the device architecture (left) and JV curves (right) for the super-20% MAPbI₃ co-evaporated devices (the n-i-p curve). Source: ref. [48].

In parallel, a main open question in the field of evaporated MHPs was how perovskite solar cells produced through vapour deposition appear to have less reliance on large grain sizes for good efficiencies as compared to solution processed devices. Indeed, contrary to spin-coated devices, good efficiencies above 15% are still obtained for devices that show very small, on the order of 100 nm grain sizes. It is generally believed that grain boundaries reduce charge transport by causing trap states to form below the band edges, and hence being sites for non-radiative recombination. The fact that evaporated devices still show very good performance could indicate that the grain boundaries in such films are better quality and less harmful to the optoelectronic properties. It is worth noting, however, that larger crystal domains and better crystallinity is still generally associated with improvements in device performance, though notably the super-20% PCE devices only had very small, order 100 nm

grains, whereas previous lower efficiency devices had grain sizes up to several μm , as illustrated in Figure 2.9. With currently no known way of controlling grain size during vapour-deposition, the effect of grain boundaries in vapour-deposited films remains an open question.

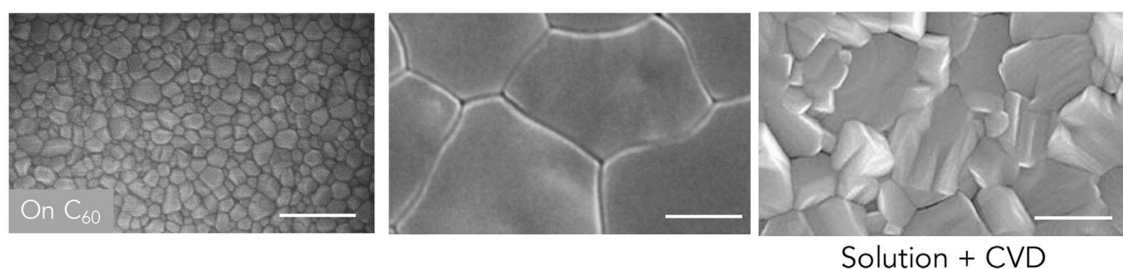


Figure 2.9: SEM scan images of high-performing evaporated devices: co-evaporation (left), sequential deposition with MAI monitored via partial pressure (middle), solution processed PbI_2 followed by MAI CVD (right). All scale bars represent 500 nm. Sources: refs. from left to right, [48, 51, 52], as modified by ref. [44].

Another issue that is prevalent in evaporated perovskite is the difficulty in controlling the MAI deposition rate through conventional quartz crystal microbalances. Indeed, as discussed above, different methods are used throughout the literature to ensure a consistent MAI coating, such as direct temperature control of the precursor crucibles, sequential deposition, or even CVD. Not only is this an issue when considering upscalability on an industrial scale, since it implies poor control over the MAI vapour, but it also makes the MAI rate needed much harder to tool and determine. While early reports of co-evaporated MAPbI_3 assumed the MAI precursor to be well-behaved under sublimation, by the time I started my research it was becoming apparent that alternative control methods needed to be developed to reproducibly control the MAI precursor, as this was another major open question in this research field.

2.2.1 Non-MAPbI₃ Perovskites

With the overall MHP research field developing more complex MHP compositions with varying bandgaps, for tandem applications, depositing these compositions also became a focus for vapour-deposition research. However, because each additional precursor requires its own deposition source, the compositions possible with existing 2-source vapour deposition equipment were more limited until said equipment was upgraded. The earliest report of a non-MAPbI₃ vapour deposited perovskites comes early 2017, by Chen et al. who produced fully vacuum processed inorganic CsPbI₃ and CsPbBrI₂ solar cells with up to 9.4% and 11.8% PCE, respectively [53]. The authors observed rather low $V_{OC} = 0.97$ V for the pure I devices given the bandgap of 1.72 eV. The V_{OC} did increase to 1.15 V for the 1.82 eV mixed halide composition, but this work showed that these inorganic compositions required significantly more optimisation than MAPbI₃, which readily forms the right perovskite phase during the deposition process. The more recent work by Borchert et al. explores the use of FAI instead of MAI as the organic precursor, preferred for its better thermal stability, forming FAPbI₃ [54]. Photovoltaic devices of area 0.0919 cm² exhibited efficiencies up to 15.8%, and the authors found FAI to sublime much more directionally than MAI, making it easier to reproducibly deposit similar thicknesses. This work was also explored large area (64 cm²) FAPbI₃ thin-films, a demonstration of the large-area conformal coating capabilities of the vapour-deposition technique that is crucial for industrial applications.

Around the same time, Longo et al. demonstrated stable mixed halide perovskite solar cells produced through vacuum co-deposition using three sources, namely MAI, PbI₂, and PbBr₂ [55]. The resulting cells show efficiencies up to 15.9% and 10.6% for MAPb(Br_{0.2}I_{0.8})₃ and MAPb(Br_{0.5}I_{0.5})₃, respectively, comparing favourably with the reference MAPbI₃ device with 17.5% PCE. The V_{OC} of the devices increases with Br content, from 1.119 to 1.207 for 20% and 50% Br content, respectively, and this comes

with a significant loss in current, with J_{SC} dropping to 17.3 and 11.4 for 20% and 50% Br content, respectively. It was hoped that the vapour-deposition process would form more homogeneous films and hence be less affected by the halide segregation observed in solution-processed devices [56], but PL measurements revealed phase segregation still occurs in the higher Br content devices of this work, though this was partially mitigated by a 30 min anneal at 90 °C. Under constant 300 mW/cm² illumination, the 20% Br films did not show a shift in the PL peak, but did show a decrease in intensity due to film degradation.

With more advanced deposition systems now ready for use, Gil-Escrig et al. went even further, producing mixed-cation perovskite films through vacuum co-evaporation of up to 4 sources [57]. The composition investigated was Cs_{0.5}FA_{0.5}Pb(I_{0.83}Br_{0.17})₃ and Cs_{0.5}FA_{0.4}MA_{0.1}Pb(I_{0.83}Br_{0.17})₃. Surprisingly, the authors found that the mix of cations resulted in the sporadic formation of larger, uneven crystallites, which is very different from the typical homogeneity observed in vapour deposited devices with simpler perovskite compositions. Ultimately, it was the addition of MAI that resulted in higher performance (16.0% PCE) and more uniform films, and allowed improved $V_{OC} = 1.146$ V for a 1.70 eV bandgap.

In general, developing these more complex MHP formulations is a necessary step for the commercial implementation of vacuum-deposition, as the production of tandem solar cells requires higher-bandgap materials than MAPbI₃. The work of Gil-Escrig et al. demonstrates the feasibility of stoichiometry control in a co-evaporation setup with more than two sources. However, it also highlights the current reliance of co-deposition on MAI, which appears to play a beneficial role in MHP film growth and morphology. MA is less thermally stable than other alternatives such as FA, so developing the deposition of MA-free multi-cation MHP became the next challenge in advancing higher-bandgap co-evaporated MHP solar cells.

Chapter 3

Experimental Techniques

3.1 Physical Vapour Deposition

3.1.1 Background

My metal-halide perovskite layers were deposited using physical vapour deposition, where the precursors are sublimed under high vacuum (10^{-6} to 10^{-5} mbar) to deposit a uniform layer on the desired substrates. For our evaporation chamber, we use radiation sources, consisting of a tungsten filament wrapped cylindrically around the inserted precursor crucible made of aluminium oxide (Al_2O_3). The crucible and wire assembly is capped by a metal cylinder, which helps contain the heat around the crucible. The tungsten filament is heated up by passing a high current directly through it (1-10 A), causing it to radiate heat to the precursor crucible, resulting in sublimation once the right temperature is reached. The sublimation rate of a particular precursor will depend on the temperature of the source, the chamber pressure, and the mass of material in the crucible. Typically, a uniform deposition rate is desired, for which quartz crystal monitors (QCMs) are used. A QCM operates by using an AC voltage to induce shear waves across a thin quartz crystal through the piezo-electric effect. As material is deposited onto the quartz crystal, the resonance frequency of the system

decreases as it becomes increasingly damped by the additional material deposited. Measuring the change in oscillation frequency of the quartz crystal hence allows very fine determination of the amount of material/mass deposited onto the QCM, in real time [58]. Therefore, the power input into the source can be changed using a PID control loop based on the input from the QCM to ensure deposition at a continuous rate throughout the deposition. Since each material has its own ratio of thickness deposited to mass, and the QCM used for deposition control is not placed directly at the substrate, each material must be tooled to determine the ratio between the mass deposited on the QCM and the thickness of material deposited on the substrate. This can be achieved straightforwardly by comparing the actual thickness deposited to the mass deposited on the QCM, and introducing the appropriate scaling “tooling factor”.

For the deposition of perovskite materials, multiple precursors are needed, namely the A-site halide compound (eg MAI, FAI, CsI) and the B-site halide compound (eg PbI_2 , PbCl_2). The two materials can be deposited either sequentially or at the same time. The former has the advantage of a more straightforward deposition process, as only one material is deposited at the same time, but relies on succesful mixing of the precursor layers, always requiring an annealing step. The latter, also called co-evaporation, produces the right stoichiometry in real time, but can be more challenging to control, as multiple precursor sources must be controlled at the same time. In my research group, we settled on using co-evaporation, as we found this method gives higher quality films, often not requiring a post-annealing step, allowing for deposition on temperature sensitive substrates such as flexible plastic films. Because the desired metal-halide perovskite composition is formed during deposition, the precursors must be evaporated at the correct stoichiometric ratio. As the QCM determines deposition rate, it is necessary to convert from thickness deposited per second to moles deposited per second. The ratio between these quantities is given by density

and molar mass of the material, denoted by ρ and m_m respectively. First, the mass M deposited over an area A during a time interval t at constant deposition rate r can be worked out by considering the thickness d of material deposited in time interval t (Figure 3.1) as

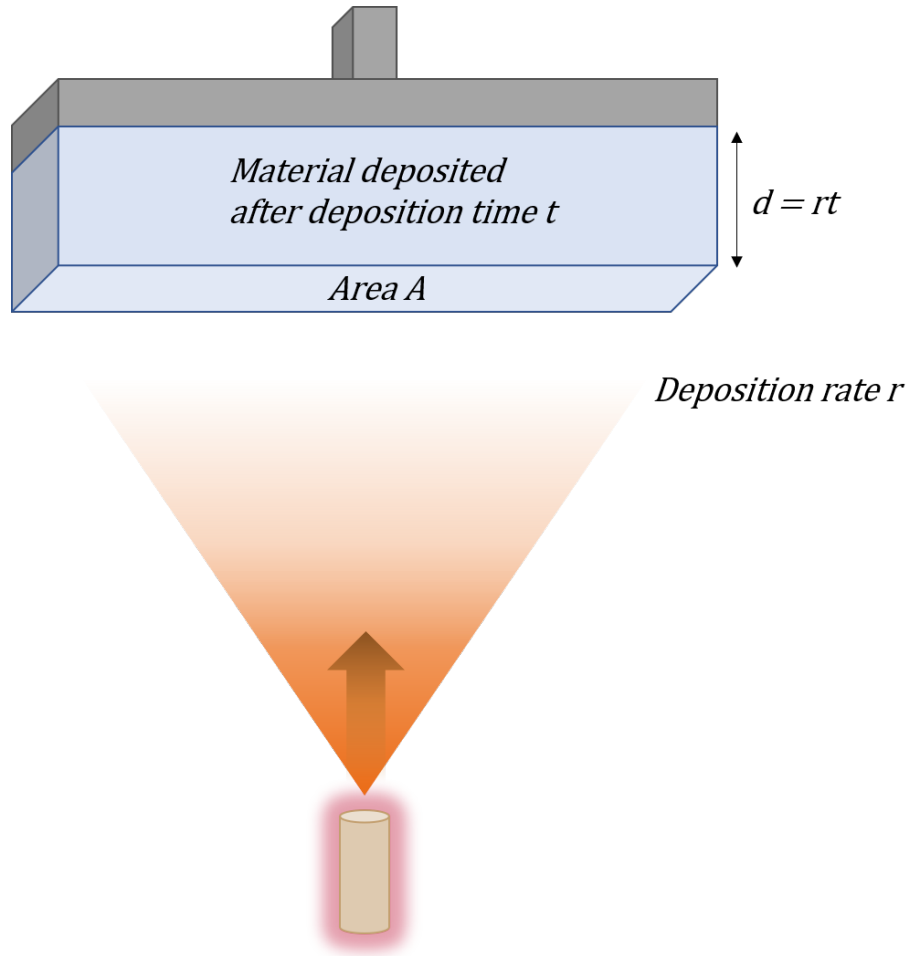


Figure 3.1: Schematic showing the volume of material deposited in time t at constant rate r over substrate area A

$$\begin{aligned} M &= \rho V \\ &= \rho A t r. \end{aligned} \tag{3.1}$$

Next, the number of moles N_m present in mass M of a material with molar mass

m_m is given by

$$N_m = \frac{M}{m_m}. \quad (3.2)$$

Substituting in the mass as a function of deposition rate from Equation 3.1 yields the following expression for the amount of moles N_m as a function of the deposition rate:

$$N_m = \frac{\rho}{m_m} Atr. \quad (3.3)$$

In co-deposition, we are interested in matching the number of moles between the precursors over the same deposition area, at each time point of the deposition. When comparing the relative deposition rate between two materials, we can hence consider the number of moles deposited per unit area and time, which is simply

$$N_m = \frac{\rho}{m_m} r. \quad (3.4)$$

For example, for the co-evaporatation of CsPbI_3 , the precursors CsI and PbI_2 must be deposited at a 1-to-1 molar ratio. Hence, the relative ratio between the CsI rate and PbI_2 rate can be calculated as follows, in terms of the CsI and PbI_2 densities and molar masses:

$$r_{\text{CsI}} = \frac{\rho_{\text{PbI}_2}}{\rho_{\text{CsI}}} \frac{m_{m\text{CsI}}}{m_{m\text{PbI}_2}} r_{\text{PbI}_2}. \quad (3.5)$$

Note that equations of the type 3.5 only hold true when the precursors are “well-behaved” under sublimation. As outlined in Chapter 2, there is significant evidence that this is not the case for MAI.

3.1.2 MHP Fabrication

I used a custom Lesker thermal evaporation chamber to deposit the semiconductor layers used for this thesis. Initially, the chamber had two radiation heater sources, which operate by passing current through a heating wire wrapped closely around a crucible (Figure 3.2 left). In this configuration, the chamber could be used to co-evaporate simple perovskite compositions such as MAPbI_3 , FAPbI_3 , or CsPbI_3 , as well as organic charge transport layers (CTL) such as C_{60} . As part of my DPhil work, the chamber was later upgraded to have five such sources, two of which were “dual-zone” sources that had two heating elements per crucible, allowing the top and bottom to be heated separately (Figure 3.2 right). After this upgrade, I was able to start depositing more complex compositions, as detailed in Chapter 6.

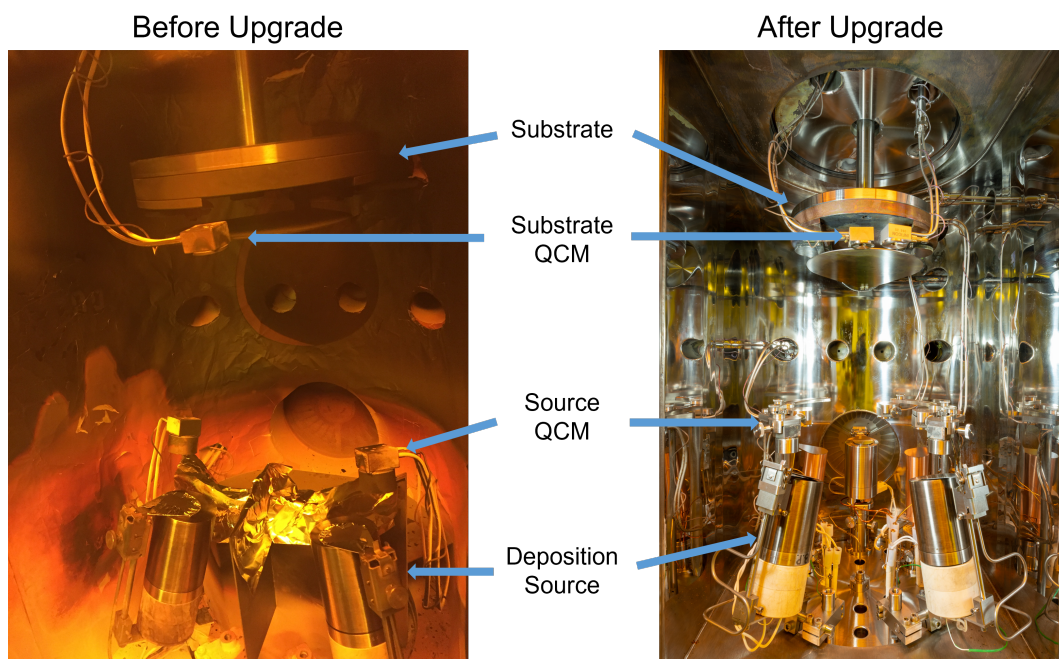


Figure 3.2: Photos of the vacuum deposition chamber I worked on, identifying the position of the key elements required to run a deposition. The precursors are heated in the deposition sources, and the rate is individually controlled by the source quartz-crystal monitors (QCM). The vapour deposits onto the substrate, while the substrate QCM gives an indication of the total deposition rate of all materials. Before the upgrade (left), the system had two sources (photo credit: Lavina Snoek). After the upgrade (right), the system had five sources (photo credit: Prof. Michael Johnston).

I used the purest precursors commercially available for my depositions. The inorganic precursors were ordered from Alfa-Aesar, and had the following purities for the metal base: PbI_2 (99.999%), PbCl_2 (99.999%), CsI (99.998%). MAI and FAI were ordered from Greatcell. Using high purity precursors reduces the batch to batch variation, and ensures good reproducibility.

For a typical deposition, the chamber was pumped down to 5×10^{-6} mbar before the I started heating the sources. During the subsequent depositions, the pressure was typically around $1\text{--}2 \times 10^{-5}$ mbar for depositions with MAI, and 10^{-6} mbar for depositions without MAI.

For the MAPbI_3 layers of Chapter 4, PbI_2 and MAI were co-evaporated in the aforementioned vapour deposition chamber. Heating of the sources starts once the chamber pressure falls below 5×10^{-6} mbar. During the subsequent evaporation, the pressure goes up to $1\text{--}2 \times 10^{-5}$ mbar. the PbI_2 rate was kept constant at $0.30 \text{ \AA/s}$ using a gold-plated quartz microbalance, while the MAI temperature was controlled such that the overall deposition rate as measured by a quartz microbalance located next to the sensor was $0.45 \text{ \AA/s}$. This rate is henceforth denoted by “substrate rate”. For a typical 420 nm deposition, this involved ramping the MAI temperature from 175.1°C to 183°C , for 1.1 g of MAI initially in the crucible. For thicker depositions, in order to match the sublimation dynamics of the thinner samples as much as possible, the amount of fresh MAI initially put in the crucible was increased according to a MAI sublimation rate of 0.05 mg/s , and the starting temperature decreased slightly.

In Chapter 5, I deposited MAPbI_3 through either co-evaporation of MAI and PbI_2 or MAI and PbCl_2 , corresponding to the PbI_2 - and PbCl_2 -route described in Chapter 2. The PbI_2 -route films were deposited in the same way as described earlier. For the PbCl_2 -route films, the PbCl_2 rate was kept constant at $0.30 \text{ \AA/s}$, while the MAI rate was still controlled with the aforementioned substrate rate control method. The chamber pressure typically rose to higher pressures of $3\text{--}4 \times 10^{-5}$ mbar during PbCl_2 -

route depositions, compared to $1\text{--}2 \times 10^{-5}$ mbar for PbI_2 -route ones. For these layers, the substrate was kept at 20 °C for all films except the ones used for scanning electron microscopy imaging, which had the substrate holder kept at 16 °C.

During deposition, MAI is known to sublime omnidirectionally and deposit on all surfaces of the vacuum chamber. To reduce contamination from MAI resublimated off the walls during a deposition, we regularly bake out both sources at 450 °C and the substrate at 150 °C, much higher than is reached during film deposition. During deposition, the temperature of the walls of the chamber is controlled to be 17 °C. Finally, the substrate rate should account for the total amount of MAI sublimed onto the substrate, including any that potentially gets resublimed off the wall.

In Chapter 6, I co-evaporated FAI, CsI, PbI_2 and PbCl_2 to deposit compositions of the form $\text{FA}_{1-y}\text{Cs}_y\text{Pb}(\text{I}_{1-x}\text{Cl}_x)_3$ by progressively substituting PbI_2 with PbCl_2 . Specifically, starting with the neat-iodide aimed composition of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{PbI}_3$, we substituted 0%, 10%, 20%, 30%, 40% of the molar deposition rate of PbI_2 with PbCl_2 , respectively. The FAI and CsI rates were kept the same for all deposition. During the evaporation, the pressure was typically $< 10^{-6}$ mbar. The source rates were kept constant using QCMs and PID-loop-control software, with set rates and typical deposition temperatures detailed in Table 3.1. The sublimation rate of the inorganic precursors was controlled using QCMs adjacent to the crucible, while the FAI sublimation rate was controlled using a QCM close to the substrate, following the method I used for MAI. Prior to every deposition, the FAI crucible was topped up to 1.1 g, adding fresh FAI to the remainder of previous deposition. For a typical 500 nm perovskite deposition, we evaporated 0.21–0.2 g of FAI. Our chamber is set up such that the walls of the chamber are cooled to 17 °C, while the substrate was held constant at 20 °C. Unless specified otherwise, all samples were annealed after deposition in an N_2 glovebox for 30 minutes at 135 °C.

Material	FAI	CsI	PbI ₂	PbCl ₂
Set rate (Å/s)	0.2	0.04	0.29-0.17	0-0.072
Temperature (°C)	150-165	390-410	265-280	305-340

Table 3.1: Set rate values for the materials vapour deposited for Chapter 6, as well as the range of temperatures typically reached by the crucibles during deposition

3.2 Solar Cell Fabrication

3.2.1 Bottom Contact

Films were deposited on TEC 15 fluorine-doped tin oxide (FTO) (Chapters 4, 5) or indium-doped tin oxide (ITO) glass (Chapter 6). The substrates were cleaned using industrial detergent Decon90 (1% vol in de-ionised water), de-ionised water, acetone, and isopropyl alcohol. Immediately prior to deposition, the FTO substrates were cleaned in an O₂ plasma chamber for 5 minutes, while the ITO substrates were cleaned under UV-ozone for 15 minutes. This same cleaning procedure was also performed on the z-cut quartz substrates used for optical characterisation.

3.2.2 Top Contact

100 nm of Ag or 80 nm of Au were thermally evaporated in a commercial Lesker nano36 chamber, at rates of 0.2–2.0 Å/s and 0.8–2.5 Å/s respectively; the rate was typically ramped up during the first 15 nm of deposition, and controlled by a gold-plated quartz microbalance. A mask was used to deposit the metal contact on the entirety of the back surface of the device, which had area 0.0919 cm² for Chapters 4, 5, and area 0.25 cm² and 1 cm² for Chapter 6.

3.2.3 n-i-p Devices

The solar cells for Chapters 4, 5 followed an n-i-p structure, using vapour deposited C₆₀ as the ETL and solution-processed Spiro-OMeTAD as the HTL (Figure 3.3 left).

C₆₀ fullerene (99.9%, Acros Organics) was thermally evaporated in the aforementioned custom thermal evaporator chamber at 0.1 Å/s, for a typical thickness of 10 nm for devices.

Spiro-OMeTAD (Lumtec) was dissolved in chlorobenzene at a concentration of 81 mg/mL, with added lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI) dissolved in 1-butanol at a concentration of 170 mg/mL, and tert-butylpyridine (tBP). For 1 mL of the spiro solution, 38 µL of the Li-TFSI solution and 21 µL of tBP were added. 40 µL of the solution was then spin-coated dynamically at 2000 rpm for 45 s. Before depositing the final electrode, the films were kept in a desiccator for 12-18 hours to oxidise the spiro-OMeTAD.

3.2.4 p-i-n Devices

The solar cells for Chapter 6 followed a p-i-n structure, using solution-processed Poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine (PTAA) as the HTL and vapour deposited C₆₀/BCP as the ETL (Figure 3.3 right). PTAA (Xi'an Polymer Light Technology) was dissolved in toluene at a concentration of 1.5 mg/mL; 100 µL of solution was applied statically onto the substrate, which was then spun up to 6000 rpm for 30 s, with an acceleration of 2000 rpm/s. After deposition, the substrate with PTAA was annealed at 100 °C for 10 mins.

C₆₀ was vacuum deposited in the same custom thermal evaporator chamber to 25 nm at 0.06 Å/s. The rate was controlled using a gold-plated quartz microbalance. Following C₆₀ deposition, without breaking vacuum, 2 nm of BCP (99.5%, Sigma-Aldrich) were deposited in the same evaporator chamber at 0.1 Å/s.

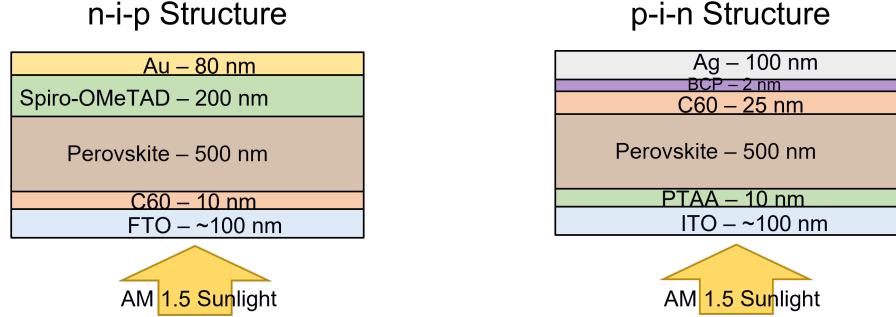


Figure 3.3: Schematic of the n-i-p (left) and p-i-n (right) solar cell structures used in this thesis. The green layer represents the HTL, while the orange layer represents the ETL.

3.3 Current Voltage Characterisation

As discussed in Chapter 2, recording the current output by a solar cell under illumination as a function of load resistance describes the JV curve of the corresponding device. The JV curve can then be analysed to determine the JV figures of merit of the solar cell, namely PCE, J_{SC} , V_{OC} , and FF. My cells were tested using the AM1.5 simulated sunlight standard described in Chapter 1, which is defined as having an intensity of 100 mW/cm^2 .

For Chapters 4 and 5, devices were measured using an ABET Technologies Sun 2000 and a Keithly 2400 sourcemeter at AM1.5 100 mW/cm^2 sunlight in ambient atmosphere. The lamp was calibrated with a KG5 Filtered silicon reference, itself calibrated by NREL. Using a mask, the active area for each device was 0.0919 cm^2 , corresponding to the top contact area. The scan rate used was 0.3 V/s for both forward and reverse scans, with no initial stabilisation time, going from 0–1.2 V. The reverse scan was performed first, followed immediately by the forward scan. Stabilised characteristics were measured after 50 s of keeping the device at the voltage of the maximum power point, as determined by the JV scan.

The solar simulator was later upgraded to an LED array able to more accurately output an AM1.5 spectrum. Devices from Chapter 6 were tested in ambient atmo-

sphere using a Wavelabs Sinus-220 solar simulator and a Keithly 2400 sourcemeter at AM1.5 100 mW/cm² sunlight. The LED array of the solar simulator was calibrated with a KG3-filtered silicon reference (Fraunhofer). Using a mask, the active area illuminated for each device was 0.25 or 1 cm², corresponding to the top contact area. Before scanning the open-circuit voltage (V_{OC}) was measured over 3 s. The scan rate used was 0.01 V/s for both forward and reverse scans. The reverse scan was performed first, going from 1.2–0 V, followed immediately by the forward scan. Steady-state characteristics were collected by measuring the current and voltage output over 30 s of keeping the device close to max power point (V_{MPP}) under illumination. After scanning the short-circuit current (J_{SC}) was recorded over a period of 3 s. The devices tended to improve slightly over the course of 1 week after deposition. All JV data shown in this work was measured 1 week after deposition of the top contact. I measured devices of both area 0.25 cm² and 1 cm².

3.4 Scanning electron microscopy

Electron microscopy refers to using a focused beam of electrons rather than visible light photons to observe the surface of a sample. Because electrons have a lower wavelength than visible light photons, this allows imaging of samples at much higher resolutions. The interaction of the beam electrons with the sample will produce a number of different signals. Scanning electron microscopy (SEM) looks at the secondary electrons, which are from the first few nanometers of the imaged sample. Hence, SEM allows imaging of the surface morphology [59].

For this thesis, top-down and cross-section images were acquired using an FEI Quanta 600 FEG, at 5 keV and 10 keV acceleration voltage, respectively, with current defined by 2.5 spot size. The chamber was pumped down to high vacuum ($< 2 \times 10^{-4}$ mbar).

3.4.1 Energy dispersive X-ray spectroscopy

In contrast to the secondary electrons used for SEM images, energy-dispersive X-ray spectroscopy (EDX) looks at the characteristic X-rays emitted by the sample as atomic electrons relax to lower energy levels left vacant by ionisation through the focused electron beam. Since these energy transitions have unique energy values for each material, EDX can be used to determine the relative chemical composition of a material. Characteristic X-rays are emitted from a much larger interaction volume than secondary electrons, typically a tear-drop shaped volume with a depth of several 100 nm [59].

The SEM EDX measurements of Chapter 6 were performed on the same system described above, using an Oxford Instruments silicon drift detector. For each sample, 9 scans were taken over areas of order 0.010 mm^2 , over a 90 s duration, using a 10 keV electron beam. To correct for differential Cl and I detection, I also prepared 500 nm thick samples of just PbI_2 and PbCl_2 . Table 3.2 shows the average relative atomic composition detected for the reference PbI_2 and PbCl_2 samples, and the calculated correction factor for I and Cl. This correction data and calculation were performed by Dr. Harry Sansom.

Reference sample	Relative Atomic Composition /%			Correction factor
	Pb	I	Cl	
PbI_2	33.649	66.351	n/a	1.0141
PbCl_2	32.232	n/a	67.768	0.9507

Table 3.2: Relative atomic composition measured using energy-dispersive X-ray spectroscopy (EDX) for the 500 nm PbI_2 and PbCl_2 reference sample, and the corresponding correction factor, as measured and calculated by Dr. Harry Sansom.

3.5 X-ray diffraction measurements

If a beam of X-rays is incident on a crystalline structure, the X-rays will diffract in specific directions dependent on the position of the electron density within the crystals. X-ray diffraction measurements (XRD) measure the X-ray intensity as a function of diffraction angle, which allows the determination of the crystal structure of the measured material. From the chemical structure it is then possible to identify the crystal phases within the material and their relative stoichiometries. Note that XRD is only sensitive to crystalline materials, and so will not detect any amorphous phases in the material.

In this thesis, XRD measurements were acquired using a Panalytical X'pert powder diffractometer equipped with a copper X-ray source (Cu-K α 1.54 Å source set to 40 kV and 40 mA). The traces were corrected for tilt by shifting the x-axis of the individual profiles such that the diffraction peak from the reference material would match the correct value. Depending on the sample, the peaks used were: FTO $2\theta = 26.583^\circ$, ITO $2\theta = 30.4^\circ$, z-cut quartz $2\theta = 16.44^\circ$. The peak position and full width at half-maximum (FWHM) for the peaks was determined by fitting a pseudo-Voigt functions to specific peaks following the formula used in ref. [60]. For Chapter 4, in the case of HL, where a shoulder appears on the (110), (220), and (130) peaks from the tetragonal phase, a double pseudo-Voigt function is fit, and the FWHM value presented corresponds to that of the higher angle, higher intensity peak. For Chapter 4, the background was additionally removed by fitting a 6th order polynomial to the entire spectrum before the pseudo-Voigt fits to the peaks.

For Chapter 4, I also measured the instrument response of the system, which defines the lowest FWHM measurable based on instrument limitations. To determine the instrument broadening, I applied the same procedure as above to a reference spectrum of a single crystal silicon sample. I then plotted FWHM against 2θ , then fit a quadratic of the form $y = ax^2 + c$ to this data to determine the instrument

broadening at any scattering angle. This plot and fit is shown in Figure 3.4. Using the fitted curve I determined the instrument broadening value at the peak position of the perovskite (130) peak of sample L, $2\theta=31.85^\circ$. At this angle, the instrument broadening was found to be 0.0628° .

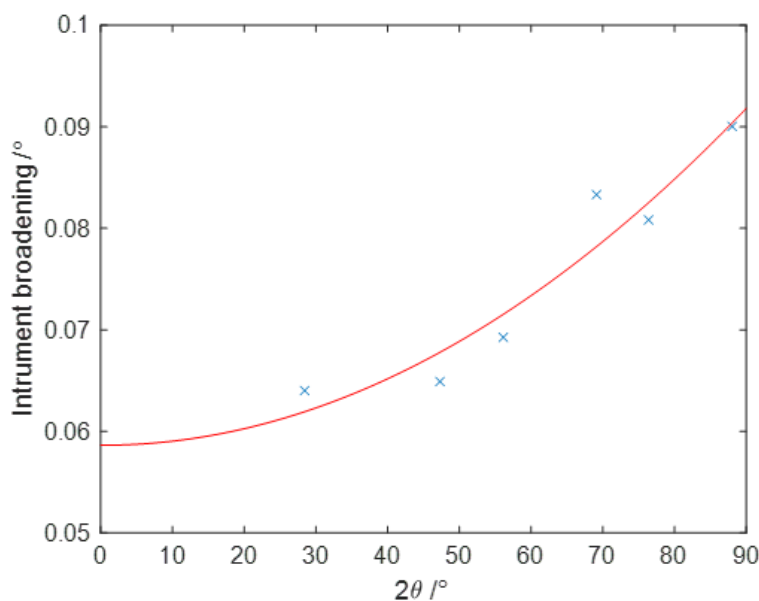


Figure 3.4: Instrument response curve for the X-ray diffractometer used in this study. The blue crosses represent the full-width at half maximum values for a reference Si sample, while the red curve represents the fitted polynomial.

3.6 X-ray photoemission spectroscopy

In X-ray photoemission spectroscopy (XPS), the photoelectric effect is used to determine the binding energies of electrons within a material. X-rays of known wavelength and hence energy are used to ionise electrons off a material. By measuring the kinetic energy of these electrons it is then possible to determine the binding energy of the electrons, as it will be equal to the difference of the incoming photon energy and the outgoing electron kinetic energy, minus a constant offset that accounts for kinetic energy losses of the electrons as it leaves the bulk material and is absorbed by the

detector. The binding energy of the atomic electrons then determines the elements present in the material, as well as their electronic configuration. XPS is most sensitive to the surface of the material, as electrons generated deeper in the film will be significantly less likely to reach the surface of the film, escape, and be collected by the detector.

The XPS experiments of this thesis were taken by Dr. Alexandra Ramadan using a Thermo Scientific $K\alpha$ X-Ray Photoelectron Spectrometer with a monochromatic Al $K\alpha$ X-Ray source at a take-off angle of 90 degrees. An area of $200\ \mu\text{m} \times 200\ \mu\text{m}$ was analysed, and the core level spectra were recorded using a pass energy of 20 eV (corresponding to an approximate resolution of 0.4 eV). Fitting procedures to extract peak positions from the XPS data were carried out using Casa XPS software suite. A Shirley background was used, and the spectra were fit with a mixture of Gaussian/Lorentzian (Lorentzian = 30%) line shapes.

3.7 Optical characterisation

With the exception of photoluminescence (PL) and optical-pump THz-probe spectroscopy (OPTPS) measurements, the following methods were taken on a Fourier transform infrared spectrometer (FTIR). An FTIR system operates by shining a broadband light source through a Michelson interferometer (Figure 3.5), and then recording the appropriate sample response as a function of the mirror displacement of the interferometer. A Fourier transform of the resulting interferogram then returns the sample response as a function of wavenumber. The sample response as a function of wavelength can be reconstructed because the incident light has a broadband spectrum, the path difference and hence interference induced by positional changes of the interferometer mirror will hence vary with wavelength. The FTIR used in this thesis was a modified Bruker Vertex 80v.

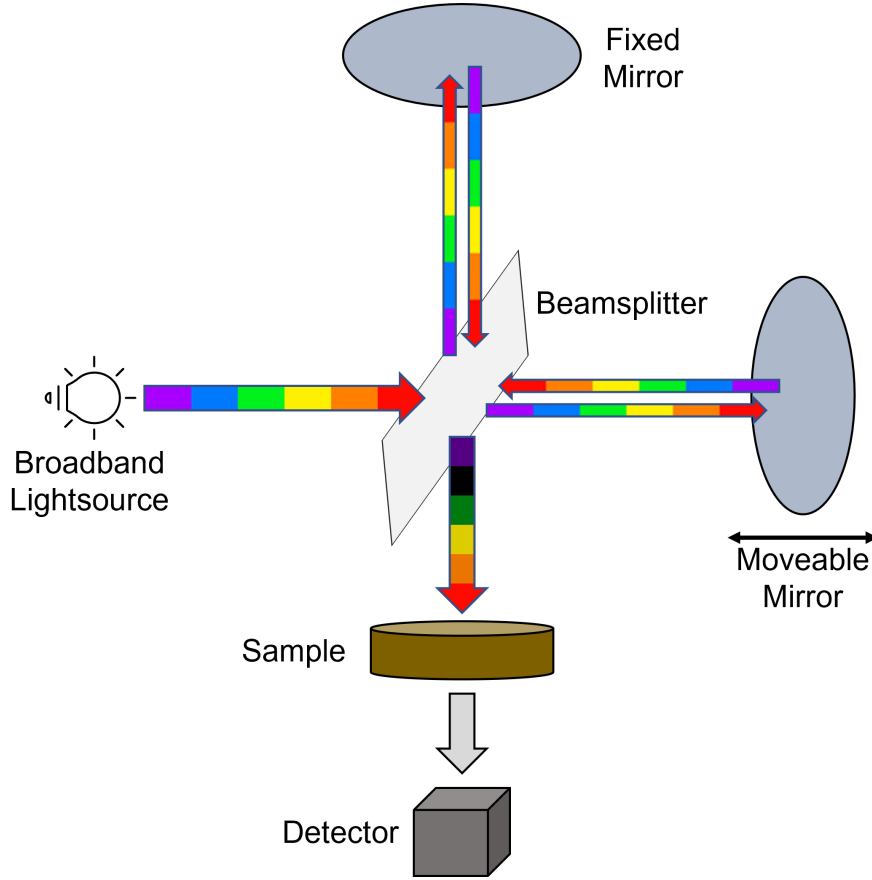


Figure 3.5: Schematic of a Michelson interferometer, as used in an FTIR experimental setup. The mirror to the right moves through a range of positions, changing the path length between the split beams. Upon recombining, differing frequencies interfere constructively or destructively. The detector measures the response of the sample to the various incident frequencies.

3.7.1 Absorbance

The absorbance of a material gives a measure of the amount of light absorbed by the material as a function of wavelength. The absorbance relative to the thickness of a sample gives its absorption coefficient. The absorption coefficient allows determination of the absorption onset and bandgap of a material, and hence plays a crucial role in most semiconductor characterisation. For this thesis, transmission and reflection measurements were taken using the aforementioned FTIR, using a tungsten halogen near-infrared source, CaF_2 beam splitter, and Si diode detector. The formula used to then calculate absorbance from transmission and reflection was $A_b = \log_{10} \left(\frac{1-R}{T} \right)$

where R is the intensity of light reflected off the sample and T is the intensity of light transmitted through the sample. Alternatively the absorption coefficient was obtained using the formula $\alpha = \frac{A_b}{t}$, where t is the film thickness.

3.7.2 Absorptance

The absorptance of the full devices was calculated from the reflection and transmission data, using the formula $A_p = 1 - R - T$, where R and T are the reflection and transmission, respectively.

3.7.3 External quantum efficiency

External quantum efficiency (EQE) refers to the number of photons that are turned into useable current by a solar cell as a function of photon wavelength, relative to the total number of photons incident on the sample. EQE measurements were taken using a modified Fourier transform photocurrent spectrometer on the same setup used for transmission reflection measurements, using a near-infrared source. The recorded spectra were calibrated using a Newport-calibrated reference silicon solar cell of known EQE value. The devices measured were the same as for the JV characterisation, with individual pixels singled out with a mask.

Using the Sun's known irradiance per wavelength for AM 1.5 it is possible to calculate the number of photons incident per wavelength on the solar cell. This then allows me to calculate the total current generated by the cell from the EQE by integrating over the current generated per wavelength.

3.7.4 Internal quantum efficiency

Internal quantum efficiency (IQE) refers to the number of photons that are turned into useable current by a solar cell as a function of photon wavelength, relative to the

total number of photons actually absorbed by the solar cell. IQE can be calculated from the absorptance and EQE using the formula $\text{IQE} = \frac{\text{EQE}}{A_p}$. IQE represents the probability of a photon leading to the collection of charge carriers once it has been absorbed by the device, i.e. the probability that the charge carriers generated by a photon of specific wavelength are collected.

3.7.5 Urbach energy

Urbach energy E_U is a measure of the slope of the absorption coefficient at the edge of the absorption onset. As such, it gives a measure of electronic disorder at and below the bandgap of a material. E_U measurements were taken on the same setup as the EQE, using a 720 nm (Chapter 4) or 700 nm (Chapter 6) low-pass filter, such that the absorption band edge could be measured at a much higher sensitivity. The single exponential $y = e^{\frac{x-a}{E_U}}$ was fitted to the data in the region near the band edge to obtain E_U .

3.7.6 Steady-state photoluminescence

PL measurements are taken by measuring the spectrum of photons emitted from a sample after photoexcitation, usually above the bandgap. The incident photons are first absorbed by the material, generating electron-hole pairs inside the material. Then, if the generated electrons and holes recombine radiatively, a new photon is emitted that can then be measured [61]. In steady-state PL measurements, all photons generated by the sample are measured, independent of their emission time relative to the photoexcitation. The PL peak position of a material is normally at energies just below the bandgap of the material. The steady-state PL spectrum of a sample can hence be used to estimate the bandgap of a material, as well as its phase uniformity.

For this thesis, the PL measurements were taken by illuminating the samples with either a 398 nm picosecond pulsed diode laser (PicoHarp, LDH-D-C-405M) (Chapters

4 and 5) or a 470 nm picosecond pulsed diode laser (PicoQuant, LDH-D-C-470M) (Chapter 6). The PL emitted by the films was coupled into a grating spectrometer (Princeton Instruments, SP-2558), and measured using an iCCD (PI-MAX4, Princeton Instruments).

3.7.7 Time-resolved photoluminescence

Time-resolved PL (TRPL) refers to measuring PL emission of a sample as a function of time after photoexcitation. Using a pulsed laser, the sample is photoexcited at a particular frequency, leaving time between pulses to collect the emitted PL. TRPL gives an estimate of how quickly the photogenerated charge-carriers recombine radiatively.

In this thesis, the TRPL was measured using time-correlated single photon counting (TCSPC), where the photons emitted by the sample are counted and binned according to their time delay with respect to the excitation pulse. TCSPC data was measured by a photon-counting detector (PDM series from MPD), using a PicoHarp300 TCSPC event timer to control its timing. The samples were photoexcited using the same lasers used for the steady-state photoluminescence, and the counts collected at the corresponding PL peak using a grating spectrometer (Princeton Instruments, SP-2558).

3.7.8 Optical-pump THz-probe spectroscopy

In optical-pump THz-probe spectroscopy (OPTPS), the sample is first excited by a high-fluence pump beam, and the sample transmission probed by a THz-pulse as a function of time after the pump excitation. In this way, the transient absorption and transmission of the sample can be measured on an ultrafast (sub-picosecond) time scale. The lateral charge-carrier mobility can then be extracted from the initial value of the change in photoconductivity immediately after the pump excitation, before

recombination occurs. Because of the ultrafast time-scales involved, OPTPS will probe the charge-carrier dynamics locally around the probe point.

For this thesis, the OPTPS measurements were performed by Dr. Chelsea Xia (Chapter 4 and Dr. Silvia Motti (Chapter 6, using the following procedure and equipment. A Spectra Physics Mai Tai–Empower–Spitfire Pro Ti:Sapphire regenerative amplifier provided 35 fs pulses centered at 800 nm at a repetition rate of 5 kHz. The 400 nm pump photoexcitation was then obtained by frequency doubling the fundamental laser output through a barium borate crystal. THz probe pulses were generated by a spintronic emitter composed of 1.8 nm of $\text{Co}_{40}\text{Fe}_{40}\text{B}_{20}$ sandwiched between 2 nm of tungsten and 2 nm of platinum, all supported by a sapphire substrate. Detection of the THz pulses was performed using electro-optic sampling in a ZnTe crystal (1 mm (110)-ZnTe). The sample, THz emitter and THz detector were held under vacuum (10^{-2} mbar) during the measurements.

Chapter 4

Effects of Growth Temperature in Methylammonium Lead Triiodide Perovskites

4.1 Introduction and Background

Despite the remarkable progress achieved in power conversion efficiencies of vacuum-deposited MHP solar cells, the actual vacuum deposition process and growth mechanism is currently poorly understood, particularly owing to the volatile and non-directional nature of the organic precursor vapour as it leaves the crucible [44]. Indeed, Borchert et al. recently demonstrated that the adsorption rate of MAI is highly sensitive to impurities present in the material, with purified precursors not depositing on some surfaces [62]. This issue presents a significant hurdle for co-deposition, the deposition process where all precursors are sublimed simultaneously [48, 49, 54, 63] as the sublimation rate of the precursors is typically controlled by tracking the material deposited on quartz microbalances placed near the crucibles. Several methods have been devised to account for the irreproducibility of MAI sublimation. These

include multi-layer sequential deposition of the precursors [64], a method where the precursors are sublimed one after the other rather than together, as well as controlling precursor sublimation rate by monitoring the chamber pressure in sequential [51] and co-evaporation routes [62, 65, 66]. However, sequential methods are less suited to automation due to the requirement of a post-deposition annealing step, while the co-evaporation pressure control routes has so far yielded poorer performance.

In parallel, a fundamental, unresolved question in the field of MHP photovoltaics is the mechanism by which crystal grain boundaries in MHP films affect solar cell performance. There are a range of studies reporting the benefits of large (micrometer size) grains in solution processed MHP devices [67–70], and these reports are consistent with grain boundaries having a negative effect on device performance through a high density of charge trapping and recombination centers. In contrast, other studies have found grain boundaries in MHP solar cells to have a benign, if not beneficial, nature [71–73], with notably Adhyaksa et al. finding both detrimental and beneficial grain boundaries within the same film [74]. Moreover, vacuum processed devices have managed to reach efficiencies up to 20.3% with very small crystal grains, having approximate lateral extent of just 100 nm [48, 49, 75]; this indicates more benign grain boundaries in these evaporated MHP films. Understanding the mechanism that causes grain boundaries to be detrimental or benign is therefore a crucial step in improving and reproducing the performance of MHP solar cells.

To elucidate these issues, I devised a method to control the grain size of vacuum deposited films by tuning and varying the temperature of the substrate on which the films form. There are numerous reports of the effects of substrate temperature on solution processed devices [68, 76–79], however for vacuum deposited films an additional complication arises. Specifically, for vacuum co-deposition the substrate temperature does not just affect crystal growth dynamics, but also the sticking coefficient and hence adsorption rate of the organic precursor vapour onto the film [62, 80]. Thus

CHAPTER 4. EFFECTS OF GROWTH TEMPERATURE IN METHYLAMMONIUM LEAD TRIIODIDE PEROVSKITES

even if the sublimation flux of an organic precursor can be controlled, the flux actually involved in forming the MHP film will change as the film's temperature varies. To investigate all effects related to substrate temperature and deal with the issue of poor process control, I have developed a vacuum co-deposition method by which the flux of organic precursor adsorbing to a MHP film is regulated.

Conventional vacuum co-deposition requires a furnace for each precursor material, with a separate quartz microbalance placed just above each furnace to measure the flux sublimed of only that precursor. This allows for the flux sublimed from each furnace to be controlled independently, by adjusting the furnace temperature based on the signal from the respective quartz microbalance. In the case of co-deposition of MAI and PbI_2 , this method works well for the inorganic precursor, but as discussed above, is problematic for controlling the flux of the organic precursor, especially if the temperature of the deposition substrate changes.

My method uses a different configuration, in which the flux of the inorganic precursor (PbI_2) is kept constant in the way described above, but the temperature of the furnace containing the organic precursor (MAI) is set based on a quartz microbalance located near the substrate, the "substrate rate" introduced in Chapter 3. Because PbI_2 is deposited on the substrate sensor as well, MAI was found to adhere much more consistently. Furthermore, as the rate of PbI_2 deposition is measured separately by the quartz microbalance situated near its crucible, the flux of MAI can be calculated by comparing the "substrate" rate to the measured PbI_2 rate. Using this method I obtained large, micrometre-sized grains at low temperatures (-2°C), and smaller, 100 nm grains at room temperature.

4.2 Effect of Changing Substrate Temperature

4.2.1 Crystallographic Characterisation

MAPbI₃ solar cells were prepared through vacuum co-evaporation using the substrate-rate control method outlined above. During the deposition, the temperature of FTO coated glass substrates was tuned according to five regimes, as represented graphically in Figure 4.2a. To demonstrate fully the effect of substrate temperature, the substrate rate was always measured on a quartz crystal monitor held at room temperature. In this way, the overall flux of vapour incident on the substrates was the same for all substrate temperatures, thereby isolating resulting differences in morphology to effects of substrate temperature on vapour adsorption and growth mechanisms. Following co-deposition the samples were not annealed, as this was found to have a negative effect on performance (Figure 4.1), for which the data comes from a run where the substrate temperature was changed from 20 °C for the first 60 nm to 0 °C for the remaining 440 nm. The device architecture followed an n-i-p structure on FTO using undoped C₆₀ as the ETL and doped Spiro-OMeTAD as the HTL.

Figure 4.2b and c show an initial inspection of the films with SEM and reveal a strong dependence of the film morphology on substrate temperature: large, micrometer-sized grains are formed at low temperatures (-2 °C) (sample L), while warmer conditions (23 °C) led to the appearance of smaller grains throughout the film (sample H). The current-voltage (JV) and steady-state PCE curves (Figures 4.2d and 4.2e) were measured from these devices under AM1.5 simulated sunlight (1000 W/m²) and show the opposite to what one would expect, with the large grains leading to the worst performance owing to a notably lower current density. To separate the effects of temperature on bulk material and interfaces, I grew three more films of MAPbI₃ at low temperature (L), but with thin layers of MAPbI₃ deposited at room-temperature (H) at either the top (LH), bottom (HL), or both (HLH) interfaces with the CTL,

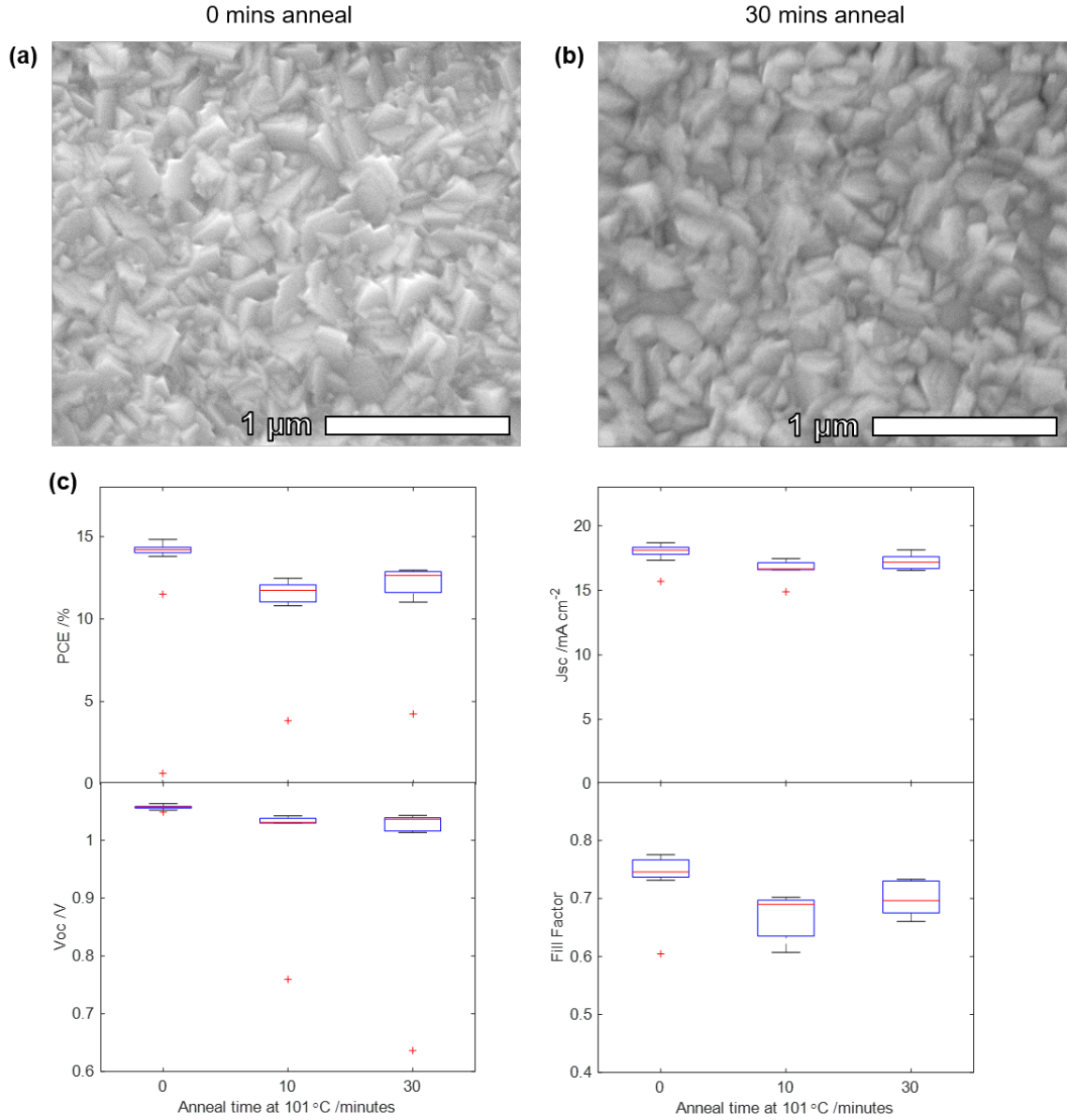


Figure 4.1: Top down SEM images of MAPbI₃ films grown on FTO at substrate temperature 20 °C for the first 60 nm, then 0 °C for the remaining 440 nm (a) no post-deposition anneal (b) annealed for 30 minutes at 101 °C (c) JV characteristics for the corresponding devices

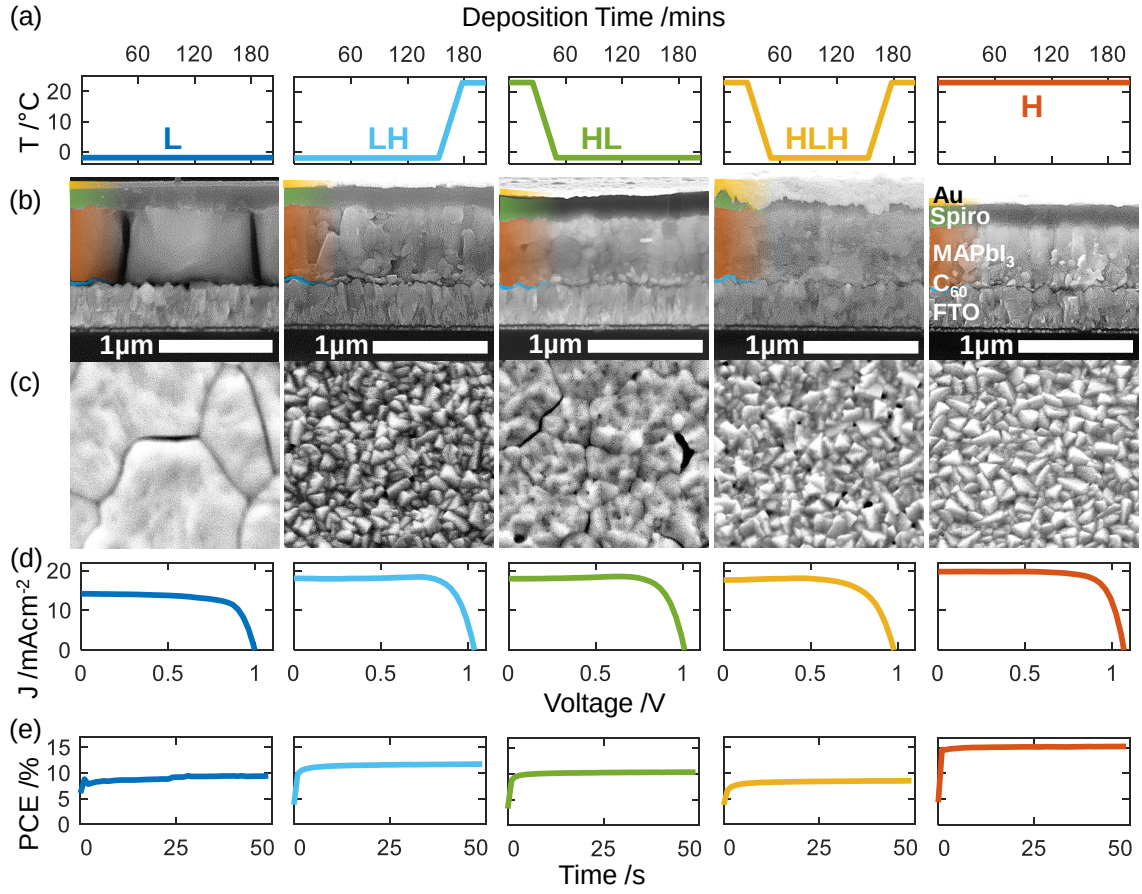


Figure 4.2: SEM images of co-evaporated MAPbI₃ devices deposited at 5 different substrate temperature conditions over 204 minutes, as graphically depicted in (a). (b) Cross-sectional SEM images of full devices with the following structure: FTO/C₆₀ (blue)/MAPbI₃ (orange)/Spiro (green)/Au (yellow) (c) Top-down images of the same devices after removal of the gold and spiro layer. The scale bar represents 1 μm for both top-down and cross-sectional images. (d) (e) JV curves and steady state PCE for the devices on which SEM was done, measured under simulated AM1.5 100 mW/cm² irradiance.

resulting in partially improved current. The effect of the temperature gradient is well demonstrated in the SEM image of the high-end to low-end temperature sample HL, which shows small grains at the interface, but larger grains throughout the rest of the film. Evidence from the other two conditions is less conclusive, but the low-end to high-end (LH) sample does show enlarged grains throughout the cross-section, while still having a surface morphology similar to HLH and H, which also finished their growth at room temperature. Lower magnification SEM images which show a larger area of the sample are shown in Figure 4.3 and 4.4 for cross-sections and top-down images, respectively.

I further investigated the nature of the gaps between the grains seen in the cross-section of L, and found them to originate from beam damage (Figure 4.5). This electron-induced damage is a well-known phenomenon [81, 82], and depends exponentially on electron dose [83]. Figure 4.5a clearly shows the gaps are only present in regions subjected to a previous scan. The smaller red-boxed areas were imaged at a 5 times higher magnification, resulting in a 25 times higher electron dose per area, leading to exponentially more beam damage. Figure 4.5b shows that the voids must have originated after deposition of the spiro, lest the latter would have infiltrated down into the gaps. The fact that sample L is more susceptible to beam damage has important ramifications on the stoichiometry of the grain boundaries, as will be discussed later on in this chapter.

In addition to the FTO/C₆₀/MAPbI₃/Spiro/Au architecture used for the champion devices, I also tried ITO/C₆₀/MAPbI₃/Spiro/Au, and p-i-n devices with FTO/Poly[N,N'-bis(4-butylphenyl)-N,N'-bisphenylbenzidine] (PolyTPD)/MAPbI₃/C₆₀/BCP/Au, as well as blank FTO and crystalline Si as substrates. Figure 4.6 shows the morphology across the different substrates. I only obtained large grains on FTO/C₆₀, and found the morphology very different on non-FTO substrates, with notably films grown on ITO showing much more columnar

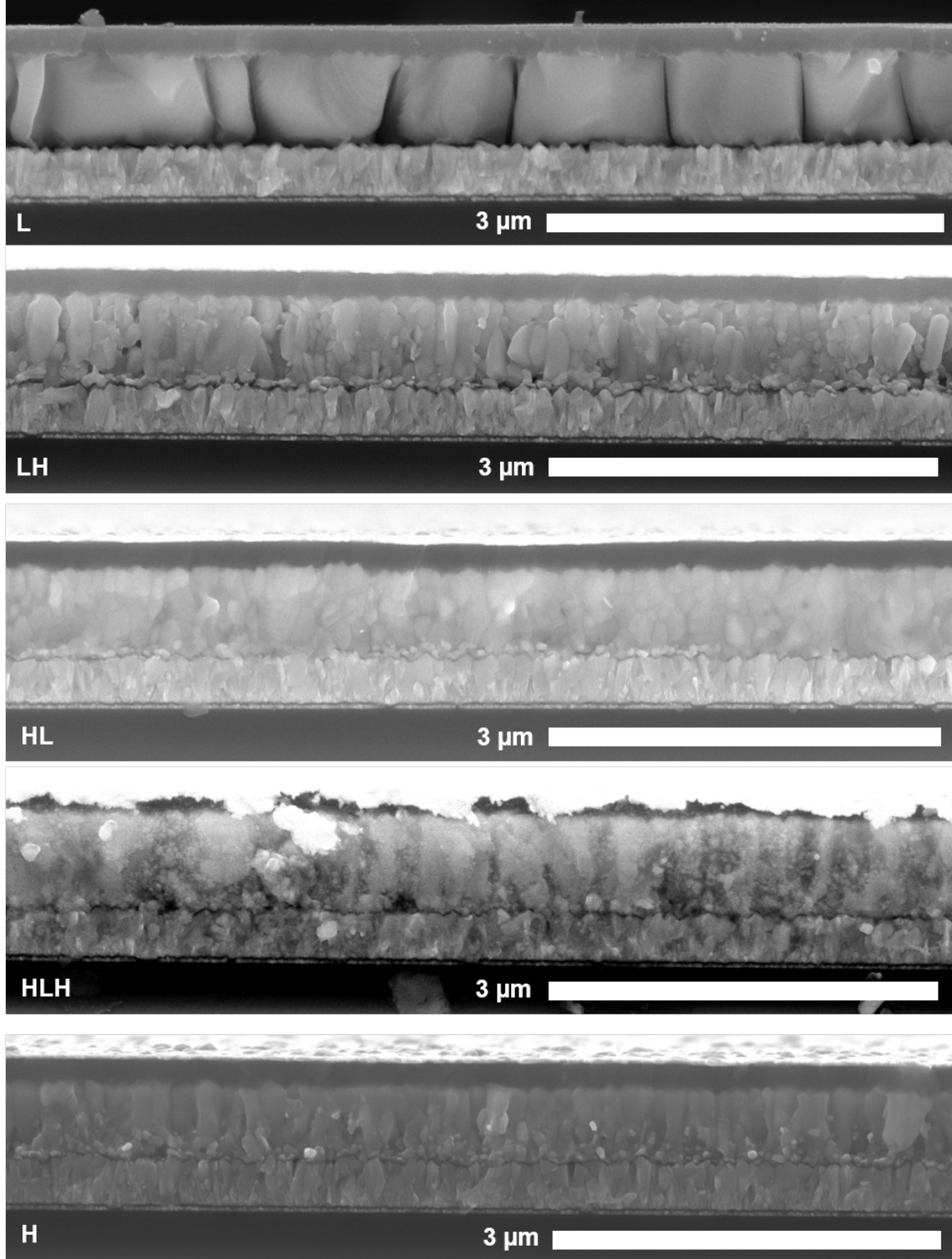


Figure 4.3: Cross-sectional scanning electron microscope images of co-evaporated MAPbI₃ devices deposited at 5 different substrate temperature conditions L,LH,HL,HLH,H, as described in the main text.

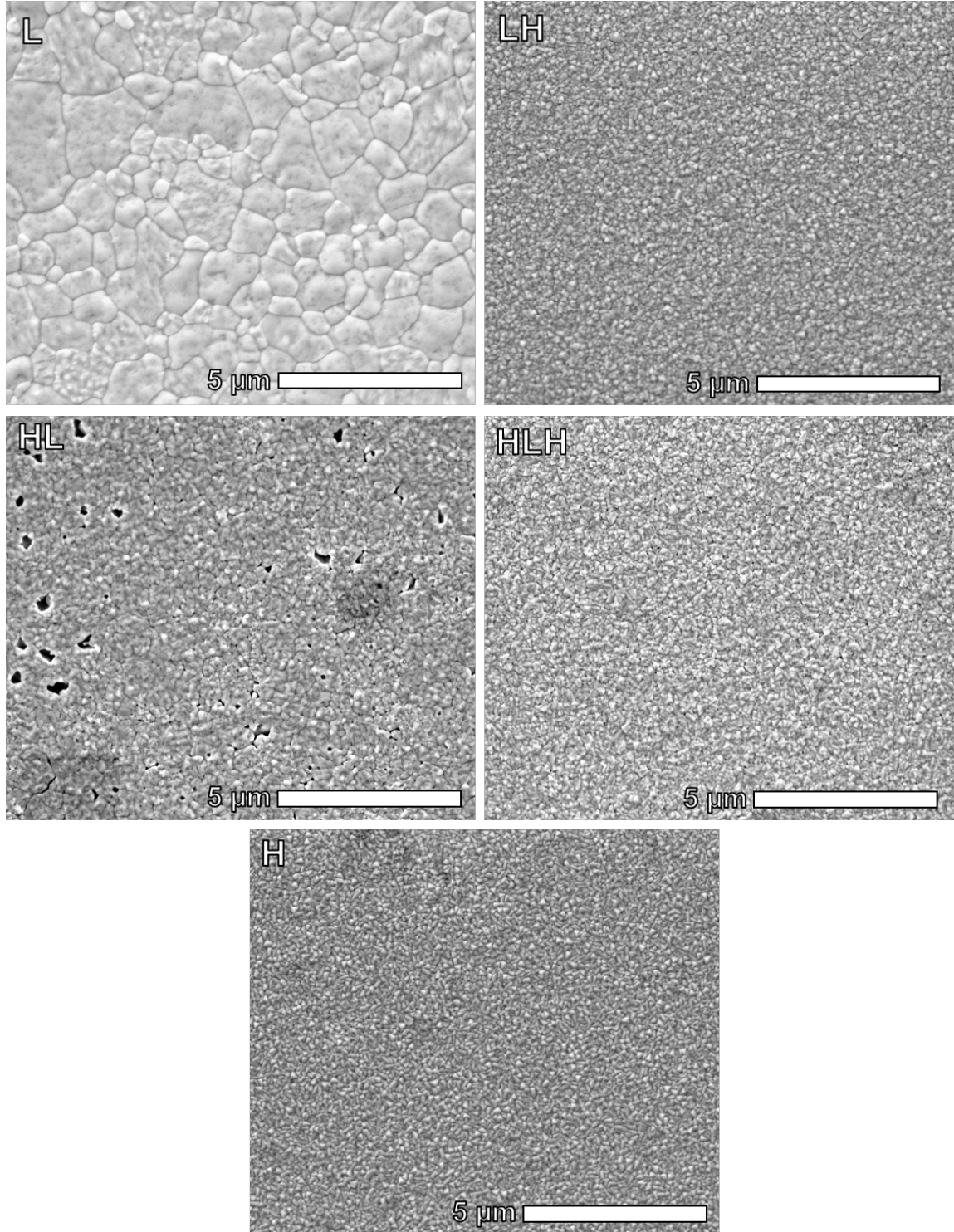


Figure 4.4: Top down view scanning electron microscope images of co-evaporated MAPbI₃ devices deposited at 5 different substrate temperature conditions L,LH,HL,HLH,H, as described in the main text.

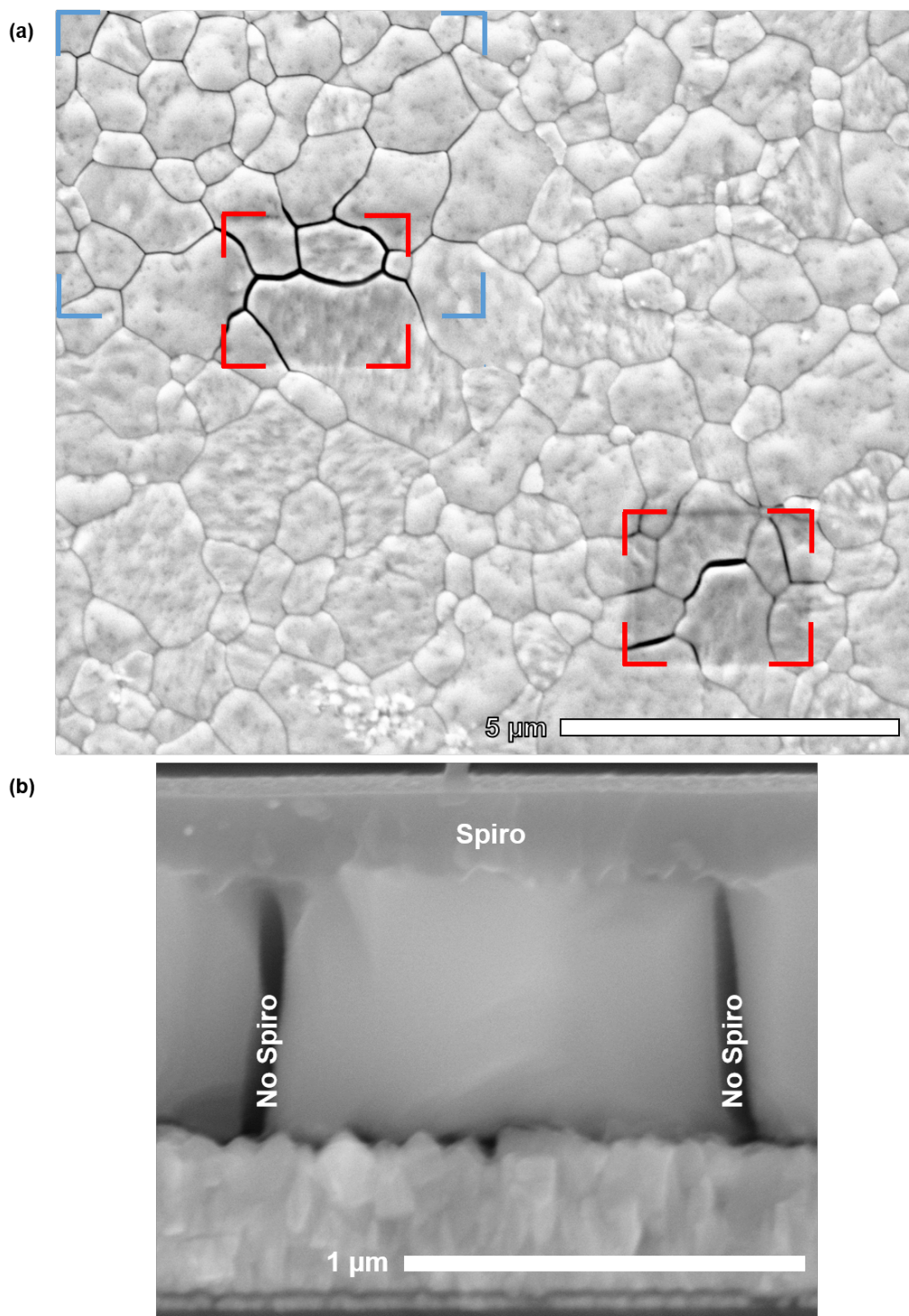


Figure 4.5: (a) SEM top down image of film L showing visible beam damage only in areas imaged previously, at the same magnification (blue rectangle) and 5 times higher magnification (red rectangles) (b) Close up of the SEM cross-section of L shown in Figure 4.2.b, showing clearly that no spiro has infiltrated down into the inter-grain voids.

grains at low substrate temperatures. Nevertheless, device performance was also worse for ITO/C₆₀ and FTO/PolyTPD, particularly for the latter, as shown in Figure 4.7. I believe that the main reason for this difference in performance, particularly between FTO/C₆₀ and ITO/C₆₀, is due to a difference in the nucleation process. Because the C₆₀ layer is only 10 nm thick, it intimately matches the roughness or smoothness of the FTO and ITO, respectively, resulting in many more nucleation sites on ITO, as evidenced by the larger number of grains seen particularly in Figure 4.61D. It is likely possible to reoptimize the rates during deposition to correct for this difference in nucleation and recover the higher performance seen on FTO/C₆₀. This finding has important consequences for the choice of contact layer on which the MHP is grown, as it will affect the crystallinity and growth of the resulting film.

The other striking difference between the layers grown at different temperatures is the thickness of the films. Indeed, sample H is noticeably thinner than the rest of the films, indicating that less material is deposited at higher substrate temperatures. Because the flux of vapour present near the substrate is controlled to be the same for all conditions, substrate temperature has a direct effect on the adsorption rate of the precursor vapour. To investigate whether this leads to any stoichiometric changes and elucidate the poor performance of large grains, the films were further characterized with crystallographic measurements.

The XRD spectra of the devices after removal of the gold electrode (Figure 4.8a) show no significant peak shifts between the different growth regimes, but films that finish at room temperature (LH, HLH, H) are characterized by the presence of a (001) PbI₂ peak at 12.7° (Figure 4.8c). The presence of this peak indicates unconverted, crystalline PbI₂ in the films, and points to a stoichiometric imbalance. Along with the evidence from SEM cross-sections indicating lower deposition rates at higher temperatures, this suggests that adsorption of MAI vapour is more affected by substrate temperature than PbI₂, and that the stoichiometry hence changes with substrate

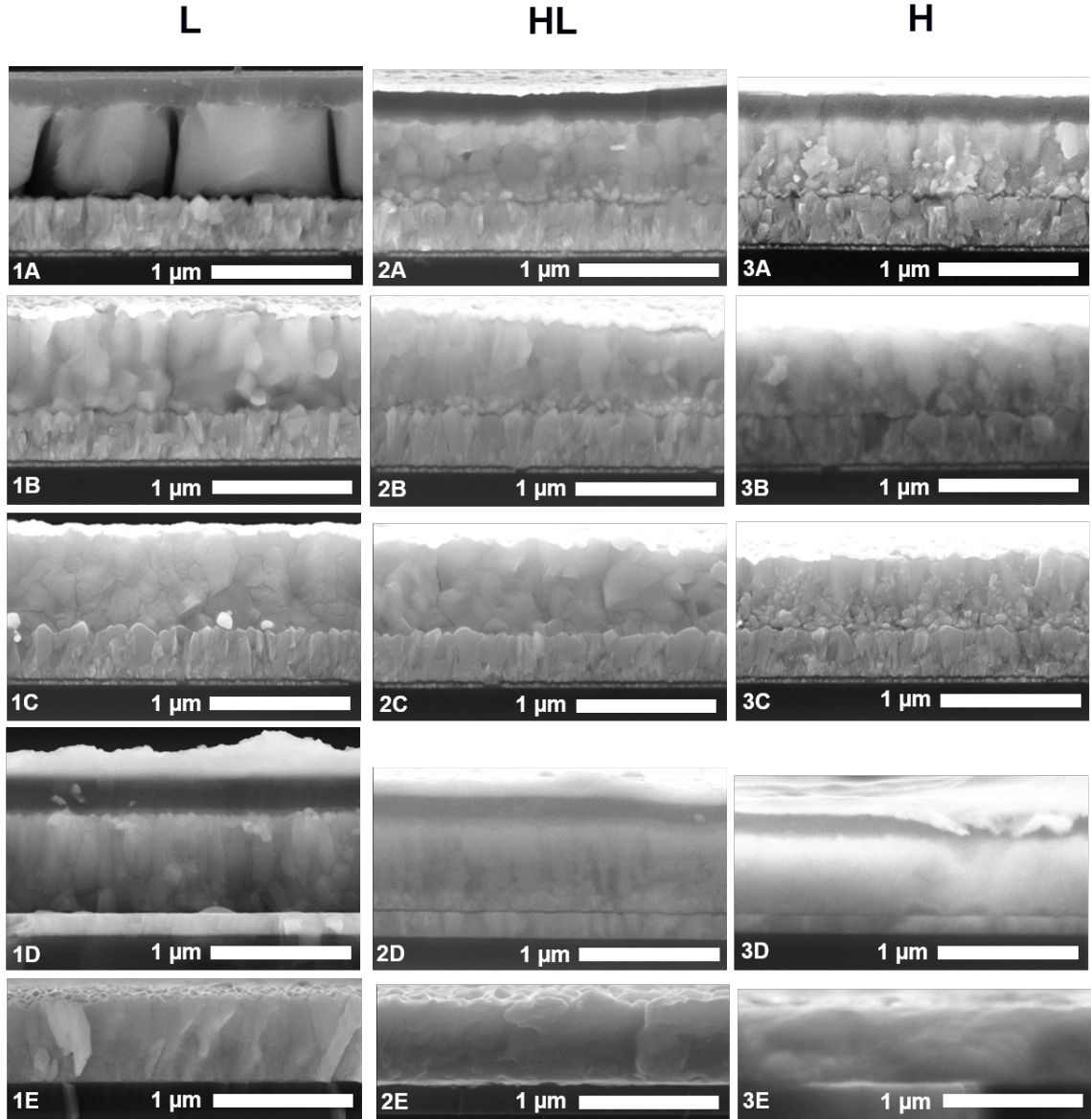


Figure 4.6: Cross-sectional scanning electron microscope images of co-evaporated MAPbI₃ devices deposited at 3 different substrate temperature conditions L (column 1), HL (column 2), H (column 3), as described in the main text. The rows correspond to the different substrates they are deposited on. A: FTO/C₆₀, B: FTO/Poly-TPD, C: FTO, D: ITO/C₆₀, E: crystalline silicon

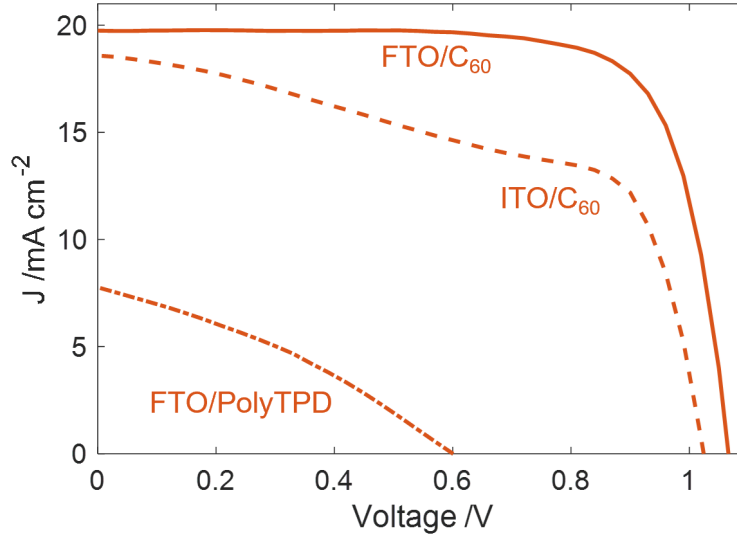


Figure 4.7: JV curves of co-evaporated MAPbI₃ devices grown at substrate temperature 23 °C on different substrates, namely FTO/C₆₀, ITO/C₆₀, FTO/PolyTPD. The device grown on FTO/C₆₀ is the one labelled “H” elsewhere.

temperature. For the dose of MAI vapour introduced into the chamber for these devices, full conversion is only achieved at low temperatures. Interestingly, HL, whose growth started at room temperature, does not have crystalline excess PbI₂. This is likely the result of excess PbI₂ from the initial room-temperature deposition phase subsequently being converted to MAPbI₃ by the additional MAI adsorbed during the low temperature deposition phase.

The FWHM of XRD peaks give a measure of crystal quality through the Scherrer equation, which shows the former to be inversely proportional to the crystallite size in the direction perpendicular to the substrate [84]. This broadening of the XRD peaks originates from the finite number of lattice planes that coherently scatter the X-rays. FWHM values were calculated by fitting a pseudo-Voigt distribution to the relevant peaks, while the instrument response was calculated from a reference measurement of a single-crystal silicon wafer. A detailed description of the fitting procedures can be found in Chapter 3. Figure 4.8d shows the values for the (222)/(130) perovskite

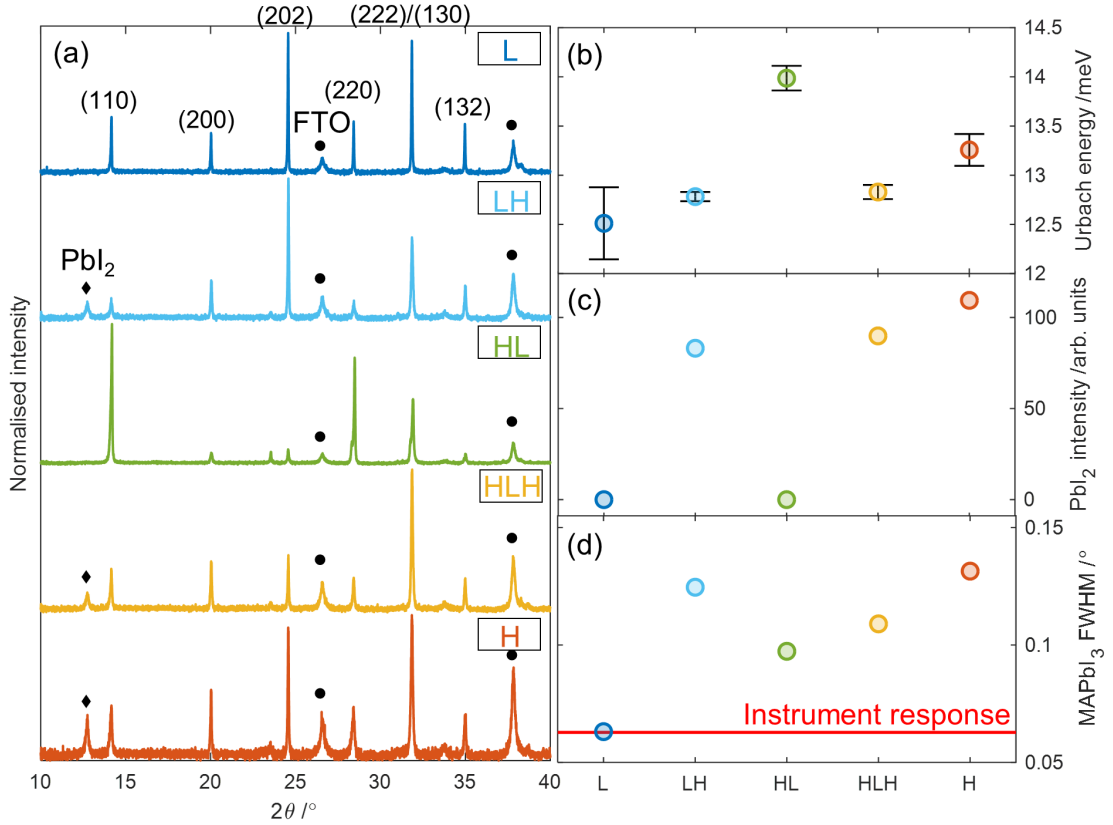


Figure 4.8: (a) XRD spectra of devices made via the 5 deposition conditions, after removal of background, normalized to the highest peak, and corrected for angular tilt by using the FTO (110) peak at 26.5° . The black diamonds represent the PbI_2 (001) peak at 12.7° , the black circles show the position of FTO peaks, while the rest of the peaks are from tetragonal MAPbI_3 , as denoted by the indices. (b) Mean Urbach energy measurements for the corresponding devices. (c) Unnormalized peak intensity of the PbI_2 (001) peak at 12.7° , as calculated from the pseudo-Voigt fit. (d) Full-width at half maximum (FWHM) of the MAPbI_3 (222)/(130) peak at 31.9° , as calculated from the pseudo-Voigt fit. The red line represents the instrument broadening, calculated from a Si reference. XRD measurements were taken with a Cu-K α X-ray source; additional information on the equipment and fitting methods is found in Chapter 3

peak at $2\theta = 31.9^\circ$, chosen because it has the highest signal to noise ratio across all films. The FWHM can again be seen to increase as the substrate temperature during growth increases, with the large grain film L having FWHM at the instrument response limit, while film H has again the highest FWHM, indicating the smallest crystallites.

To further probe the crystal quality of the different films, I also performed Urbach energy (E_U) measurements (Figure 4.8b) from the photocurrent onsets of the EQE spectra (Figure 4.11), which give a measure of electronic disorder. My data shows that the large grain, low substrate temperature film L does indeed have the lowest E_U at 12.5 meV, increasing to 13.3 meV for the room temperature sample, indicating that the largest grains do correspond to the least energetic disorder. However, detailed analysis has shown that in the case where $E_U < kT = 26$ meV for $T = 298$ K (where k is the Boltzmann constant, and T is the temperature), the expected change in V_{OC} is small [85], such that only minor improvements are expected from the E_U decrease in this case.

Together, the E_U and XRD measurements confirm that the large crystals seen in SEM directly reflect better crystal quality within the material, with lower E_U and XRD FWHM that falls below the instrument response. The samples with the largest grains, L and HL, also do not show the presence of crystalline excess PbI_2 , suggesting that a balanced stoichiometry could play a part in the growth of larger grains. All of these factors could be expected to be indicative of improved performance, and a more in depth study of the device operation is now needed to understand why this is not the case.

4.2.2 Solar Cell Characterisation

Figure 4.9a shows boxplots of the JV characteristics measured from devices L, HL, LH, and HLH. As outlined previously, the large-grain devices L have lower J_{SC} and

V_{OC} than the small grain devices H, resulting in a decrease in PCE from 16.0% (15.2% steady-state) for the latter to 10.1% (9.4% steady-state) for the former. The J_{SC} increases in spite of the perovskite film thickness decreasing for H. Indeed, when the small grain MAPbI₃ layer thickness was increased to a more optimal thickness of 600 nm I produced a champion device of efficiency 18.2% (17.5% steady-state) (Figure 4.10), showing that the difference in performance is even greater for comparable light absorption.

4.2.3 Optoelectronic Characterisation

To better understand the origin of the difference in performance across the devices, I performed IQE measurements (Figure 4.9b). IQE measures the probability that an electron-hole pair will be generated and collected as photocurrent by a photon of a specific wavelength absorbed in the device, and is obtained by normalizing the EQE (Figure 4.11) with respect to the absorptance (Figure 4.12) of the devices. This corrects the EQE for losses due to photons reflected off or transmitted through the device, and means IQE only drops as a result of losing photocurrent via charge trapping or recombination of photo-generated charge. For my devices, most notably L and HL, the loss in charge carriers collected is not uniform across the photon energy spectrum, but rather drops off with increasing wavelength. Because the absorption coefficient of MAPbI₃ increases rapidly with photon energy above the bandgap (Figure 4.13), in my devices, high-energy photons (short-wavelength light) will be absorbed and produce free-carriers with a sharp exponentially decaying density profile, peaked at the interface with C₆₀. In contrast, lower-energy photons (longer-wavelength light) will be absorbed more uniformly over the thickness of the MAPbI₃ layer. The slanted IQE curve hence indicates that there is a fundamental problem collecting charges generated deeper in the large grain device L.

Because the cells are oriented in such a way that the light passes through the

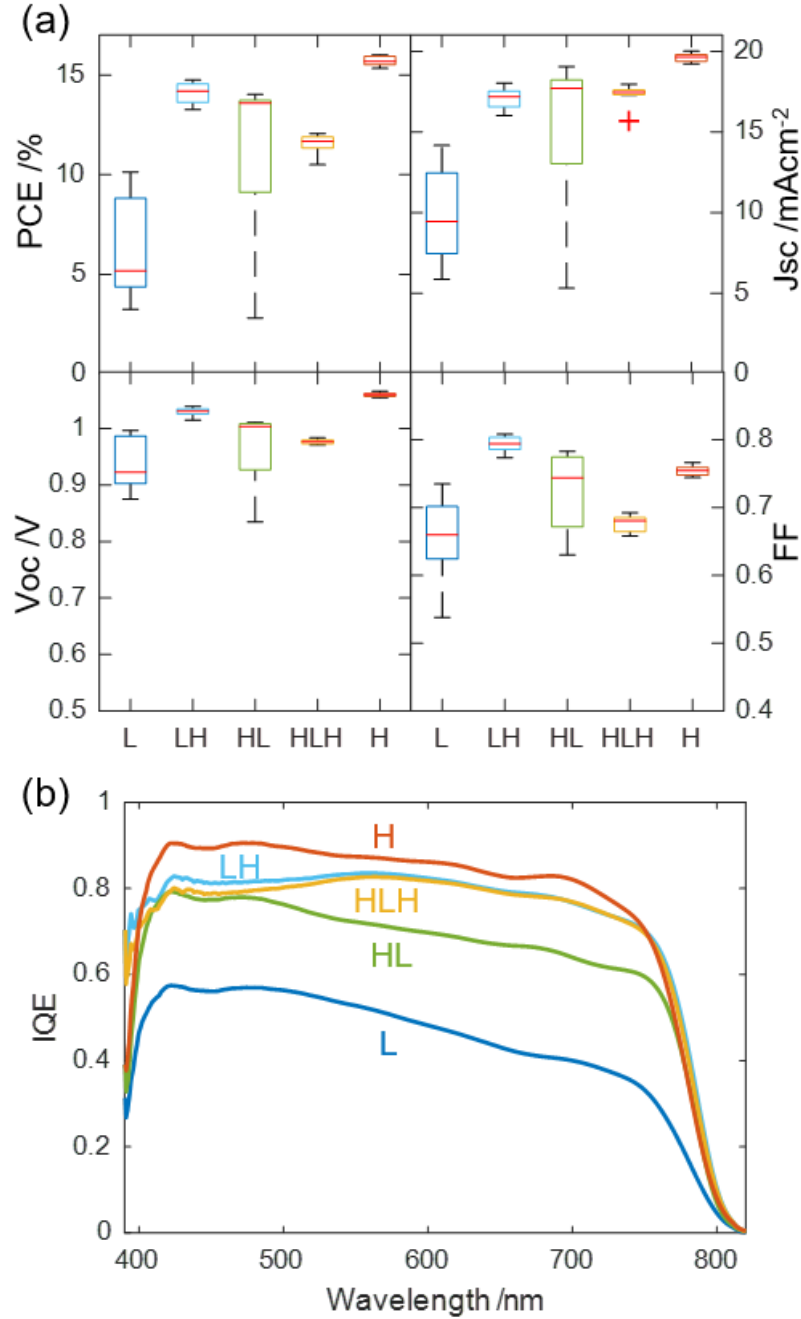


Figure 4.9: (a) Boxplots of the JV characteristics taken from 8 devices made according to the 5 different deposition conditions. (b) Internal quantum efficiency (IQE) curves of the highest performing device measured from each of the 5 different deposition conditions.

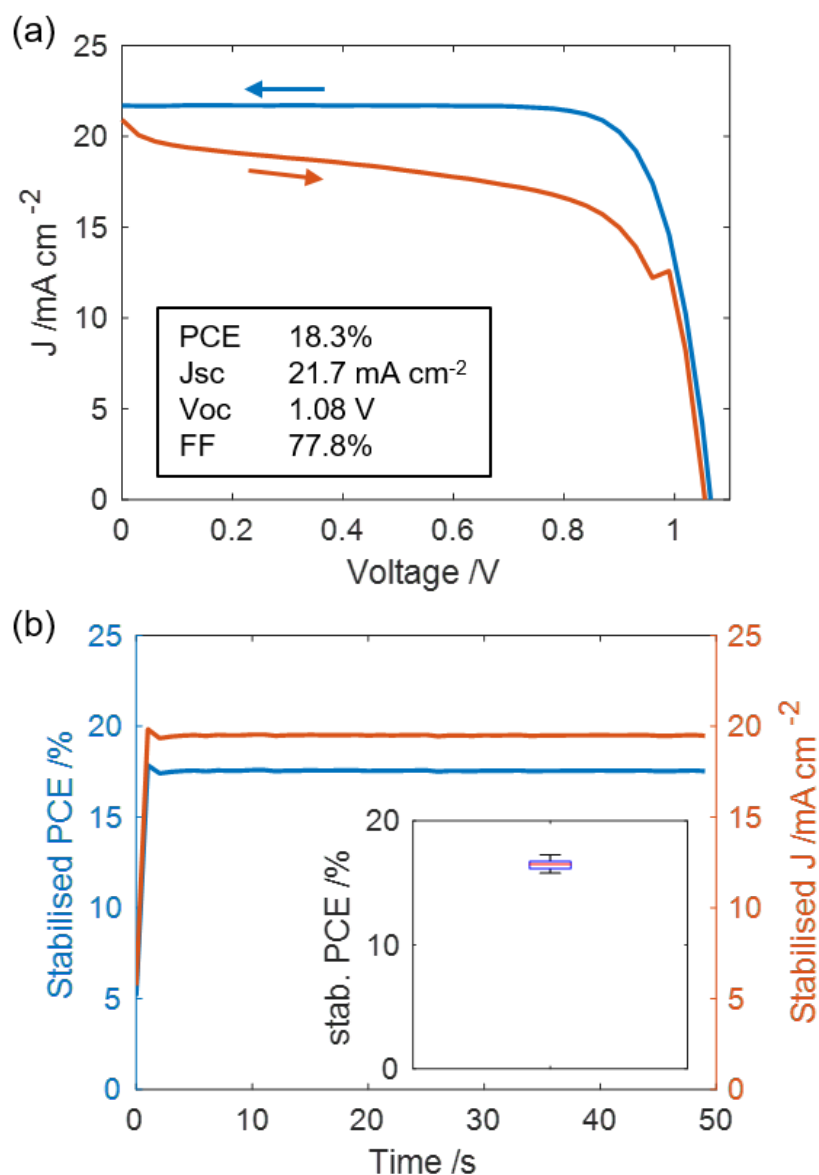


Figure 4.10: (a) JV curve of the champion device, with the reverse scan (V_{OC} to J_{SC}) in blue, and the forward scan (J_{SC} to V_{OC}) in red. The inset is a table of the JV characteristics taken from the reverse scan (b) Stabilised power conversion efficiency (PCE) and current at max power point voltage over 50 seconds. The inset represents the stabilised PCE data for the devices made in the batch that included the champion device.

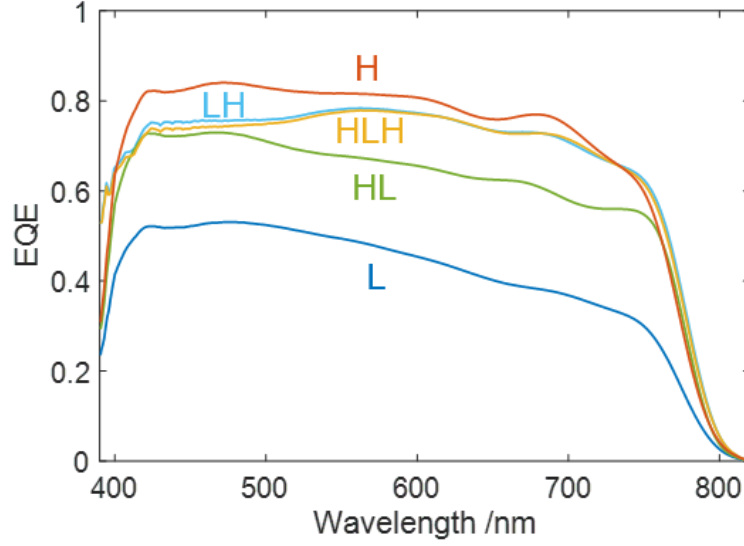


Figure 4.11: External quantum efficiency (EQE) of co-evaporated MAPbI₃ devices deposited at 5 different substrate temperature conditions L,LH,HL,HLH,H, as described in the main text.

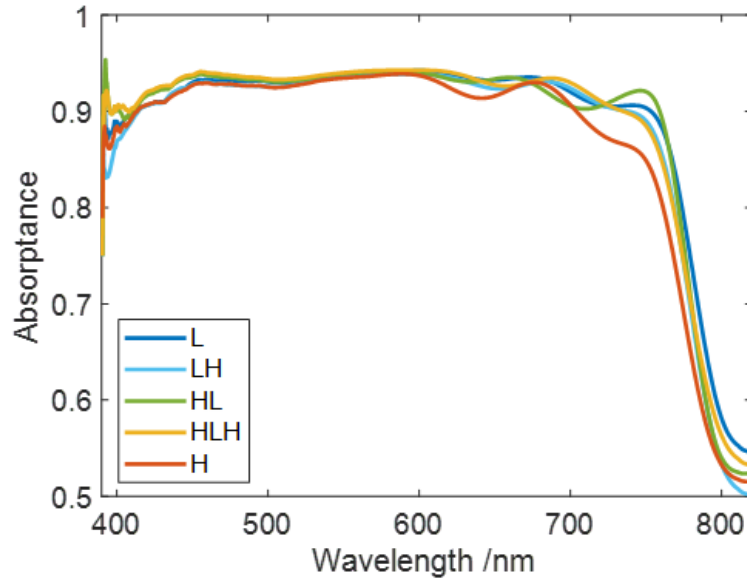


Figure 4.12: Absorptance of co-evaporated MAPbI₃ devices deposited at 5 different substrate temperature conditions L,LH,HL,HLH,H, as described in the main text.

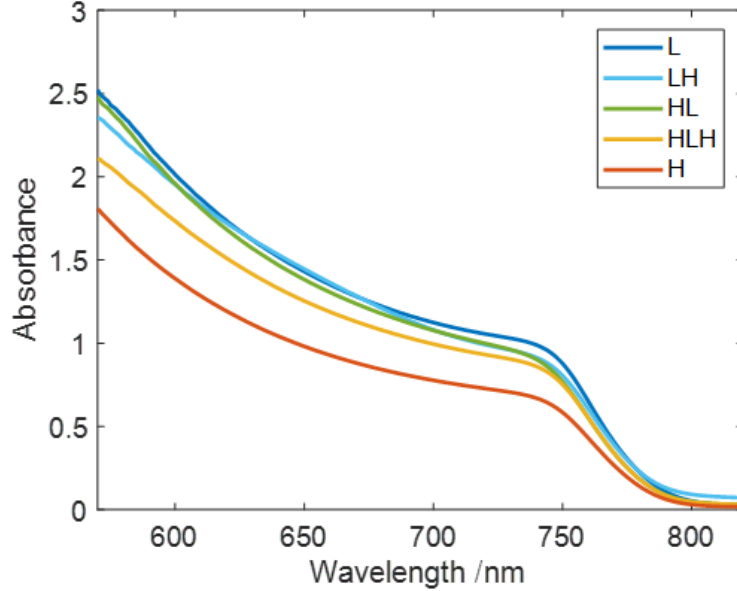


Figure 4.13: Absorbance of co-evaporated MAPbI_3 thin films on FTO/C_{60} , deposited at 5 different substrate temperature conditions L, LH, HL, HLH, H, as described in the main text.

C_{60} /perovskite interface first, these results point to a problem with the collection of electrons. Indeed, electrons are the charge-carriers that on average need to travel a shorter distance if light is absorbed near the interface, but comparatively further if light is absorbed deeper in the film. This could be due to either poorer electron mobility or lifetime in the larger grains preventing the electrons generated deeper in the film from reaching the ETL, or a result of poor interface optimization resulting in increased back surface recombination at the HTL leading to non-radiative recombination.

The OPTPS measurements performed by Dr. Chelsea Xia suggest that it is a combination of both effects (Figure 4.14). OPTPS revealed lower charge-carrier mobilities for films grown on low-temperature substrates ($6.87 \text{ cm}^2/\text{Vs}$) compared with those grown at room temperature ($13.0 \text{ cm}^2/\text{Vs}$), providing evidence that contrary to expectations, the intrinsic electrical properties are poorer for the large-crystal devices. It should be noted, however, that OPTPS probes the charge carrier mobility locally

rather than across the entire film. Furthermore, these OPTPS measurements were performed on samples grown on z-cut quartz due to its optimal transmission in the THz frequency range. Z-cut quartz is a very smooth substrate, so the grain growth of these samples is likely to be significantly different than for the devices grown on FTO, as shown in Figure 4.6.

On the other hand, analysis of the J_{SC} and integrated current from the EQE measurements, displayed in Figure 4.15, show improved current and EQE for the LH, HL, and HLH devices, where the perovskite material at the interface with the CTL has been grown at a different temperature than the bulk. This indicates that interface morphology also significantly affects device performance, with the most benefit obtained when growing the perovskite near the HTL at a higher temperature than the bulk. Strikingly, the comparatively worse performance of HLH shows that it is significantly better to only change the composition of the perovskite near one interface rather than both.

To get a more complete overview of the optoelectronic properties of the films, steady-state PL measurements on full devices deposited on FTO/C₆₀ after removal of the gold and spiro layer (Figure 4.16), and I performed TCSPC experiments on bare films grown on z-cut quartz (Figure 4.17). As with the OPTPS data, it is likely that the different substrate leads to a different morphology, so the films shown here, grown at substrate temperature -5 °C and 23 °C, won't necessarily correspond to L and H. It should also be noted that evaporated films generally have very low PLQY, below 0.1%, which means that the dynamics of the PL recorded correspond to an equally small fraction of the actual recombination events. Nevertheless, the low temperature film can be seen to have a longer charge carrier lifetime, which is in agreement with the improved electronic quality of L as measured by the lower E_U (Figure 4.8b), which is a more reliable measurement as it was taken on the actual large-grain devices.

Longer charge carrier lifetimes should lead to improved solar cell performance,

but this is not the case for L. This can be resolved by the work of Chirvony et al. [86], who showed that the short lifetimes generally observed in vacuum processed metal halide perovskite films are due to fast diffusion of the photogenerated carriers to the interfaces. As such, the longer photoluminescence lifetimes of the low temperature film could indicate poorer diffusion of the charge carriers in this material, and hence worse performance. The difference between the dynamics of charge carriers generated at the surface versus the bulk could be determined through 2-photon excitation spectroscopy, or determining the surface recombination velocity through numerical fitting. Possible further work to get around the issue of spatial charge separation includes transient photovoltage, though at the moment more work is needed to disentangle the effects of ion migration on this measurement technique [87].

The simplest explanation for this phenomenon is that the larger grains present more traps for the electrons, limiting their diffusion lengths and hence collection. The partial recovery of the EQE when incorporating smaller grains at the perovskite-CTL interfaces indicates either that these traps are mainly located at these interfaces, or that the material grown on a small grain template is simply less prone to traps in the case of HL. This seemingly goes against the idea that traps are associated with grain boundaries, since the large grain samples necessarily have significantly fewer boundaries, so possibly the answer lies more in the stoichiometry of the boundary, as outlined by Jacobsson et al. [88]. Indeed, in contrast to the other films, film L shows larger, darker regions between the grains, both in cross-section and top-down image. These regions are probably a result of electron beam damage, and hence a likely indicator of excess organic material, which is more vulnerable to this damage than the rest of the film [83]. Excess PbI_2 has previously been associated with higher-performance solution processed devices [89], specifically being linked with trap passivation, at the grain boundaries [90] or at the ETL interface, mesoporous TiO_2 in this case [91]. Notably, Jacobsson et al. associate the worse photovoltaic

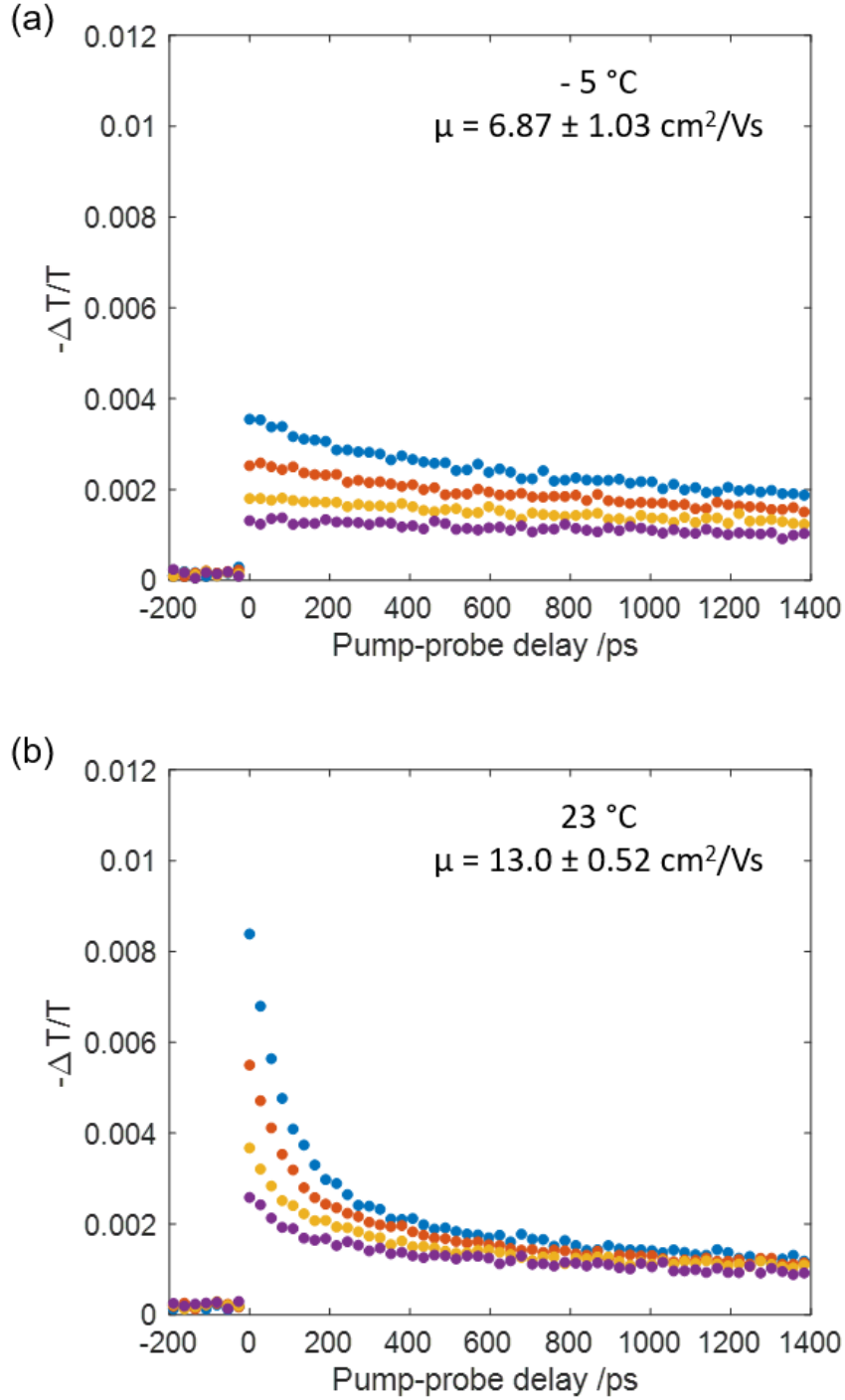


Figure 4.14: OPTPS measurements of bare MAPbI₃ films grown on quartz at different substrate temperatures (a) -5 °C (b) 23 °C as measured at different pump fluences 6 (purple) – 22 (blue) $\mu\text{J}/\text{cm}^2$, and the mobility extracted from the measurements. This data was collected, analysed and plotted by Dr. Chelsea Xia.

CHAPTER 4. EFFECTS OF GROWTH TEMPERATURE IN METHYLAMMONIUM LEAD TRIIODIDE PEROVSKITES

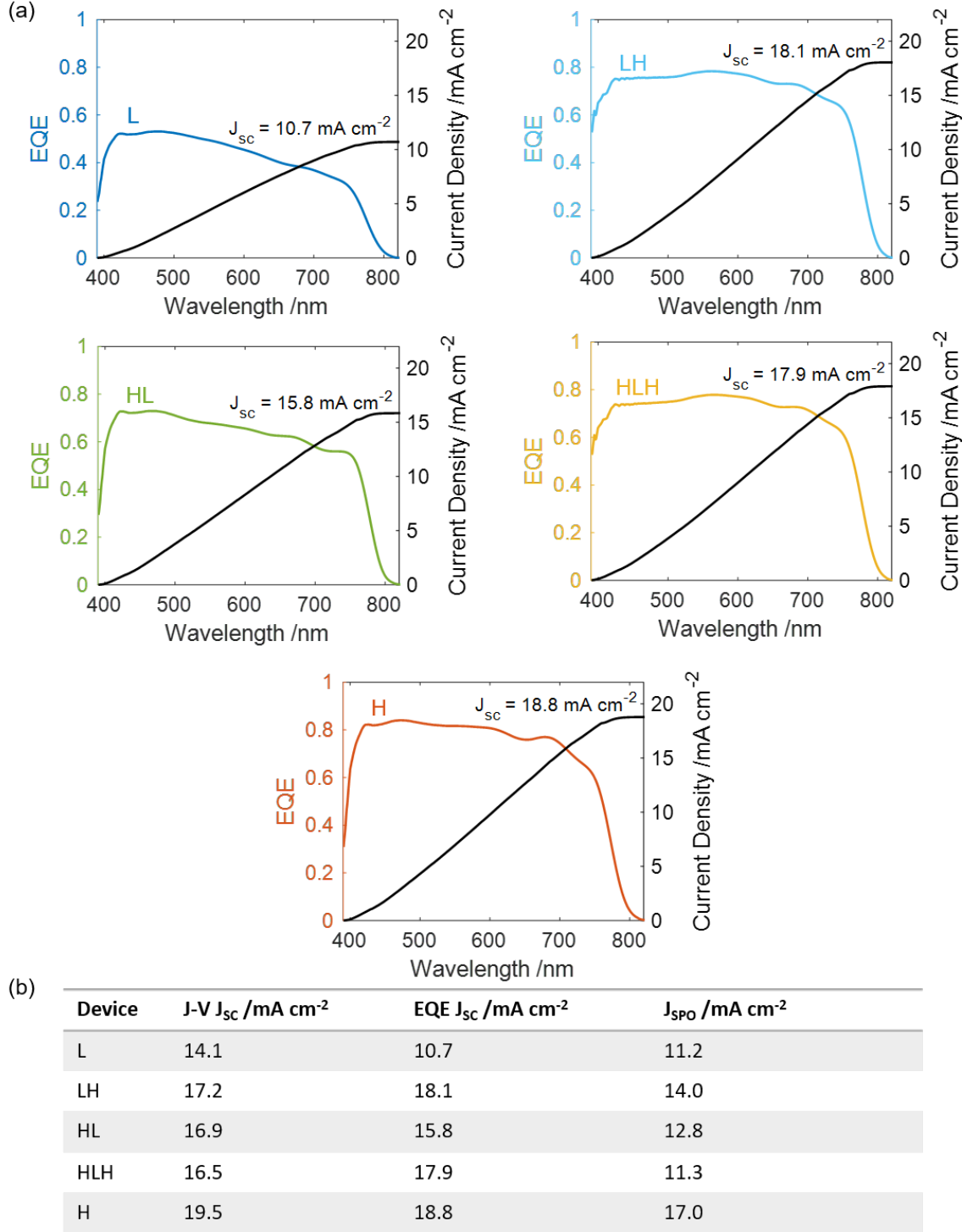


Figure 4.15: (a) External quantum efficiency (EQE) measurements along with the cumulative current extracted over the EQE spectrum, as measured from the champion devices deposited at 5 different substrate temperature conditions L,LH,HL,HLH,H, as described in the main text. (b) Comparison of current extracted from the devices from the JV scan (average of forward and reverse), the EQE spectrum, and the steady-state current density measured after 50 s of constant operation at applied bias corresponding to the maximum power point, as determined by the JV scan (J_{SPO}).

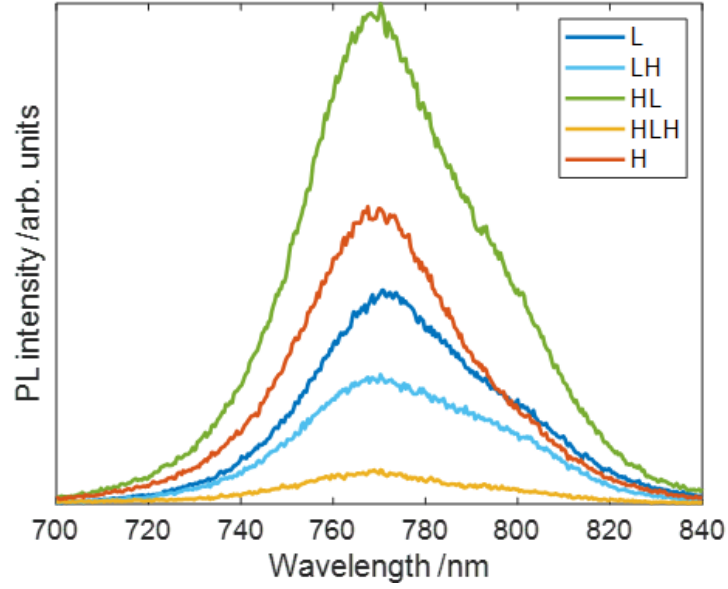


Figure 4.16: Steady-state photoluminescence of co-evaporated MAPbI_3 thin films on FTO/C_{60} , deposited at 5 different substrate temperature conditions L, LH, HL, HLH, H, as described previously.

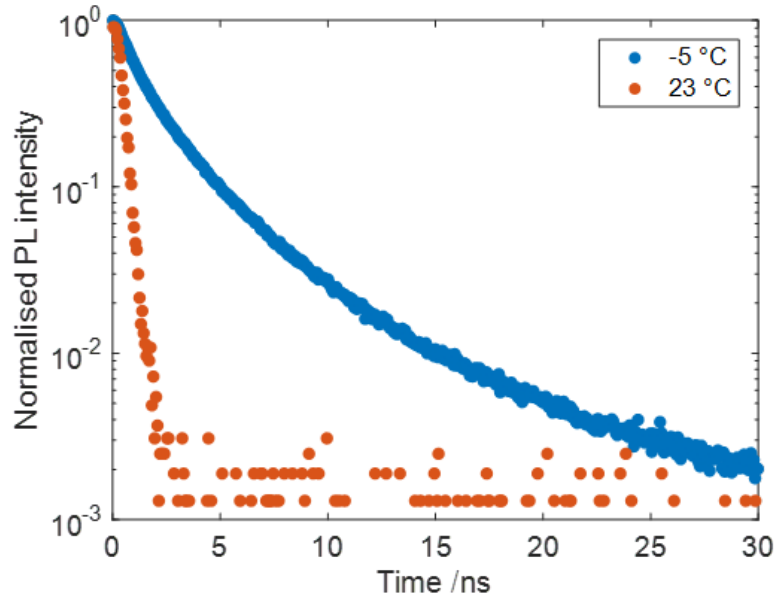


Figure 4.17: Time correlated single photon counting (TCSPC) traces of bare co-evaporated MAPbI_3 thin films deposited on quartz at different substrate temperatures, namely $-5\text{ }^\circ\text{C}$ (blue dots) and $23\text{ }^\circ\text{C}$ (red dots).

performance without a PbI_2 excess with excess organic molecules at grain boundaries [88]. I believe this to be the case here as well given my direct evidence from the XRD (Figure 4.8c) linking higher performance devices with excess PbI_2 and the increased susceptibility to electron beam damage of the grain boundaries in the films grown at low temperature (L) (Figure 4.5). This is in contrast to the work previously done by Xu et al. that showed improved performance when the PbI_2 layer at the n-type interface was removed, though this work was performed on devices with TiO_2 rather than C_{60} as the n-type contact, which could play a large role in the crystallization dynamics [92]. In vacuum co-evaporated devices, remnant PbI_2 has also been shown to directly contribute to photocurrent [93]. It is worth noting that excess unreacted PbI_2 has also been associated with photo-instability of the resulting films [94], and previous reports agree that it is only beneficial up to a point [89].

4.3 Effect of Changing MAI Flux

I now address the mechanism that determines crystal size in evaporated polycrystalline films of MAPbI_3 . In particular, does substrate temperature simply affect crystal size by changing the film stoichiometry as a result of changed MAI adsorption, or does temperature also play a more direct role in crystallization? One of the differences between L and H is stoichiometry, as H shows an excess of crystalline PbI_2 . It stands to reason to wonder whether the morphological differences arise simply due to stoichiometry. I hence increased the MAI flux at substrate temperature 23°C while keeping the PbI_2 rate constant to see whether I could replicate the large grains seen in L. As shown in Figure 4.18, I found that I was unable to do so, even when increasing the dose of MAI evaporated by 90% as measured by the final weight of MAI left in the crucible (H2), at which point there was no sign of any unreacted crystalline PbI_2 in the XRD pattern. Instead, it looks like increasing MAI leads to the disappearance

of the small bright grains seen along the otherwise columnar grains, pointing to those grains being linked to excess PbI_2 . Performance of the devices remained relatively unchanged, with a small increase in J_{SC} being balanced by a small decrease in V_{OC} .

Conversely, I find that when decreasing the MAI at low temperature, I do recover the morphology seen at room temperature, with a scattering of smaller grains on more columnar grains, indicating that stoichiometry does play a role in the resulting morphology (Figure 4.19). Interestingly, for decreased MAI flux, the performance of H is only recovered when the initial interface is grown at room temperature (LH1 and LH2). The substrate temperature used to grow these films was the following: L1, like L, was deposited entirely at -2°C . HL1 and HL2 followed the same temperature variation as HL, with the exception that HL1 only went down to 0°C rather than -2°C .

These results show that both low temperature and a balanced stoichiometry are needed to grow large grains, and is clear evidence that the benefits of excess PbI_2 for vacuum co-evaporation come not only in the form of direct passivation in the bulk or at grain boundaries, but that it also plays a crucial role in templating the growth of a material with better charge carrier properties. Indeed, HL shows no excess crystalline PbI_2 but still exhibits improved J_{SC} on par with the other samples that have at least one interface grown at room temperature (LH and HLH). Thus it is likely that the presence of PbI_2 domains during the growth of the films leads to better growth conditions for photovoltaic performance, irrespective of whether the PbI_2 gets converted in the end.

I hypothesize that the beneficial effects of excess PbI_2 during MAPbI_3 growth via co-evaporation come from PbI_2 domains templating the growth of MAPbI_3 . Indeed, I found that the presence of PbI_2 greatly enhances the adsorption of MAI, as when depositing MAI on its own, I did not observe MAI sticking to either FTO or glass. This hypothesis is also consistent with my observation of a higher adsorption rate of

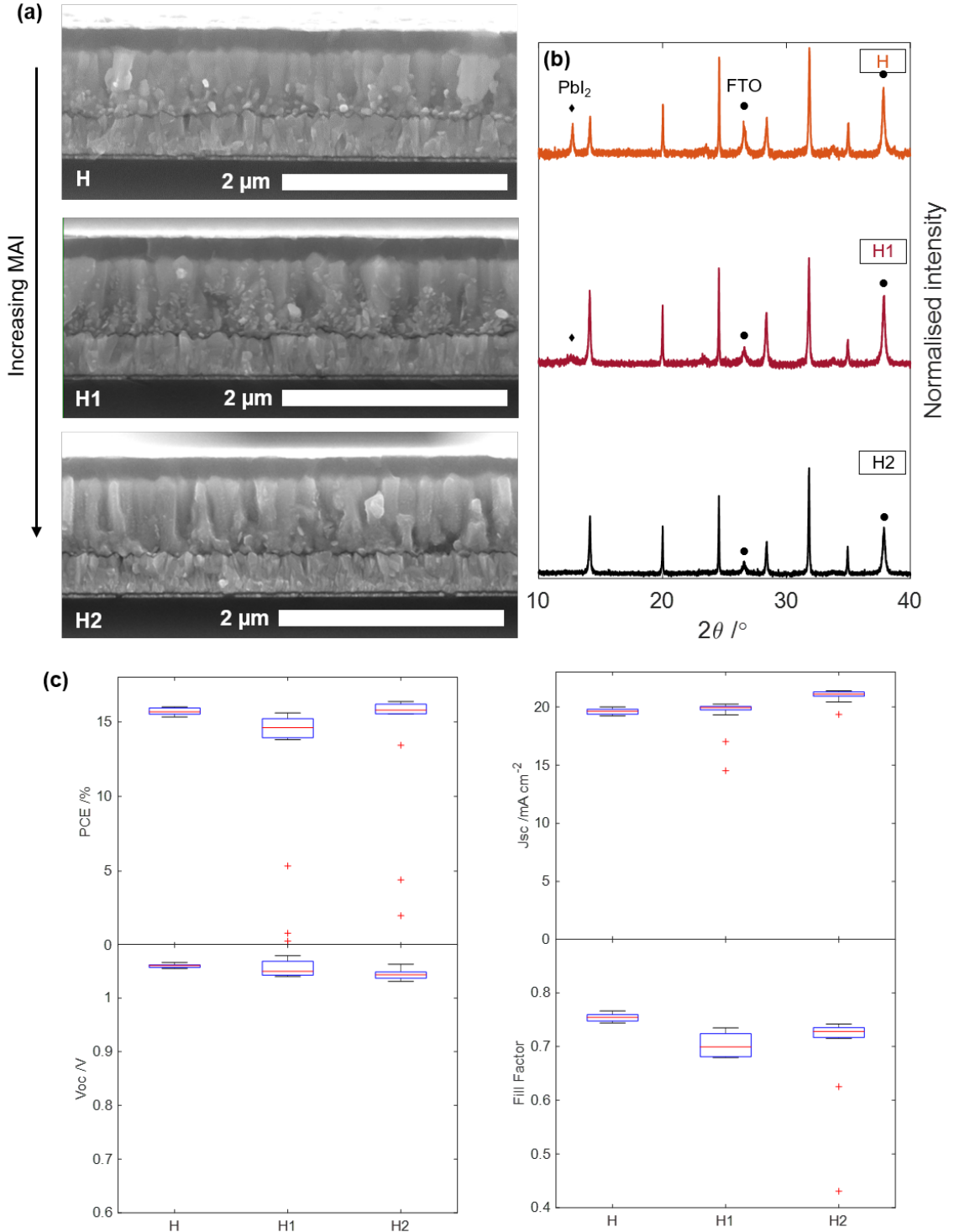


Figure 4.18: (a) cross-sectional SEM images of MAPbI₃ films grown at substrate temperature 23°C with increasing MAI flux. H1 and H2 were deposited by evaporating 30% and 90% more MAI than H as measured from the weight lost during the evaporation. (b) XRD patterns for the corresponding devices. The diamonds denote the PbI₂ peak at 12.7°, the circles the FTO peaks. All other peaks are perovskite peaks. (c) JV characteristics for the corresponding devices.

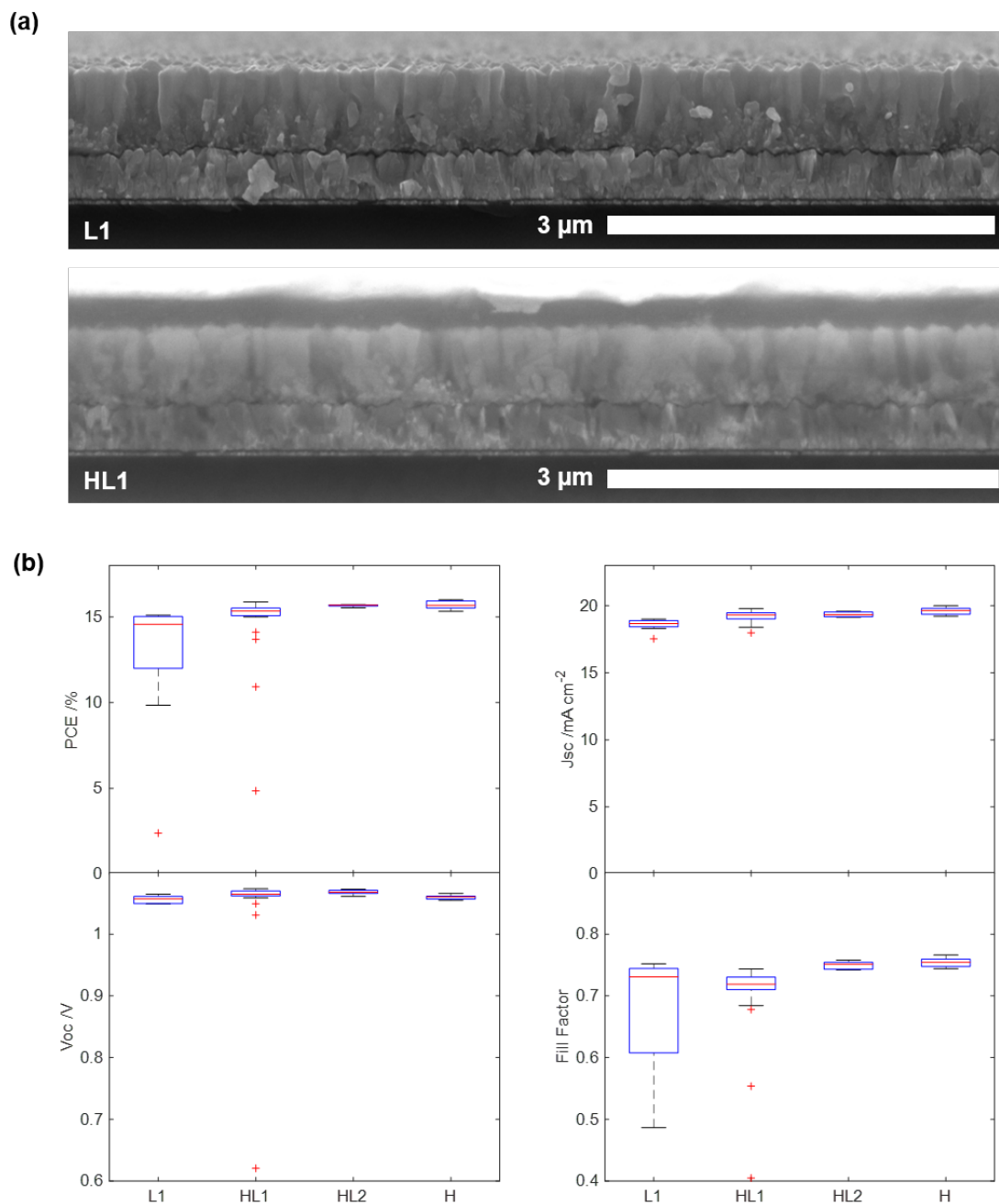


Figure 4.19: (a) cross-sectional SEM images of MAPbI_3 films grown at various substrate temperatures, as described previously, with reduced MAI flux. (c) JV characteristics for the corresponding devices.

MAI to a quartz microbalance thickness monitor in the vicinity of the substrate where PbI_2 is present, compared with one in the PbI_2 -free region near the MAI crucible. Together, these results suggest that PbI_2 deposits first on the substrate, subsequently adsorbing MAI and converting to MAPbI_3 . Lower substrate temperatures then directly increase the sticking coefficient of MAI onto PbI_2 . As such, while previous reports had found growth to vary with stoichiometry [51, 65, 66] I find that both a balanced stoichiometry and rapid perovskite conversion is needed to produce large grains. This also explains why increasing substrate temperature above 20 °C does not lead to the desired performance boost (Figure 4.20)[95], due to too much excess PbI_2 present during film formation, even if it is entirely converted by the end of the deposition [96]. It is worth noting that I did not increase the MAI flux to balance the reduced MAI adsorption, but the more detailed study done by Kottokkaran et al. shows that the performance never fully recovers even when increasing the MAI flux to account for this [96].

4.4 Substrate Rate Control

Finally, to address the substrate rate control method more generally, I found it a direct and versatile way of reproducibly controlling MAI flux. Indeed, using substrate rate control, I found consistent and reproducible performance for devices co-deposited using MAI precursors from different suppliers, which had very different adsorption behavior on their own. Figure 4.21 shows that very similar results are obtained for solar cells fabricated using homemade MAI (homemade MAI and MAPbI_3 layers produced by Dr. Jay Patel), which easily adheres to quartz microbalances, and Greatcell MAI, which doesn't stick on its own at all on quartz microbalances. The table shows the raw (untooled) data from the quartz microbalances near the MAI source, the PbI_2 source, and the substrate, respectively, for these two depositions. It shows how sim-

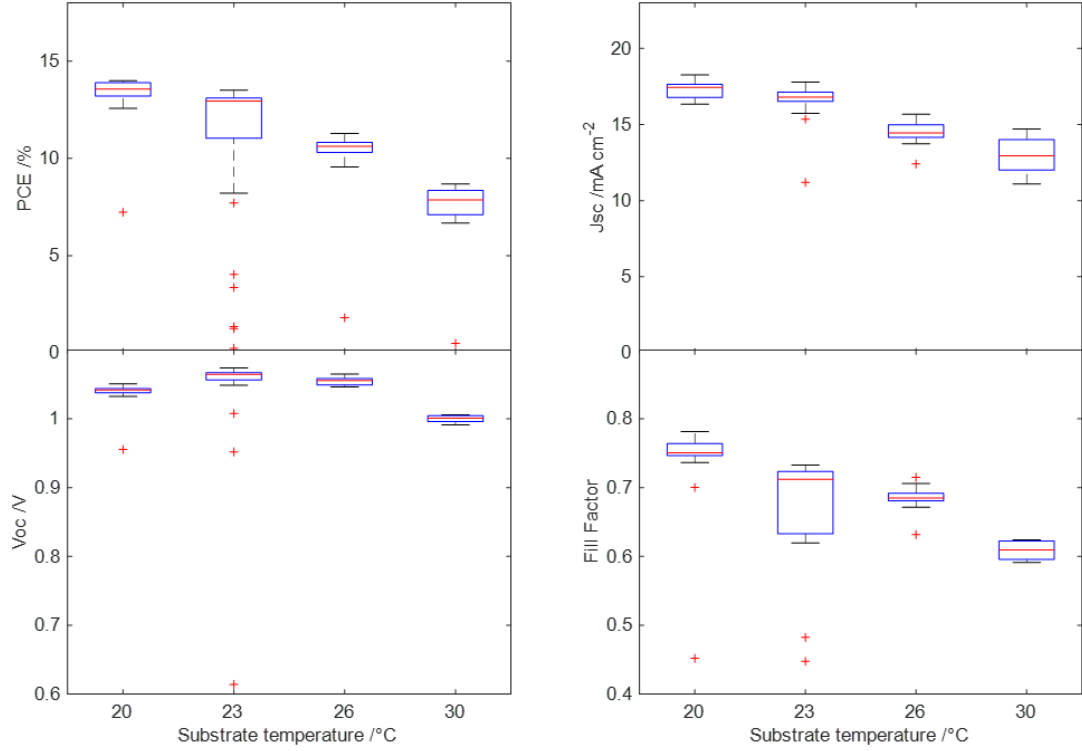


Figure 4.20: JV characteristics for MAPbI₃ devices grown at the same MAI flux but different substrate temperature

ilar the amount of material deposited near the substrate is even though the amount measured by the sensor near the MAI source is vastly different, and hence how the substrate rate is independent of the sticking rate of the MAI on its own because of how significant of an effect the presence of PbI₂ has. Increasing the thickness for device optimization also proved as simple as running the evaporation for longer, and continuing to ramp up the MAI crucible temperature to keep the substrate rate constant. This method works well because, as discussed previously, MAI has significantly increased adsorption in the presence of PbI₂, as I found much higher rates measured near the substrate than the individual contributions of PbI₂ and MAI when heating them up alone. The champion device achieved via my substrate rate control deposition method is the 18.2% PCE device grown at room temperature (20 °C) presented earlier (Figure 4.10), and shows the potential of this technique as a novel way of

tuning MHP vacuum co-deposition.

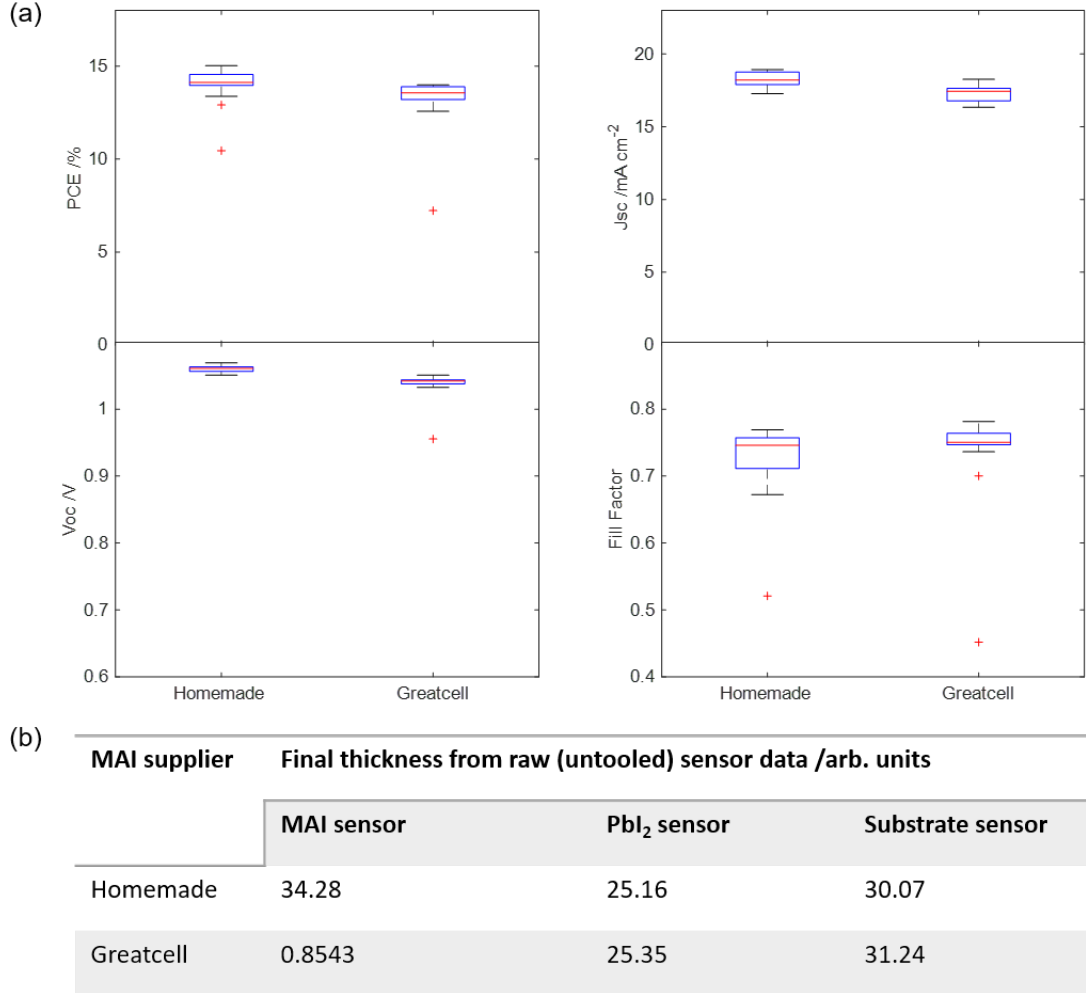


Figure 4.21: (a) JV characteristics for MAPbI₃ devices grown using homemade MAI (homemade MAI and devices fabricated by Dr. Jay Patel) and Greatcell MAI (b) Final thicknesses as measured from the raw (untooled) sensor data for the three sensors in the chamber

4.5 Conclusion

In conclusion, my work demonstrates control of crystallite size in vacuum co-evaporated films of MAPbI₃ by tuning the temperature of the substrate during deposition. Films grown at low temperatures (-2 °C) exhibited large, micrometer-sized grains, but significantly reduced J_{SC} , dropping the performance from PCE

16.0% to 10.1% as compared to films grown at room temperature (23 °C). I find changing the substrate temperature directly affects MAI adsorption rate, changing both the conversion rate of PbI_2 to MAPbI_3 as well as final stoichiometry. Grain growth and morphology is then a result of both these parameters, which can both be tuned individually by also changing the MAI sublimation rate at the MAI source. Furthermore, I find strong evidence to suggest that the deposition process happens through deposition of PbI_2 on the substrate first, followed by subsequent conversion to MAPbI_3 , as opposed to a simultaneous process. The difference in performance of my devices indicates that excess PbI_2 is beneficial to device performance both during deposition by seeding growth and in the final film by passivating charge carrier traps at grain boundaries. To achieve optimal performance, both the amount of MAI vapour incident on the substrate and the conversion rate of PbI_2 to MAPbI_3 must be optimized, which can only be done through changing the substrate temperature. This work provides a significant advancement in understanding the growth mechanism of vacuum co-evaporated MAPbI_3 , and offers a new avenue to optimise solar cells made from both this and more complex MHP formulations. With the ability to control grain size through substrate temperature, further advancements can be achieved with subsequent passivation methodologies, to obtain large crystalline domains with low defect densities and long carrier lifetimes, thereby leading to scalable, more efficient and highly reproducible MHP solar cell devices.

Chapter 5

Cl Passivation in Vapour Deposited MAPbI₃

5.1 Introduction and Background

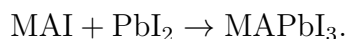
The remarkable progress of solution-processed MHP solar cells in the last few years has in a large part resulted from the development and improvement of thin-film crystallization and passivation techniques, aimed at reducing the defect density in the semi-conducting perovskite layers and minimizing non-radiative recombination at defects within the bulk of the crystal, at its surfaces and at interfaces with other materials. Improving the thin-film growth has been enabled by controlling “precursor-phases” during the thin-film deposition and crystallization, typically by employing mixed solvent systems [97, 98], and tuning the solvent lead-halide complexation [99, 100]. In particular, the introduction of an “antisolvent quenching” step, resulted in a step improvement in thin-film quality and reproducibility [97, 98]. The most successful passivation routes have been through a combination of molecular passivation [101], typically with primary amines or ammonium molecules [102], or via the creation of extremely thin 2D layered phase perovskites on top of or mixed within the 3D per-

ovskite film [103]. While a lot of the advancements in vapour deposited MHPs have benefited from the learning gained with the solution processed perovskites, most of the methodologies for thin-film growth control and passivation are not translatable to dry solvent-free processing.

For vapour deposited MHPs, considerable work has been undertaken on optimising the charge transport and contact layers within the solar cell stack [48, 63], and thickness of the active perovskite layer [42]. However few studies have been performed on translating the passivation techniques developed for solution-processed devices to vacuum deposition. This omission derives in part from challenges to finding dry passivation methods that do not introduce solvents back into an otherwise solvent-free system, and requiring an additional deposition source for every passivant in the case of in-situ passivation. However, developing passivation techniques compatible with vacuum deposition is a necessary step to improve the performance of vacuum deposited MHP solar cells. Indeed, Chapter 4 shows the necessity of passivating grain boundaries in vapour deposited MHP solar cells. A promising way of resolving both of these challenges is to use the so called “PbCl₂-route” introduced in Chapter 2, a co-evaporation procedure during which the precursors MAI and PbCl₂ are used. The latter are co-evaporated together at a 3:1 molar ratio, predominantly resulting in MAPbI₃ through the reaction:



This approach is in contrast to the PbI₂-route, which uses PbI₂ instead of PbCl₂ as the inorganic precursor, and a lower flux of MAI to directly produce MAPbI₃ through the reaction:



Indeed, I- or Cl-based compounds have shown significant passivation effects in solution-processed MHP solar cells [90, 102, 104, 105], with the incorporation of Cl being one of the earliest and best demonstrated of these for lab-scale spin-coated devices [106–112]. Originally, Cl was used in spin-coated films because it promoted enhanced grain growth through the formation of a precursor phase which subsequently converts into the ABX₃ perovskite phase after annealing and removal of the excess material [99, 100, 106, 109]. While this method of controlling grain growth and crystallization was ultimately replaced in favor of solvent engineering techniques [97, 98], Cl-based additives have recently regained popularity due to their performance and stability enhancements reaching beyond just improvements to grain growth [113]. Notably, the addition of Cl has been shown to also aid in phase stabilization of more complex MHP formulations [110], leading to significant improvements in perovskite films for tandem applications [39].

The PbCl₂-route was used in the first report of vacuum co-evaporated MHP solar cells [49], at the time because of its similarity to then state-of-the-art solution processed films. The PbCl₂-route was ultimately abandoned in favor of the PbI₂-route, since the latter produced equally homogenous, higher performance films [41, 48, 63]. However, given the renewal of interest in Cl-based additives and advancements in co-evaporation protocols, the PbCl₂-route warrants revisiting, as additional work is required to understand how it affects the optoelectronic and material properties, to guide further improvements and optimization of the passivating effects.

In this chapter, I performed a series of comparisons between the PbI₂-route and PbCl₂-route for MAPbI₃ films, to better understand the effects of Cl addition and test its potential as a passivating agent in vacuum-deposited MHP solar cells. The MAPbI₃ films were co-deposited according to a “substrate-rate control” method discussed in Chapter 4, for which the inorganic precursor is controlled by a film-thickness sensor near its source, but the MAI is controlled by a film-thickness sensor near the

substrate that monitors both MAI and the inorganic precursor. MAPbI₃ films fabricated via the PbI₂-route were grown by co-evaporating MAI and PbI₂, while MAPbI₃ films fabricated via the PbCl₂-route were grown by co-evaporating PbCl₂ with a higher flux of MAI. Following co-evaporation, the PbCl₂ route films were optionally annealed at 101 °C for 0, 30, 60 or 90 minutes in a nitrogen filled glove box. PbI₂ route films were not annealed, as I previously found this to decrease performance, with no significant morphology change (Figure 4.1). Full solar cell devices were fabricated according to the following n-i-p architecture: FTO as the bottom contact; followed by C₆₀ as the ETL; the perovskite; doped Spiro-OMeTAD as the HTL; and capped by Ag as the top contact.

5.2 Comparing the PbI₂- and PbCl₂-routes

5.2.1 Thin-Film Characterisation

Initial characterization of the MAPbI₃ films reveals strong optoelectronic differences, but negligible bulk crystallographic differences. Indeed, Figure 5.1a shows typical TRPL spectra of MAPbI₃ films made via the PbCl₂- and PbI₂-routes, and reveals lifetimes of over 12 ns for the PbCl₂-route MAPbI₃ film, but of only 0.85 ns for the PbI₂-route film. The very short lifetimes of the latter are typical for vacuum-deposited PbI₂-route MAPbI₃ films [86], even for high-performance devices [42, 48], and so it is even more impressive that the use of Cl during fabrication boosts the photogenerated charge-carrier lifetime by over an order of magnitude. The lifetimes were obtained by fitting a stretched exponential to the experimental data [54, 114]. The inset of Figure 5.1a shows the fits for the PbI₂-route and the early time decay of the PbCl₂-route MAPbI₃ films. The TRPL trace of the PbI₂-route MAPbI₃ film has been cut to only show sample signal above the noise threshold, with the full PbI₂-route TRPL trace shown in Figure 5.2. My results clearly show that incorporating Cl during the

deposition process has a substantial effect on the optoelectronic properties of the films, and demonstrates a passivating effect by reducing non-radiative recombination pathways.

XRD measurements, on the other hand, indicate negligible difference between MAPbI₃ films made via the PbCl₂- and PbI₂-routes. No shift in peak position is observed, the only difference being a stronger signal from the PbCl₂-route sample, and a slightly reduced full-width at half maximum (FWHM): 0.07 ° for the PbCl₂-route versus 0.11 ° for the PbI₂-route, for the perovskite (110) peak at $2\theta = 14.1^\circ$, indicating slightly enhanced grain size [84]. This finding suggests that a significant amount of Cl does not incorporate into the perovskite crystal structure during evaporation and post curing of the perovskite films, but rather has an influence upon the crystallization and final quality of the as crystallized films. This observation matches previous conclusions for spin-coated films fabricated from solution formulations of the type MAPbI_{3-x}Cl_x, for which starting with a molar excess of methylammonium and Cl has been shown to aid in the nucleation and crystallization process through the formation of a precursor phase, but little or no Cl incorporation into the bulk [99, 100, 108, 109, 115–117]. In contrast to the solution processing methods, I find that perovskite phase MAPbI₃ forms directly during deposition, even before post annealing (Figure 5.3), in agreement with the in-situ XRD study of this material during co-evaporation by Pistor et al. [118]. My results hence indicate that it is possible to form directly the perovskite phase of MAPbI₃ from thermal evaporation of PbCl₂ and MAI, and obtain thin films with significantly better optoelectronic properties than those fabricated via the PbI₂-route.

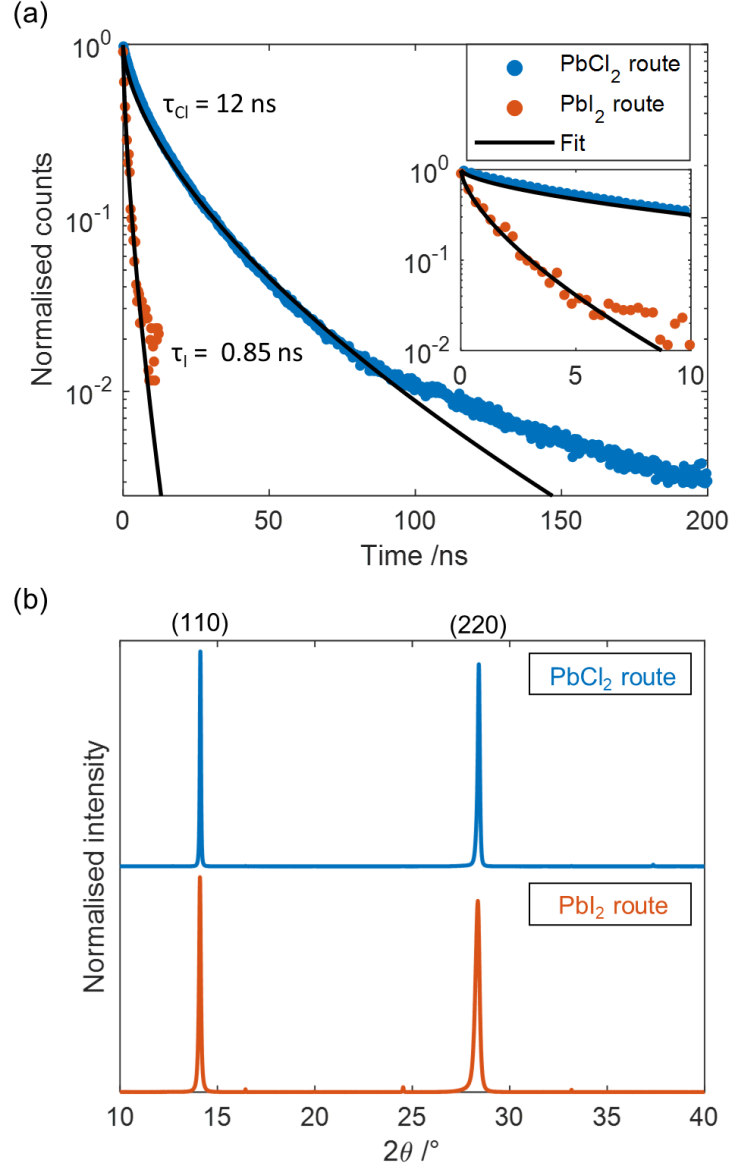


Figure 5.1: (a) TRPL traces for MAPbI₃ thin films grown via the PbCl₂-route (blue) and PbI₂-route (red), thin films grown on z-cut quartz. The data shows PbCl₂-route devices after 1h annealing at 101 °C, whereas PbI₂-route devices were not annealed; which are these conditions that gave the highest PCE. The inset shows the same traces, for a more limited time range. The PbI₂-route trace is cut-off to only show sample signal; the full trace is shown in Figure 5.2, fitting methods are described in Chapter 3. (b) XRD traces for PbCl₂-route MAPbI₃ and PbI₂-route MAPbI₃ thin films grown on z-cut quartz. The curves have been normalised to their respective highest peaks, and corrected for angular tilt by fitting the quartz peak at $2\theta = 16.4^\circ$. The data was obtained using a Cu-K α X-ray source with wavelength 1.54 Å.

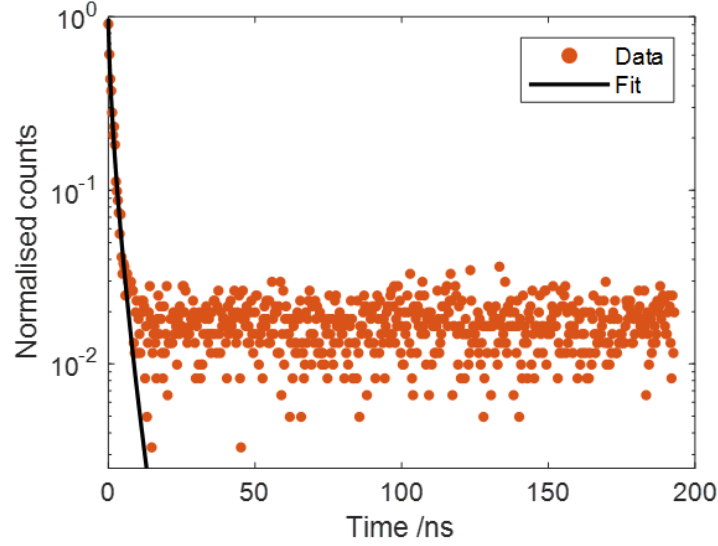


Figure 5.2: Full TRPL traces for MAPbI₃ thin films deposited via the and PbI₂-route, with the black line corresponding to a stretched exponential fit.

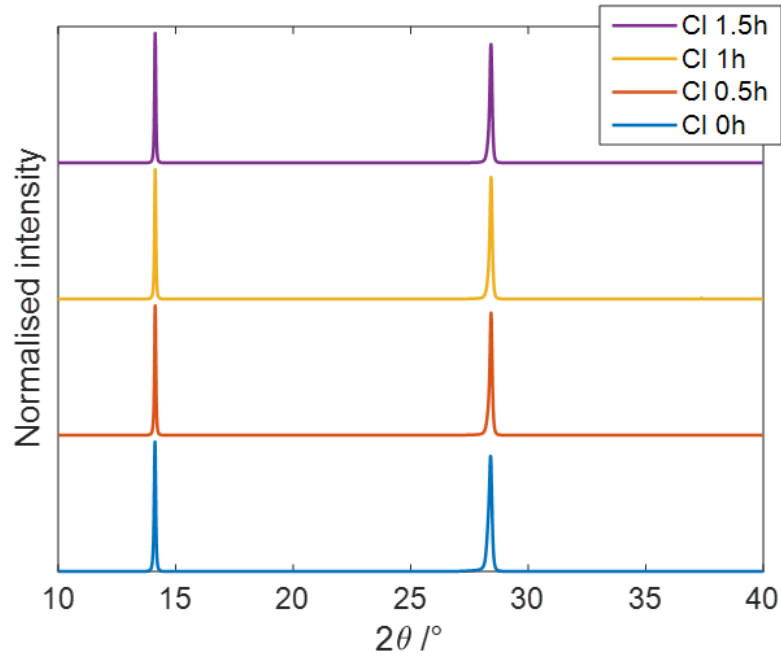


Figure 5.3: Normalised XRD traces for PbCl₂-route MAPbI₃ films grown on z-cut quartz, for different annealing times at 101 °C in an N₂ glovebox: as deposited (Cl 0h, blue), 0.5h (Cl 0.5h, orange), 1h (Cl 1h, yellow), 1.5h (Cl 1.5h, purple). The curves have been corrected for angular tilt by fitting the quartz peak at $2\theta = 16.4^\circ$. The data was obtained using a Cu-K α X-ray source of wavelength 1.54 Å.

5.2.2 Solar Cell Characterisation

While the material properties and particularly the optoelectronic properties are substantially improved for the PbCl₂-route MAPbI₃ films, this does not lead to the expected performance increase in solar cells. Figure 5.4a shows the JV characteristics of tested devices for MAPbI₃ films fabricated through the PbCl₂- or PbI₂-routes, and shows that the best PbCl₂-route devices are only marginally better than those fabricated via the PbI₂-route, with a higher short-circuit current density (J_{SC}) but a lower open-circuit voltage (V_{OC}). The steady-state efficiency of the champion MAPbI₃ devices are 14.5% for the PbCl₂-route and 14.0% for the PbI₂-route. Figure 5.4b displays the JV curve of the corresponding devices, with the inset showing the steady-state performance of these devices over a time of 50 s. The loss of V_{OC} with the addition of Cl is surprising given the significantly longer PL lifetimes observed in these films in Figure 5.1. Indeed, the longer PL lifetimes imply reduced non-radiative recombination, which is expected to lead to improved V_{OC} owing to a reduced density of trap states and surface recombination [85, 119]. Furthermore, Cl has also been associated with better charge transport across the interfaces with the CTL in spin-coated devices [109], which would also result in a higher V_{OC} . Even more striking is the much larger spread in performance in the batch of PbCl₂-route solar cells, with only a few achieving over 10% PCE, and most producing less than 5% PCE. This spread is the result of a large variation in the measured V_{OC} , with the high-performing devices recording a V_{OC} around 1 V, but the poor performing devices exhibiting only 0.4 V V_{OC} . In contrast, the J_{SC} is similar across all of the devices. The uniformly high J_{SC} indicates that the problem does not lie in charge extraction. Instead, the large spread in V_{OC} indicates there may be an increase in interfacial trap states or shunts through for example pinholes, which would lower the V_{OC} . This is illustrated in Figure 5.5, which shows the numerically averaged JV curves for each device type, confirming significant shunting for the PbCl₂-route MAPbI₃ devices. More generally, the large spread

in device statistics points to the PbCl₂-route producing less homogeneous MAPbI₃ films. Investigating the small-scale morphology is hence the next step required, to understand the nature of the inhomogeneity and performance limiting shunts.

5.3 MACl Loss in Annealing

Figure 5.6 shows scanning electron microscope top-down images for MAPbI₃ films made through the PbCl₂- and PbI₂-routes, before and after annealing. Both films show a similar morphology prior to annealing, consisting of a dense film with grains of order 100 nm, the typical grain size reported previously for vapour deposited MAPbI₃ [48, 75, 120]. After annealing, however, the PbCl₂-route film changes morphology dramatically, while the PbI₂-route film stays unchanged. Indeed, the PbCl₂-route film develops into a clustered network of grains with large voids in between. The origin of this transformation is unclear, but indicates a loss of material during the annealing step. This is likely to be associated with the presence of reactive components in PbCl₂-route films that are not present in PbI₂-route films. The most obvious candidate is MACl, which forms by the reaction of MAI + PbCl₂. MACl is more volatile than MAI [121], so readily evaporates from the perovskite when heated, deforming grains and creating voids. Furthermore, I found that PbCl₂ can result in MACl formation during annealing even if the MA⁺ ions are in the perovskite MAPbI₃ structure, which results in loss of MA⁺ and formation of excess PbI₂. Indeed, when I deposited a thin layer of PbCl₂ on top of a PbI₂-route MAPbI₃ film, I found that, during annealing, the PbCl₂ readily mixes with the MAPbI₃ and leads to an increase in PbI₂ in the film, indicating MA⁺ loss (Figure 5.7, 5.8). This generalizes the work of Yu et al. [121] to show that Cl-ions can lead to the release of MA⁺ ions during annealing even if the MA⁺ is already in a stable perovskite structure. This finding has considerable implications, since it allows for a new approach to passivating stoichiometric MAPbI₃ films: depositing a

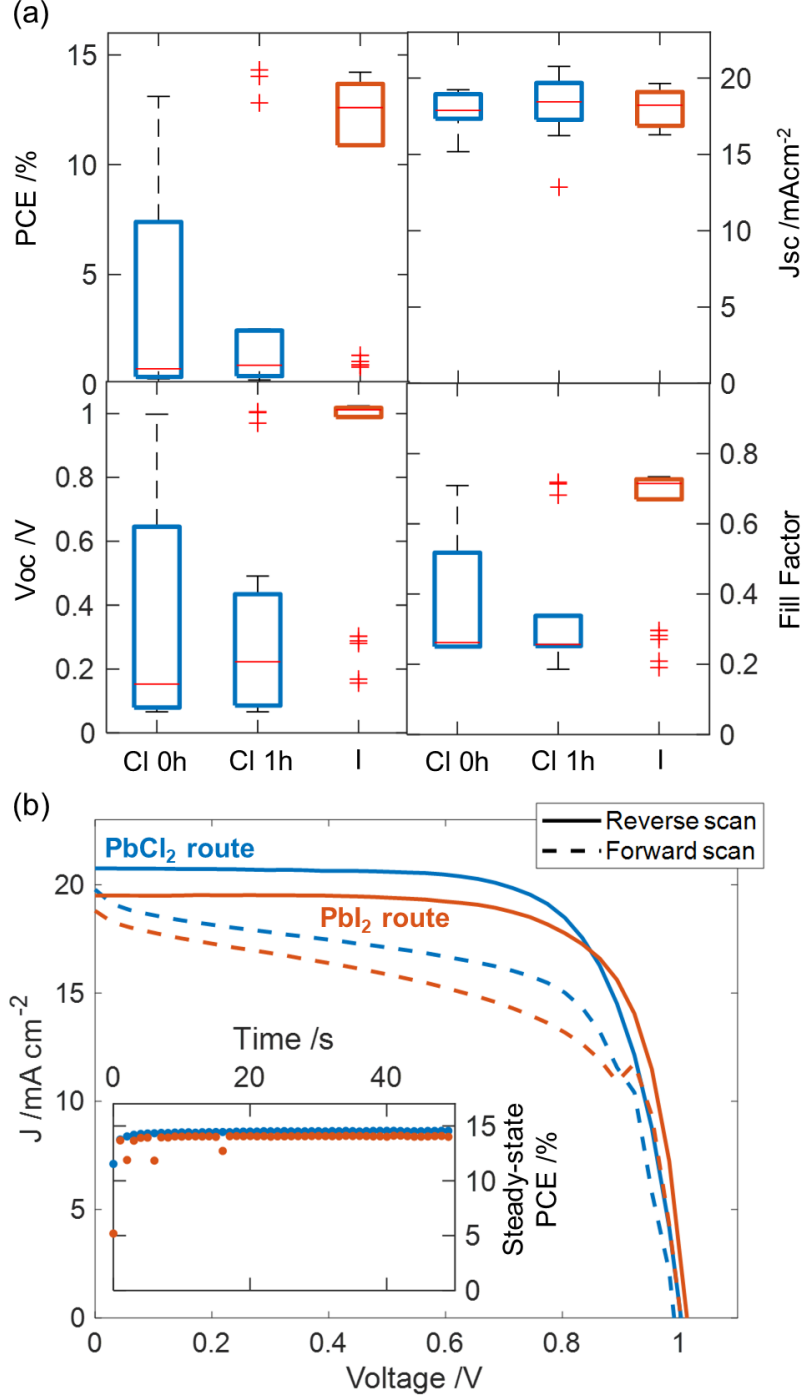


Figure 5.4: (a) JV characteristics for MAPbI₃ devices grown via the PbCl₂-route (Cl, blue) and PbI₂-route (I, red). The data shows PbCl₂-route devices as deposited (Cl 0h) and after 1h annealing at 101 °C (Cl 1h). The PbI₂-route devices were not annealed (b) JV curve for the best PbCl₂-route (blue) and PbI₂-route devices (orange) as measured by steady-state performance. The solid curves represent the reverse scans from V_{OC} to J_{SC}, while the dashed lines represent the forward scans from J_{SC} to V_{OC}. The inset shows the steady-state PCE measured over 50 s for the same devices.

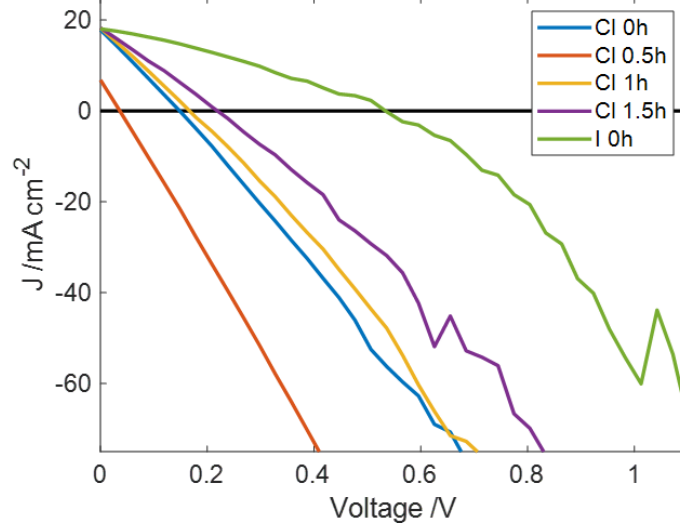


Figure 5.5: Numerically averaged JV curves for PbI_2 -route MAPbI_3 devices (I 0h, green) and PbCl_2 -route MAPbI_3 devices for different annealing times: as deposited (Cl 0h, blue), 0.5h (Cl 0.5h, red), 1h (Cl 1h, yellow), 1.5h (Cl 1.5h, purple). The curves were obtained by averaging over the current values of the reverse scan (V_{OC} to J_{SC}) of every device for a corresponding anneal time.

thin layer of PbCl_2 on top of a finished MAPbI_3 film to induce formation of the slight PbI_2 excess associated with passivation and improved performance [88–90, 120].

The mixing of the PbCl_2 and MAPbI_3 layers through annealing can also be seen to result in a change of strain in the MAPbI_3 lattice along the (110)/(002) direction. Indeed, in Figure 5.8, nearly all peaks of the perovskite phase line up, with the notable exception of the (220)/(004) peak around $2\theta = 28.2^\circ$, which shifts to slightly higher diffraction angles. This shift indicates a reduction in the lattice constant along this direction. Since the other crystallographic orientations remain invariant, this implies that the annealing, mixing of the PbCl_2 with the MAPbI_3 , and subsequent MACl loss has strained the perovskite. This exemplifies how the loss of MACl changes the material properties even though it is no longer present in the final film.

The change in morphology with annealing shown in Figure 5.6 explains the poor V_{OC} of the devices. If the HTL spin-coated on top of the MAPbI_3 films is able to traverse pinholes and contact the ETL below the perovskite, this would result in lower

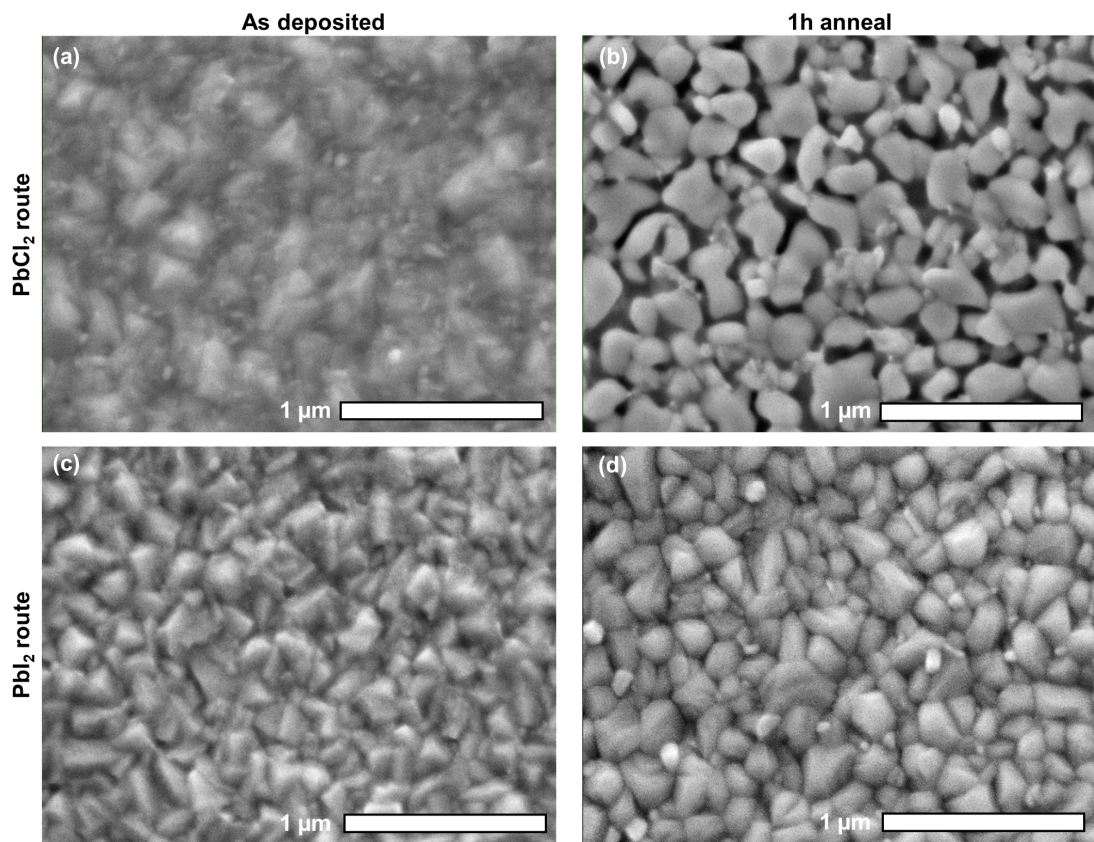


Figure 5.6: Top down view scanning electron microscope images of co-evaporated MAPbI₃ thin films grown via the PbCl₂-route (a and b) and PbI₂-route (c and d), deposited on FTO. The first column represents films as deposited (a and c), while the second column represents films after 1h anneal (b and d).

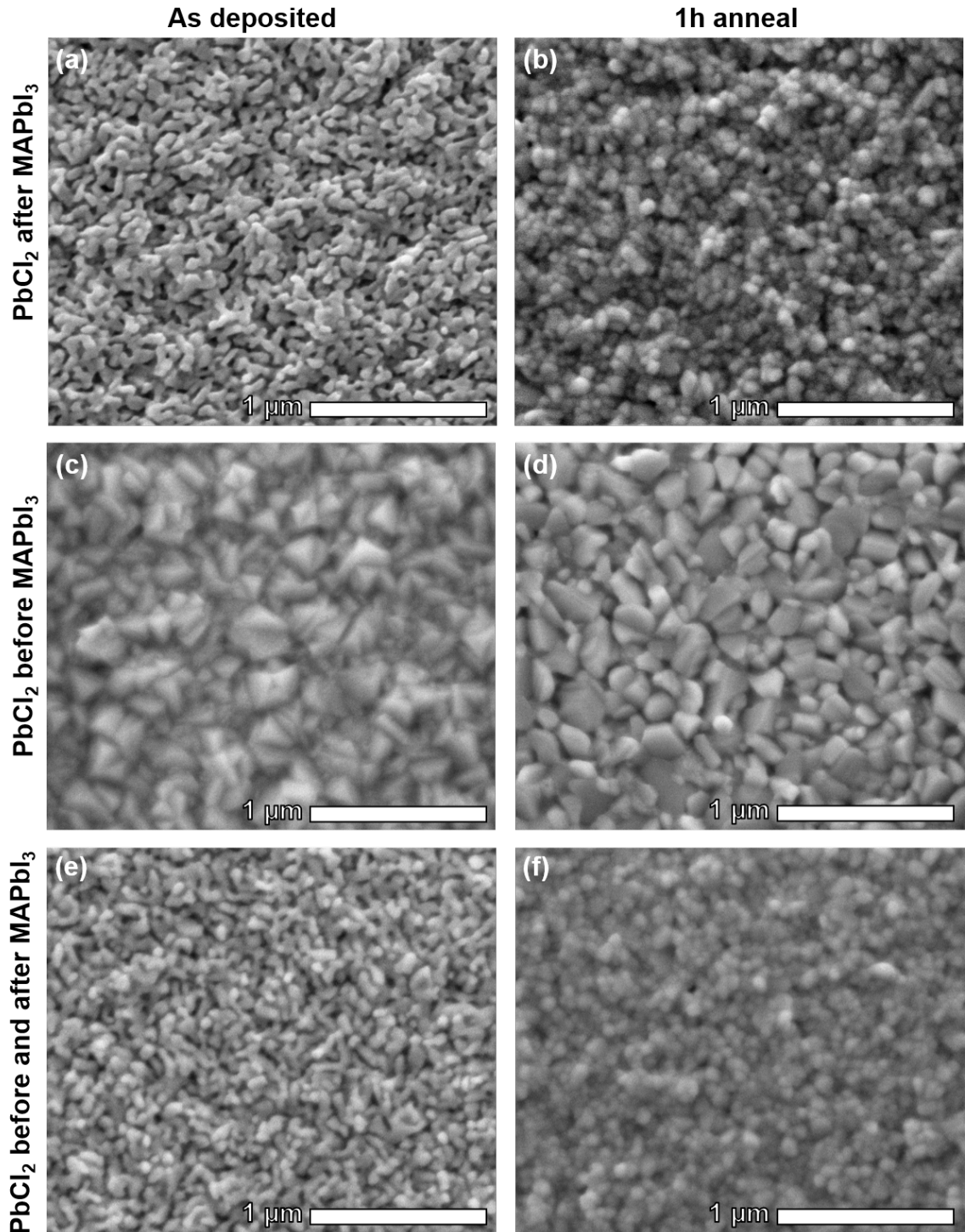


Figure 5.7: Top down view scanning electron microscope images of co-evaporated PbI₂-route MAPbI₃ thin-films with a 30 nm PbCl₂ interlayer deposited after (a and b), before (c and d), or before and after (e and f) the 400 nm MAPbI₃ layer. Images from the first column represent the as-deposited films (a, c and e), the second column after a 1h anneal in N₂ at 101 °C (b, d and f).

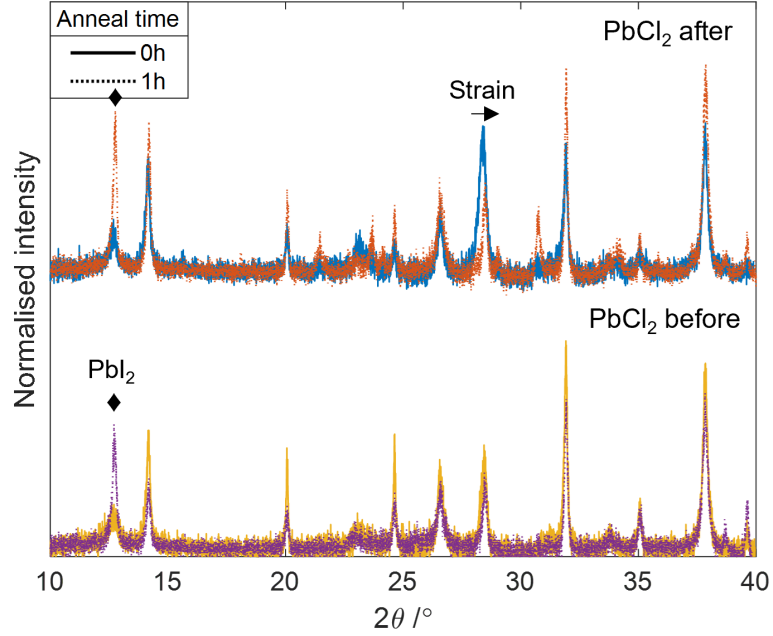


Figure 5.8: XRD spectra of co-evaporated PbI₂-route MAPbI₃ thin films on FTO, with 30 nm of PbCl₂ deposited before (bottom row: yellow/purple) or after (top row: orange/blue) the MAPbI₃ layer. The solid lines (yellow, blue) represent the as deposited films, while the dashed lines (purple, orange) represent the films after annealing for 1h at 101 °C. The black diamond represents the position of the PbI₂ (001) peak at $2\theta = 12.7^\circ$. The films were normalised with respect to their highest intensity peak, and corrected for angular tilt using the FTO (110) peak at $2\theta = 26.6^\circ$. The data was obtained using a Cu-K α X-ray source with wavelength 1.54 Å

shunt resistance, decreasing the V_{OC} and fill factor. This effect is demonstrated in Figure 5.9, which shows an example of a poor performance JV curve, with a very high forward bias current density and “spikes” in the JV curve, consistent with low shunt resistance and pinholes being present which sporadically “burn-out” during the JV scanning process. In the case of the unannealed films, the poor performance is likely caused by excess MACl trapped within the film [121]. Optimising device performance of PbCl₂-route MAPbI₃ films can thus be described as a compromise between achieving ideal composition and continuous coverage. The unannealed films have continuous coverage, but contain trapped excess MACl, whereas the annealed films allow the MACl to escape at the cost of pinholes in the film. This highlights

the issue of using just PbCl₂ as the inorganic precursor. Indeed, very recently Babei et al. demonstrated that using a mix of PbI₂ and PbCl₂ produced more uniform MAPbI₃ films while maintaining the beneficial effects of Cl [122]. Overall, the relative indifference between the JV data shows that there is no notable benefit of annealing the devices in my case (Figure 5.10).

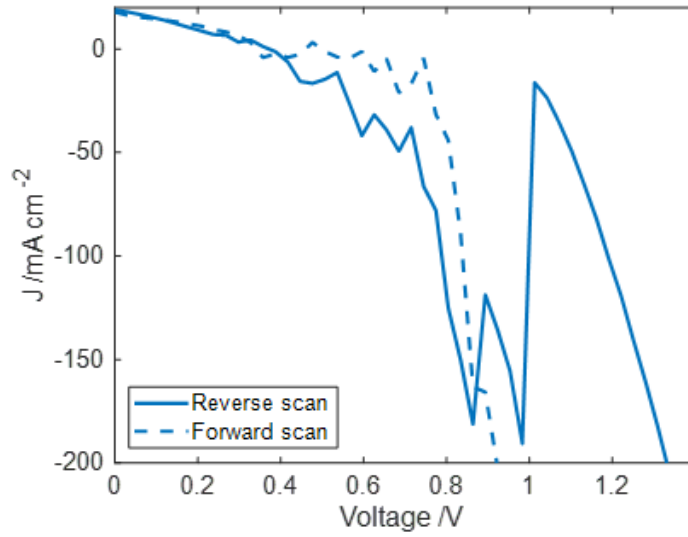


Figure 5.9: JV curve for a PbCl₂-route MAPbI₃ device showing a characteristic kink as it approaches power-generating currents. This particular curve comes from a device annealed at 1h.

It is worth noting that the PL lifetimes of the PbCl₂-route MAPbI₃ films are also generally independent of anneal duration, as shown in Figure 5.11. This observation is quite remarkable, as it implies that the morphology change resulting from annealing does not induce a significant change in charge-carrier recombination dynamics. In general, the presence of voids and crevices in the annealed films imply a change in surface area, typically an increase. Assuming a similar surface trap density in all MAPbI₃ films, a larger surface area would be expected to lead to increased non-radiative surface recombination through a larger number of surface traps and defects, but my data show no sign of increased non-radiative recombination. Therefore, my results suggest that the PbCl₂-route MAPbI₃ films have a well passivated surface,

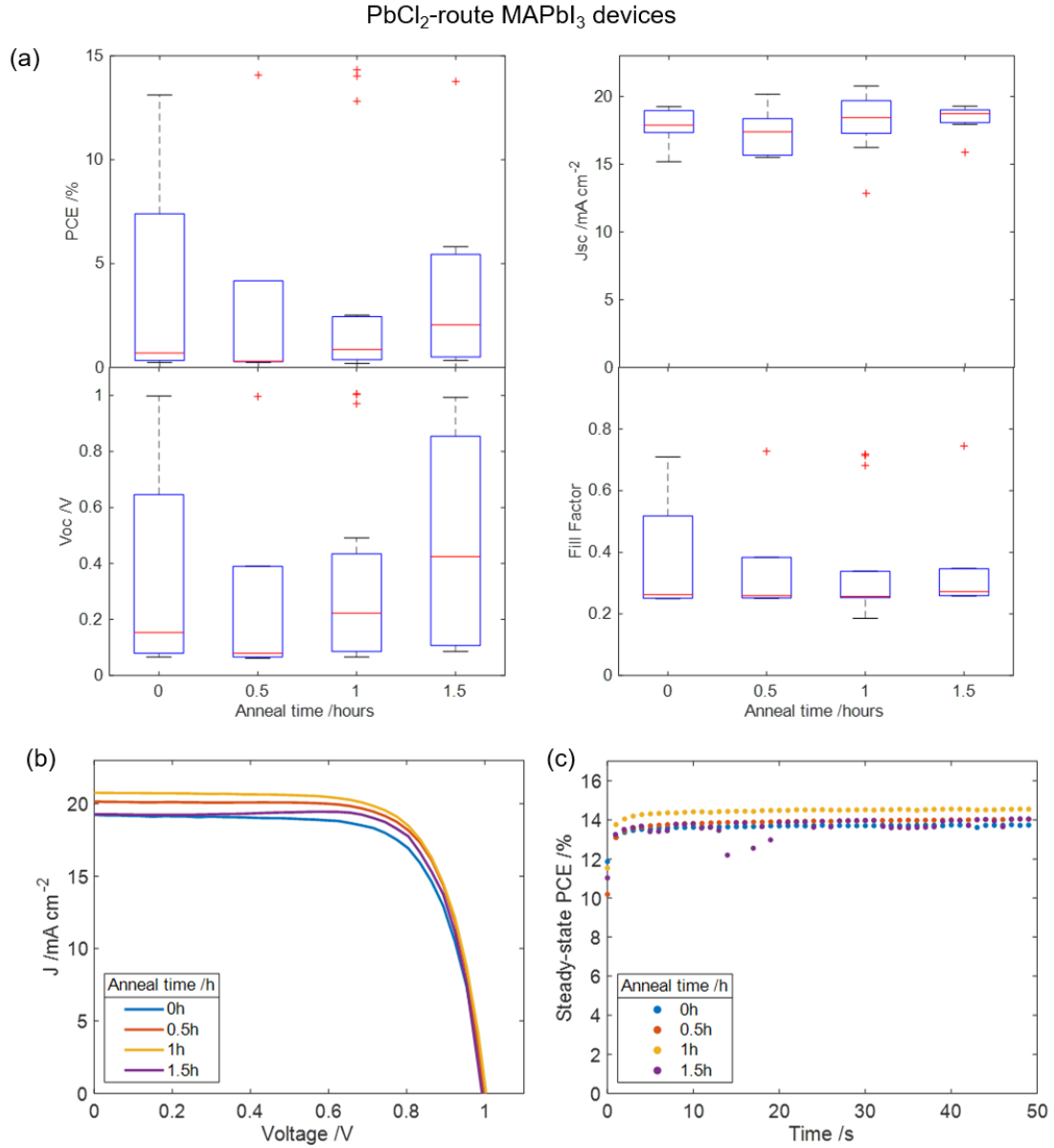


Figure 5.10: (a) JV characteristics for PbCl₂-route MAPbI₃ devices as a function of annealing time at 101 °C (b) JV curve for the best device as measured by steady-state performance for each of the annealing times. The curves shown are the reverse scans from V_{OC} to J_{SC} . (c) Steady-state PCE measured over 50 s for the best devices as measured by best steady-state PCE for each of the annealing times.

reducing the usually detrimental effects of a larger surface area, which is consistent with the increased PL lifetimes shown in Figure 5.1a.

Together with the rest of my results, these observations give a consistent picture of the role of Cl in vapour deposited PbCl₂-route MAPbI₃ films, namely as inducing the growth of films with well-passivated surfaces. Indeed, my XRD measurements showed that if Cl is incorporated into the bulk structure, it is at such a low level that it does not cause any measurable change in the crystal lattice parameters, meaning that any Cl left in the film is likely to be present and acting interstitially or on the surface. Effective surface passivation of MAPbI₃ via the PbCl₂-route also explains why the device performance is not significantly affected by the increased surface area of the annealed films, with Cl passivating the surface trap states that would otherwise hamper device performance. Moreover, I believe that improved surface passivation is also the main reason behind the much longer bulk photoexcited carrier lifetimes observed in the PbCl₂-route MAPbI₃ films as compared to the PbI₂-route films. An in-depth study on the short photogenerated charge-carrier lifetimes typically observed in vacuum-deposited MAPbI₃ films by Chirvony et al. demonstrated that these short lifetimes are due to efficient charge carrier separation and subsequent non-radiative recombination at the surfaces [86]. Therefore, if surface recombination is the main non-radiative pathway for photogenerated charges, the well-passivated surface of the PbCl₂-route MAPbI₃ would significantly improve overall charge-carrier lifetimes, which is indeed what I observed in 5.1a.

5.4 PbCl₂ Interlayer

It is clear from the results of sections 5.2 and 5.3 that relying on PbCl₂ as the sole inorganic precursor for MAPbI₃ is not an ideal way of passivating the resulting material. Indeed, while the PbCl₂-route provides clear benefits to the crystallographic

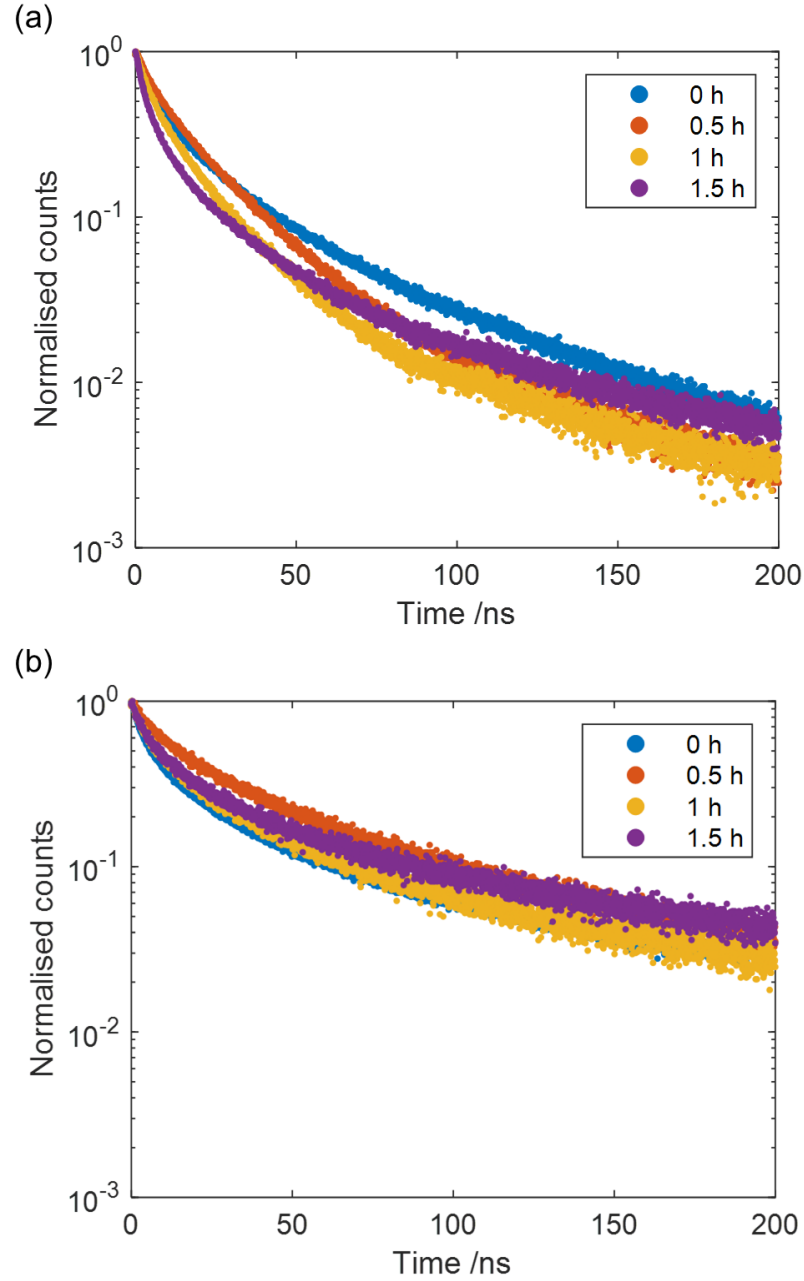


Figure 5.11: TRPL traces for MAPbI₃ thin films grown via the PbCl₂-route on z-cut quartz annealed for different times at 101 °C: 0 h (blue), 0.5 h (orange), 1 h (yellow), 1.5 h (purple). The different figures show this data for different excitation fluences (a) 40 nJ/cm^2 (b) 4 nJ/cm^2

and optoelectronic properties of the films, relying on the sublimation of substantial amounts of MACl is ultimately detrimental to the thin-film morphology and solar cell performance. Because my deposition system only had two sources at the time, I could not explore using a mix of PbCl₂ and PbI₂ as the inorganic precursors for co-evaporated MAPbI₃. An alternative method of introducing small amounts of PbCl₂ to PbI₂-route MAPbI₃ with my setup is to instead deposit thin layers of PbCl₂ before or after the MHP, and see if the chloride is able to diffuse into the iodide perovskite. This method follows the benefits observed from introducing growth interlayers in Chapter 4. This interlayer approach has the additional benefit of depositing the chloride directly where surface passivation is most beneficial, i.e. close to the interfaces.

To test this approach, I deposited 30 nm of PbCl₂ before and/or after a PbI₂-route MAPbI₃ deposition. The morphological effects were already shown in Section 5.3 in Figure 5.7 and 5.8, in the context of showing the solid-state miscibility of PbCl₂ and PbI₂. To summarise, the SEM data showed that PbCl₂ mixes with MAPbI₃ during annealing, while the XRD data showed the formation of significant amounts of PbI₂ during annealing, consistent with the formation and loss of MACl. This indicates that the PbCl₂ is able to mix with MAPbI₃, and react with the MA⁺ therein. Further to the SEM and XRD data, I also tested solar cells made with the PbCl₂ interlayers to test this approach as an alternative to introducing Cl into the MAPbI₃ perovskite. Figure 5.12 shows the corresponding solar cell performance for films with 30 nm of PbCl₂ deposited after, as well as before and after the 500 nm PbI₂-route MAPbI₃ layer, after 5 or 15 minutes annealing time at 101 °C. Unfortunately the PbCl₂ layer clearly blocked charge extraction, as the photovoltaic devices with the interlayers showed a significant reduction in J_{SC} , leading to significantly worse PCE than the control device. However, both longer annealing and light soaking appeared to help diffusion of the PbCl₂ to form a more uniform perovskite layer, as seen in Figure 5.12c. This implies that a PbCl₂ interlayer can successfully mix with PbI₂-route MAPbI₃

and be used to introduce Cl into the perovskite, but that the 30 nm layers used in this experiment were too thick. I expect improvements in PCE could be obtained by using thinner PbCl₂ interlayers, and using this approach in MA-free films, which would not be affected by MACl formation and loss.

5.5 Conclusion

In conclusion, I demonstrate the ability to enhance the optoelectronic properties of vapour deposited MAPbI₃ through incorporation of Cl during deposition via the PbCl₂-route. I find photogenerated charge-carrier lifetimes improved by an order of magnitude, from 0.85 ns for the PbI₂-route MAPbI₃ films to over 12 ns for MAPbI₃ films grown by the PbCl₂-route. Crystallographically, the bulk MAPbI₃ material is the same for films fabricated via the PbI₂- and PbCl₂-routes, within the resolution limit of the instrument, indicating that the Cl does not incorporate into the bulk at a significant concentration, but likely passivates the surface. I find the morphology of MAPbI₃ films grown by the PbCl₂-route changes substantially with annealing, developing from a dense small crystallite film, to a grain network separated by pinholes. Remarkably, this change does not significantly affect either the optoelectronic properties or device performance, even as the exposed surface area of the film increases. This is clear evidence for the surface passivating effects of Cl when making films using the PbCl₂-route. Surprisingly, the passivated films do not lead to significantly improved solar cell device performance, most likely due to remnant MACl in the unannealed MAPbI₃ films, and the pinhole morphology in the case of the annealed film. Remarkably, I found that PbCl₂ can react with MAPbI₃ directly to induce formation of PbI₂ through loss of MA, allowing for new ways of thin-film passivation. Overall, I have demonstrated the beneficial effects of Cl incorporation via the PbCl₂-route for vacuum deposited MAPbI₃. The addition of Cl to solution processed perovskite PV cells,

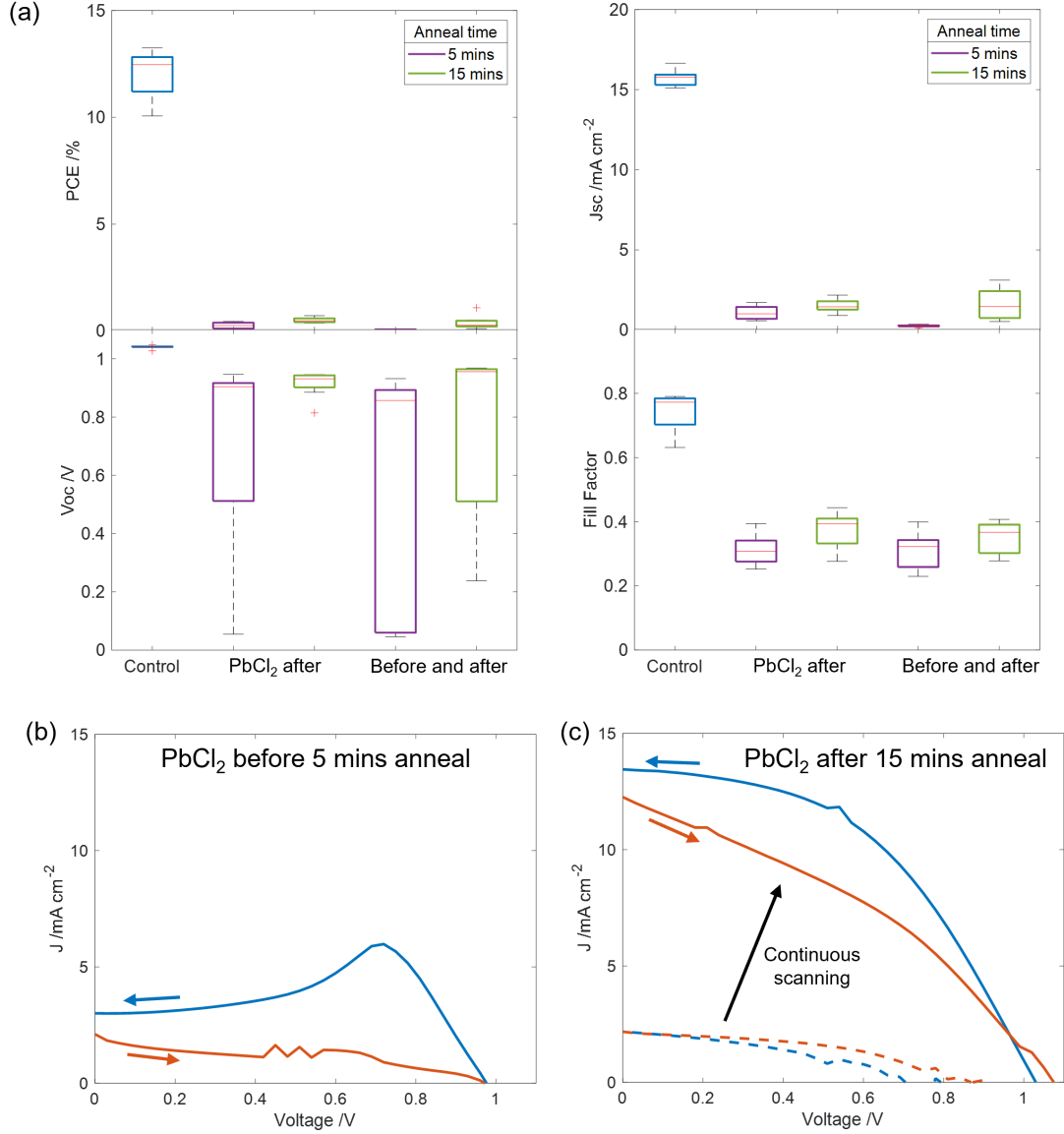


Figure 5.12: (a) JV characteristics for CH₃NH₃PbI₃ (MAPbI₃) devices grown without (control) or with a 30 nm PbCl₂ layer after or before and after the 400 nm MAPbI₃ layer. The control device is not annealed, the devices with a PbCl₂ interlayer are annealed for 5 (purple) or 15 minutes (green) (b) JV curve for the best MAPbI₃ device with 30 nm of PbCl₂ deposited before the MAPbI₃ layer, annealed for 5 minutes. The blue curve represents the reverse scan from V_{OC} to J_{SC} , while the orange line represents the forward scan from J_{SC} to V_{OC} . (c) JV curves for the MAPbI₃ layer with 30 nm of PbCl₂ deposited after the MAPbI₃ layer, annealed for 15 minutes, showing changes in the J-V curve under continuous scanning. Dashed lines: 1st scan, solid lines: 30th scan.

is well established for record efficiency devices. I expect that this work will renew interest in incorporating Cl into vapour-deposited perovskite PV cells, and expect that further work understanding and minimizing the morphological change brought on by annealing will pave the way for highly efficient, passivated, vacuum-deposited perovskite solar cells.

Chapter 6

Vapour deposited perovskites beyond 2 sources

6.1 Introduction and Background

Despite being highly compatible with large-scale manufacturing, the cost of research scale equipment for vapour deposition is significantly higher than the cost of a spin-coater. This has led to a vast asymmetry in the amount of research effort undertaken on MHP vapour deposition, in comparison to solution processing. Nevertheless, equipment and expertise in vapour-deposition has continued to develop in recent years, with groups installing newer multi-source systems allowing co-deposition of up to 3, 4, or even 5 materials at once. This has allowed significant progress to be made replicating the more complex formulations used in state-of-the-art solution-processed films and needed for tandem devices, including mixed cation [57, 123–125], mixed halide [55, 126], Pb-Sn [127, 128], and 2D-3D perovskites [129]. High-efficiency vacuum processed MHP solar cells (PCE 21.3%) have been demonstrated through sequential sublimation of the precursor materials to form $\text{FA}_{0.95}\text{Cs}_{0.05}\text{PbI}_3$ [130], while large-area (21 cm^2) MAPbI_3 mini-modules deposited through precursor co-evaporation have

reached a respectable 18.1% PCE [41]. However, the move to more complex formulations for MHPs has only exacerbated the need for bulk passivation. Indeed, in their investigation of mixed FA-Cs and I-Br compositions, Gil-Escrig et al. find that most of the non-radiative recombination losses occur within the bulk material rather than the already-optimised interfaces [126]. The presence of electronic traps has been shown to be the driving factor behind I-Br phase segregation [56, 131], a hurdle that must be overcome to achieve higher-bandgap (1.72 eV) [132] materials ideal for tandem applications [133].

In Chapter 5 I demonstrated the passivating effects of using PbCl_2 as a precursor for MAPbI_3 , but also showed that relying on the sublimation of significant amounts of MACl to obtain the correct stoichiometry was detrimental to the film morphology, limiting solar cell performance. In solution-processed films, it is the addition of a small excess of chloride salt to the starting solution that has been shown to enhance crystallization of the perovskite thin-films, leading to improved optoelectronic properties [39, 134, 135]. However, it is not clear if this Cl addition is simply a component that aids the crystallization, or if the residual presence of Cl is playing an active role in the crystallized films. Notably, significant Cl miscibility has been demonstrated in state-of-the-art $\text{FA}_{0.75}\text{Cs}_{0.25}\text{Pb}(\text{I}_{0.8}\text{Br}_{0.2})_3$ compositions, leading to significant improvements in perovskite films for tandem applications [39]. After the work undertaken in Chapter 5, the vacuum-deposition chamber I work on was significantly upgraded to be able to deposit up to 5 materials at once, as detailed in Chapter 3. This allowed me to not only start investigating the more complex FA-Cs mixed-cation formulations, but also use PbCl_2 as an additive rather than the sole Pb precursor, in an attempt to improve bulk passivation of evaporated MHP films.

In this chapter, I investigate if the addition of controllable amounts of Cl-salts to the growth of lead-triiodide perovskite thin films can influence the crystallization and eventual optoelectronic quality of the vapour deposited thin films. I discover that

substituting varying amounts of PbI_2 for PbCl_2 in a co-evaporated mixed-cation tri-iodide system, namely $\text{FA}_{0.83}\text{Cs}_{0.17}\text{PbI}_3$, results in a profoundly positive impact upon both optoelectronic quality and subsequent solar-cell performance. I then discuss the origin of these improvements and find evidence that Cl is retained in the final perovskite films.

I fabricated a series of $\text{FA}_{1-y}\text{Cs}_y\text{Pb}(\text{I}_{1-x}\text{Cl}_x)_3$ perovskite thin films, via simultaneous co-deposition of 4 precursors (FAI , CsI , PbI_2 , PbCl_2), each in its own independently controlled vacuum furnace in a custom-built vacuum deposition system. I started with the neat iodide system of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{PbI}_3$. Then, for each growth run the PbI_2 precursor was progressively substituted by PbCl_2 , such that the total dose of Pb and halide atoms remained the same for all depositions. For example, a 30% PbCl_2 substitution film was formed from 70% PbI_2 and 30% PbCl_2 by molar amount. FAI and CsI deposition rates were kept the same for all films. After deposition, films were annealed in an N_2 glovebox, at 135 °C for 30 mins [124]. The compositions investigated were 0% (neat I), 10%, 20%, 30%, and 40% PbCl_2 substitution. Because additional I is introduced by the A-site precursors, the actual amount of Cl sublimated as a percentage of total halide is given by given by 0%, 7%, 13%, 20%, 27% respectively (rounded to the nearest integer percentage). As discussed later there is uncertainty as to where and how much Cl ends up in the final film, and how it affects the FA:Cs ratio in the perovskite phase; Thus I will henceforth use the former nomenclature of PbCl_2 substitution percentage to denote the films. In addition, the films are made with a slight lead halide excess, even for the neat iodide sample, in accordance to state-of-the-art practices for vapour deposited MHPs [120, 124, 130].

6.2 Material and Electronic Properties

As eluded to above, the first aspect of interest is if any of the chloride from the PbCl_2 remains in the final film, and if it can substitute iodide in a $\text{FA}_{1-y}\text{Cs}_y\text{Pb}(\text{I}_{1-x}\text{Cl}_x)_3$ perovskite structure, since chloride ions have a significantly smaller ionic radius than iodide ions. Indeed, there has been much debate previously as to what extent chloride can substitute iodide in the similar $\text{MAPb}(\text{I}_{1-x}\text{Cl}_x)_3$ structure [29, 109, 115–117, 121, 122], with the most generous reports finding Cl can substitute only up to 3-4% [115]. In Figure 6.1a I show the XRD traces between $2\theta = 12.4^\circ$ and 16.0° (full traces Figure 6.2), which include the PbI_2 (001) peak at $2\theta = 12.7^\circ$ the (100) $\text{FA}_{1-y}\text{Cs}_y\text{Pb}(\text{I}_{1-x}\text{Cl}_x)_3$ bulk perovskite peak at $2\theta = 14.0^\circ$, and the (100) CsPbCl_3 impurity peak at $2\theta = 15.8^\circ$. I observe a reduction in the lattice constant of the bulk perovskite as more PbCl_2 is added, up to 30% PbCl_2 , after which the lattice constant increases again, as shown in Figure 6.1b. Furthermore, as shown in Figure 6.1c, substantial amounts of Cl are detectable in the final films through X-ray photoemission spectroscopy (XPS) measurements, and that the amount of Cl detected in the film increases as more PbCl_2 is added. This change in lattice constant is accompanied by a monotonic increase in CsPbCl_3 impurity phase scattering intensity, for Cl contents above 10% (Figure 6.3). At the same time, I find the excess PbI_2 peak to decrease at first for 10% and 20% PbCl_2 substitution, then increase again for 30% and 40% PbCl_2 , as shown in Figure Figure 6.3. I believe the PbI_2 excess drops initially because of the overall reduction in PbI_2 sublimated, while the subsequent increase is due to the formation and re-evaporation of FACl at the substrate, as discussed in Section 6.3.3. The lattice refinement of my XRD traces was carried out by Dr. Harry Sansom, while the XPS measurements were performed by Dr. Alexandra Ramadan. The Elliot fits to the absorption edges I measured were performed by Karim Elmestekawy.

In Figures 6.1d and e, I show the PL and optical absorption spectra for the same series of films. Up until 30% PbCl_2 substitution I observe a monotonic blue

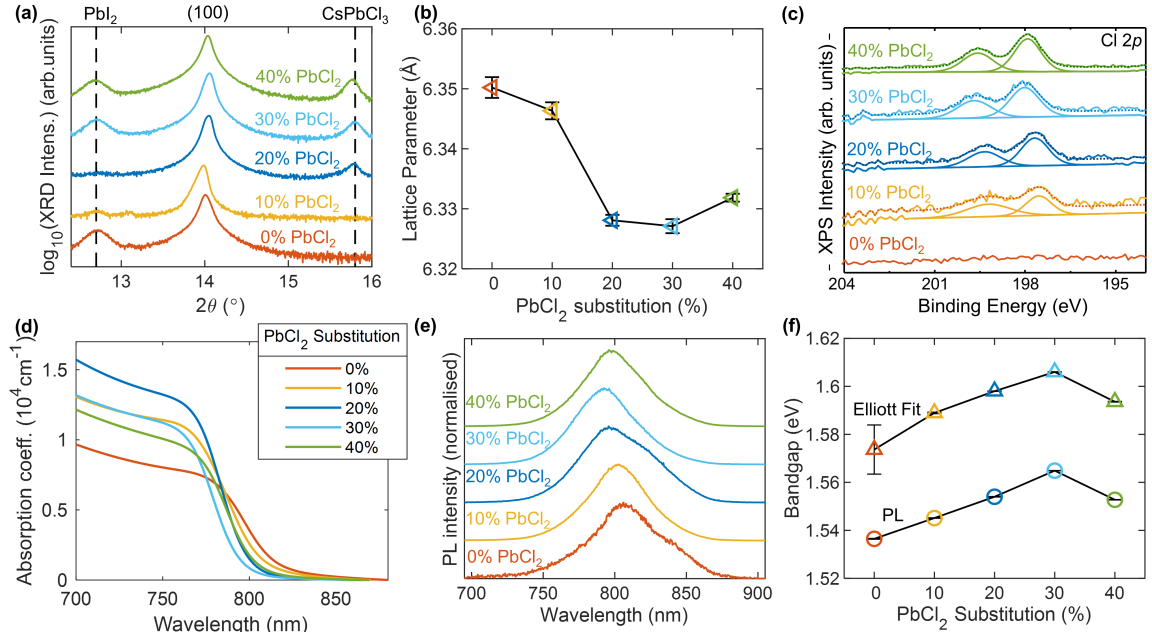


Figure 6.1: Evidence for incorporation of Cl into bulk perovskite. (a) X-ray diffraction patterns of $\text{FA}_{1-y}\text{Cs}_y\text{Pb}(\text{I}_{1-x}\text{Cl}_x)_3$ full photovoltaic devices after testing, grown with varying amounts of PbI_2 substituted for PbCl_2 , as depicted in the legend. The y-axis shows the logarithm of the measured intensity to be able to show both the large perovskite peak and the much smaller PbI_2 and CsPbCl_3 peaks. The XRD spectra were taken with $\text{Cu-K}\alpha$ 1.54 Å X-ray source (b) Lattice parameter obtained from the XRD traces in (a) for the bulk perovskite fitted to a cubic unit cell. Lattice refinement done by Dr. Harry Sansom (c) X-ray photoemission (XPS) high-resolution spectra for thin films of the aforementioned compositions deposited on ITO/PTAA, showing the Cl 2p region. Subfigure and measurements done by Dr. Alexandra Ramadan (d) Absorption coefficient of the aforementioned bare films on quartz (e) Normalized photoluminescence (PL) of the aforementioned bare films on quartz after photoexcitation at 470 nm. (f) Optical bandgap obtained from fits to the PL, and electronic bandgap obtained from Elliott fits to the absorption edge, for the aforementioned bare films on quartz. The Elliot fits were done by Karim Elmostekawy. The error bars in (b) and (f) represent the 1 standard deviation range (68% confidence interval) for the respective fit parameters.

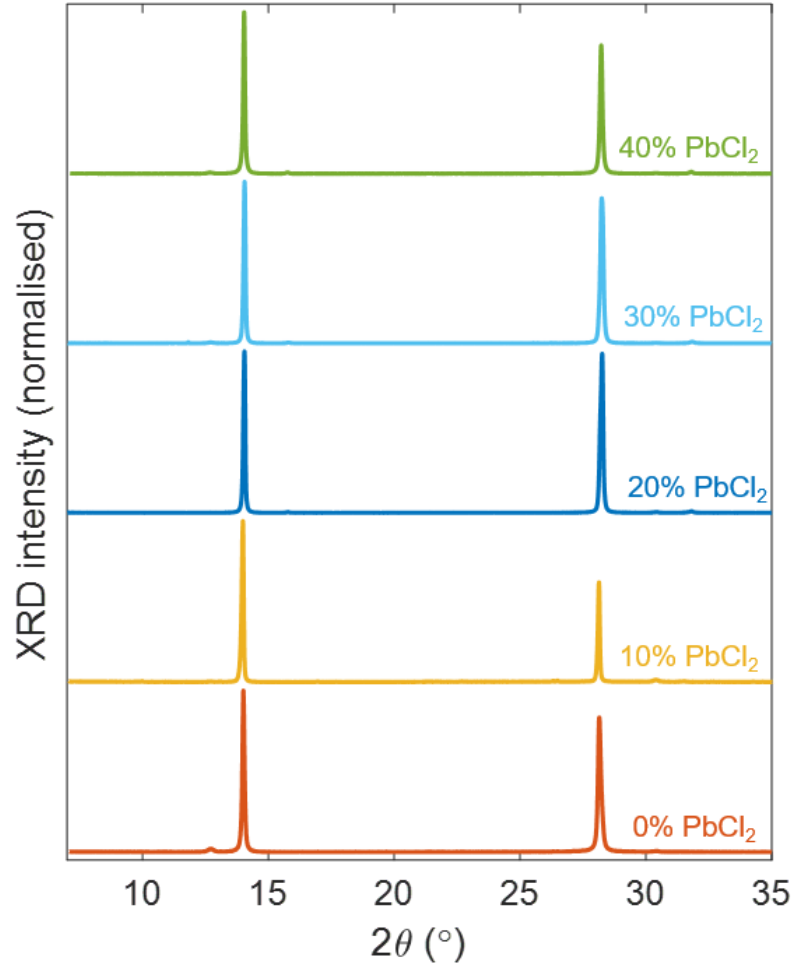


Figure 6.2: X-ray diffraction patterns of vapour deposited $\text{FA}_{1-y}\text{Cs}_y\text{Pb}(\text{I}_{1-x}\text{Cl}_x)_3$ full devices after testing, grown with varying amounts of the PbI_2 substituted for PbCl_2 . Each trace has been normalized with respect to its highest peak.

shift in absorption onset and PL peak position, consistent with a widening of the band gap. This is summarized in Figure 6.1f, which shows a clear trend of the bandgap of the bulk perovskite, obtained either from the PL peak position or fits of the absorption spectra to Elliot's model, increasing as more PbCl_2 is added, up to 30%, after which the bandgap decreases again. The widening of the band gap is consistent with a shrinking of the lattice constant and/or an increased octahedral tilting of the lead-halide octahedra [136]. This is in excellent agreement with the XRD

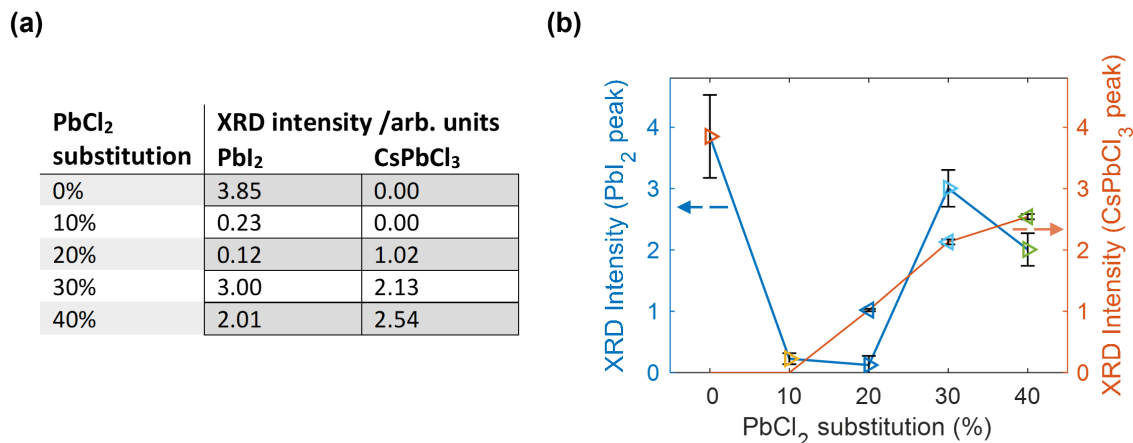


Figure 6.3: (a) Table showing the intensity of the PbI₂ (001) peak and CsPbCl₃ (100) peak of vapour deposited FA_{1-y}Cs_yPb(I_{1-x}Cl_x)₃ full devices after testing, grown with various amounts of PbI₂ substituted for PbCl₂ PbI₂ and CsPbCl₃ intensity. These values were obtained from pseudo-Voigt fits to the corresponding XRD peaks and normalized with respect to the ITO peak of each sample. These values graphically represented in (b)

patterns, which also demonstrate a reduction in lattice spacing. Since this is a multi-component perovskite, the changes in lattice constant and bandgap could originate from multiple sources. Specifically, this widening of the bandgap and reduction of the lattice constant could either originate either from an increase in the Cs content at the perovskite A site or a chloride substitution for iodide at the X site. There have been many studies of Cs substitution of FA at the A site [34, 35]. However, since chloride ions have a significantly smaller ionic radius than iodide ions it is not immediately clear if the X site substitution is possible. Furthermore, the formation of CsPbCl₃ significantly complicates this system, as the latter will remove Cs from the bulk perovskite, causing a red-shift opposing a blue-shift from loss of FA or Cl substitution. As such, the next section explores the amount of Cs and Cl substitution occurring for different CsPbCl₃ formation scenarios. Finally, I find the presence of Cl leads to a slight increase in grain size for low amounts of PbCl₂ substitution, as seen in top-down (Figure 6.4) and cross-sectional SEM (Figure 6.5).

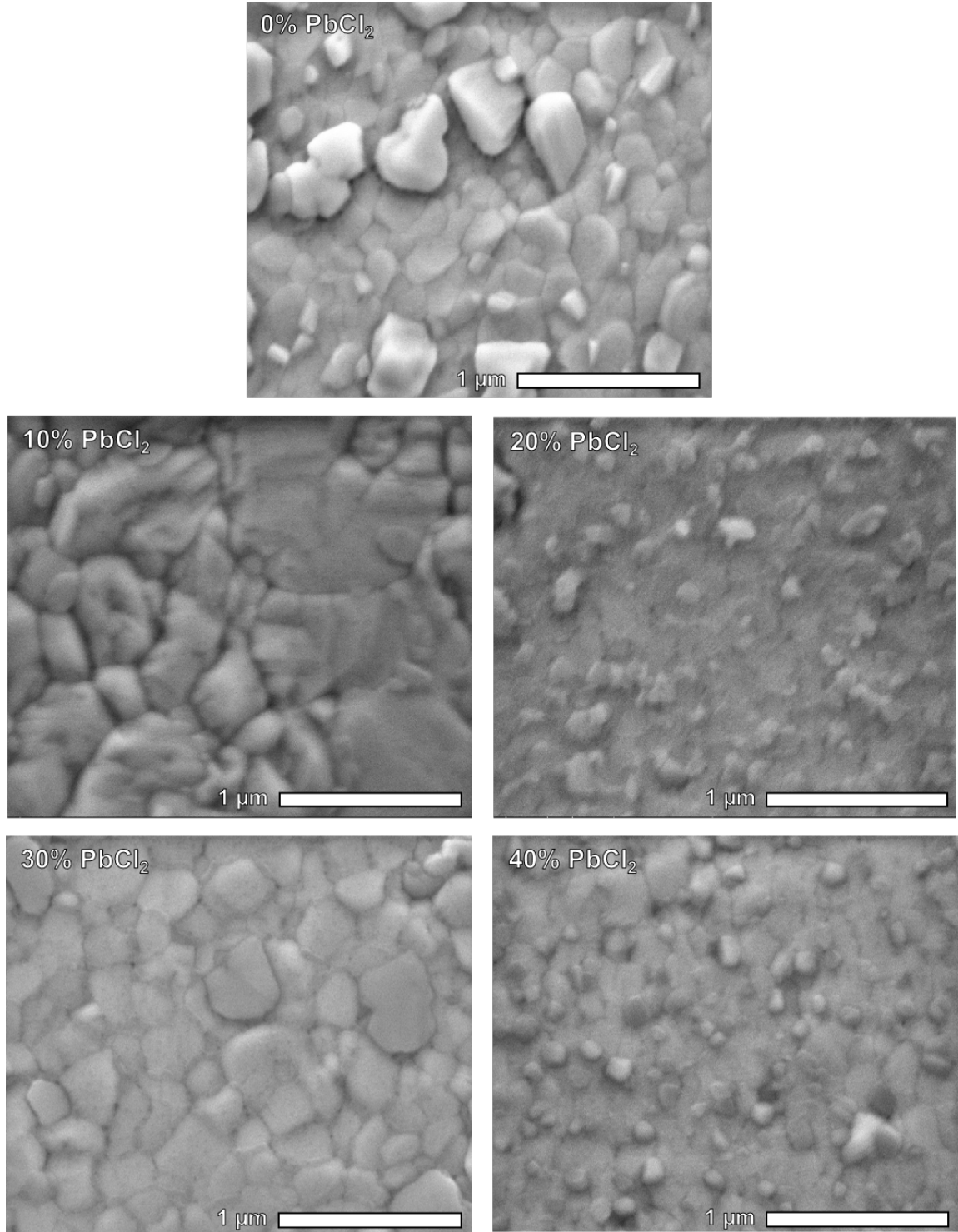


Figure 6.4: Top-down view scanning electron microscope images of vapour-deposited $\text{FA}_{1-y}\text{Cs}_y\text{Pb}(\text{I}_{1-x}\text{Cl}_x)_3$ thin films on ITO/PTAA, grown with varying amounts of PbI_2 substituted for PbCl_2 , as denoted in the top left corner of each image. The scale bars at the bottom left of each image are 1 μm long.

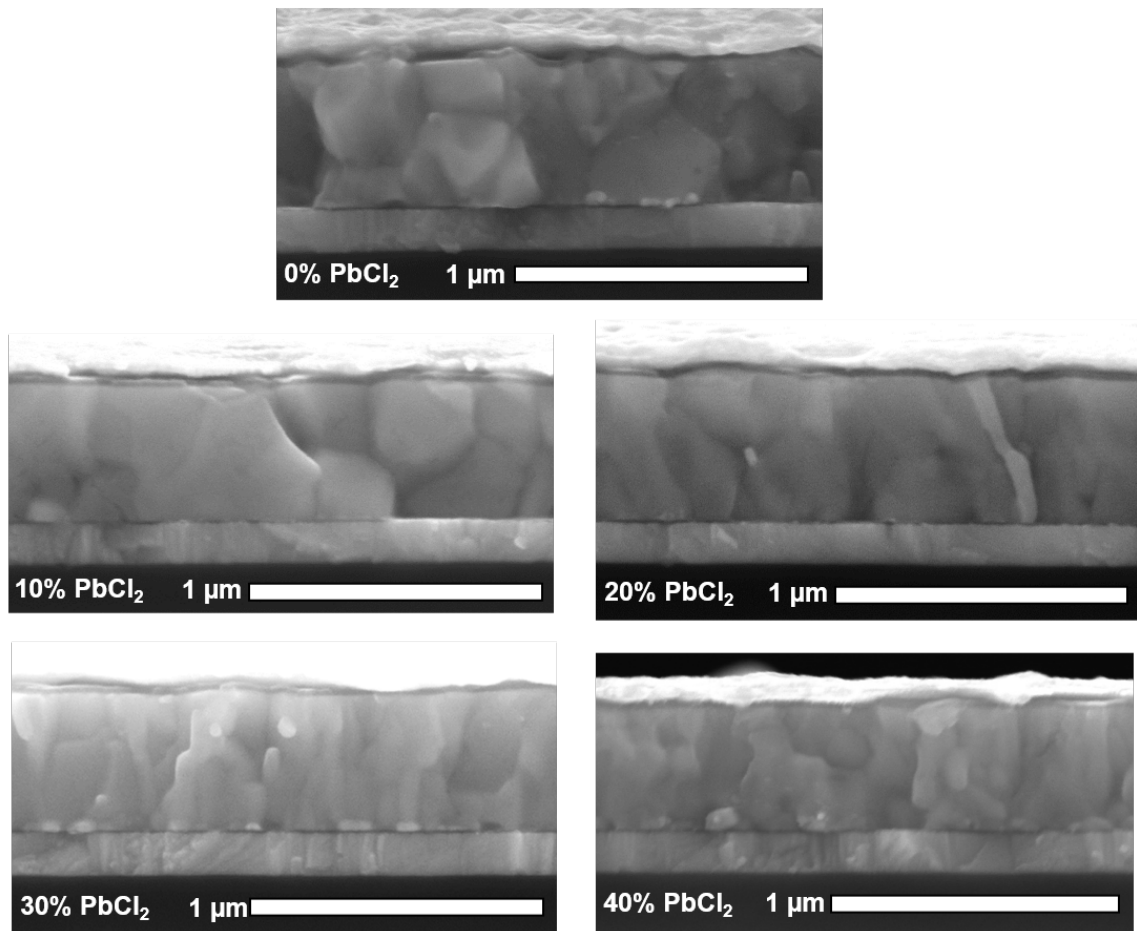


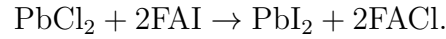
Figure 6.5: Cross-section view scanning electron microscope images of vapour-deposited $\text{FA}_{1-y}\text{Cs}_y\text{Pb}(\text{I}_{1-x}\text{Cl}_x)_3$ full devices, grown with varying amounts of PbI_2 substituted for PbCl_2 , as denoted in the bottom left corner of each image. The scale bars at the bottom left of each image are $1\text{ }\mu\text{m}$ long.

6.3 Cl incorporation

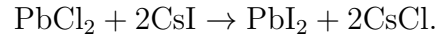
6.3.1 Theory

Because the final perovskite layer consists of multiple components and phases, there are multiple ways for Cl to be used during film formation without ending up in the bulk perovskite. The raw PbCl_2 precursor can have the following reactions with the other precursors:

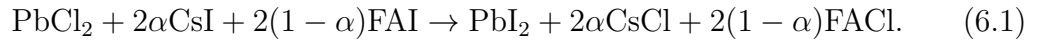
1. React with FAI to form PbI_2 and FACl , according to the following reaction



2. React with CsI to form PbI_2 and CsCl , according to the following reaction

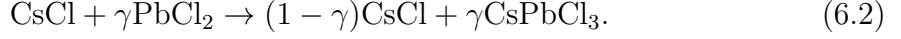


In general these first two equations can be combined by introducing a factor α representing the preference for CsCl formation over FACl , with $0 < \alpha < 1$:

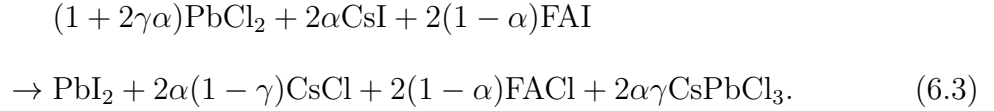


3. Remain unreacted

From my XRD results, I find the phases present in the final film to be PbI_2 , CsPbCl_3 , and some FA/Cs I/Cl mixed perovskite with general formula $\text{FA}_{1-y}\text{Cs}_y\text{Pb}(\text{I}_{1-x}\text{Cl}_x)_3$, where $0 < x, y < 1$. As such, it can be ruled out that large amounts of PbCl_2 remain unreacted. Instead, the possible formation of CsPbCl_3 opens a new pathway for any CsCl formed, namely



Where $0 < \gamma < 1$ represents the percentage of formed CsCl that reacts with PbCl₂ to form CsPbCl₃ i.e. if $\gamma = 0$ no CsPbCl₃ is formed, if $\gamma = 1$ only CsPbCl₃ is formed. By multiplying equation 6.2 by 2α , it can be substituted into equation 6.1, yielding



It is now possible to write down a general equation for the ratio of products based on the factors a, b, α, γ , which define the relative amount of CsI to FAI, the relative amount of PbI₂ to PbCl₂, the relative amount of CsCl formed to FACl formed, and the relative amount of CsPbCl₃ formed for each CsCl. Starting from the precursors evaporated,

$$\begin{aligned} & (1 - a)\text{FAI} + a\text{CsI} + (1 - b)\text{PbI}_2 + b\text{PbCl}_2 \\ & = (1 - a)\text{FAI} + a\text{CsI} + (1 - b)\text{PbI}_2 + \frac{b}{1 + 2\gamma\alpha}(1 + 2\gamma\alpha)\text{PbCl}_2 \\ & \quad + \frac{b}{1 + 2\gamma\alpha}[2\alpha\text{CsI} + 2(1 - \alpha)\text{FAI}] - \frac{b}{1 + 2\gamma\alpha}[2\alpha\text{CsI} + 2(1 - \alpha)\text{FAI}] \\ & \rightarrow [1 - a - 2f(1 - \alpha)]\text{FAI} + (a - 2f\alpha)\text{CsI} + (1 - b + f)\text{PbI}_2 \\ & \quad + 2f\alpha(1 - \gamma)\text{CsCl} + 2f(1 - \alpha)\text{FACl} + 2f\alpha\gamma\text{CsPbCl}_3. \end{aligned} \quad (6.4)$$

Here, the terms highlighted in gray (which sum to 0) have been added to obtain a multiple $f = \frac{b}{1+2\gamma\alpha}$ of equation 6.3 with the terms in blue. Note that this equation is only valid for sufficient amounts of CsI, i.e. $a \geq 2f\alpha$. This represents the moment

when all CsI has reacted to form either CsCl or CsPbCl₃. These cases will be discussed later on. From equation 6.4, it can be seen that Cl could enter the bulk perovskite through CsCl or FACl. If it is assumed that FACl is volatile enough to leave the film during deposition or annealing, but CsCl is able to integrate the bulk perovskite, equation 6.4 can be rearranged into the following products:

$$\begin{aligned} & \text{FA}_{[1-a-2f(1-\alpha)]} \text{Cs}_{(a-2f\alpha\gamma)} \text{Pb}_{[1-b+f(2\alpha-1)]} \text{I}_{[3-2b-4f(1-\alpha)]} \text{Cl}_{2f\alpha(1-\gamma)} \\ & + 2f\alpha\gamma \text{CsPbCl}_3 + f(1-\alpha) \text{PbI}_2 + 2f(1-\alpha) \text{FACl}. \end{aligned} \quad (6.5)$$

From this, it is possible to deduce the fraction of Cs to FA and Cl to I in the bulk perovskite, denoted by y and x respectively in a composition of the form

$$\begin{aligned} y &= \frac{a - 2f\alpha\gamma}{1 - b + f(2\alpha - 1)} \\ x &= \frac{2f\alpha(1 - \gamma)}{3[1 - b + f(2\alpha - 1)]}. \end{aligned}$$

These values can then be used to determine the expected bandgap and lattice parameter of the resulting perovskite. As mentioned earlier, this relationship only holds true while there is enough CsI in the precursors to allow both the desired CsCl and CsPbCl₃ fraction to form. Should this no longer be the case, when $a < 2f\alpha$, there are two scenarios available:

1. Fix the current fraction of CsCl and CsPbCl₃, meaning all additional PbCl₂ reacts with FAI only
2. Allow the CsPbCl₃ to continue to grow, now removing CsCl from the bulk perovskite, until all Cs is in the CsPbCl₃ phase, at which point all additional PbCl₂ reacts with FAI only.

My data shows an initial increase in the bandgap and lattice constant, with the trend reaching a maximum around 20–30% PbCl_2 substitution, followed by a reversal in the trend. Because the only process that could reduce the bandgap and increase the lattice size in this system is the removal of Cs and Cl from the bulk perovskite, I expect the second process to be dominant in this system. With these assumptions I can do simple modelling of the expected lattice parameter and bandgap as a function of PbCl_2 substitution. Figure 6.6 shows 4 different scenarios based on the fraction of CsPbCl_3 formed. The model calculates the Cs and Cl fraction in the bulk perovskite according to the relationships derived above. The bandgap is then calculated assuming linear shifts from one material to the next. Here, I use values of 1.54 eV for FAPbI_3 , previously reported for vapour-deposited films using Elliott fits [137], 1.81 eV for CsPbI_3 , previously reported at room temperature from Elliot fits [138], and 3.00 eV for CsPbCl_3 [139]. To summarize, I obtain the following expression for the bandgap as a function of Cs and Cl substitution (denoted by $0 < y, x < 1$ respectively) of FAPbI_3 ,

$$E_g = 1.54 + 0.27y + 1.19x.$$

I note that my coefficient of y , 0.27, is very similar to that previously reported by Li et al. of 0.28 [35], even though I derive mine from Elliott fits where theirs comes from Tauc plots. In reality, there may be band-bending occurring, especially for the poorly understood I-Cl substitution, since it is observed for I-Br substitution [32]. Band-bending for I-Cl substitution in the same direction as I-Br substitution would result in an underestimate of I-Cl substitution for low x values, so I expect the numerical values obtained to be approximate. Nevertheless, the trends obtained should still reflect the ones observed in my material. The resulting bandgap was calculated for a variety of α and γ values across a range of PbCl_2 substitution. For ease of understanding, the curves were grouped according to the fraction of CsPbCl_3

grown per 3 Cl atoms in the starting products. The resulting bulk perovskite can be seen to vary wildly depending on the formation of CsPbCl_3 , FACl , and the latter's volatility. Comparing to the trends found for my samples in Figure 6.1b and f, it can be seen that I am likely forming a medium amount of CsPbCl_3 per 3 Cl atoms in the starting products, between 0.4 and 0.8 CsPbCl_3 per 3 Cl, depending on how much FACl is formed versus CsCl . Importantly, it can be seen that, in order to obtain the trends I observe, I need some amount of Cl to incorporate into the lattice and increase the bandgap, such that not all Cl I detect in the films can come from CsPbCl_3 . In the following sub-sections I will explore what can be deduced about the formation of FACl and CsCl .

6.3.2 Evidence for Cl in the final films

To determine how much Cl is present in the final films, Dr. Alexandra Ramadan performed XPS measurements, while Dr. Harry Sansom and I performed EDX measurements on the series of films going from 0% to 40% PbCl_2 substitution. The high-resolution spectra of the Cl $2p$ region measured in XPS are shown in Figure 6.1c. Figure 6.7a shows the calculated I:Pb:Cl ratios from the XPS measurements, normalized to the amount of Pb, and Figure 6.7b graphically shows the calculated $\text{Cl}/(\text{I}+\text{Cl})$ ratio as a function of PbCl_2 substitution. It can be seen that we are clearly detecting substantial amounts of Cl in the final films, of the order of 1-10%, with the amount of Cl detected increasing as more PbCl_2 is added. However, the numerical value of Cl detected is only about half of what was originally evaporated.

Lab-based XPS measurements, like the ones carried out in this work, probe depths of up to 10 nm therefore to ensure the detection of Cl was not limited to the surface of the films Dr. Harry Sansom and I also performed EDX measurements on another set of films. Table 6.1 and Figure 6.8a shows the calculated $\text{Cl}/(\text{I}+\text{Cl})$ ratio as a function of PbCl_2 measured from films used for devices (ITO/PTAA/Perovskite/ C_{60} /BCP),

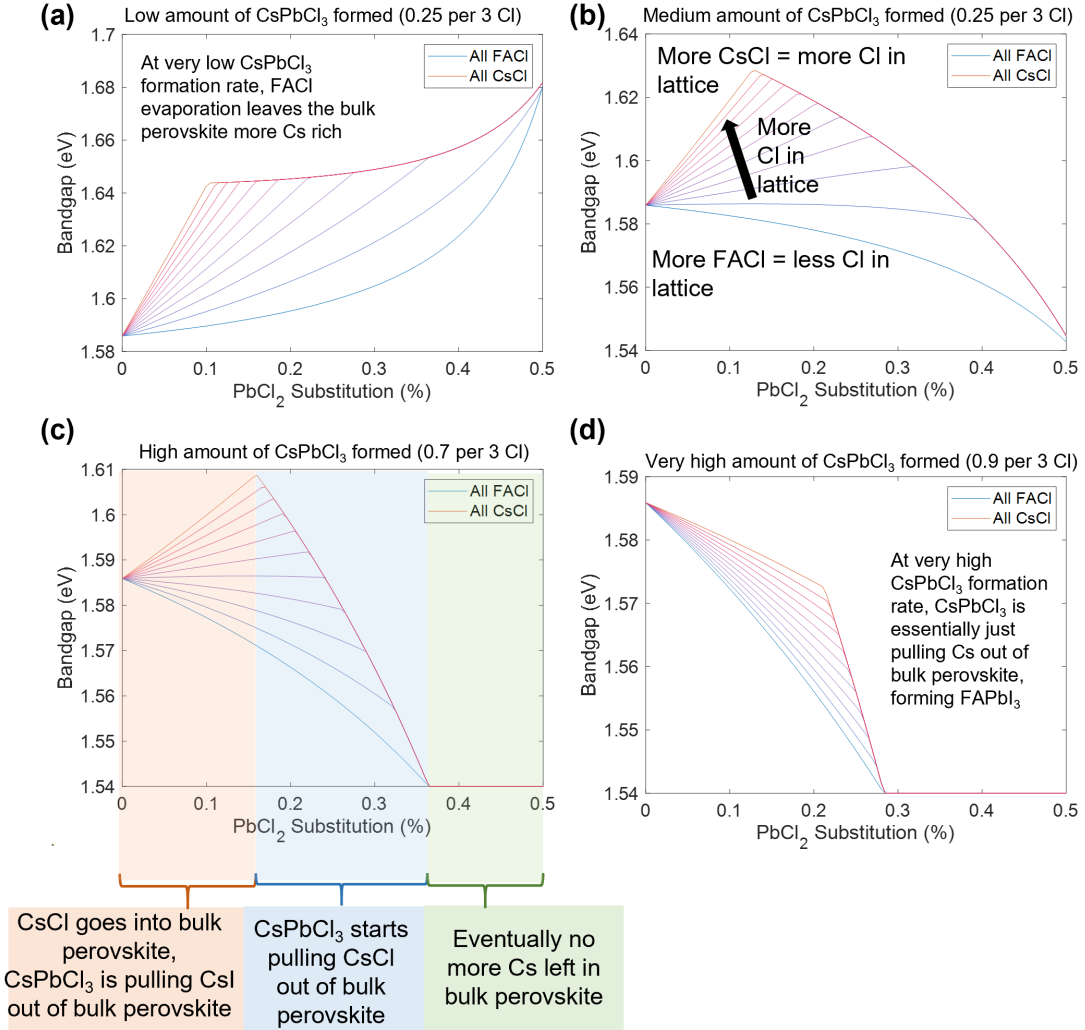


Figure 6.6: Modelling of expected bandgap of $\text{FA}_{1-y}\text{Cs}_y\text{Pb}(\text{I}_{1-x}\text{Cl}_x)_3$, depending on PbCl_2 substitution of PbI_2 , CsPbCl_3 formation, and relative preference of PbCl_2 to form FAPbI₃ or CsPbCl_3 . The CsPbCl_3 formation rate is defined as the fraction of CsPbCl_3 formed per 3 Cl added, i.e. at 1 all Cl goes to form CsPbCl_3 . The CsPbCl_3 formation rates shown here are (a) 0.25 (b) 0.5 (c) 0.7 (d) 0.9. Within each individual graph, the blue line represents the scenario where, other than CsPbCl_3 , only FAPbI₃ is formed. The red line represents the opposite scenario, where only CsPbCl_3 is formed, while the gradient of lines in between represents mixed scenarios with more or less CsPbCl_3 , as depicted in (b). Effectively, the “all FAPbI₃” scenario depicted by the blue line represents no Cl substituting into the bulk perovskite, while the “all CsPbCl_3 ” scenario represents all Cl not forming CsPbCl_3 substituting into the bulk perovskite.

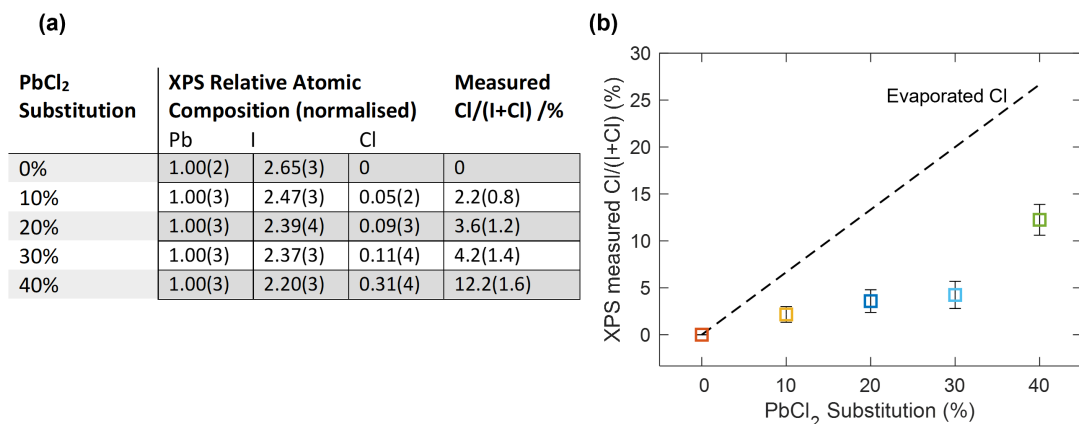


Figure 6.7: (a) Relative atomic composition measured using X-ray photoemission spectroscopy (XPS), normalized to Pb content. (b) Graphical representation of the relative Cl percentage measured in XPS, using the values from the last column of (a). The dashed line represents the Cl/(I+Cl) ratio of the precursors evaporated.

while Figure 6.8b shows EDX measurements for a bare film of the champion 20% PbCl₂ composition before and after annealing. A similar trend to the XPS measurements is observed, with the Cl detected increasing with added PbCl₂, but also more Cl in general, up to 20% for the film with 40% PbCl₂ substitution. We also find only a small change in Cl content before and after annealing, with the final annealed 20% PbCl₂ thin film showing 11.5% Cl, very close to the amount of Cl evaporated, 13.3% (Figure 6.8). Overall, these results show that most of the Cl sublimated ends up in the final film, with only a few percent lost during deposition or annealing.

6.3.3 Evidence for FACl formation

The relative amount of FACl formed during growth and how much of it is re-sublimated has important consequences on the amount of chloride and iodide present in the final films. I believe that, if formed, FACl is likely volatile enough to escape the film during deposition or annealing, based on the behavior observed for MACl in MAPbI₃ grown from MAI and PbCl₂. Specifically, early solution processed perovskite recipes [29], and indeed the first thermal evaporation perovskite PV

PbCl₂ Substitution	Corrected Relative Atomic Composition (normalized)			Measured Cl/(I+Cl) /%
	Pb	I	Cl	
20% as deposited	1.00(2)	2.64(4)	0.43(4)	14.0(1.2)
20% annealed	1.00(2)	2.69(4)	0.35(3)	11.5(1.2)
0% device	1.00(2)	2.96(2)	n/a	0
10% device	1.00(4)	3.09(4)	0.12(4)	3.8(1.2)
20% device	1.00(4)	2.96(3)	0.20(5)	6.2(1.5)
30% device	1.00(3)	2.97(5)	0.27(3)	8.2(0.9)
40% device	1.00(2)	2.63(5)	0.66(4)	20.0(1.3)

Table 6.1: Relative atomic composition measured using energy-dispersive X-ray spectroscopy (EDX) for 500 nm films of $\text{FA}_{1-y}\text{Cs}_y\text{Pb}(\text{I}_{1-x}\text{Cl}_x)_3$ grown with varying amounts of PbI_2 substituted for PbCl_2 . The atomic composition values have been corrected using the factors derived in Table 3, and normalized to the measured Pb content. The table entries labeled as device were all annealed, and capped by C_{60}/BCP .

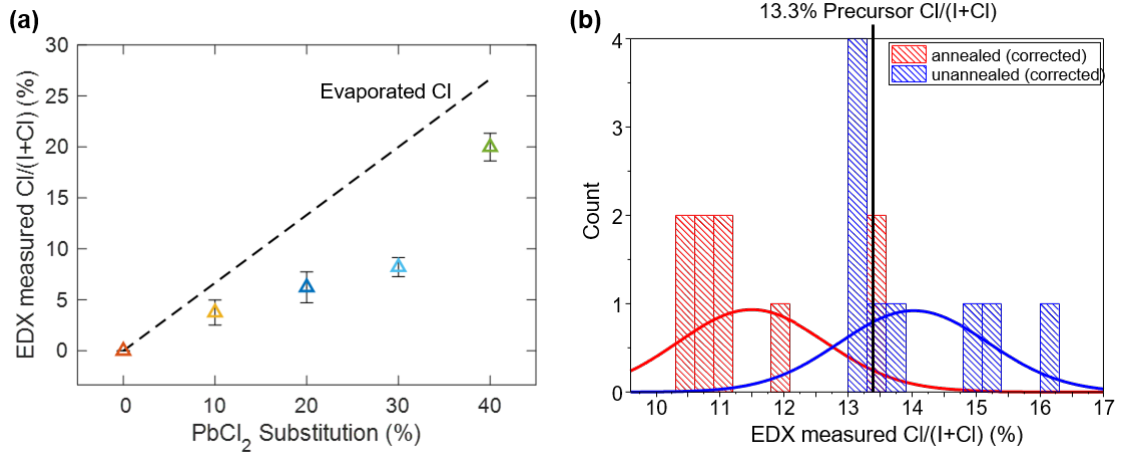


Figure 6.8: (a) Graphical representation of the relative Cl content measured using energy dispersive X-ray spectroscopy (EDX), from the $\text{FA}_{1-y}\text{Cs}_y\text{Pb}(\text{I}_{1-x}\text{Cl}_x)_3$ devices grown with varying amounts of PbI_2 substituted for PbCl_2 . The corresponding numerical values are found in Table 6.1. The dashed line represents the $\text{Cl}/(\text{I}+\text{Cl})$ ratio of the precursors evaporated. (b) Histogram of the relative Cl content measured using EDX for the annealed and unannealed film with 13% Cl at the precursor stage. The black line shows the Cl content present at the precursor stage. Subfigure and measurements done by Dr. Harry Sansom.

publication [49] employed PbCl_2 as the sole Pb source, and relied on volatilization of excess MACl to result in a post annealed film comprising predominantly MAPbI_3 , with only a small amount of Cl substitution. In fact, as discussed in Chapter 5 I found that MAPbI_3 grown via MAI and PbCl_2 already forms pure phase neat I MAPbI_3 before annealing, demonstrating how the high vacuum during deposition is enough to expel MACl already during deposition. Figure 6.9 shows the neat Cl perovskite phase XRD peak for films before and after annealing, and reveals that, while after annealing the position matches that of CsPbCl_3 in all cases, the position shifts to lower angles before annealing for higher PbCl_2 substitution. This reduction in XRD peak position implies an increase in lattice size of the neat Cl perovskite phase, consistent with the increased presence of FA in this phase. As such, this shows this is evidence that, for higher amounts of PbCl_2 , I am indeed forming FACl during deposition, that not all FACl is lost through the high-vacuum during deposition, but that it is all lost through the annealing process.

Equation 6.5 shows that PbI_2 formation is associated with loss of FACl . I find that the XRD PbI_2 peak intensity drops for low amounts of PbCl_2 substitution but increases again from 30% PbCl_2 onwards (Figure 6.3). This is in good agreement with the evidence from the neat Cl phase XRD peak, specifically that there is little FACl loss for PbCl_2 substitution below 30%, but noticeable FACl formation and loss for PbCl_2 substitution over 30%. Finally, I expect the thickness of the resulting films to decrease as more FACl is lost, which can be observed in the SEM cross-sections (Figure 6.5). It is clear that, while the films from 0% to 30% PbCl_2 substitution generally have the expected thickness of 500 nm, the 40% PbCl_2 film is noticeably thinner than the others, consistent with increased loss of material.

The most striking observation is that, while the 30% PbCl_2 and especially the 40% PbCl_2 films show evidence for FACl formation and loss, this is not the case for the 10% and 20% PbCl_2 films. From equation 6.5, it can be deduced that this is likely

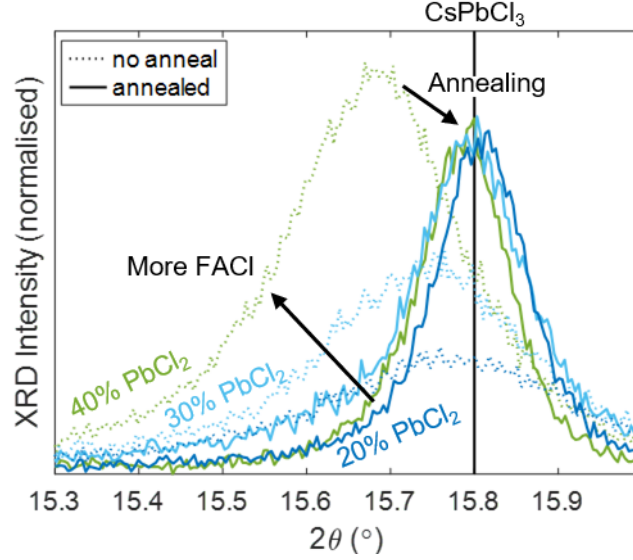


Figure 6.9: X-ray diffraction traces of vapour-deposited $\text{FA}_{1-y}\text{Cs}_y\text{Pb}(\text{I}_{1-x}\text{Cl}_x)_3$ films on ITO/PTAA, grown with 20-40% of the PbI_2 substituted for PbCl_2 . The dashed lines represent films before annealing, the solid lines represent films after a 30 minute anneal at 135°C . The solid black line represents the position of the CsPbCl_3 (100) peak.

related to preferential formation of CsCl over FAPbI_3 i.e., larger values of α . Since the amount of Cs in the film is limited, FAPbI_3 formation will dominate once all CsI has reacted with PbCl_2 , and this is exactly what I observe.

6.3.4 Role of Cl

As mentioned previously, the results I see could be due either to sublimation of FAPbI_3 forming a more Cs -rich bulk perovskite, or direct Cl substitution into the bulk perovskite. However, as discussed in this section, I find no evidence of FAPbI_3 sublimation for composition under 30% PbCl_2 (Figure 6.3, 6.9), and instead evidence of substantial amounts of Cl present in the final films, close to the amount of Cl precursor sublimated, through XPS and EDX (Figure 6.7, 6.8). As such, the simplest interpretation is a mix of direct Cl substitution in the bulk perovskite coupled with growth of CsPbCl_3 , with the latter also causing a decrease in the relative Cs fraction of the bulk perovskite. As the amount of Cs is limited, this last process will eventually lead

to an increase in the lattice constant and decrease in bandgap of the bulk perovskite as more CsPbCl_3 is formed (Figure 6.6). I cannot say from my results exactly how much of the Cl present in the films ends up in CsPbCl_3 versus integrating in the bulk perovskite, but from Figure 6.6 I expect the latter to be of the order of 0.5 to 0.8 CsPbCl_3 formed per 3 Cl sublimated. This corresponds to slightly more than half the Cl sublimated ending up in CsPbCl_3 . This would put the maximum amount of Cl substitution, x , in the bulk perovskite around 5% of the total halide content, for the 30% PbCl_2 film.

6.4 Importance of CsPbCl_3 formation

I investigated the phase stability of the perovskite compositions outlined in this study by measuring the XRD of bare films grown on ITO/PTAA over the course of 30 days, with the films stored in ambient air in the dark (40-50% relative humidity). Figure 6.10 and 6.11 show this data for films before and after annealing, respectively. Note that the unannealed 10% PbCl_2 substitution film proved particularly unstable, and turned completely yellow after 1 week, so this data point is shown instead. In general, I found the films grown with small amounts of Cl, before the formation of CsPbCl_3 to be less crystallographically stable than films with CsPbCl_3 . Notably, the 10% PbCl_2 film, which does not show a CsPbCl_3 peak in XRD, is very unstable before annealing, in contrast to the other films (Figure 6.10).

I was able to replicate this instability in films where the PbCl_2 was introduced separately from the bulk perovskite deposition, as a thin interlayer between the ITO/PTAA and the perovskite. Specifically, I deposited 3 nm and 9 nm of PbCl_2 followed by 500 nm of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{PbI}_3$, grown without PbI_2 excess to account for the additional PbCl_2 . I found that, for 3 nm of PbCl_2 , the films are very unstable, quickly turning into δ -phase CsPbI_3 (Figure 6.12b), in contrast with the films grown

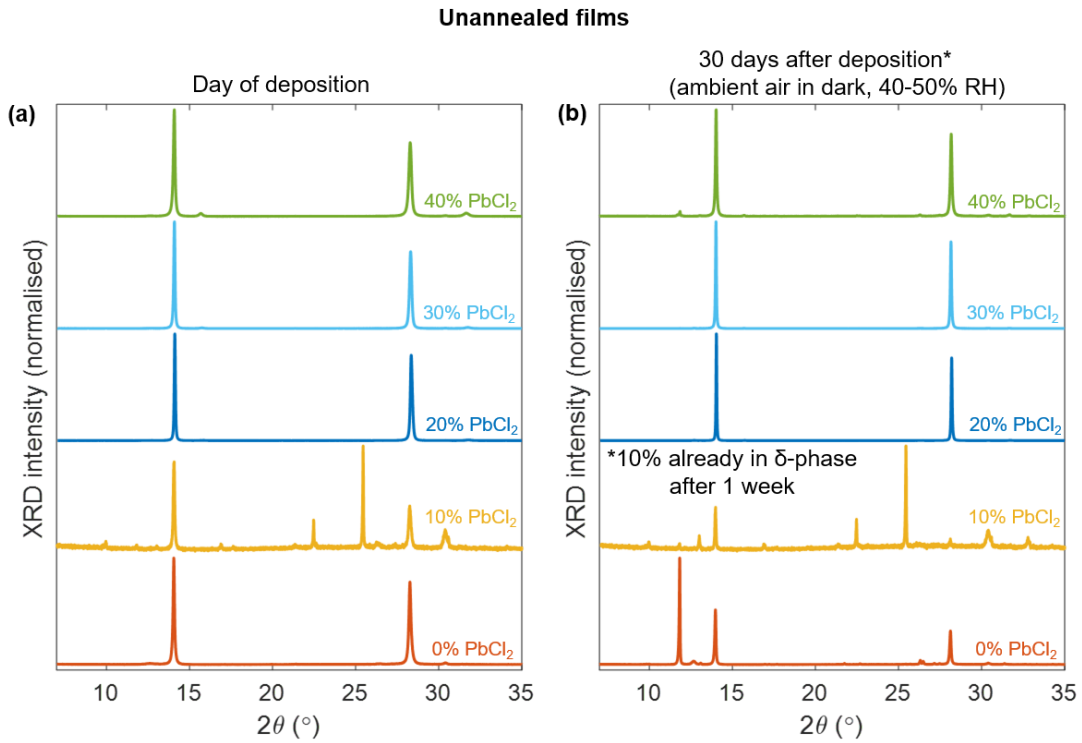


Figure 6.10: X-ray diffraction patterns of vapour deposited $\text{FA}_{1-y}\text{Cs}_y\text{Pb}(\text{I}_{1-x}\text{Cl}_x)_3$ thin films grown with varying amounts of PbI_2 substituted for PbCl_2 , on ITO/PTAA. The films were not annealed before or after measurement. (a) shows the films on the day of deposition, (b) shows the films after 30 days stored in the dark, in ambient air (40-50% RH), apart from the 10% PbCl_2 film, which is shown already after 1 week.

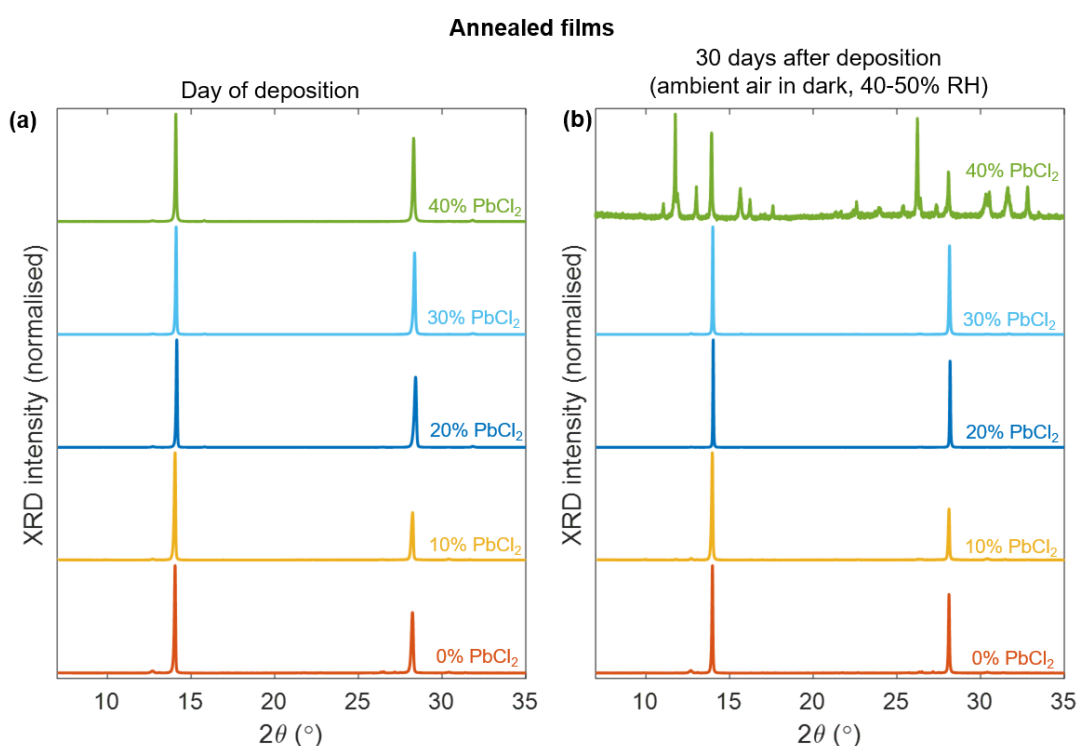


Figure 6.11: X-ray diffraction patterns of vapour deposited $\text{FA}_{1-y}\text{Cs}_y\text{Pb}(\text{I}_{1-x}\text{Cl}_x)_3$ thin films grown with varying amounts of PbI_2 substituted for PbCl_2 , on ITO/PTAA. After deposition, the films were annealed for 30 mins at 135°C . (a) shows the films on the day of deposition, (b) shows the films after 30 days stored in the dark, in ambient air (40-50% RH)

on 9 nm of PbCl_2 , which showed improved photovoltaic performance (Figure 6.13), accompanied by the appearance of a CsPbCl_3 peak (Figure 6.12a). As such, I speculate that the formation of at least some CsPbCl_3 is necessary to stabilize a mixed I-Cl perovskite phase. However, it is worth noting that once larger amounts of CsPbCl_3 are present for the 30% and 40% PbCl_2 films, after annealing the films tend to be less stable again than when CsPbCl_3 just begins to form at 20% PbCl_2 (Figure 6.11), likely due to the loss of FACl described previously.

While the introduction of a 9 nm PbCl_2 interlayer significantly improves the PCE of the devices, the PCE doesn't quite reach that of the films deposited with 20% PbCl_2 substitution, demarked by the grey column in Figure 6.13. Note that, as a baseline for the latter, the performance of the 0% PbCl_2 sample, deposited with excess PbI_2 , should be used, which reaches up to 16.4% PCE, as shown in Figure 6.16. The performance of these devices and the full range of PbCl_2 substitutions investigated is discussed in Section 6.6.

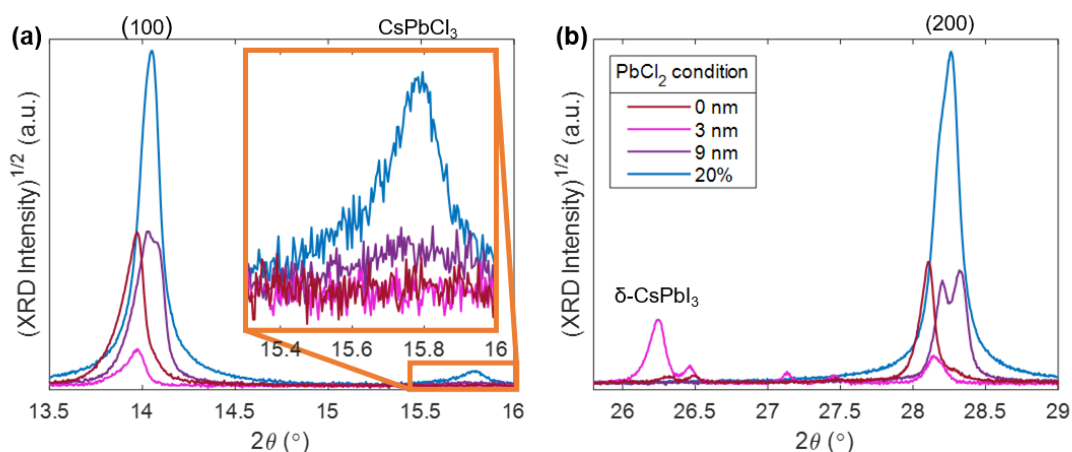


Figure 6.12: X-ray diffraction (XRD) patterns of vapour-deposited $\text{FA}_{1-y}\text{Cs}_y\text{Pb}(\text{I}_{1-x}\text{Cl}_x)_3$ full devices after testing, grown either on top of a PbCl_2 interlayer or with 20% PbI_2 substituted for PbCl_2 , as denoted by the legend. The y-axis shows the square root of the measured intensity to be able to show both the large perovskite peak and the much smaller CsPbCl_3 or δ -phase CsPbI_3 peak. (a) shows the XRD pattern around the bulk perovskite (100) peak, with the inset showing the same pattern zoomed in on the CsPbCl_3 (100) peak. (b) shows the XRD pattern around the (200) bulk perovskite peak

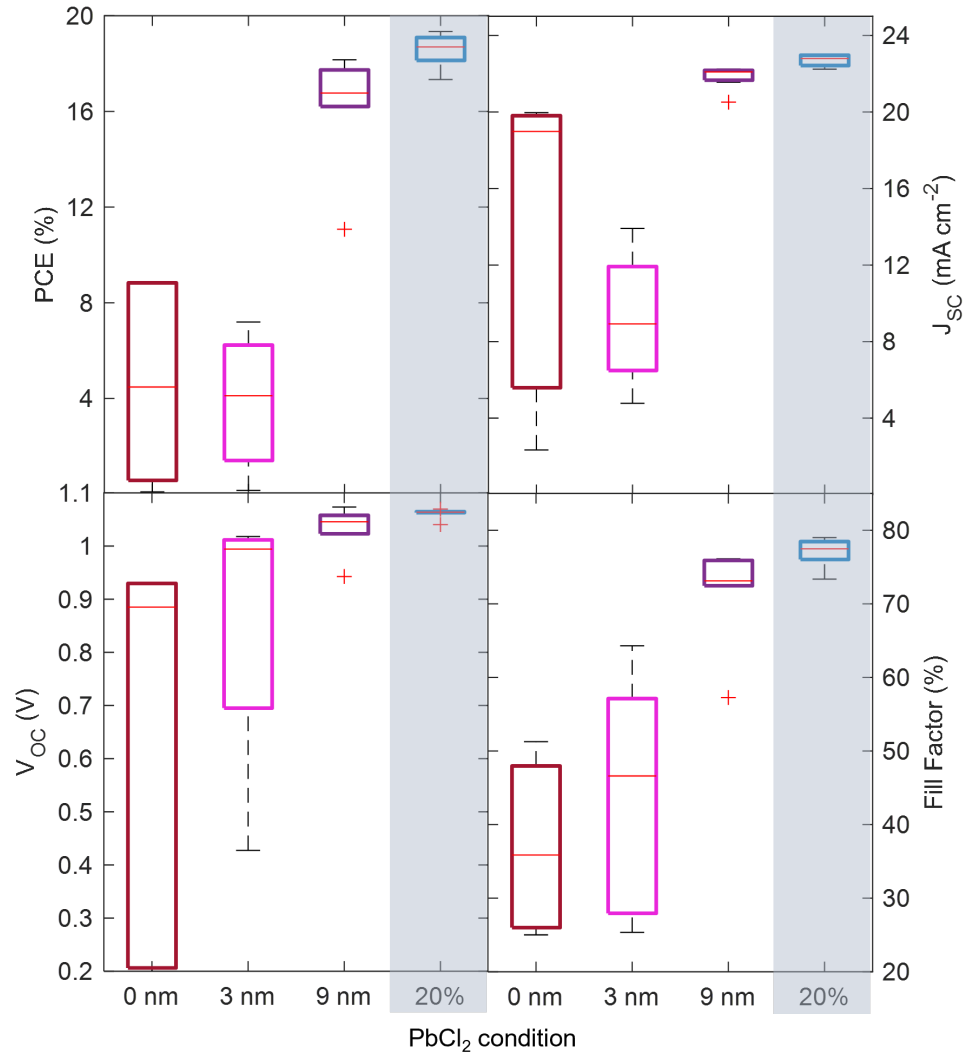


Figure 6.13: JV characteristics of the reverse scan for co-evaporated $\text{FA}_{0.83}\text{Cs}_{0.17}\text{PbI}_3$ devices, grown with either a 0, 3, 9 nm PbCl_2 interlayer before the perovskite, or with 20% of the PbI_2 substituted for PbCl_2 . The grey column demarks how the data from the latter comes from a batch with a different 0% PbCl_2 control sample, shown in Figure 6.16.

6.5 Charge-Carrier Dynamics

I now investigate if the substitution of PbI_2 for PbCl_2 influences the optoelectronic quality of the as crystalized perovskite films. In Figure 6.14a I show the TRPL transients for the 5 compositions investigated in this work. I observe a dramatic increase in the PL decay lifetime over the entire concentration range, consistent with a significant reduction in the nonradiative trap-assisted recombination rate, and consequent enhancement in the charge-carrier lifetimes for $\text{FA}_{1-y}\text{Cs}_y\text{Pb}(\text{I}_{1-x}\text{Cl}_x)_3$ films. I summarize the charge-carrier lifetimes obtained from stretched exponential fits to these TRPL decays in Figure 6.14c, which reveal an increase of over an order of magnitude even when only a small fraction of Cl is added. A similar trend is observed for PL quantum yield (PLQY) measurements of neat films acquired by Robert Oliver following the procedure by Mello et al. [140] (Figure 6.14c), which show a jump from values close to the experimental detection limit of 0.02% for the neat iodide films to 0.3% for the 40% PbCl_2 film. Together, these measurements clearly demonstrate that processing with fractional substitution of PbI_2 for PbCl_2 has an effect of reducing non-radiative recombination in the co-evaporated $\text{FA}_{1-y}\text{Cs}_y\text{Pb}(\text{I}_{1-x}\text{Cl}_x)_3$ films. This may be due to fewer crystalline defects being present in the film grown with PbCl_2 , or an active passivation effect of the Cl ions. The order of magnitude increase in photocarrier lifetimes matches that previously observed between the vapour deposited MAPbI_3 [86, 120] and $\text{MAPbI}_{3-x}\text{Cl}_x$ [122, 141] I investigated in Chapter 5, though even the latter only displayed TRPL lifetimes up to 83 ns [141].

To probe the charge carrier mobility in the perovskite films, Dr. Silvia Motti performed OPTPS measurements [141], which are shown in Figure 6.14b and d, with the full decays shown in Figure 6.15. A monotonic increase in mobility is observed when increasing the Cl fraction up to 20%, with the charge carrier mobility increasing from $46 \text{ cm}^2/\text{Vs}$ for the neat iodide perovskite to $56 \text{ cm}^2/\text{Vs}$ for the sample made with 20% Cl. Charge carrier mobility in metal halide perovskites is controlled by a

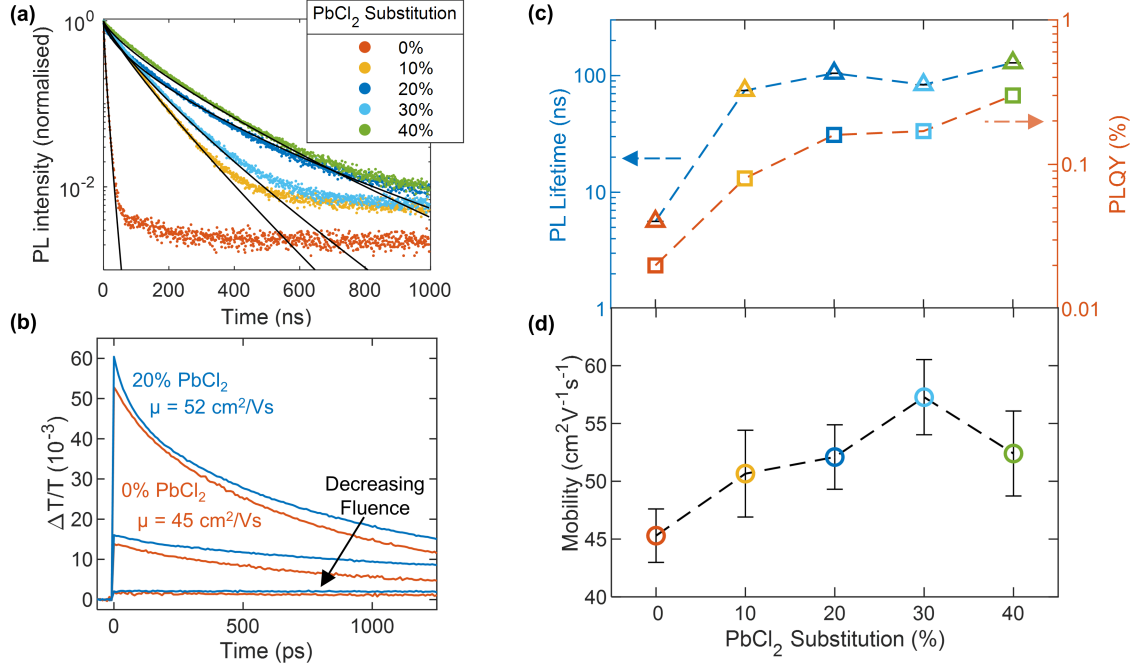


Figure 6.14: Evidence for defect passivation with Cl addition. (a) Time-resolved photoluminescence (TRPL) traces of $\text{FA}_{1-y}\text{Cs}_y\text{Pb}(\text{I}_{1-x}\text{Cl}_x)_3$ thin films on z-cut quartz, grown with various amounts of PbI_2 substituted with PbCl_2 , after photoexcitation by a 1 MHz-pulsed 470 nm laser, at fluence $20 \mu\text{J}/\text{cm}^2$. The solid lines show the stretched exponential fits. (b) Optical-pump THz-probe (OTTP) photoconductivity transients of the aforementioned bare films for 0% and 20% PbCl_2 , on quartz after photoexcitation at 400 nm, as a function of fluence (1.0, 10, $42 \mu\text{J}/\text{cm}^2$). Measurements performed by Dr. Silvia Motti. (c) Photocarrier lifetimes (blue, left) and photoluminescence quantum yield (PLQY) (red, right) of the aforementioned bare films on quartz. The lifetimes were obtained from stretched exponential fits to time-resolved photoluminescence (TRPL) traces, which were obtained by photoexciting the samples with a 1 MHz pulsed 470 nm laser with fluence $20 \mu\text{J}/\text{cm}^2$. The PLQY was obtained through 532 nm photoexcitation at 24 mWcm^{-2} intensity, and performed by Robert Oliver. (d) Charge carrier mobilities obtained from optical-pump THz-probe spectroscopy done on the aforementioned bare films. Data collection and analysis performed by Dr. Silvia Motti.

combination of phonon scattering and scattering from defects. The estimated limiting mobilities for a material only governed by phonon scattering is on the order to $100 \text{ cm}^2/\text{Vs}$ [142, 143], hence the charge carrier mobility in the materials measured here is likely to be limited by defect scattering. The increase in mobility with increasing PbCl_2 fraction, is therefore consistent with a reduction of the defect density, on the length-scale relevant to charge carrier scattering. Notably, these mobility values are much larger than those reported previously for other thermally evaporated perovskites, which have been reported at $13.0 \text{ cm}^2/\text{Vs}$ for MAPbI_3 [120], $33 \text{ cm}^2/\text{Vs}$ for $\text{MAPbI}_{3-x}\text{Cl}_x$ [141] and $26 \text{ cm}^2/\text{Vs}$ for FAPbI_3 [54]. This first of all highlights the benefits of moving from FAPbI_3 to $\text{FA}_{0.83}\text{Cs}_{0.17}\text{PbI}_3$ even in the absence of Cl passivation, and then exemplifies how much of an improvement these $\text{FA}_{1-y}\text{Cs}_y\text{Pb}(\text{I}_{1-x}\text{Cl}_x)_3$ films represent over the previous state-of-the-art. These findings also imply that the growth of the higher-bandgap $\sim 3.0 \text{ eV}$ CsPbCl_3 phase [139, 144] does not introduce additional charge-carrier traps in the film. In fact CsPbCl_3 may even play a role in passivating these traps, specifically because it has a higher bandgap and seemingly forms a good interface with the iodide bulk perovskite.

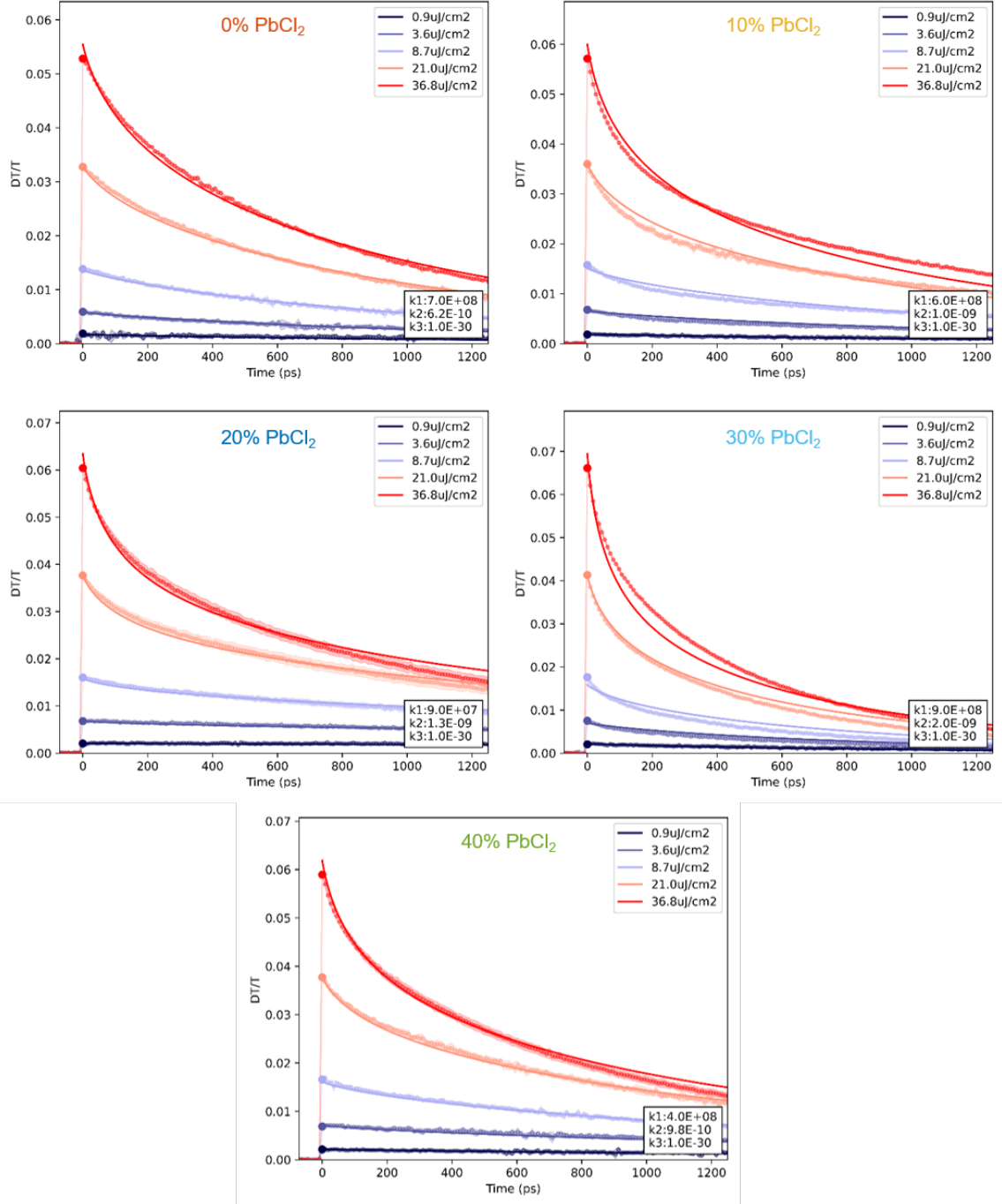


Figure 6.15: OPTPS photoconductivity transients obtained from vapour-deposited $\text{FA}_{1-y}\text{Cs}_y\text{Pb}(\text{I}_{1-x}\text{Cl}_x)_3$ thin films on z-cut quartz, grown with varying amounts of PbI_2 substituted for PbCl_2 . The thin solid lines represent the fits to the data. Data collection, fitting performed by Dr. Silvia Motti.

6.6 Solar Cell Performance

I now investigate how PbCl_2 substitution and the improved crystallographic and optoelectronic properties affect the performance of solar cells based on co-evaporated $\text{FA}_{1-y}\text{Cs}_y\text{Pb}(\text{I}_{1-x}\text{Cl}_x)_3$. I fabricated devices with the following p-i-n architecture: indium-doped tin oxide (ITO) as the bottom contact; followed by PTAA as the HTL; the perovskite $\text{FA}_{1-y}\text{Cs}_y\text{Pb}(\text{I}_{1-x}\text{Cl}_x)_3$; C_{60} as the ETL with a thin BCP buffer layer; and capped by Ag as the top contact. In Figure 6.16a I show boxplots for JV scans obtained from solar cells made using the PbCl_2 -substituted perovskite compositions, demonstrating significant enhancement in all JV figures-of-merit for the mid-range of PbCl_2 substitution. Indeed, the champion device PCE improves from 16.5% (14.1% steady-state) for the neat iodide film to 19.3% (18.7% steady state) for 20% PbCl_2 substitution, through improvements in J_{SC} , V_{OC} , and FF (Figure 6.16b, 6.17, EQE Figure 6.18). The values of the JV figures-of-merit are shown in Table 6.2. I tested both 0.25 and 1 cm^2 devices, and found that the increased area only lowered efficiencies slightly, with the champion 1 cm^2 device reaching 18.0% PCE (18.0% steady-state) (Figure 6.19). While performance initially improves as more PbCl_2 is added, the PCE of the devices drops after 20% PbCl_2 substitution, primarily driven by a drop in FF. In addition, I observed that, surprisingly, some of the 30% PbCl_2 devices showed a phase instability under illumination, resulting in significantly reduced performance. These devices are not included in Figure 6.16a, but are shown in Figure 6.20. The initial boost in both J_{SC} and V_{OC} are consistent with the reduced non-radiative recombination, increased charge carrier lifetime and improvement in charge carrier mobility.

It is worth noting that even though optoelectronic properties generally continue to improve for higher Cl concentrations, this is not reflected in the PCE, largely due to a significant drop in FF. The main culprit for this drop is likely to be the increased presence of CsPbCl_3 in the higher percentage PbCl_2 films: while optoelectronic properties

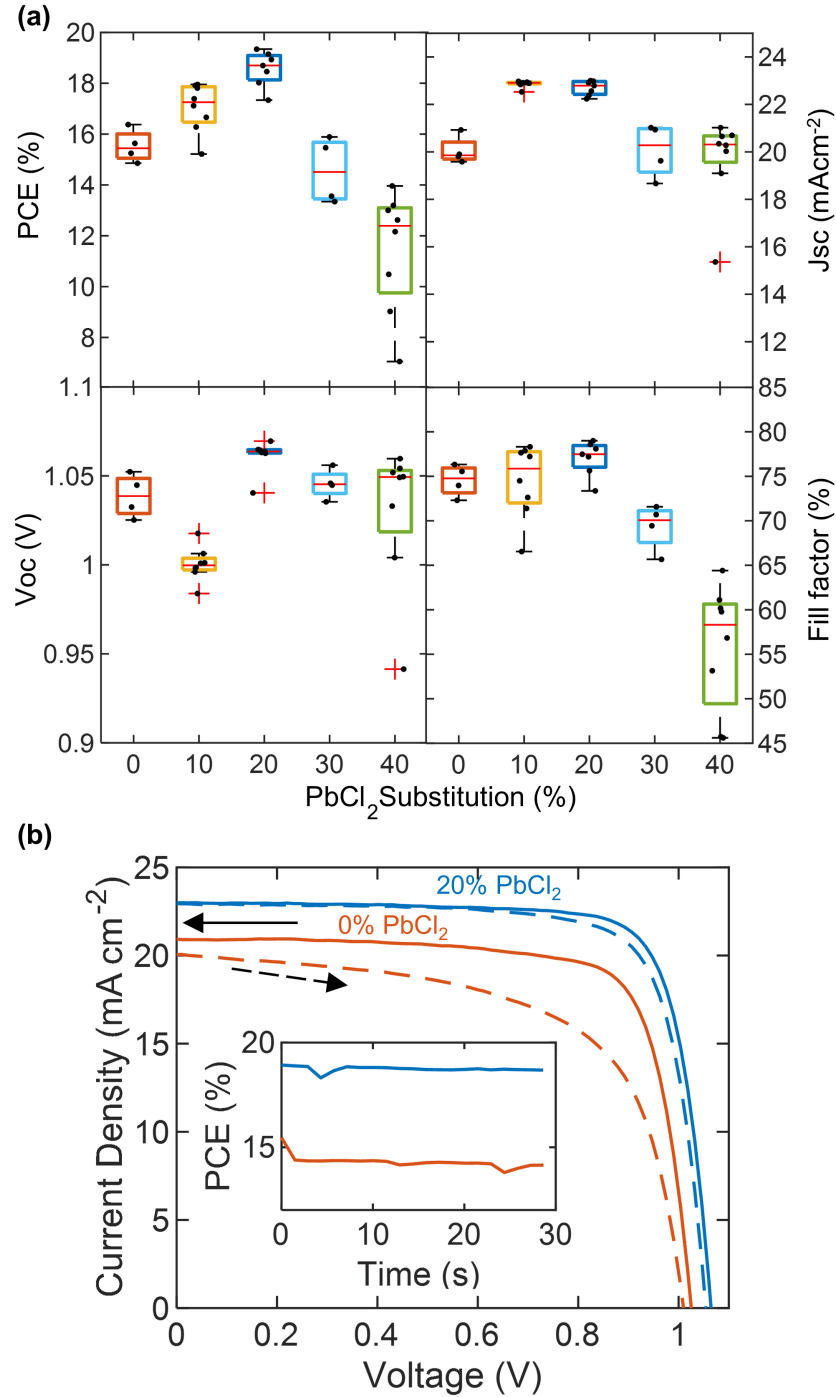


Figure 6.16: Solar cell performance optimal at 20% PbCl_2 . (a) Current-voltage (JV) characteristics for reverse scans of 0.25 and 1 cm^2 devices made from $\text{FA}_{1-y}\text{Cs}_y\text{Pb}(\text{I}_{1-x}\text{Cl}_x)_3$, tested under simulated AM1.5 solar irradiance. The solar cells were made with the following p-i-n structure ITO/PTAA/perovskite/ C_{60} /BCP/Ag. (b) Current-voltage (JV) measurements of the champion 0% and 20% PbCl_2 devices, as measured under reverse bias (solid line) and forward bias (dashed line). The inset shows the power conversion efficiency (PCE) measured at max power point under continuous illumination over 30 s.

PbCl ₂ Substitution /%	PCE /%	J _{SC} /mAcm ⁻²	V _{OC} /V	FF /%
0	16.4 (15.53)	20.9 (20.05)	1.03 (1.038)	76.3 (74.54)
10	18.0 (17.04)	23.0 (22.86)	1.01 (1.000)	77.7 (74.51)
20	19.3 (18.56)	23.0 (22.70)	1.06 (1.061)	79.0 (77.05)
30	15.9 (14.56)	21.0 (20.06)	1.06 (1.046)	71.6 (69.35)
40	14.0 (11.44)	20.7 (19.68)	1.05 (1.030)	64.4 (55.85)

Table 6.2: JV characteristics of the reverse scans of evaporated FA_{1-y}Cs_yPb(I_{1-x}Cl_x)₃ devices with various amounts of Cl. The table shows the champion device data with the average device data in italics, in parentheses.

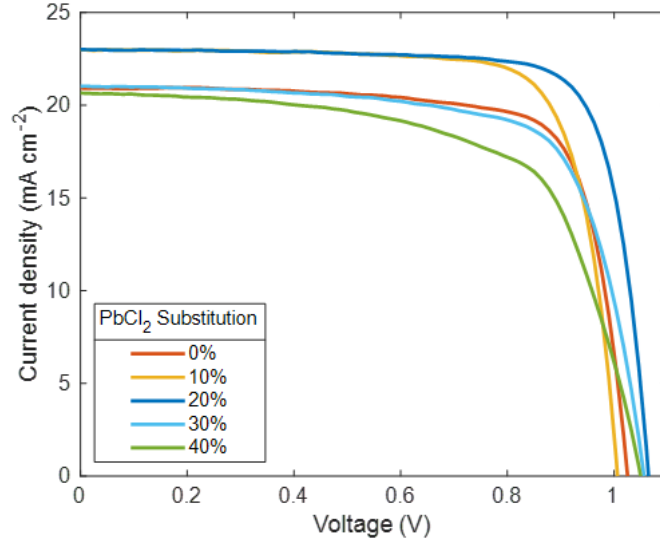


Figure 6.17: Reverse JV scans for the champion device of the champion FA_{0.83}Cs_{0.17}PbI₃ devices, grown with varying amounts of PbI₂ substituted with PbCl₂, as denoted in the legend.

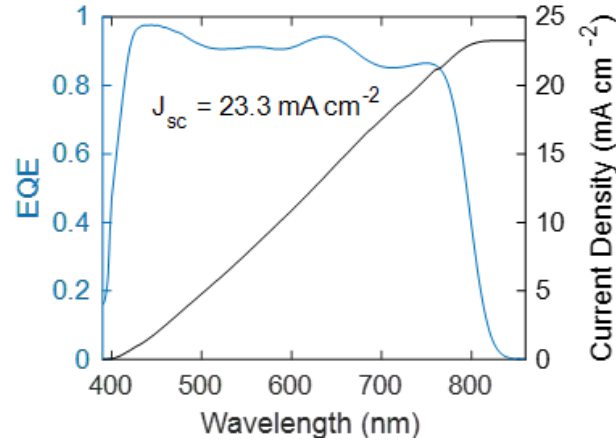


Figure 6.18: EQE (blue line) and the corresponding integrated current density (black line) at AM1.5 for a $\text{FA}_{1-y}\text{Cs}_y\text{Pb}(\text{I}_{1-x}\text{Cl}_x)_3$ device grown with 20% of the PbI_2 substituted with PbCl_2 .

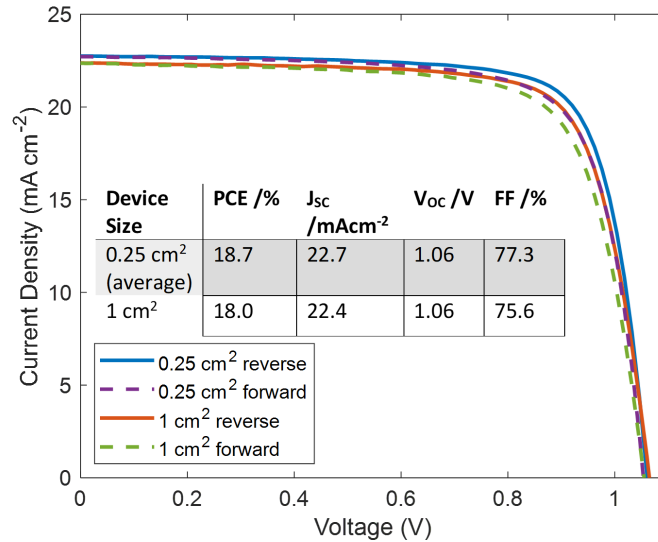


Figure 6.19: JV scans for vapour-deposited $\text{FA}_{1-y}\text{Cs}_y\text{Pb}(\text{I}_{1-x}\text{Cl}_x)_3$ devices, grown with 20% of the PbI_2 substituted with PbCl_2 at the precursor stage, according to device size. The JV curve for the 0.25 cm² devices was calculated by averaging the JV curves of all 0.25 cm² devices. The inset table shows the JV figures of merit for the reverse scans shown in the figure

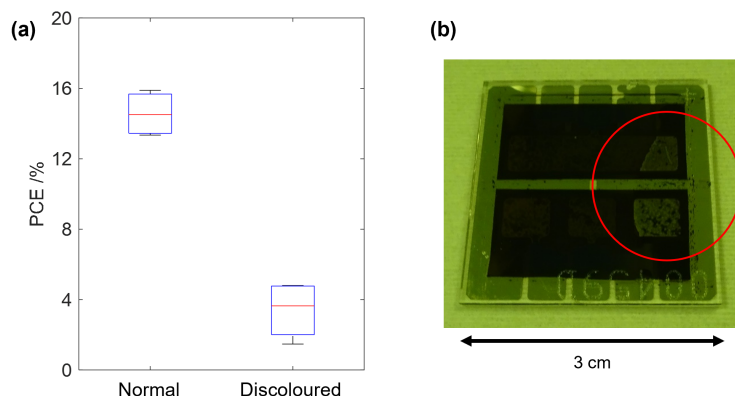


Figure 6.20: (a) JV characteristics for vapor-deposited $\text{FA}_{1-y}\text{Cs}_y\text{Pb}(\text{I}_{1-x}\text{Cl}_x)_3$ devices, grown with 30% of the PbI_2 substituted with PbCl_2 at the precursor stage, according to whether the devices showed normal behavior, or discolouration after illumination. (b) A photograph of one of the solar cells tested, showing two discoloured devices circled in red.

show CsPbCl_3 to be benign or beneficial for reducing non-radiative recombination, inclusions of higher bandgap CsPbCl_3 will act as high-energy obstacles for charge-carrier transport in the surrounding iodide-rich perovskite phase. As such, I conclude that the optimum amount of PbCl_2 substitution is around 20%, when small inclusions of a CsPbCl_3 phase just begin to form. This is in a good agreement with a series of films where the PbCl_2 was introduced as a thin interlayer before the $\text{FA}_{0.83}\text{Cs}_{0.17}\text{PbI}_3$ perovskite, which also show improved PCE when CsPbCl_3 first starts to form (Figure 6.12, 6.13 in Section 6.4), and the recent results of Min et al. showing the benefits of a thin FASnCl_x layer at the ETL [145].

6.7 Conclusion

In conclusion, I demonstrated PbCl_2 as a viable in-situ defect passivant for $\text{FA}_{0.83}\text{Cs}_{0.17}\text{PbI}_3$ vapour deposited MHP solar cells, effective both as an interlayer before deposition and deposited in the bulk. I observed Cl retention with the as-processed films, and show evidence of a small fractional substitution of Cl at

the X site of the perovskite crystal with maximum uptake observed for 30% PbCl_2 processed film exhibiting a Cl substitution in the perovskite crystal of 5%, resulting in an electronic bandgap of 1.6 eV. In general, PbCl_2 substitution resulted in films of excellent optoelectronic properties. These films show extremely low energetic disorder, and exhibited improved crystallinity as well as increased radiative efficiency, PL lifetimes and charge-carrier mobility. These enhancements led to solar cells with significantly improved PCE of up to 19.3% (18.7% steady-state) for devices with 20% PbCl_2 substitution. I expect that this work will lay the foundations for incorporating Cl into vapour deposited perovskite PV cells, and expect that further efficiency improvements may result from extending this approach to Br-based MHPs to yield highly efficient, passivated, vacuum deposited multijunction solar cells.

To date the performance of MHP solar cells fabricated via vapour-deposition has lagged behind solution-processed cells, despite vapour deposition being a process that can easily deliver highly conformal MHP thin films. This has largely been due to the much shorter charge-carrier lifetimes typically observed in vapour-deposited MHP films. My work here has shown a clear and effective strategy to achieving the highest quality thin films from vapour deposition and will lead to significant improvements in the performance of vapour-deposited MHP solar cells in the near future. Moreover, this “dry” solvent-free processing methodology is already compatible with high-volume manufacturing.

Chapter 7

Conclusions and Outlook

In conclusion, this thesis presents the potential of vacuum co-evaporation as a viable, upscalable technique for MHP solar cells, and how the optoelectronic properties of the MHP films can be tuned by changing various deposition parameters. Over the past few years, highly efficient single-junction-perovskite, silicon-perovskite-tandem and perovskite-perovskite-tandem solar cells and modules have been demonstrated. As a result, a major research focus is now how to upscale these lab-based successes into widespread real-world applications. Vacuum co-evaporation is an ideal candidate for this, as it allows for uniform depositions over large areas, and has already been used in other commercial semiconductor applications. The main challenges facing vacuum-deposited MHP solar cells are the difficulty in reproducibly controlling the deposition of the organic precursors such as MAI, and forming high-efficiency low-bandgap Sn-based and high-bandgap Br-based perovskite formulations for use in tandem cells. For the latter, a necessary step is to find passivation methods compatible with large-area vacuum deposition. In this thesis, I started by focusing on the issue of MAI deposition control, then moving to investigating pathways to improving the optoelectronic properties of these materials.

In Chapter 4 I investigated the effects of changing the substrate temperature on

the resulting MAPbI₃ thin films. I found MAI adsorption rate to be very sensitive to substrate temperature. Indeed, when lowering the temperature of the substrate, MAI adhesion significantly increased, leading to formation of thin-films with significantly enhanced grain-growth. This allowed me to compare the effects of grain size on the optoelectronic properties and device performance. While the larger-grain material showed improved photoluminescence lifetimes, the charge-carrier mobility was significantly hampered, which I attributed to the enhanced grain-growth coming at the cost of more organic-rich grain boundaries detrimental to charge transport. This is because I found that a small excess of PbI₂ in the film is crucial to good charge transport and high solar cell PCE. As such, for evaporated perovskites, the absolute grain size appears less important than the stoichiometry of the grain boundaries, with a slight PbI₂ excess being the most desirable condition. Finally, in order to carry out this work, I devised a new method of controlling the MAI sublimation rate, using a sensor located near the substrate that also sees PbI₂. The presence of PbI₂ on the sensor leads to more consistent MAI adhesion, allowing better reproducibility through the substrate rate. Using this method, I was able to fabricate champion devices of 18.3% PCE. This method of substrate rate control has since been successfully used by another group [126], exemplifying the validity of this method.

In Chapter 5, I explored the use of PbCl₂ as a replacement for PbI₂ in the vapour-deposition of MAPbI₃. I found that MAPbI₃ deposited through MAI and PbCl₂ resulted in films of substantially enhanced photogenerated charge-carrier lifetimes of over an order of magnitude, as compared to films deposited through MAI and PbI₂. However, the MAcl that is formed as a by-product of the PbCl₂-route was detrimental to film morphology, resulting in devices with similar performance to the control ones deposited with PbI₂. Surprisingly, the high charge-carrier lifetimes observed for the PbCl₂-route devices appeared independent of surface morphology, consistent with a well passivated surface. Overall, this indicated the potential of PbCl₂ as a passivant in

vapour-deposited perovskites, but showed that it was likely better used as an additive in small quantities rather than relying on the sublimation of large amounts of MA₂Cl. To that end, I also briefly explored alternative methods of incorporating Cl into the vapour-deposition process, namely as an interlayer before and after the perovskite. I found that there is good miscibility between MAPbI₃ and PbCl₂, but that the thickness of the PbCl₂ layer would need careful optimisation to obtain working solar cells.

In Chapter 6 I extended my work from 2 source co-deposition to 3 and 4 source co-deposition. In general the resulting FA_{0.83}Cs_{0.17}PbI₃ MHP proved more stable than the MAPbI₃ layers I previously deposited, with higher charge-carrier mobilities. Furthermore, by substituting small amounts of PbI₂ for PbCl₂ in the former composition, I was able to significantly improve the optoelectronic properties and hence performance of the resulting FA_{1-y}Cs_yPb(I_{1-x}Cl_x)₃. Indeed, PL lifetimes improved by over an order of magnitude, while charge-carrier mobilities also increased. Most strikingly, I found I was able to incorporate up to about 5% Cl into the I perovskite structure, slightly increasing the bandgap of the material, with the rest of the Cl predominantly forming CsPbCl₃. However, in small amounts the latter appeared to have a stabilising effect on the perovskite crystal structure. Overall, I found optimum performance for 20% PbCl₂ substitution, which improved solar cell performance from 16.4% PCE to 19.3% PCE. As an alternative to this 4 source co-deposition method, I was able to keep some of these performance improvements by introducing the PbCl₂ as a 9 nm interlayer before the FA_{0.83}Cs_{0.17}PbI₃ perovskite. By not relying on significant amounts of MA₂Cl sublimation, it is clear that the addition of PbCl₂ in small quantities helps passivate defects and non-radiative recombination in the bulk perovskite.

The exceptional rise in efficiencies of perovskite solar cells in the last few years has been dominated by solution-processing methods which increasingly rely on innova-

tive defect passivation techniques to reduce parasitic loss in solar cells. Unfortunately, these passivation techniques are mostly not transferrable to “dry” vapour deposition. The method of PbCl_2 addition I introduced in this thesis solves this problem by providing a route to the in situ defect passivation of MHP solar cells. In small amounts, PbCl_2 substitutes PbI_2 as the inorganic precursor, yielding significant improvements to optoelectronic properties and hence solar cell performance. This method of defect passivation is intrinsic to the vapour deposition process, so can readily be applied and upscaled in larger systems. Coupled with the improved control over organic precursors presented through the substrate rate control method, this thesis opens the pathway for more reproducible, higher efficiency MHP solar cells, decoupled from solution-processing pathways for thin-film passivation.

I expect that my methodology can be applied to vacuum-deposited higher-bandgap mixed I-Br systems, which are required for efficient tandem cells, paving the way for systems with reduced trap densities and reduced halide segregation. Defect passivation is particularly important for mixed I-Br systems, because these suffer from light-induced halide segregation, which severely hampers device performance. With electronic trap states largely responsible for this halide segregation, I expect vacuum-deposited I-Br-Cl systems to be particularly resilient to these losses. As such a future project could look at the effect of PbCl_2 addition to mixed I-Br MHPs.

Another aspect of interest is the role of Cs and CsPbCl_3 in the final perovskite. Chapter 6 provides evidence that small amounts of CsPbCl_3 are necessary for the crystallographic stability of the films with PbCl_2 , and that the amount of CsPbCl_3 formed depends on the amount of Cs present in the final film. As such, a future project could investigate the dependence of CsPbCl_3 formation on the amount of Cs precursor present, and the effect of said CsPbCl_3 on the optoelectronic properties and solar cell performance of these layers. Of particular interest would also be the direct deposition of a thin CsPbCl_3 layer to template the perovskite growth.

Finally, this thesis only briefly looked at the stability of the evaporated MHP layers. As another major focus of the MHP research community, solar cell stability under sunlight illumination of my MHP thin-films would provide further insights into the potential advantages of solvent-free deposition methods such as vacuum co-deposition. In conjunction with the investigation of the effect of CsPbCl_3 on film stability, research in this area could lead to improvements in not only solar cell PCE, but also long term operational stability.

Bibliography

- [1] BP Statistical Review of World Energy 2021, <https://www.bp.com/en/global/corporate/energy-economics/statistical-review-of-world-energy.html> Accessed 17/02/2022 .
- [2] European Comission, “Paris Agreement 2015”, *21st Conference of the Parties*, 2015. <https://unfccc.int/process/conferences/pastconferences/paris-climate-change-conference-november-2015/paris-agreement> .
- [3] The Intergovernmental Panel on Climate Change (IPCC), *Special Report – Global Warming of 1.5 °C*, 2018. <https://www.ipcc.ch/sr15/> Accessed 17/02/2022 .
- [4] The Intergovernmental Panel on Climate Change (IPCC) Working Group 1, *Sixth Assesment Report*, 2021. <https://www.ipcc.ch/report/ar6/wg1/> Accessed 17/02/2022 .
- [5] M. Perez and R. Perez, “A fundamental look at supply side energy reserves for the planet,” *IEA/SHC Solar Update*, vol. 62, pp. 4–6, 2015.
- [6] H. Ritchie and M. Roser, “Energy,” *Our World in Data*, 2020. <https://ourworldindata.org/energy>.
- [7] D. J. C. MacKay, *Sustainable Energy – without the Hot Air*. UIT Cambridge, 2009. Accessible online at <https://www.withouthotair.com/>.

- [8] O. Coddington, J. Lean, P. Pilewskie, M. Snow, and D. Lindholm, “A solar irradiance climate data record,” *Bulletin of the American Meteorological Society*, vol. 97, no. 7, pp. 1265–1282, 2016.
- [9] F. Kasten and A. T. Young, “Revised optical air mass tables and approximation formula,” *Applied optics*, vol. 28, no. 22, pp. 4735–4738, 1989.
- [10] C. A. Gueymard, D. Myers, and K. Emery, “Proposed reference irradiance spectra for solar energy systems testing,” *Solar energy*, vol. 73, no. 6, pp. 443–467, 2002.
- [11] NREL, ASTM G-173-03 reference solar spectrum, <https://www.nrel.gov/grid/solar-resource/spectra.html> Accessed 20/01/2022 .
- [12] Ivanpah Solar Power Facility, California, USA <https://www.energy.gov/lpo/ivanpah> Accessed 20/01/2022 .
- [13] Noor Ouarzazate Solar Complex, Morocco <https://www.power-technology.com/projects/noor-ouarzazate-solar-complex/> Accessed 20/01/2022 .
- [14] J. Nelson, *The Physics of Solar Cells*. Imperial College Press, 2003.
- [15] W. Shockley and H. J. Queisser, “Detailed balance limit of efficiency of p-n junction solar cells,” *Journal of Applied Physics*, vol. 32, no. 3, pp. 510–519, 1961.
- [16] S. Rühle, “Tabulated values of the Shockley–Queisser limit for single junction solar cells,” *Solar Energy*, vol. 130, pp. 139–147, 2016.
- [17] A. De Vos, “Detailed balance limit of the efficiency of tandem solar cells,” *Journal of Physics D: Applied Physics*, vol. 13, p. 839, 1980.

- [18] F. Dimroth, M. Grave, P. Beutel, U. Fiedeler, C. Karcher, T. N. D. Tibbits, E. Oliva, G. Siefert, M. Schachtner, A. Wekkeli, A. W. Bett, R. Krause, M. Piccin, N. Blanc, C. Drazek, E. Guiot, B. Ghyselen, A. T. T. Salvetat, T. Signarmarcheix, A. Dobrich, T. Hannappel, and K. Schwarzburg, “Wafer bonded four-junction GaInP/GaAs/GaInAsP/GaInAs concentrator solar cells with 44.7% efficiency,” *Progress in Photovoltaics*, vol. 22, p. 277, 2014.
- [19] M. Anaya, G. Lozano, M. E. Calvo, and H. Míguez, “ABX₃ perovskites for tandem solar cells,” *Joule*, vol. 1, p. 769, 2017.
- [20] “This month in physics history,” *APS News*, vol. 18, p. 2, 2009.
- [21] C. E. Fritts, “On a new form of selenium cell, and some electrical discoveries made by its use,” *American Journal of Science*, vol. 3, pp. 465–472, 1883.
- [22] D. M. Chapin, C. S. Fuller, and G. L. Pearson, “A new silicon p-n junction photocell for converting solar radiation into electrical power,” *Journal of Applied Physics*, vol. 25, pp. 676–677, 1954.
- [23] S. Philipps and W. Warmuth, “Fraunhofer ISE Photovoltaics Report,” 2021. <https://www.ise.fraunhofer.de/en/publications/studies/photovoltaics-report.html> Accessed 20/01/2022.
- [24] R. Kapadnis, S. Bansode, A. Supekar, P. Bhujbal, S. Kale, S. Jadkar, and H. Pathan, “Cadmium telluride/cadmium sulfide thin films solar cells: A review,” *ES Energy & Environment*, vol. 10, pp. 3–12, 2020.
- [25] J. Ramanujam and U. P. Singh, “Copper indium gallium selenide based solar cells – a review,” *Energy Environ. Sci*, vol. 10, p. 1306, 2017.
- [26] A. R. Murad, A. Iraqi, S. B. Aziz, S. N. Abdullah, and M. A. Brza, “Con-

- ducting polymers for optoelectronic devices and organic solar cells: A review,” *Polymers*, vol. 12, p. 2627, 2020.
- [27] Z. I. Alferov, V. M. Andreev, and V. D. Rumyantsev, “III-V solar cells and concentrator arrays,” in *High-Efficient Low-Cost Photovoltaics*, pp. 101–141, Springer, 2009.
- [28] A. Kojima, K. Teshima, Y. Shirai, and T. Miyasaka, “Organometal halide perovskites as visible-light sensitizers for photovoltaic cells,” *J. Am. Chem. Soc.*, vol. 131, p. 6050, 2009.
- [29] M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami, and H. J. Snaith, “Efficient hybrid solar cells based on meso-superstructured organometal halide perovskites,” *Science*, vol. 338, p. 643, 2012.
- [30] NREL, Best Research-Cell Efficiency Chart, <https://www.nrel.gov/pv/cell-efficiency.html> Accessed 20/01/2022 .
- [31] M. L. Petrus, J. Schlipf, C. Li, T. P. Gujar, N. Giesbrecht, P. M”uller-Buschbaum, M. Thelakkat, T. Bein, S. H”uttner, and P. Docampo, “Capturing the sun: A review of the challenges and perspectives of perovskite solar cells,” *Adv. Energy Mater.*, vol. 7, p. 1700264, 2017.
- [32] J. H. Noh, S. H. Im, J. H. Heo, T. N. Mandal, and S. I. Seok, “Chemical management for colorful, efficient, and stable inorganic-organic hybrid nanostructured solar cells,” *Nano. Lett.*, vol. 13, p. 1764, 2013.
- [33] C. C. Stoumpos, C. D. Malliakas, and M. G. Kanatzidis, “Semiconducting tin and lead iodide perovskites with organic cations: Phase transitions, high mobilities, and near-infrared photoluminescent properties,” *Inorg. Chem.*, vol. 52, p. 9019, 2013.

- [34] D. P. McMeekin, G. Sadoughi, W. Rehman, G. E. Eperon, M. Saliba, M. T. Hörantner, A. Haghighirad, N. Sakai, L. Korte, B. Rech, M. B. Johnston, L. M. Herz, and H. J. Snaith, “A mixed-cation lead mixed-halide perovskite absorber for tandem solar cells,” *Science*, vol. 351, p. 151, 2016.
- [35] Z. Li, M. Yang, J.-S. Park, S.-H. Wei, J. J. Berry, and K. Zhu, “Stabilizing perovskite structures by tuning tolerance factor: Formation of formamidinium and cesium lead iodide solid-state alloys,” *Chem. Mater.*, vol. 28, p. 284, 2016.
- [36] I. Levchuk, A. Osvet, X. Tang, M. Brandl, J. D. Perea, F. Hoegl, G. J. Matt, R. Hock, M. Batentschuk, and C. J. Brabec, “Brightly luminescent and color-tunable formamidinium lead halide perovskite FAPbX_3 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) colloidal nanocrystals,” *Nano. Lett.*, vol. 17, p. 2765, 2017.
- [37] G. E. Eperon, T. Leijtens, K. A. Bush, R. Prasanna, T. Green, J. T.-W. Wang, D. P. McMeekin, G. Volonakis, R. L. Milot, R. May, A. Palmstrom, D. J. Slotcavage, R. A. Belisle, J. B. Patel, E. S. Parrott, R. J. Sutton, W. Ma, F. Moghadam, B. Conings, A. Babayigit, H.-G. Boyen, S. Bent, F. Giustino, L. M. Herz, M. B. Johnston, M. D. McGehee, and H. J. Snaith, “Perovskite-perovskite tandem photovoltaics with optimized bandgaps,” *Science*, vol. 354, p. 861, 2016.
- [38] Z. Yang, A. Rajagopal, C.-C. Chueh, S. B. Jo, B. Liu, T. Zhao, and A. K.-Y. Jen, “Stable low-bandgap Pb-Sn binary perovskites for tandem solar cells,” *Adv. Mater.*, vol. 28, p. 8990, 2016.
- [39] J. Xu, C. C. Boyd, Z. J. Yu, A. F. Palmstrom, D. J. Witter, B. W. Larson, R. M. France, J. Werner, S. P. Harvey, E. J. Wolf, W. Weigand, S. Manzoor, M. F. A. M. v. Hest, J. J. Berry, J. M. Luther, Z. C. Holman, and M. D. McGehee,

- “Triple-halide wide-band gap perovskites with suppressed phase segregation for efficient tandems,” *Science*, vol. 367, p. 1097, 2020.
- [40] B. Chen, S.-W. Baek, Y. Hou, E. Aydin, M. D. Bastiani, B. Scheffel, A. Proppe, Z. Huang, M. Wei, Y.-K. Wang, E.-H. Jung, T. G. Allen, E. V. Kerschaver, F. P. G. d. Arquer, M. I. Saidaminov, S. Hoogland, S. D. Wolf, and E. H. Sargent, “Enhanced optical path and electron diffusion length enable high-efficiency perovskite tandems,” *Nat. Commun.*, vol. 11, p. 1257, 2020.
- [41] J. Li, H. Wang, X. Y. Chin, H. A. Dewi, K. Vergeer, T. W. Goh, J. W. M. Lim, J. H. Lew, K. P. Loh, C. Soci, T. C. Sum, H. J. Bolink, N. Mathews, S. Mhaisalkar, and A. Bruno, “Highly efficient thermally co-evaporated perovskite solar cells and mini-modules,” *Joule*, vol. 4, p. 1035, 2020.
- [42] J. B. Patel, A. D. Wright, K. B. Lohmann, K. Peng, C. Q. Xia, J. M. Ball, N. K. Noel, T. W. Crothers, J. Wong-Leung, H. J. Snaith, L. M. Herz, and M. B. Johnston, “Light absorption and recycling in hybrid metal halide perovskite photovoltaic devices,” *Adv. Energy Mater.*, vol. 10, p. 1903653, 2020.
- [43] Y. Vaynzof, “The future of perovskite photovoltaics – thermal evaporation or solution processing?,” *Advanced Energy Materials*, vol. 10, no. 48, p. 2003073, 2020.
- [44] J. Ávila, C. Momblona, P. P. Boix, M. Sessolo, and H. J. V.-D. P. Bolink, “The route to high-performance solar cell production?,” *Joule*, vol. 1, p. 431, 2017.
- [45] D. Forgács, L. Gil-Escrig, D. Pérez-Del-Rey, C. Momblona, J. Werner, B. Niesen, C. Ballif, M. Sessolo, and H. J. Bolink, “Efficient monolithic perovskite/perovskite tandem solar cells,” *Adv. Mater.*, vol. 7, p. 1602121, 2017.
- [46] S. M. SZE, *Semiconductor Devices Physics and Technology*. John Wiley & Sons, 1985.

- [47] G.-W. Kim and A. Petrozza, “Defect tolerance and intolerance in metal-halide perovskites,” *Adv. Energy Mater.*, vol. 10, no. 37, p. 2001959, 2020.
- [48] C. Momblona, L. Gil-Escrig, E. Bandiello, E. M. Hutter, M. Sessolo, K. Lederer, J. Blochwitz-Nimoth, and H. J. Bolink, “Efficient vacuum deposited p-i-n and n-i-p perovskite solar cells employing doped charge transport layers,” *Energy Environ. Sci.*, vol. 9, p. 3456, 2016.
- [49] M. Liu, M. B. Johnston, and H. J. Snaith, “Efficient planar heterojunction perovskite solar cells by vapour deposition,” *Nature*, vol. 501, p. 395, 2013.
- [50] Q. Lin, A. Armin, R. C. R. Nagiri, P. L. Burn, and P. Meredith, “Electro-optics of perovskite solar cells,” *Nature Photonics*, vol. 9, p. 106, 2014.
- [51] S.-Y. Hsiao, H.-L. Lin, W.-H. Lee, W.-L. Tsai, K.-M. Chiang, W.-Y. Liao, C.-Z. Ren-Wu, C.-Y. Chen, and H.-W. Lin, “Efficient all-vacuum deposited perovskite solar cells by controlling reagent partial pressure in high vacuum,” *Adv. Mater.*, vol. 28, p. 7013, 2016.
- [52] J. Yin, J. C. H. Qu, H. Tai, J. Li, and N. Zheng, “Vapor-assisted crystallization control toward high performance perovskite photovoltaics with over 18% efficiency in the ambient atmosphere,” *J. Mater. Chem.*, vol. 4, p. 13203, 2016.
- [53] C.-Y. Chen, H.-Y. Lin, K.-M. Chiang, W.-L. Tsai, Y.-C. Huang, C.-S. Tsao, and H.-W. Lin, “All-vacuum-deposited stoichiometrically balanced inorganic cesium lead halide perovskite solar cells with stabilized efficiency exceeding 11%,” *Adv. Mater.*, vol. 29, p. 1605290, 2017.
- [54] J. Borchert, R. L. Milot, J. B. Patel, C. L. Davies, A. D. Wright, L. M. Maestro, H. J. Snaith, L. M. Herz, and M. B. Johnston, “Large-area, highly uniform evaporated formamidinium lead triiodide thin films for solar cells,” *ACS Energy Lett.*, vol. 2, p. 2799, 2017.

- [55] G. Longo, C. Momblona, M.-G. La-Placa, L. Gil-Escrig, M. Sessolo, and H. J. Bolink, “Fully vacuum-processed wide band gap mixed-halide perovskite solar cells,” *ACS Energy Lett.*, vol. 3, p. 214, 2018.
- [56] E. T. Hoke, D. J. Slotcavage, E. R. Dohner, A. R. Bowring, H. I. Karunadasa, and M. D. McGehee, “Reversible photo-induced trap formation in mixed-halide hybrid perovskites for photovoltaics,” *Chemical Science*, vol. 6, pp. 613–617, 2015.
- [57] L. Gil-Escrig, C. Momblona, M.-G. La-Placa, P. P. Boix, M. Sessolo, and H. J. Bolink, “Vacuum deposited triple-cation mixed-halide perovskite solar cells,” *Adv. Energy Mater.*, vol. 8, p. 1703506, 2018.
- [58] C. Lu and A. W. Czanderna, *Applications of Piezoelectric Quartz Crystal Microbalances*. Elsevier, 1984.
- [59] D. Stokes, *Principles and practice of variable pressure/environmental scanning electron microscopy (VP-ESEM)*. John Wiley & Sons, 2008.
- [60] P. Thompson, D. E. Cox, and J. B. Hastings, “Rietveld refinement of Debye-Scherrer synchrotron X-ray data from Al₂O₃,” *J. Appl. Cryst.*, vol. 20, p. 79, 1987.
- [61] P. Landsberg, *Recombination in Semiconductors*. Cambridge University Press, 1991.
- [62] J. Borchert, I. Levchuk, L. C. Snoek, M. U. Rothmann, R. Haver, H. J. Snaith, C. J. Brabec, L. M. Herz, and M. B. Johnston, “Impurity tracking enables enhanced control and reproducibility of hybrid perovskite vapour deposition,” *ACS Appl. Mater. Interfaces*, vol. 11, p. 28851, 2019.

- [63] J. B. Patel, J. Wong-Leung, S. Van Reenen, N. Sakai, J. T. W. Wang, E. S. Parrott, M. Liu, H. J. Snaith, L. M. Herz, and M. B. Johnston, "Influence of interface morphology on hysteresis in vapor-deposited perovskite solar cells," *Adv. Electron. Mater.*, vol. 3, p. 1600470, 2017.
- [64] M. M. Tavakoli, A. Simchi, X. Mo, and Z. Fan, "High-quality organohalide lead perovskite films fabricated by layer-by-layer alternating vacuum deposition for high efficiency photovoltaics," *Mater. Chem. Front.*, vol. 1, p. 1520, 2017.
- [65] D. J. Teuscher, D. A. Ulianov, P. O. Müntener, P. M. Grätzel, and D. N. Tétreault, "Control and study of the stoichiometry in evaporated perovskite solar cells," *ChemSusChem*, vol. 8, p. 3847, 2015.
- [66] V. Arivazhagan, J. Xie, Z. Yang, P. Hang, M. M. Parvathi, K. Xiao, C. Cui, D. Yang, and X. Yu, "Vacuum co-deposited $\text{CH}_3\text{NH}_3\text{PbI}_3$ films by controlling vapor pressure for efficient planar perovskite solar cells," *Sol. Energy*, vol. 181, p. 339, 2019.
- [67] H. D. Kim, H. Ohkita, H. Benten, and S. Ito, "Photovoltaic performance of perovskite solar cells with different grain sizes," *Adv. Mater.*, vol. 28, p. 917, 2016.
- [68] W. Nie, H. Tsai, R. Asadpour, J.-C. Blancon, A. J. Neukirch, G. Gupta, J. J. Crochet, M. Chhowalla, S. Tretiak, M. A. Alam, H.-L. Wang, and A. D. Mohite, "High-efficiency solution-processed perovskite solar cells with millimeter-scale grains," *Science*, vol. 347, p. 522, 2015.
- [69] C. Chiang and C. Wu, "Film grain-size related long-term stability of inverted perovskite solar cells," *ChemSusChem*, vol. 9, p. 2666, 2016.
- [70] Q. Han, Y. Bai, J. Liu, K.-z. Du, T. Li, D. Ji, Y. Zhou, C. Cao, D. Shin, J. Ding, A. D. Franklin, J. T. Glass, J. Hu, M. J. Therien, J. Liu, and D. B.

- Mitzi, “Additive engineering for high-performance room-temperature-processed perovskite absorbers with micron-size grains and microsecond-range carrier lifetimes,” *Energy Environ. Sci.*, vol. 10, p. 2365, 2017.
- [71] W.-J. Yin, T. Shi, and Y. Yan, “Unique properties of halide perovskites as possible origins of the superior solar cell performance,” *Adv. Mater.*, vol. 26, p. 4653, 2014.
- [72] J. S. Yun, A. Ho-Baillie, S. Huang, S. H. Woo, Y. Heo, J. Seidel, F. Huang, Y.-B. Cheng, and M. A. Green, “Benefit of grain boundaries in organic-inorganic halide planar perovskite solar cells,” *J. Phys. Chem. Lett.*, vol. 6, p. 875, 2015.
- [73] J. S. Yun, J. Seidel, J. Kim, A. M. Soufiani, S. Huang, J. Lau, N. J. Jeon, S. I. Seok, M. A. Green, and A. Ho-Baillie, “Critical role of grain boundaries for ion migration in formamidinium and methylammonium lead halide perovskite solar cells,” *Adv. Energy Mater.*, vol. 6, no. 16003, p. 30, 2016.
- [74] G. W. P. Adhyaksa, S. Brittman, H. Āboliņš, A. Lof, X. Li, J. D. Keelor, Y. Luo, T. Duevski, R. M. A. Heeren, S. R. Ellis, D. P. Fenning, and E. C. Garnett, “Understanding detrimental and beneficial grain boundary effects in halide perovskites,” *Adv. Mater.*, vol. 30, p. 1804792, 2018.
- [75] T. W. Crothers, R. L. Milot, J. B. Patel, E. S. Parrott, J. Schlipf, P. Müller-Buschbaum, M. B. Johnston, and L. M. Herz, “Photon reabsorption masks intrinsic bimolecular charge-carrier recombination in $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite,” *Nano Lett.*, vol. 17, p. 5782, 2017.
- [76] W. Nie, H. Tsai, J. Blancon, F. Liu, C. C. Stoumpos, B. Traore, M. Kepenekian, O. Durand, C. Katan, S. Tretiak, J. Crochet, P. M. Ajayan, M. G. Kanatzidis, J. Even, and A. D. Mohite, “Critical role of interface and crystallinity on the

- performance and photostability of perovskite solar cell on nickel oxide,” *Adv. Mater.*, vol. 30, p. 1703879, 2018.
- [77] J. Chen, L. Zuo, Y. Zhang, X. Lian, W. Fu, J. Yan, J. Li, G. Wu, C. Li, and H. Chen, “High-performance thickness insensitive perovskite solar cells with enhanced moisture stability,” *Adv. Energy Mater.*, vol. 8, p. 1800438, 2018.
- [78] S. Song, M. T. Hörantner, K. Choi, H. J. Snaith, and T. Park, “Inducing swift nucleation morphology control for efficient planar perovskite solar cells by hot-air quenching,” *J. Mater. Chem. A*, vol. 5, p. 3812, 2017.
- [79] Y.-K. Ren, X.-H. Ding, Y.-H. Wu, J. Zhu, T. Hayat, A. Alsaedi, Y.-F. Xu, Z.-Q. Li, S.-F. Yang, and S.-Y. Dai, “Temperature-assisted rapid nucleation: a facile method to optimize the film morphology for perovskite solar cells,” *J. Mater. Chem. A*, vol. 5, p. 20327, 2017.
- [80] M. J. Bækbo, O. Hansen, I. Chorkendorff, and P. C. K. Vesborg, “Deposition of methylammonium iodide via evaporation – combined kinetic and mass spectrometric study,” *RSC Adv.*, vol. 8, p. 29899, 2018.
- [81] M. Yang, Y. Zhou, Y. Zeng, C.-S. Jiang, N. P. Padture, and K. Zhu, “Square-centimeter solution-processed planar $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite solar cells with efficiency exceeding 15%,” *Adv. Mater.*, vol. 27, p. 6363, 2015.
- [82] H. Yuan, E. Debroye, K. Janssen, H. Naiki, C. Steuwe, G. Lu, M. Moris, E. Orgiu, H. Uji-i, F. D. Schryver, P. Samorì, J. Hofkens, and M. Roeffaers, “Degradation of methylammonium lead iodide perovskite structures through light and electron beam driven ion migration,” *J. Phys. Chem. Lett.*, vol. 7, p. 561, 2016.
- [83] M. U. Rothmann, W. Li, Y. Zhu, A. Liu, Z. Ku, U. Bach, J. Etheridge, and

- Y.-B. Cheng, “Structural and chemical changes to $\text{CH}_3\text{NH}_3\text{PbI}_3$ induced by electron and gallium ion beams,” *Adv. Mater.*, vol. 30, p. 1800629, 2018.
- [84] P. Scherrer, “Bestimmung der Größe und der inneren Struktur von Kolloidteilchen mittels Röntgenstrahlen,” *Göttinger Nachrichten Math. Phys.*, vol. 2, p. 98, 1918.
- [85] P. K. Nayak, S. Mahesh, H. J. Snaith, and D. Cahen, “Photovoltaic solar cell technologies: analysing the state of the art,” *Nature Reviews Materials*, vol. 4, p. 269, 2019.
- [86] V. S. Chirvony, K. S. Sekerbayev, D. P. del Rey, J. P. Martínez-Pastor, F. Palazon, P. P. Boix, T. I. Taurbayev, M. Sessolo, and H. J. Bolink, “Short photoluminescence lifetimes in vacuum-deposited $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite thin films as a result of fast diffusion of photogenerated charge carriers,” *J. Phys.*, vol. 10, p. 5167, 2019.
- [87] D. Walter, A. Fell, Y. Wu, T. Duong, C. Barugkin, N. Wu, T. White, and K. Weber, “Transient photovoltage in perovskite solar cells: Interaction of trap-mediated recombination and migration of multiple ionic species,” *J. Phys. Chem C*, vol. 122, p. 11270, 2018.
- [88] T. J. Jacobsson, J.-P. Correa-Baena, E. H. Anaraki, B. Philippe, S. D. Stranks, M. E. F. Bouduban, W. Tress, K. Schenk, J. Teuscher, J.-E. Moser, H. Rensmo, and A. Hagfeldt, “Unreacted PbI_2 as a double-edged sword for enhancing the performance of perovskite solar cells,” *J. Am. Chem. Soc.*, vol. 138, p. 10331, 2016.
- [89] Y. C. Kim, N. J. Jeon, J. H. Noh, W. S. Yang, J. Seo, J. S. Yun, A. Ho-Baillie, S. Huang, M. A. Green, J. Seidel, T. K. Ahn, and S. I. Seok, “Beneficial effects

- of PbI_2 incorporated in organo-lead halide perovskite solar cells,” *Adv. Energy Mater.*, vol. 6, p. 1502104, 2016.
- [90] L. Wang, C. McCleese, A. Kovalsky, Y. Zhao, and C. Burda, “Femtosecond time-resolved transient absorption spectroscopy of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite films: Evidence for passivation effect of PbI_2 ,” *J. Am. Chem. Soc.*, vol. 136, p. 12205, 2014.
- [91] D. H. Cao, C. C. Stoumpos, C. D. Malliakas, M. J. Katz, O. K. Farha, J. T. Hupp, and M. G. Kanatzidis, “Remnant PbI_2 an unforeseen necessity in high-efficiency hybrid perovskite-based solar cells?,” *APL Mater.*, vol. 2, p. 091101, 2014.
- [92] H. Xu, F. Xu, W. Wang, Y. Zhu, Z. Fang, B. Yao, F. Hong, J. Cui, F. Xu, R. Xu, C.-C. Chen, and L. Wang, “Resolving the detrimental interface in co-evaporated MAPbI_3 perovskite solar cells by hybrid growth method,” *Org. Electron.*, vol. 69, p. 329, 2019.
- [93] J. B. Patel, Q. Lin, O. Zadvorna, C. L. Davies, L. M. Herz, and M. B. Johnston, “Photocurrent spectroscopy of perovskite solar cells over a wide temperature range from 15 to 350 K,” *J. Phys. Chem. Lett.*, vol. 9, p. 263, 2018.
- [94] F. Liu, Q. Dong, M. K. Wong, A. B. Djurišić, A. Ng, Z. Ren, Q. Shen, C. Surya, W. K. Chan, J. Wang, A. M. C. Ng, C. Liao, H. Li, K. Shih, C. Wei, H. Su, and J. Dai, “Is excess PbI_2 beneficial for perovskite solar cell performance?,” *Adv. Energy Mater.*, vol. 6, p. 1502206, 2016.
- [95] S. Wang, L. K. Ono, M. R. Leyden, Y. Kato, S. R. Raga, M. V. Lee, and Y. Qi, “Smooth perovskite thin films and efficient perovskite solar cells prepared by the hybrid deposition method,” *J. Mater. Chem. A*, vol. 3, p. 14631, 2015.

- [96] R. Kottokkaran, H. A. Gaonkar, H. A. Abbas, M. Noack, and V. Dalal, "Performance and stability of co-evaporated vapor deposited perovskite solar cells," *J. Mater. Sci.: Mater. Electron*, vol. 30, p. 5487, 2019.
- [97] N. J. Jeon, J. H. Noh, Y. C. Kim, W. S. Yang, S. Ryu, and S. I. Seok, "Solvent engineering for high-performance inorganic-organic hybrid perovskite solar cells," *Nature Mater.*, vol. 13, p. 897, 2014.
- [98] Y. Rong, Z. Tang, Y. Zhao, X. Zhong, S. Venkatesan, H. Graham, M. Patton, Y. Jing, A. M. Guloy, and Y. Yao, "Solvent engineering towards controlled grain growth in perovskite planar heterojunction solar cells," *Nanoscale*, vol. 7, p. 10595, 2015.
- [99] D. T. Moore, H. Sai, K. W. Tan, D.-M. Smilgies, W. Zhang, H. J. Snaith, U. Wiesner, and L. A. Estroff, "Crystallization kinetics of organic-inorganic trihalide perovskites and the role of the lead anion in crystal growth," *J. Am. Chem. Soc.*, vol. 137, p. 2350, 2015.
- [100] K. H. Stone, A. Gold-Parker, V. L. Pool, E. L. Unger, A. R. Bowring, M. D. McGehee, M. F. Toney, and C. J. Tassone, "Transformation from crystalline precursor to perovskite in PbCl_2 -derived MAPbI_3 ," *Nat. Commun.*, vol. 9, p. 3458, 2018.
- [101] N. K. Noel, A. Abate, S. D. Stranks, E. S. Parrott, V. M. Burlakov, A. Goriely, and H. J. Snaith, "Enhanced photoluminescence and solar cell performance via lewis base passivation of organic-inorganic lead halide perovskites," *ACS Nano*, vol. 8, p. 9815, 2014.
- [102] Q. Jiang, Y. Zhao, X. Zhang, X. Yang, Y. Chen, Z. Chu, Q. Ye, X. Li, Z. Yin, and J. You, "Surface passivation of perovskite film for efficient solar cells," *Nat. Photonics*, vol. 13, p. 460, 2019.

- [103] S. Gharibzadeh, B. A. Nejand, M. Jakoby, T. Abzieher, D. Hauschild, S. Moghadamzadeh, J. A. Schwenzler, P. Brenner, R. Schmager, A. A. Haghighirad, L. Weinhardt, U. Lemmer, B. S. Richards, I. A. Howard, and U. W. Paetzold, "Record open-circuit voltage wide-bandgap perovskite solar cells utilizing 2D/3D perovskite heterostructure," *Adv. Energy Mater.*, vol. 9, p. 1803699, 2019.
- [104] T. Zhao, C.-C. Chueh, Q. Chen, A. Rajagopal, and A. K.-Y. Jen, "Defect passivation of organic-inorganic hybrid perovskites by diammonium iodide toward high-performance photovoltaic devices," *ACS Energy Lett.*, vol. 1, p. 757, 2016.
- [105] X. Zheng, B. Chen, Y. F. JunDai, Y. Bai, Y. Lin, H. Wei, X. C. Zeng, and J. Huang, "Defect passivation in hybrid perovskite solar cells using quaternary ammonium halide anions and cations," *Nat. Energy*, vol. 2, p. 17102, 2017.
- [106] S. D. Stranks, G. E. Eperon, G. Grancini, C. Menelaou, M. J. P. Alcocer, T. Leijtens, L. M. Herz, A. Petrozza, and H. J. Snaith, "Electron-hole diffusion lengths exceeding 1 micrometer in an organometal trihalide perovskite absorber," *Science*, vol. 342, p. 341, 2013.
- [107] P. Docampo, F. C. Hanusch, S. D. Stranks, M. D"obliger, J. M. Feckl, M. Ehrensperger, N. K. Minar, M. B. Johnston, H. J. Snaith, and T. Bein, "Solution deposition-conversion for planar heterojunction mixed halide perovskite solar cells," *Adv. Energy Mater.*, vol. 4, p. 1400355, 2014.
- [108] S. T. Williams, F. Zuo, C.-C. Chueh, C.-Y. Liao, P.-W. Liang, and A. K.-Y. Jen, "Role of chloride in the morphological evolution of organo-lead halide perovskite thin films," *ACS Nano*, vol. 8, p. 10640, 2014.
- [109] Q. Chen, H. Zhou, Y. Fang, A. Z. Stieg, T.-B. Song, H.-H. Wang, X. Xu, Y. Liu, S. Lu, J. You, P. Sun, J. McKay, M. S. Goorsky, and Y. Yang, "The

- optoelectronic role of chlorine in $\text{CH}_3\text{NH}_3\text{PbI}_3(\text{Cl})$ -based perovskite solar cells,” *Nat. Commun.*, vol. 6, p. 7269, 2015.
- [110] F. Xie, C.-C. Chen, Y. Wu, X. Li, M. Cai, X. Liu, X. Yang, and L. Han, “Vertical recrystallization for highly efficient and stable formamidinium-based inverted-structure perovskite solar cells,” *Energy Environ. Sci.*, vol. 10, p. 1942, 2017.
- [111] D. B. Khadka, Y. Shirai, M. Yanagida, T. Masudaa, and K. Miyanoa, “Enhancement in efficiency and optoelectronic quality of perovskite thin films annealed in MACl vapor,” *Sustainable Energy Fuels*, vol. 1, p. 755, 2017.
- [112] K. O. Kosmatos, L. Theofylaktos, E. Giannakaki, D. Deligiannis, M. Konstantakou, and T. Stergiopoulos, “Methylammonium chloride: A key additive for highly efficient, stable, and up-scalable perovskite solar cells,” *Energy Environ. Mater.*, vol. 2, p. 79, 2019.
- [113] M. I. Saidaminov, J. Kim, A. Jain, R. Quintero-Bermudez, H. Tan, G. Long, F. Tan, A. Johnston, Y. Zhao, O. Voznyy, and E. H. Sargent, “Suppression of atomic vacancies via incorporation of isovalent small ions to increase the stability of halide perovskite solar cells in ambient air,” *Nat. Energy*, vol. 3, p. 648, 2018.
- [114] D. W. deQuilettes, S. M. Vorpahl, S. D. Stranks, H. Nagaoka, G. E. Eperon, M. E. Ziffer, H. J. Snaith, and D. S. Ginger, “Impact of microstructure on local carrier lifetime in perovskite solar cells,” *Science*, vol. 348, p. 683, 2015.
- [115] S. Colella, E. Mosconi, P. Fedeli, A. Listorti, F. Gazza, F. Orlandi, P. Ferro, T. Besagni, A. Rizzo, G. Calestani, G. Gigli, F. D. Angelis, and R. Mosca, “ $\text{MAPbI}_{3-x}\text{Cl}_x$ mixed halide perovskite for hybrid solar cells: The role of chloride

- as dopant on the transport and structural properties,” *Chem. Mater.*, vol. 25, p. 4613, 2013.
- [116] S. Colella, E. Mosconi, G. Pellegrino, A. Alberti, V. L. P. Guerra, S. Masi, A. Listorti, A. Rizzo, G. G. Condorelli, F. D. Angelis, and G. Gigli, “Elusive presence of chloride in mixed halide perovskite solar cells,” *J. Phys. Chem. Lett.*, vol. 5, p. 3532, 2014.
- [117] M. I. Dar, N. A. Gao, S. Ahmad, M. Grätzel, and M. K. Nazeeruddin, “Investigation regarding the role of chloride in organic-inorganic halide perovskites obtained from chloride containing precursors,” *Nano Lett.*, vol. 14, p. 6991, 2014.
- [118] P. Pistor, J. Borchert, W. Fraänzel, R. Csuk, and R. Scheer, “Monitoring the phase formation of coevaporated lead halide perovskite thin films by in situ X-ray diffraction,” *J. Phys. Chem. Lett.*, vol. 5, p. 3308, 2014.
- [119] I. L. Braly, D. W. deQuilettes, L. M. Pazos-Outón, S. Burke, M. E. Ziffer, D. S. Ginger, and H. W. Hillhouse, “Hybrid perovskite films approaching the radiative limit with over 90% photoluminescence quantum efficiency,” *Nature Photon*, vol. 12, p. 355, 2018.
- [120] K. B. Lohmann, J. B. Patel, M. U. Rothmann, C. Q. Xia, R. D. J. Oliver, L. M. Herz, H. J. Snaith, and M. B. Johnston, “Control over crystal size in vapor deposited metal-halide perovskite films,” *ACS Energy Lett.*, vol. 5, p. 710, 2020.
- [121] H. Yu, F. Wang, F. Xie, W. Li, J. Chen, and N. Zhao, “The role of chlorine in the formation process of ” $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ ” perovskite,” *Adv. Funct. Mater.*, vol. 24, p. 7102, 2014.

- [122] A. Babaei, W. Soltanpoor, M. A. Tesa-Serrate, S. Yerci, M. Sessolo, and H. J. Bolink, “Preparation and characterization of mixed halide MAPbI_{3-x}Cl_x perovskite thin films by three-source vacuum deposition,” *Energy Technol.*, vol. 8, p. 1900784, 2020.
- [123] M. M. Tavakoli, P. Yadav, D. Prochowicz, R. Tavakoli, and M. Saliba, “Multi-layer evaporation of MAFAPbI_{3-x}Cl_x for the fabrication of efficient and large-scale device perovskite solar cells,” *J. Phys. D: Appl. Phys.*, vol. 52, p. 034005, 2019.
- [124] Y.-H. Chiang, M. Anaya, and S. D. Stranks, “Multisource vacuum deposition of methylammonium-free perovskite solar cells,” *ACS Energy Lett.*, vol. 5, p. 2498, 2020.
- [125] L. Gil-Escrig, C. Dreessen, I. C. Kaya, B.-S. Kim, F. Palazon, M. Sessolo, and H. J. Bolink, “Efficient vacuum-deposited perovskite solar cells with stable cubic FA_{1-x}MA_xPbI₃,” *ACS Energy Letters*, vol. 5, pp. 3053–3061, 2020.
- [126] L. Gil-Escrig, C. Dreessen, F. Palazon, Z. Hawash, E. Moons, S. Albrecht, M. Sessolo, and H. J. Bolink, “Efficient wide-bandgap mixed-cation and mixed-halide perovskite solar cells by vacuum deposition,” *ACS Energy Letters*, vol. 6, pp. 827–836, 2021.
- [127] J. M. Ball, L. Buizza, H. C. Sansom, M. D. Farrar, M. T. Klug, J. Borchert, J. Patel, L. M. Herz, M. B. Johnston, and H. J. Snaith, “Dual-source coevaporation of low-bandgap FA_{1-x}CS_xSn_{1-y}Pb_yI₃ perovskites for photovoltaics,” *ACS Energy Lett*, vol. 4, p. 2748, 2019.
- [128] A. M. Igual-Muñoz, A. Castillo, C. Dreessen, P. P. Boix, and H. J. Bolink, “Vacuum-deposited multication tin-lead perovskite solar cells,” *ACS Appl. Energy Mater*, vol. 3, p. 2755, 2020.

- [129] M.-G. La-Placa, L. Gil-Escrig, D. Guo, F. Palazon, T. J. Savenije, M. Sessolo, and H. J. Bolink, “Vacuum-deposited 2D/3D perovskite heterojunctions,” *ACS Energy Lett.*, vol. 4, p. 2893, 2019.
- [130] J. Feng, Y. Jiao, H. Wang, X. Zhu, Y. Sun, M. Du, Y. Cao, D. Yang, and S. F. Liu, “High-throughput large-area vacuum deposition for high-performance formamidine-based perovskite solar cells,” *Energy Environ. Sci.*, vol. 14, p. 3035, 2021.
- [131] A. J. Knight, A. D. Wright, J. B. Patel, D. P. McMeekin, H. J. Snaith, M. B. Johnston, and L. M. Herz, “Electronic traps and phase segregation in lead mixed-halide perovskite,” *ACS Energy Letters*, vol. 4, pp. 75–84, 2018.
- [132] T. J. Coutts, K. A. Emery, and J. Scott Ward, “Modeled performance of polycrystalline thin-film tandem solar cells,” *Progress in Photovoltaics: Research and Applications*, vol. 10, pp. 195–203, 2002.
- [133] A. J. Knight and L. M. Herz, “Preventing phase segregation in mixed-halide perovskites: a perspective,” *Energy & Environmental Science*, vol. 13, pp. 2024–2046, 2020.
- [134] M. M. Tavakoli, P. Yadav, D. Prochowicz, M. Sponseller, A. Osherov, V. Bulović, and J. Kong, “Controllable perovskite crystallization via antisolvent technique using chloride additives for highly efficient planar perovskite solar cells,” *Adv. Energy Mater.*, vol. 9, p. 1803587, 2019.
- [135] H. T. Pham, Y. Yin, G. Andersson, K. J. Weber, T. Duong, and J. Wong-Leung, “Unraveling the influence of CsCl/MACl on the formation of nanotwins, stacking faults and cubic supercell structure in FA-based perovskite solar cells,” *Nano Energy*, vol. 87, p. 106226, 2021.

- [136] M. R. Filip, G. E. Eperon, H. J. Snaith, and F. Giustino, “Steric engineering of metal-halide perovskites with tunable optical band gaps,” *Nat Commun*, vol. 5, p. 5757, 2014.
- [137] A. D. Wright, G. Volonakis, J. Borchert, C. L. Davies, F. Giustino, M. B. Johnston, and L. M. Herz, “Intrinsic quantum confinement in formamidinium lead triiodide perovskite,” *Nature Materials*, vol. 19, p. 1201, 2020.
- [138] R. J. Sutton, M. R. Filip, A. A. Haghighirad, N. Sakai, B. Wenger, F. Giustino, and H. J. Snaith, “Cubic or orthorhombic? revealing the crystal structure of metastable black-phase CsPbI₃ by theory and experiment,” *ACS Energy Lett.*, vol. 3, pp. 1787–1794, 2018.
- [139] K. Heidrich, W. Schafer, M. Schreiber, J. Sochtig, G. Trendel, and J. Treusch, “Electronic structure, photoemission spectra, and vacuum-ultraviolet optical spectra of CsPbCl₃ and CsPbBr₃,” *Physical Review B*, vol. 24, pp. 5642–5649, 1981.
- [140] D. J. C. d. Mello, D. H. F. Wittmann, and P. R. H. Friend, “An improved experimental determination of external photoluminescence quantum efficiency,” *Adv. Mater*, vol. 9, p. 230, 2004.
- [141] C. Wehrenfennig, M. Liu, H. J. Snaith, M. B. Johnston, and L. M. Herz, “Homogeneous emission line broadening in the organo lead halide perovskite CH₃NH₃PbI_{3-x}Cl_x,” *J. Phys. Chem. Lett.*, vol. 5, p. 1300, 2014.
- [142] S. Ponc  , M. Schlipf, and F. Giustino, “Origin of low carrier mobilities in halide perovskites,” *ACS Energy Lett.*, vol. 4, p. 456, 2019.
- [143] C. Q. Xia, J. Peng, S. Ponc  , J. B. Patel, A. D. Wright, T. W. Crothers, M. U. Rothmann, J. Borchert, R. L. Milot, H. Kraus, Q. Lin, F. Giustino, L. M. Herz,

- and M. B. Johnston, “Limits to electrical mobility in lead-halide perovskite semiconductors,” *J. Phys. Chem. Lett.*, vol. 12, p. 3607, 2021.
- [144] G. Nedelcu, L. Protesescu, S. Yakunin, M. I. Bodnarchuk, M. J. Grotevent, and M. V. Kovalenko, “Fast anion-exchange in highly luminescent nanocrystals of cesium lead halide perovskites (CsPbX_3 , $X = \text{Cl, Br, I}$),” *Nano Lett.*, vol. 15, p. 5635, 2015.
- [145] H. Min, D. Y. Lee, J. Kim, G. Kim, K. S. Lee, J. Kim, M. J. Paik, Y. K. Kim, K. S. Kim, M. G. Kim, T. J. Shin, and S. I. Seok, “Perovskite solar cells with atomically coherent interlayers on SnO_2 electrodes,” *Nature*, vol. 598, p. 444, 2021.