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Investigating Compositions and Fabrication Methodology for Efficient and Stable Wide-Bandgap Perovskite Solar Cells

Xinyi SHEN

The Queen's College



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Declaration of Authorship

I, Xinyi SHEN, declare that this thesis is my own work and that, to the best of my knowledge and belief, it contains no material previously published or written by another person nor material which has been accepted for the award of any other degree or diploma at any university or other institute of higher learning, except where due acknowledgement has been made in the text.

Abstract

Investigating Compositions and Fabrication Methodology for Efficient and Stable Wide-Bandgap Perovskite Solar Cells

Xinyi SHEN

Metal halide perovskite-based tandem solar cells are promising for achieving power conversion efficiency beyond the theoretical limit of their single-junction counterparts. However, the mediocre absolute efficiency and poor operational lifetime of wide-bandgap perovskite solar cells remain major hurdles for realising efficient and stable perovskite tandem cells. These issues can be attributed to non-radiative losses, heterogeneous crystallisation of the mixed-ion perovskites required for wide-bandgap, and light-induced halide segregation.

In Chapter 4, we report a holistic approach to overcoming challenges in 1.8-eV perovskite solar cells by engineering the perovskite crystallisation pathway by means of chloride additives. In conjunction with employing a self-assembled monolayer as the hole transport layer, we achieved a V_{OC} of 1.25 V and a η_{MPPT} of 17.0%. We elucidate the key role of methylammonium chloride addition in facilitating the growth of a chloride-rich intermediate phase that directs crystallisation of the desired cubic perovskite phase and induces more effective halide homogenization. The as-formed 1.8-eV perovskite demonstrates suppressed halide segregation and improved optoelectronic properties.

In Chapter 5, we demonstrate the first intermediate phase formed in co-evaporated 1.7-eV perovskites with a dimethylammonium iodide additive. The modified perovskite film achieved grain sizes of a few micrometers, which is around 5 times larger than the control film, implying the great

promise of using intermediate phase-assisted crystallisation to control the morphology of co-evaporated perovskites. Nevertheless, the sublimation of dimethylammonium iodide contaminated the evaporation chamber, hence, alternative molecules are required.

Finally, in Chapter 6, we establish the correlations between the optoelectronic and crystallographic properties of evaporated and solution-processed 1.67-eV perovskites and their macroscopic device performance and operational longevity. Interestingly, the evaporated perovskites have high crystallinity, uniaxial orientation, horizontally and vertically homogeneous grains, as well as solvent-free nature, leading to exceptional intrinsic stability under heat and light. For the first time, we demonstrate an evaporated 1.67-eV perovskite solar cell with comparable efficiency and stability to the state-of-the-art solution-processed cells. Furthermore, we demonstrate a fully-evaporated perovskite-Si tandem solar cell on a 1 cm² micro-textured Si wafer with a η_{MPPT} over 23%. We further show that our co-evaporated perovskite-Si tandem devices achieve excellent field-lifetime stability, maintaining 80% of their initial performance over eight months of continuous operation.

This thesis provides effective approaches to address the issues of wide-bandgap perovskites and an in-depth understanding of the underlying mechanisms that affect the performance and stability of solution-processed and evaporated wide-bandgap perovskite solar cells. This will help significantly in the successful advancement of efficient and stable perovskite tandem technologies in the future.

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List of Publications

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List of Abbreviations

ALD Atomic layer deposition

BCP Bathocuproine

E_g Bandgap energy

EDX Energy dispersive X-ray spectroscopy

EQE External quantum efficiency

ETL Electron transport layer

η Efficiency

FA Formamidinium

FF Fill factor

FTO Fluorine-doped tin oxide

GIWAXS Grazing-incidence wide-angle X-ray scattering

HTL Hole transport layer

ITO Indium-doped tin oxide

IZO Indium zinc oxide

J_{SC} Short-circuit current density

JV Current density voltage

Me-4PACz [4-(3,6-dimethyl-9H-carbazol-9-yl)butyl]phosphonic acid

MeO-2PACz [2-(3,6-Dimethoxy-9H-carbazol-9-yl)ethyl]phosphonic acid

MPPT Maximum power point tracking

NMR Nuclear magnetic resonance

2PACz [2-(9H-Carbazol-9-yl)ethyl]phosphonic acid

PCE Power conversion efficiency

PL Photoluminescence

PLQE Photoluminescence quantum efficiency

PMMA poly(methyl methacrylate)

PSC Perovskite solar cells

PTAA Poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine]

PV Photovoltaic

QCM Quartz-crystal microbalance

QFLS Quasi-Fermi level splitting

SAM Self-assembled monolayer

SEM Scanning electron microscopy

Spiro-TTB 2,2',7,7'-Tetra(N,N-di-p-tolyl)amino-9,9-spirobifluorene

SnO₂ Tin oxide

ToF-SIMS Time-of-flight secondary ion mass spectroscopy

V_{OC} Open-circuit voltage

WBG Wide-bandgap

WDXRF Wavelength dispersive X-ray fluorescence

XRD X-ray diffraction

Chapter 1

Introduction

1.1 The Global Energy Issue and Climate Dilemma

Since the late 18th century, following the onset of the Industrial Revolution, human society has undergone swift economic expansion propelled by technological progress. This era also witnessed a shift from agrarian-based communities to industrialised ones. Reflected in the global average gross domestic product (GDP) per capita over the long run (See Figure 1.1) [1], which is commonly utilised to assess economic growth and societal prosperity, surged significantly. The metric increased by more than 10-fold from 1300 dollars per capita in 1820 to 16997 dollars per capita in 2021. The drastic increase in GDP is primarily due to the intensive industrial activities (e.g. sourcing, processing, assembly, and repair of manufactured products), accompanied by a substantial increase in energy consumption in all sectors.

In Figure 1.2, I present the change in the global primary energy consumption by source from 1820 to 2022 [2]. A discernible pattern emerges indicating a transition from renewable sources (traditional biomass, wind, and hydropower) to non-renewable fossil fuels as the primary energy sources over the past two centuries. However, in order to maintain the rapid increase in GDP, human society has developed a heavy reliance on depletable

Global average GDP per capita over the long run

These historical estimates of GDP per capita are adjusted for inflation.

Our World
in Data

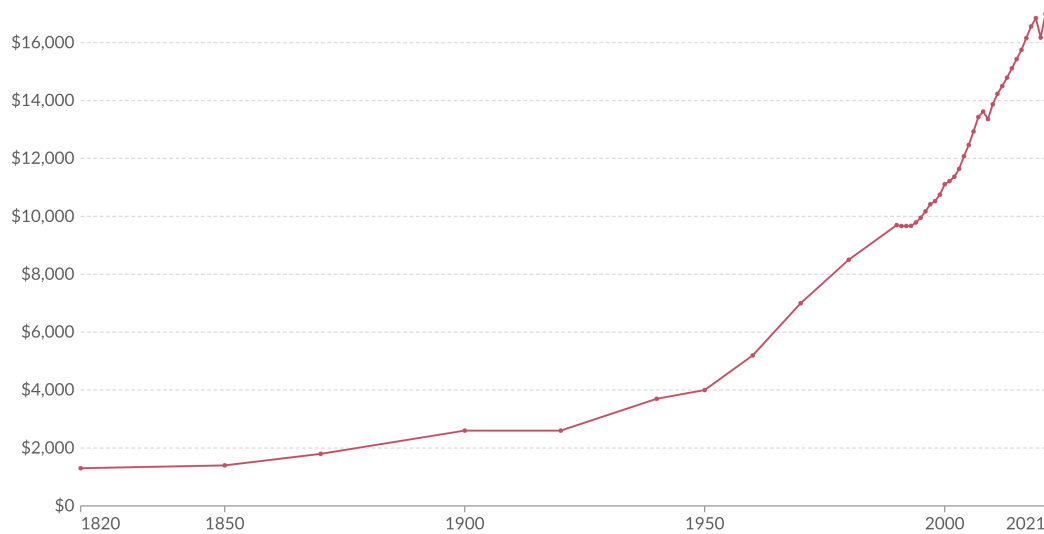


FIGURE 1.1: Global average GDP per capita in the long run (1820-2021). (Copyright - Max Roser, Pablo Arriagada, Joe Hasell, Hannah Ritchie and Esteban Ortiz-Ospina (2023) - "Economic Growth". Published online at OurWorldInData.org. Source: World Bank (2023); Maddison Project Database 2020 (Bolt and van Zanden, 2020); Maddison Database 2010 (Maddison, 2009)) [1].

Global primary energy consumption by source

Primary energy¹ is based on the substitution method² and measured in terawatt-hours³.

Our World
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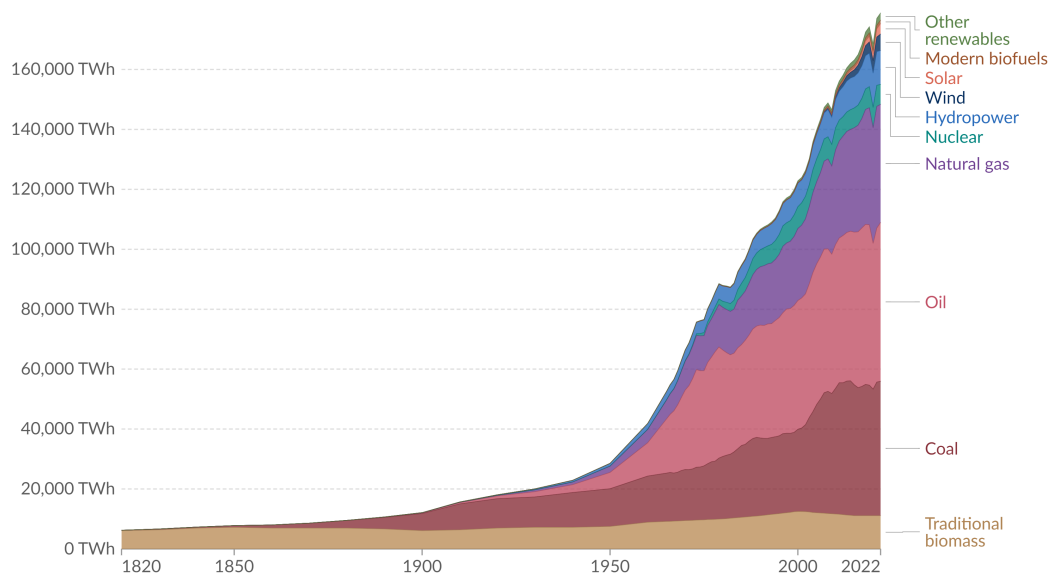


FIGURE 1.2: Global primary energy consumption from 1820 to 2022 (Copyright – Hannah Ritchie and Max Roser. Published online at OurWorldInData.org. Source: Energy Institute - Statistical Review of World Energy (2023), Vaclav Smil (2017) [2].

resources for power production activities, which is not a sustainable solution for long-term economic growth and human well-being.

Global warming: monthly temperature anomaly

The combined land-surface air and sea-surface water temperature anomaly is given as the deviation from the 1951–1980 mean.

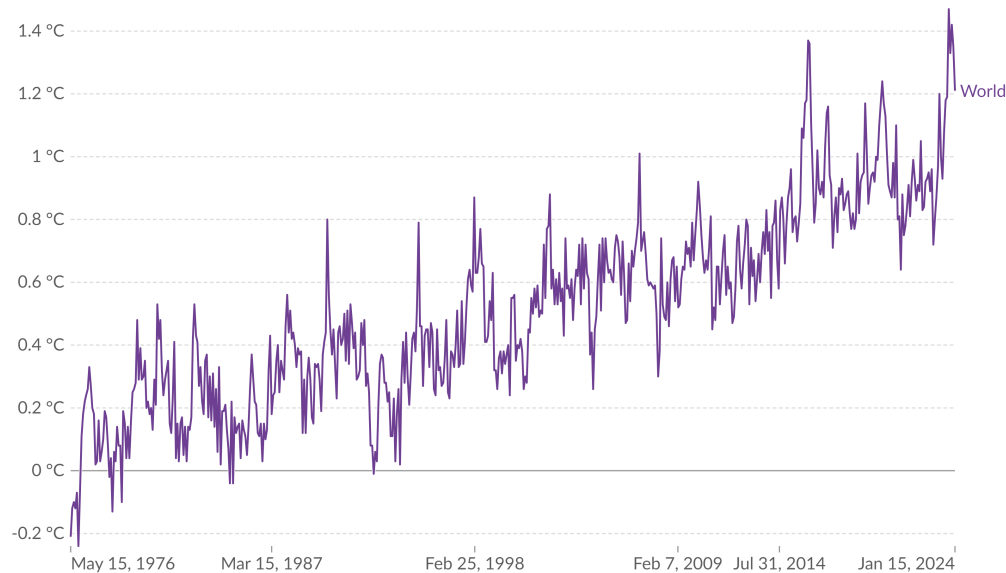


FIGURE 1.3: Global average temperature change from 1976 to 2024 (Published online at OurWorldInData.org. Source: NASA Goddard Institute for Space Studies - GISS Surface Temperature Analysis [3].

The utilisation of non-renewable fossil fuels, often through combustion, releases substantial heat as an energy source, inevitably producing carbon dioxide (CO₂) as a byproduct. CO₂, a well-known greenhouse gas, can absorb infrared radiation and trap heat, influencing the Earth's surface temperature. While greenhouse gases are crucial for maintaining an optimal temperature essential to the survival of animals and plants, an excessive concentration can lead to adverse effects. When the level of greenhouse gases surpasses a safe threshold, it triggers a cascade of global warming impacts, exerting immense pressure on the environmental and ecological systems vital for sustaining human life on Earth. One of the most immediate consequences is the global average temperature that has risen by 1.4 °C in less than 50 years (Figure 1.3) along with an increase in the annual CO₂ emission due to the burning of fossil fuels (Figure 1.4) [3], [4]. Such an insignificant

Annual CO₂ emissions

Carbon dioxide (CO₂) emissions from fossil fuels and industry¹. Land-use change is not included.

Our World
in Data

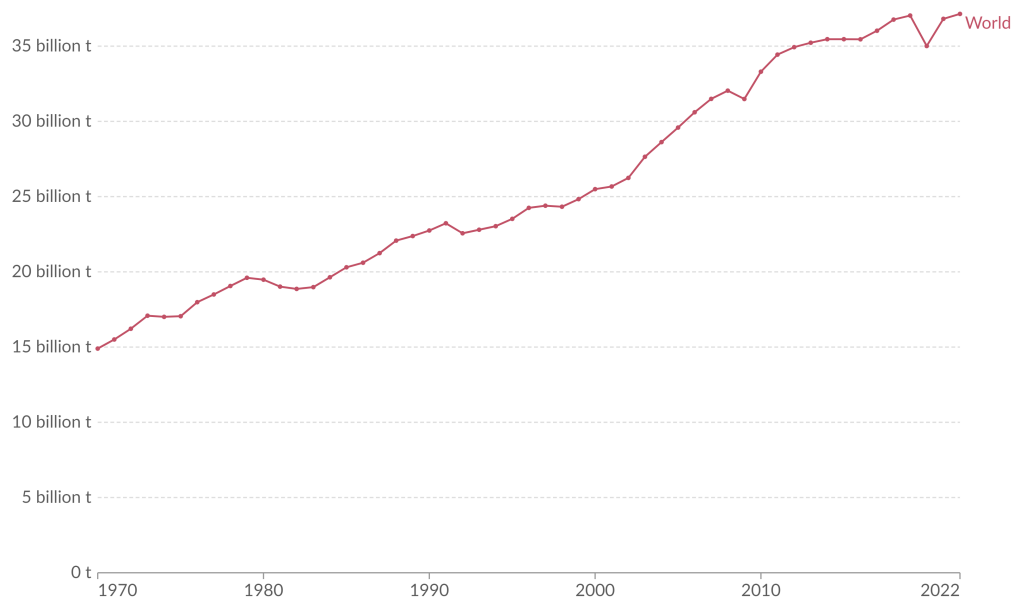


FIGURE 1.4: Global CO₂ emission due to the burning of fossil fuels between 1970 and 2022 (Copyright – Hannah Ritchie and Max Roser. Published online at OurWorldInData.org. Source: Global Carbon Budget (2023)) [4].

temperature change has led to noticeable consequences in our daily lives, including more frequent extreme weathers, an increase in sea level due to the melting of the polar ice caps and mountain glaciers, changing animal migration patterns, etc. [5]. To prevent the occurrence of more severe consequences (e.g. species extinction and humanitarian crisis) in the future, more attention and efforts are required to reduce the consumption of fossil fuels and the emission of greenhouse gases.

1.2 Harnessing Solar Power with Photovoltaic Technology

To recap, in section 1.1, I emphasise the importance of reducing reliance on fossil fuels to address the escalating climate crisis. To facilitate a seamless

transition from finite fossil fuel energy sources to renewable ones, it's imperative to develop alternative renewable technologies that are both efficient and cost-effective, comparable to fossil fuels. The sun, with its virtually boundless energy reserve, presents us with opportunities to harness energy with high efficiency and low cost. Various attempts have been made in the past to convert sunlight into usable energy for our society, such as using mirrors to concentrate sunlight to heat water for electricity production [6]. However, this method predominantly utilises infrared light from the solar spectrum, resulting in the wastage of a significant portion of photons in the visible and ultraviolet range [7]. Moreover, the inclusion of redundant energy conversion processes leads to further energy losses, limiting the power conversion efficiency (PCE).

An alternative approach involves the direct conversion of sunlight into electricity with photovoltaic (PV) technology using semiconducting materials [9]. PV materials can absorb photons with energy equal to or greater than their bandgaps, converting them into electron-hole pairs at the bandgap energy level, while the excess energy carried by photons above their bandgap is lost as heat via thermalisation [10]. Therefore, achieving optimal performance in PV systems requires a balance between maximising the optical absorption and minimising the thermalisation loss [10]. In 1961, William Shockley and Hans-Joachim Queisser conducted the first calculation of the theoretical PCE achievable by a single-junction PV cell, also known as the Detailed Balance (DB) limit [11]. This limit sets a theoretical threshold of 33.7% for the ideal single-junction PV cell ($E_g = 1.34$ eV) under the AM1.5 solar spectrum [7]. In most developed countries where solar panels are deployed, which are often located significantly away from the equator, the AM1.5 solar spectrum serves as the standard for characterising solar irradiance in research on solar cells [7]. The AM1.5 spectrum represents sunlight after traversing 1.5

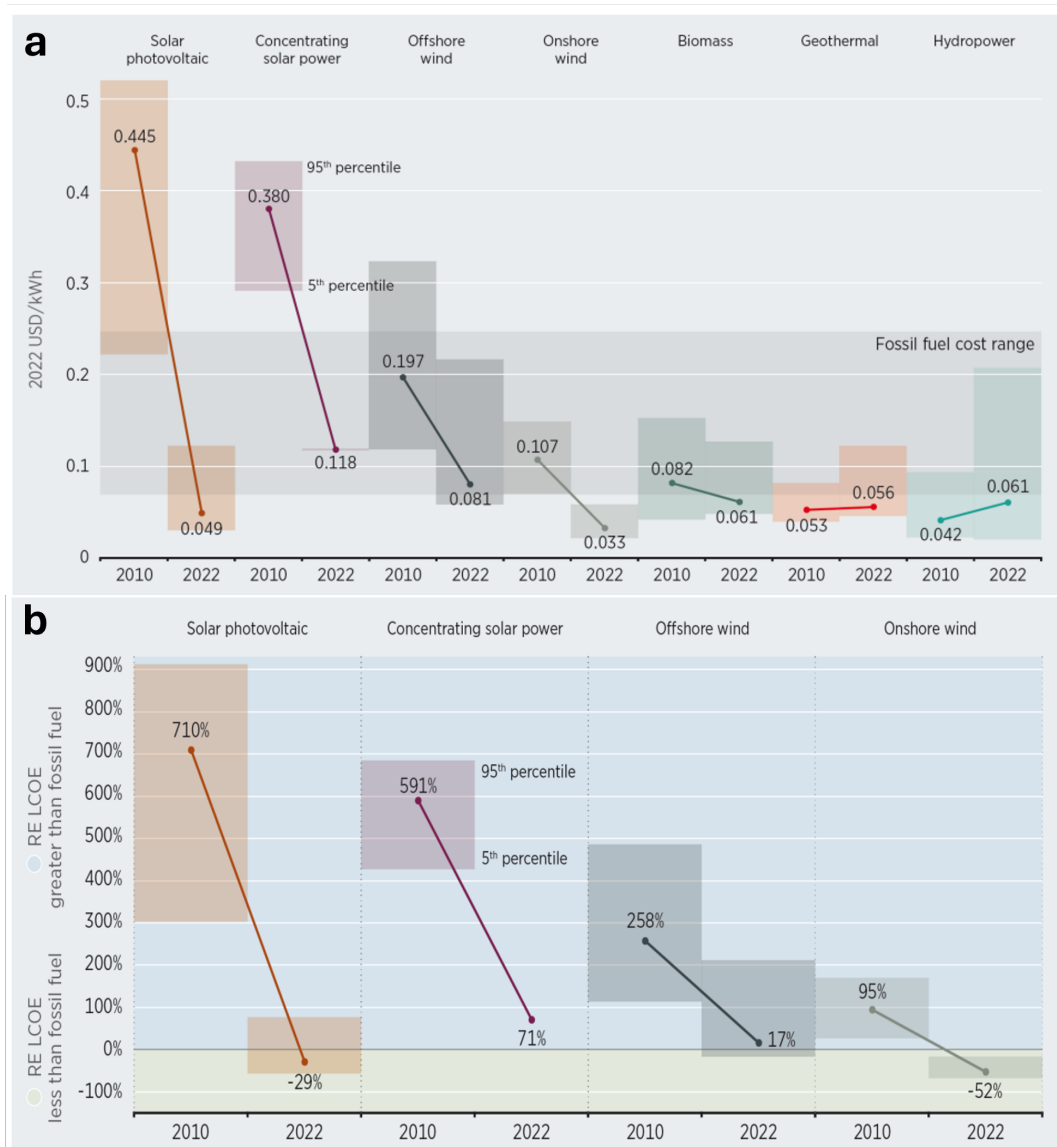


FIGURE 1.5: (a) Global weighted-average LCOE of renewable energy technologies (b) compared to that of fossil fuels (2010-2022) (Copyright – International Renewable Energy Agency (IRENA). Published online at www.irena.org. [8].

atmospheric lengths, with a solar zenith angle of 48.2° , corresponding to an illuminance of 1000 W/m^2 at 1 Sun [12], [13]. Nowadays, multi-junction PV cells offer a practical means to surpass the DB limit [14]. Essentially, by stacking several solar cells on top of each other, multi-junction PV cells can achieve higher efficiencies by capturing a broader spectrum of sunlight and minimising thermal losses [14]. The theoretical efficiency limit of two-junction (tandem), three-junction and infinite junction PV devices is raised to 46 % ($E_{g1} = 1.9 \text{ eV}$, $E_{g2} = 1.0 \text{ eV}$), 52 % ($E_{g1} = 2.3 \text{ eV}$, $E_{g2} = 1.4 \text{ eV}$, $E_{g3} = 0.8 \text{ eV}$)

and 86.8 % (68.7 % under unconcentrated sunlight), respectively [14]. The successful demonstration of highly efficient multi-junction solar cells across various systems has positioned it as a primary focus for the advancement of next-generation PV technologies [15], [16].

Due to their high efficiency, stability, and environmental safety, silicon-based solar cells have dominated the PV market for the past few decades [17], [18]. The levelized cost of electricity (LCOE) serves as a common indicator in the energy industry for evaluating the economic viability of different energy sources consistently [19]. It considers the average net present cost of electricity generation for a generator over its assumed operational lifespan.

According to a report from the International Renewable Energy Agency (IRENA) (refer to Figure 1.5) [8], the cost of solar PV has plummeted by an order of magnitude over 12 years due to enhancements in efficiency, economies of scale, and improved production yields of silicon solar cells. It is now even 29% cheaper than the least expensive fossil fuels, indicating significant potential for reshaping the energy market. However, achieving the ultimate goal of carbon neutrality by 2050 requires the urgent establishment of a terawatt-scale PV market [20]. Despite 60 years of research, the manufacturing cost of silicon PV still poses a barrier to large-scale global deployment [21]. Moreover, their PCE is already approaching the theoretical limit [18], further constraining their power output-to-cost ratio.

Next-generation PV materials like Cadmium Indium Gallium Selenide (CIGS) and Indium Gallium Arsenide (InGaAs) have made significant progress in overcoming the theoretical limitations of silicon PV [22], [23]. However, they are still produced using similar techniques, resulting in high production costs [22], [23]. In contrast, metal halide perovskites have emerged in the

past decade as a remarkable class of materials [24], [25]. They not only possess many desirable optoelectronic properties similar to CIGS and InGaAs [26]–[28], but also can be easily fabricated using extremely low-cost solution processing or thermal evaporation techniques [29].

1.3 Perovskites for PV Applications

Since their introduction as photovoltaic materials in 2009 [24], metal halide perovskite solar cells (PSCs) have already achieved single-junction certified PCEs of up to 27% [18], matching those of industrially dominant single crystalline silicon [18]. Metal halide perovskites have the general formula ABX_3 , where A is a large cation (e.g. methylammonium, MA^+ , formamidinium, FA^+ ; caesium, Cs^+), B is a metal cation (e.g. lead, Pb^{2+} , tin, Sn^{2+}), and X is a halide anion (chloride, Cl^- ; bromide, Br^- ; iodide, I^-) [30]. To minimise the coulomb repulsion between A and B, perovskites normally adopt a 3D network of corner-sharing $[BX_6]^{4-}$ octahedrons, and the A-site cation can fit into the vacancies (as depicted in Figure 1.6). This imposes a design rule for A-site cations: A stable perovskite crystal lattice can form only when the Goldschmidt tolerance factor, t , is within the range of 0.71 – 1.0 [31]. Goldschmidt tolerance factors are widely used to pseudo-quantify the phase stability and degree of distortion expected in the cubic ABX_3 perovskite crystal structure [31].

$$t = (r_A + r_X) / \sqrt{2(r_B + r_X)} \quad (1.1)$$

where r_A , r_B , r_X are the ionic radii of the A cation, B cation and X anion respectively.

In contrast to conventional semiconducting materials, like Si, which

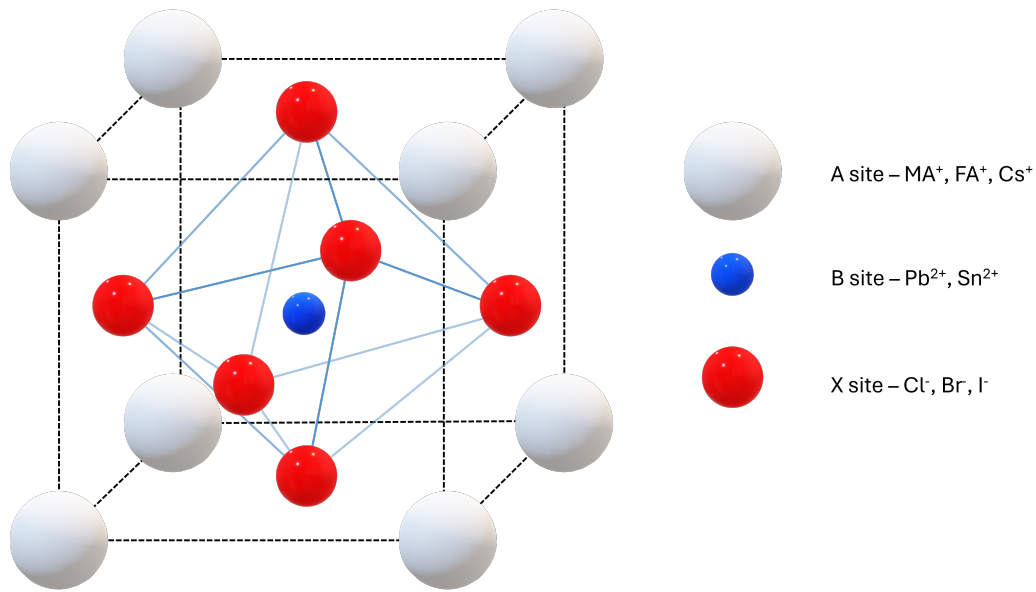


FIGURE 1.6: Crystalline ABX_3 structure of metal halide perovskites. Commonly used molecules for A, B, and X sites are also listed. MA^+ : methyammonium cation, FA^+ : formamidinium cation.

typically have fixed bandgaps [32], perovskite materials offer the advantage of tunable bandgaps across a wide range [33]–[35]. This tunability is achieved by adjusting the ratio between different ions in the perovskite compositions, allowing for the harvesting of different parts of the solar spectrum [33]–[35]. For example, increasing the bromide content is a commonly used technique to widen the material bandgap [33]. Similarly, narrow bandgap perovskites (with $E_g = 1.2$ eV) can be produced by incorporating a mixture of Pb and Sn at the B-sites [35].

Furthermore, perovskites can be manufactured using various methods, making them compatible with a range of production approaches [29], [36], [37]. Coupled with their bandgap tunability, this versatility positions them as ideal candidates for tandem applications [38]–[41]. This includes both all-perovskite configurations and combinations with established silicon

technologies [38]–[41]. The latter is especially significant for the commercial viability of perovskite materials, as they can be deposited onto existing silicon wafers at relatively low cost to enhance the PCE of the established market-leading technology. It's worth noting that the certified PCE of perovskite-Si tandem solar cells has recently reached 34.6% [39], marking perovskites as the next promising game-changer for the PV industry.

One major hurdle remaining for the commercialisation and global adoption of PSCs is the development of a manufacturing route compatible with high-throughput and large-scale industrial production. While spin coating is the most commonly used fabrication method for small-area PSCs at the lab scale due to its lower capital investment requirement, upscaling such technology and other solution-based fabrication methods to the industrial level is unrealistic [29], [42]. The main bottleneck lies in the significantly increased economic and environmental costs of solvent procurement and disposal [43].

Alternatively, these issues can be effectively addressed by utilising thermal evaporation, a method that has demonstrated its viability in other commercial optoelectronic devices such as OLED displays and thin-film PV modules [22], [30], [44]. Thermal evaporation, also known as "the dry process" for PSCs, involves heating the precursor materials under vacuum to sublime them and allow for crystallisation on substrates without the use of any toxic solvents [29], [45]. Furthermore, thermal evaporation facilitates the uniform growth of high-quality perovskite films over large-area substrates with precise thickness control [42], [46]. These characteristics make this technique especially well-suited for producing tandem devices [46], where multiple layers need to be deposited sequentially without compromising the quality of underlying layers. In contrast, solution-based routes require careful

consideration of solvent orthogonality to prevent damage to underlying layers [29]. Additionally, the thickness of each layer can be finely tuned to optimise photon absorption, thereby enhancing the overall device PCE [46].

1.4 Layout of Thesis

This thesis focuses on developing high-efficiency and operationally stable wide-bandgap (WBG) PSCs for tandem applications. In this work, I comprehensively address many bottlenecks present in both solution processing and thermal evaporation of compositional complex mixed-cation, mixed-halide WBG perovskite systems, which are essential to coupled with crystalline silicon and other perovskites to create high-performing multi-junction solar cells.

Chapter 1 highlights the significance and motivation of developing renewable energy sources, especially photovoltaic technology as an alternative to fossil fuels. I also introduce perovskite materials as a promising candidate for PV applications.

Chapter 2 provides an overview of the theory and concepts essential to this thesis. In this chapter, I first cover the working principle of solar cells and the significance of utilising tandem PV technology to surpass the Detailed Balance limit. I then provide a detailed literature review to systematically discuss the advantages and limitations of using solution processing and thermal evaporation for the fabrication of PSCs and the resultant optoelectronic properties of the perovskite films made via corresponding methods. I also outline the causes of the limited operational stability of PSCs.

Chapter 3 describes the experimental techniques used throughout the thesis in detail. This includes the fabrication of perovskite films and full

devices as well as the characterisation techniques used to study the sample properties.

Chapter 4 comprehensively investigates the impacts of various chloride additives on the crystallisation process of a 1.8-eV mixed-halide perovskite which has an ideal bandgap for making all-perovskite tandem solar cells. I unveil the role of MACl additive in promoting halide homogenisation via a more controlled crystallisation of perovskite materials. The MACl-modified perovskites demonstrate enhanced resistance to light-induced halide segregation and better ambient stability. The optimised PSCs also show reduced photovoltage deficit as well as improved steady-state power output.

In Chapter 5, I demonstrate a successful proof of concept by introducing an intermediate-phase assisted crystallisation pathway into co-evaporated WBG perovskites with a DMAI additive. The optimised perovskite films show substantially enlarged grain size in the order of a few μm . This method sheds light on manipulating the crystallographic properties of co-evaporated perovskites with additive engineering, which has been widely employed in solution-processed perovskites but rarely reported in evaporated perovskites.

Chapter 6 thoroughly investigates the optoelectronic and crystallographic properties of evaporated and solution-processed WBG perovskites (1.67 eV). I also discuss their impacts on the device efficiency and operational lifetime. For the first time, I present full-evaporated PSCs that achieve efficiency and stability on par with state-of-the-art solution-processed solar cells. Furthermore, I demonstrate a fully evaporated perovskite-Si tandem solar cell with excellent outdoor stability under real operational conditions.

Chapter 7 summarises the works present in this thesis and provides an outlook for future research directions.

Chapter 2

Theory and Background

2.1 Fundamentals of Photovoltaic Devices

2.1.1 Single Junction Solar Cell

A single-junction solar cell operates by generating voltage and current simultaneously through the absorption of photons. This process relies on the use of a semiconducting material and involves three key steps: absorption of light, separation of charge carriers, and extraction of charge carriers to an external electric circuit. Each step will be introduced in more detail below:

When a semiconductor is exposed to light, the presence of a bandgap (the energy difference between its valence band and conduction band, E_g) allows only photons with energy equal to or greater than the material's bandgap to be absorbed. Subsequently, the absorbed photon energy excites an electron from the valence band to the conduction band, creating an electron-hole pair in the process. Although the electron initially gains energy equivalent to the absorbed photon's energy, it quickly relaxes back to the bottom of the conduction band, with any excess energy dissipating as heat (i.e., in the form of phonons) to the crystal lattice. Therefore, the net energy gain can only be equal to or less than the bandgap energy [10].

In addition to absorption, incident photons may also be reflected at an interface or transmitted through the material, leading to optical loss. When light passes through a solar cell with multiple layers of different refractive indices, both reflection and refraction occur, reducing the number of photons reaching the absorber layer [10]. In commercial PV technologies such as silicon solar cells, textured pyramidal structures are employed as effective anti-reflective strategies to minimise the optical loss [47], [48]. Additionally, low-energy photons that do not contribute to the electricity generation in a single-junction solar cell can be harnessed with a multi-junction device configuration (i.e., tandem solar cell), which will be discussed in section 2.1.4.

Following the generation of an electron-hole pair, the opposite charges they carry make them subject to Coulomb attraction and tend to undergo a recombination process. However, the current can only be produced when charges are effectively separated and extracted at different ends of the solar cell. Hence, for solar cell application, semiconductors with high dielectric constants are preferentially selected to screen the Coulomb interaction between the electron-hole pairs [10], [32]. For instance, the high dielectric constant of Si allows electrons and holes to be separated readily at ambient temperature [10], [49].

In a single-junction solar cell, the transport of free charge carriers occurs through two processes: drift and diffusion. In the drift mode, charge movement is driven by an electric field, causing electrons and holes to move in the opposite directions towards their respective electrodes [10]. Electrons move towards the positive electrode (anode), while holes move towards the negative electrode (cathode). In the diffusion mode, charge carriers move down their concentration gradients throughout the materials, travelling from areas of high concentration to areas of low concentration. In traditional solar

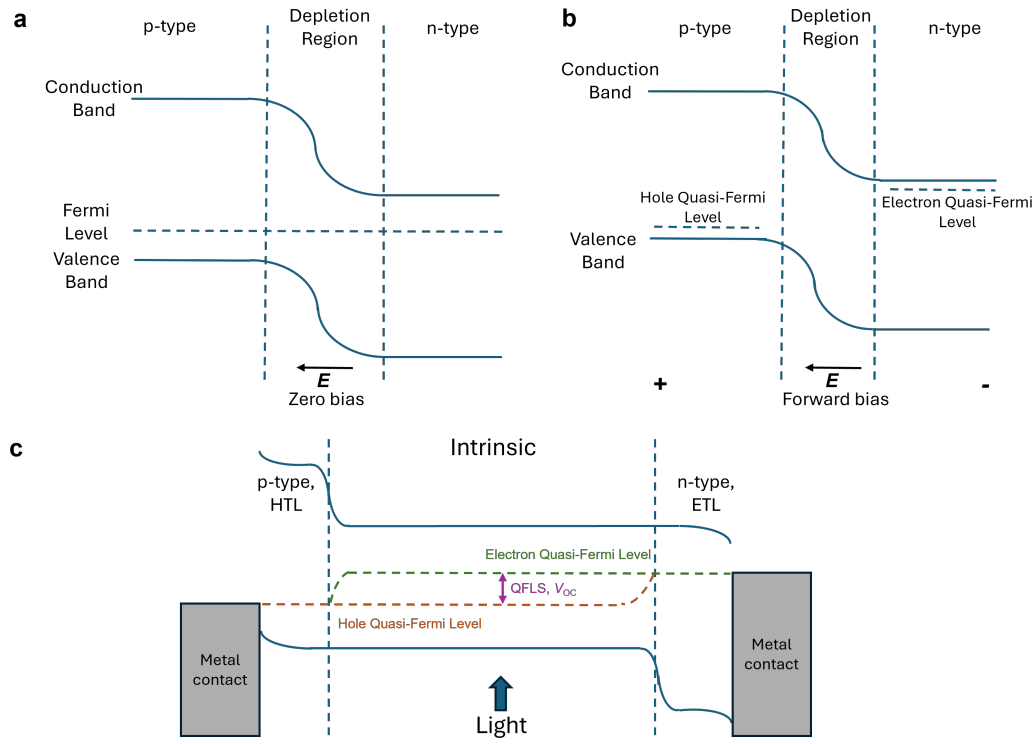


FIGURE 2.1: Band structure of a conventional p-n junction (a) at equilibrium, or (b) under forward bias. (c) A p-i-n junction solar cell under open-circuit and illumination. The holes in the valence band and the electrons in the conduction band now have distinct quasi-Fermi levels. The quasi-Fermi level splitting (QFLS) gives the V_{OC} of the device.

cells, selective extraction of electrons and holes is achieved using a p-n junction, which consists of p-type and n-type semiconductors (See Figure 2.1a and b). The asymmetric doping of an intrinsic semiconductor material can create materials containing either an excess amount of holes (p-type) or electrons (n-type) at room temperature. This results in the formation of a depletion region and a built-in potential at the interface of the p-n junction. Charge carriers can only flow through the junction in one direction.

Under dark conditions (Figure 2.1a), the charge carriers in the p-n junction are at equilibrium with zero bias. Electrons and holes share a single Fermi level, indicating identical electrochemical potentials for both carrier types, hence, there is no net current flow. The Fermi level position depends on doping and it is nearer to the conduction band in n-type materials

and valence band in p-type materials [10]. Under illumination, generation of electron-hole pairs because of the absorption of photons with energy higher than the semiconductor bandgap, will disrupt the equilibrium. An electric field is naturally formed due to the redistribution of charge carriers: electrons are pushed towards the p-type side, and holes are pushed towards the n-type side. This instant separation of charges creates an electrochemical potential difference and separate electron Quasi-Fermi level and hole Quasi-Fermi level. The difference between these levels is called Quasi-Fermi Level Splitting (QFLS). QFLS represents the gradient in electrochemical potential that drives electrons and holes towards opposite contacts, which is the primary force enabling charge extraction. As such, QFLS represents the maximum usable energy per photogenerated carrier pair [10]. This electrochemical potential gradient can be maintained while electron-hole pairs are generated continuously upon illumination. Meanwhile, when an external circuit is connected, separated charges can flow through it to recombine, thus giving rise to an electric current. The simultaneous production of voltage and current in such a passive device under light irradiation is known as the photovoltaic effect and the miracle of solar cells [10]. Owing to the photovoltaic effect, sunlight can be directly converted into electric power, making solar cells more efficient compared to other solar power harvesting technologies, such as hot water panels, which require additional energy conversion steps with more potential energy losses [50].

However, heavy doping required to form the p-n junction has been found to be detrimental to device performance [10]. Therefore, emerging PV technologies, particularly perovskite solar cells (PSCs), commonly use a p-i-n heterojunction structure instead (See Figure 2.1c). In this configuration, an intrinsic semiconductor (perovskite) is sandwiched between a p-type (hole transport layer, HTL) and an n-type (electron transport layer, ETL) contact.

As the absorber layer, perovskite materials exhibit high absorption coefficients, enabling efficient photon capture even in thin films [27]. In addition, perovskites have weak exciton binding energy (around 2-50 meV), allowing excitons to dissociate into free electrons and holes at room temperature [51]. As implied by their names, the HTL and ETL selectively collect holes and electrons, respectively, while acting like blocking layers to the opposite charge carriers [10]. The alignment of the Fermi levels of the materials, along with the gradients in the conduction and valence bands, effectively guides free carriers to move towards the selective contacts. This can be achieved by carefully selecting the charge transport materials. The electron transport material should have a deeper valence band relative to the intrinsic layer to create an energetic barrier to hole flow while maintaining low hole conductivity to minimise the hole transport. On the contrary, the hole transport material should have a shallower conduction band relative to the intrinsic layer to block the electron flow and facilitate hole transport [10]. In PSCs, the use of selective charge transport layers enables efficient charge collection at the opposite contacts to maintain the QFLS. The QFLS sustains voltage potential while enabling current flow with an external circuit connected. Hence, simultaneous current and voltage generation can be realised in PSCs. Poor selectivity will cause interfacial recombination and reduce the QFLS [10].

2.1.2 Current Voltage Characterisation of Solar Cells

In section 2.1.1, I provided a brief overview of how solar cells can be utilised for power generation. To assess the quality of a solar cell as a practical energy source for both laboratory research and industrial applications, it is essential to quantitatively measure the device performance. Hence, PCE is introduced as a key parameter that evaluates how effectively the incident photons can be converted into electricity by a solar cell with a known active area.

The AM1.5 spectrum, which accounts for optical filtration by Earth's atmosphere and incident angles, with an illuminance power density of 1000 W/m^2 (1-sun intensity) and an ambient temperature of 25°C , is chosen as the global standard conditions for characterising the efficiency of solar cells. By measuring the electrical power output generated by a solar cell while a photon flux shines onto the surface area of the solar cell, the PCE of a solar cell can be calculated using the following equation:

$$\text{PCE} = \frac{\text{maximum electrical power output}}{\text{incident photon power}} = \frac{P_{\text{mpp}}}{P_{\text{in}}} \quad (2.1)$$

where P_{mpp} is the maximum power density generated by the solar cell, and P_{in} is the incident photon power density.

The power density output, P , is calculated by multiplying the current density (J) and voltage (V). To find the maximum power density output (P_{mpp}), the point on the current voltage (JV) curve that delivers the maximum power must be determined. This can be accomplished by sweeping the solar cell with a bias voltage and monitoring the change in current density. The maximum power point is found at the JV pair that yields the highest power. For an ideal solar cell (or an ideal diode), the relationship between J and V can be described by the diode equation:

$$J = J_{\text{SC}} - J_0(e^{qV/k_{\text{B}}T} - 1) \quad (2.2)$$

where J_{SC} is the short-circuit current, which is the maximum current generated in a solar cell when there is no applied voltage (the applied bias is set to 0) under standard illumination conditions. It represents the maximum current the solar cell can produce. J_0 is the dark saturation current, which is the current flowing through the diode when no light is incident on the cell. q is

the electric charge carried by an electron, k_B is the Boltzmann's constant, and T is the temperature of the solar cell.

The open-circuit voltage (V_{OC}) is the maximum voltage built up in a solar cell while no current flows (i.e., the circuit is at open condition, and the bias is effectively infinite) under standard illumination conditions, which can be given as:

$$V_{OC} = \frac{k_B T}{q} \ln \left(\frac{J_{SC}}{J_0} - 1 \right) \quad (2.3)$$

As shown in Figure 2.1b, the quasi-Fermi level, which is a measure of the population of electrons and holes in the conduction band and the valence band, respectively, is different when a semiconducting layer is under illumination. The photoexcited electrons in the conduction band and the holes in the valence band can be considered as isolated systems internally in equilibrium because of the slow intra-band recombination rate compared with the inter-band relaxation rate. Their separate quasi-Fermi levels give rise to the quasi-Fermi level splitting (QFLS), which represents the intrinsic chemical potential and can be further interpreted as the ceiling of the V_{OC} of a solar cell. In the practical scenario, the V_{OC} is always lower than QFLS due to contact losses [32].

The maximum power point of a solar cell can thus be determined by J_{SC} , V_{OC} , and an additional parameter called the fill factor (FF). The FF is defined as the ratio of the power produced at the maximum power point to the product of V_{OC} and J_{SC} . Mathematically, it's given by the equation:

$$FF = \frac{P_{mpp}}{J_{SC} V_{OC}} = \frac{J_{mpp} V_{mpp}}{J_{SC} V_{OC}} \quad (2.4)$$

where FF is the fill factor, P_{mpp} is the power generated at the maximum power point, which is the highest power output of the solar cell, J_{mpp} is the current density at maximum power point, V_{mpp} is the voltage at maximum power point.

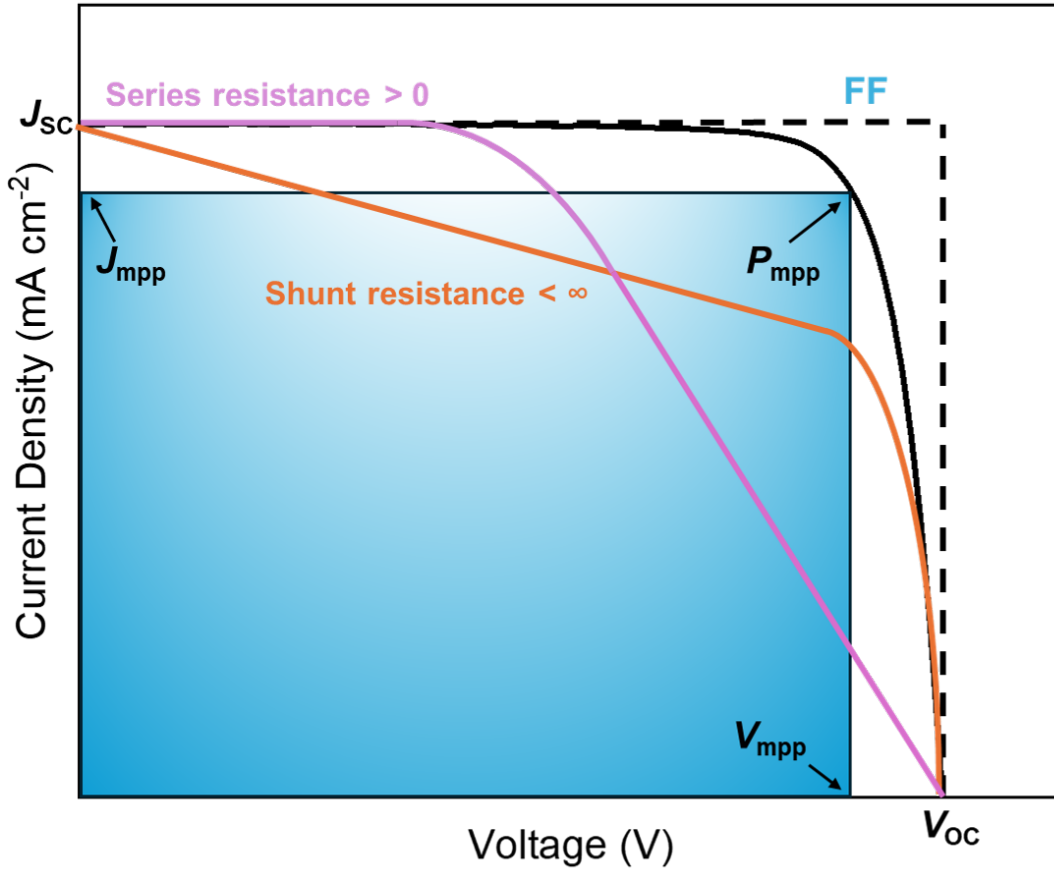


FIGURE 2.2: JV curve of a typical solar cell (black) under illumination. The blue rectangle is delimited by the voltage and current at max power point (J_{mpp} , V_{mpp} , and P_{mpp} , respectively). The area of the blue rectangle compared to the area delimited by the V_{OC} and the J_{SC} represents the FF. The purple and orange lines demonstrate the impact of higher series resistance and lower shunt resistance, respectively, on the JV curve and the cell's performance.

The fill factor provides an indication of the quality of the solar cell, as it measures how efficiently the solar cell converts sunlight into electricity at the maximum power point. A higher fill factor generally indicates a better-performing solar cell. The fill factor of a solar cell is primarily influenced by two key factors: series resistance and shunt resistance. The series resistance accounts for all the parasitic resistance present within the bulk material, at

the interfaces, and at the contacts, which can impede the flow of current. In an ideal scenario, the series resistance should be zero. However, if there is any resistance, it can decrease the steepness of the JV curve near the V_{OC} and negatively impact the overall performance of the device. The shunt resistance represents the existence of alternative shunt paths across the solar cell. Ideally, the shunt resistance should be close to infinity to prevent any leakage current. However, fabrication defects such as pinholes in the device structure can create direct contact between charge transport layers or between the absorber layer and electrodes. This can reduce the shunt resistance, create leakage current, and reduce net current density [10].

Both series and shunt resistances play critical roles in determining the overall efficiency and fill factor of a solar cell. Keeping series resistance low and shunt resistance high helps maintain a high fill factor, which in turn contributes to better device performance. A JV curve of a typical solar cell along with V_{OC} , J_{SC} , P_{mpp} , and the impacts of high series resistance/ low shunt resistance on the JV curve are visually demonstrated in Figure 2.2.

2.1.3 Detailed Balance Limit

The theoretical efficiency limit of a single-junction solar cell, also known as the detailed balance limit, was first calculated by William Shockley and Hans-Joachim Queisser in 1961 [11]. This limit establishes the relationship between the semiconductor bandgap and the maximum power output an ideal solar cell can deliver. The origin of this efficiency limit is based on the fact that only photons with energy equal to or greater than the material bandgap can be absorbed by the semiconductor. Furthermore, the maximum energy that can be harvested from these photons is equal to or less than the material bandgap energy. This creates a balance between maximising absorption and maximising the bandgap energy. A semiconductor material with a

smaller bandgap can absorb a broader spectrum of photons, but each photon will generate a smaller amount of energy. On the other hand, a larger bandgap material can absorb only a limited range of photons, but each absorbed photon provides more energy. This trade-off influences the choice of bandgap in designing solar cells and sets the upper limit for the power conversion efficiency of single-junction solar cells. In practice, this efficiency limit varies depending on the specific material and design of the solar cell, but it provides a theoretical benchmark for the maximum performance that can be achieved [11].

The detailed balance limit is based on a series of idealised assumptions about a solar cell's operation. In real-world solar cells, these assumptions often do not hold, leading to additional efficiency losses. Here are some factors that contribute to efficiency loss in actual solar cells. Firstly, the detailed balance model assumes that all the incident photons with energy above E_g can be absorbed. In reality, optical losses due to reflection and transmission can occur, reducing the number of photons absorbed by the cell. Additionally, the optimal absorber layer thickness must be within the charge diffusion length to ensure efficient charge collection at the contacts, which can further limit absorption. Furthermore, the parasitic absorption by the charge transport layers or any passivation layers is not negligible in real solar cells. Secondly, all recombination in an ideal solar cell is assumed to be radiative, which means all the generated electron-hole pairs under illumination will contribute to electricity generation. In principle, the charge recombination rate is dependent on the temperature of the cell through the so-called thermal voltage (V_c), where $V_c = k_B T_c / q$. In the extreme scenario, the open-circuit voltage of a solar cell can be equal to E_g if the sun is infinitely hotter than the solar cell. Indeed, this is not true in the real world. Hence, the maximum V_{OC} is always lower than E_g , reducing the maximum theoretical efficiency.

Moreover, in practice, non-radiative recombination occurs due to defects in the bulk material or charge-selective materials, leading to additional performance losses. Thirdly, each photon absorbed by an ideal solar cell is assumed to give rise to exactly one electron-hole pair. However, in actual devices with imperfect external quantum efficiency (EQE), this process may not be entirely efficient, reducing the cell's overall performance. Also, high-energy photons can undergo thermalisation losses to lose excess energy as heat, resulting in further performance loss. In some cases, a single high-energy photon can undergo photon downconversion to create multiple charge carriers, offering an effective method to reduce the thermalisation losses and surpass the detailed balance limit [52]. Lastly, all the charge carriers in an ideal solar cell can be effectively extracted at the contacts. In a real device, factors such as non-zero series resistance due to contact resistance and non-infinite shunt resistance due to fabrication defects also impede charge extraction and decrease efficiency [10].

In conclusion, the detailed balance limit serves as a useful guide for selecting semiconducting materials with optimal bandgaps for achieving the highest potential efficiency. It provides a theoretical benchmark for solar cell performance and helps inform decisions about material choices in solar cell design. However, real-world applications come along with additional challenges, which are outlined above, that need to be addressed to optimise solar cells and approach their theoretical limit. By carefully considering these factors and employing advanced materials and manufacturing techniques, it is possible to enhance the efficiency of solar cells in practice. In the past, a series of strategies have been explored to circumnavigate the detailed balance limit for single-junction solar cells, including: 1. Integrating non-reciprocal photonics to redirect emitted photons back into the solar cells for reabsorption [53]. 2. employing multi-junction/tandem architecture to split the solar

spectrum and reduce thermalisation losses [54]. 3. Using photon downconversion to create multiple charge carriers with one high-energy photon [52]. 4. Mimicking photosynthetic coherence to suppress recombination, as explored in bio-inspired PSCs [55]. Despite some progress having been made, continuous research and development efforts are still essential to push the boundaries of solar cell efficiency and make solar energy an even more viable and sustainable energy source [10].

In addition to the detailed balance limit, there are other limits which also provide predictions of the theoretical efficiency ceilings for solar energy conversion systems. For example, the Carnot limit treats the Sun and the Earth as two heat sinks, and the temperature differential (5800 K vs 300 K) between them determines the maximum efficiency of any solar energy converter to be 95% [56]. However, this limit is based on an assumption that the energy transfer between the two heat reservoirs is reversible with no increase in entropy. Given that solar cells are quantum converters that convert photon energy directly to electricity, rather than heat engines, this limit is fundamentally unattainable for solar cells, including idealised infinite-junction designs [56]. If we take the irreversible entropy generation in photon absorption and re-emission into account, and treat the sunlight as blackbody radiation with lossless absorption and emission, we get the blackbody efficiency limit set by the second law of thermodynamics for a solar cell to be 93.1% [56]. Furthermore, as processing the incident solar energy current is not possible without entropy generation, the upper limit for a solar cell under maximally concentrated solar radiation is 86% [56].

Moreover, since PSCs typically use ultra-thin absorber layers (300–1,000 nm) to minimise recombination losses. However, thin films inherently suffer from incomplete light absorption, especially near the bandgap. In this scenario, the Yablonovitch limit provides a reasonable estimate of the maximum

device efficiency enabled by the maximum light path enhancement [57]. The Yablonovitch limit assumes that the solar cell is optically thin and features Lambertian light-trapping, no external reflection losses, and a perfect back mirror. In this case, radiative recombination is the only energy loss mechanism. Under these assumptions the maximum path length enhancement of light is $4n^2$, where n is the refractive index [58]. For a typical lead halide perovskite, n near the band edge is equal to 2.6 [59], thus the maximum voltage gain is around 83 mV with perfect photon recycling of internally re-emitted photons. With the assistance of advanced light-trapping structures, which can alter the acceptance angle and exploit photon recycling [57], the limit set by Yablonovitch can be further increased.

2.1.4 Tandem Solar Cells

A tandem solar cell is an effective approach to circumvent the detailed balance limit of single-junction solar cells by combining semiconducting materials with different bandgaps. This configuration allows a broader range of the solar spectrum to be harvested and converted into electricity, thereby improving overall device efficiency [14]. To illustrate the working principle of a tandem solar cell, I consider a perovskite-Si tandem solar cell as an example (see Figure 2.3a). The incident light first passes through the top cell, which is a perovskite solar cell with a wider bandgap ($E_g = 1.7$ eV). This cell absorbs high-energy photons (blue area) and converts them into high-voltage electron-hole pairs. The low-energy photons that are not absorbed by the top cell pass through to the bottom cell, which is a silicon solar cell with a narrower bandgap ($E_g = 1.1$ eV), and get absorbed. By using this tandem structure, a wider range of the solar spectrum can be effectively utilised. Each cell absorbs photons with energy closer to its bandgap energy, minimising energy loss through thermalisation in the narrow bandgap material. This approach

allows for the generation of electricity with higher efficiency, as each cell operates optimally within its specific bandgap range. The combined effect of the two cells working together in a tandem configuration leads to improved overall device efficiency compared to single-junction solar cells. This makes tandem solar cells a promising avenue for achieving higher PCE in PV devices and surpassing the single junction detailed balance limit.

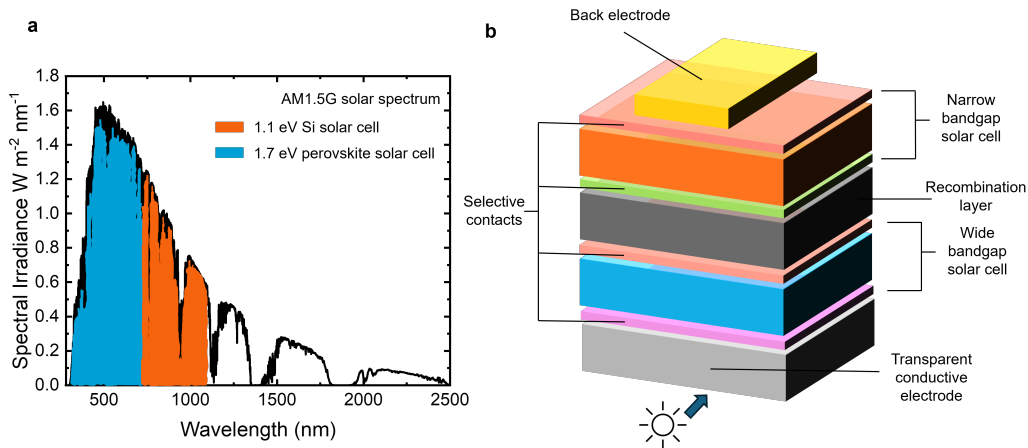


FIGURE 2.3: (a) AM1.5G solar spectrum with different regions absorbed by materials of wide-bandgap (perovskite, orange area), and narrow bandgap (silicon, blue area) used in a perovskite-Si 2-terminal tandem solar cell. (b) Schematic of a 2-terminal tandem solar cell.

There are two common ways to couple the different materials: 2-terminal tandem solar cell and 4-terminal tandem solar cell. Each type has its own set of advantages and disadvantages which will be discussed in detail later. A commonly employed architecture in perovskite-Si tandem solar cells is the 2-terminal tandem solar cell. This approach is also known as a monolithic tandem solar cell because multiple layers are directly stacked on top of each other to create a monolithic structure. The device architecture is illustrated in Figure 2.3b. The monolithic tandem solar cell consists of a WBG solar cell (such as a perovskite cell) stacked on top of a narrow bandgap solar cell (such as a silicon cell). The two cells are connected by a recombination buffer layer. In this design, the cells are electrically connected in series, with the generated current collected only at the transparent front terminal (where

light enters the cell) and the opaque back terminal (e.g., copper, silver, gold). Since the cells are connected in series, the current density flowing through the entire structure must be the same and is limited by the subcell with the lowest current density. This requirement is known as current matching, and it is crucial for achieving high performance in tandem solar cells. The recombination layer acts as an intermediary between the two subcells. Its primary role is to balance the current between the subcells, ensuring that the current flowing from one cell to the other is optimised for efficient operation [10], [16].

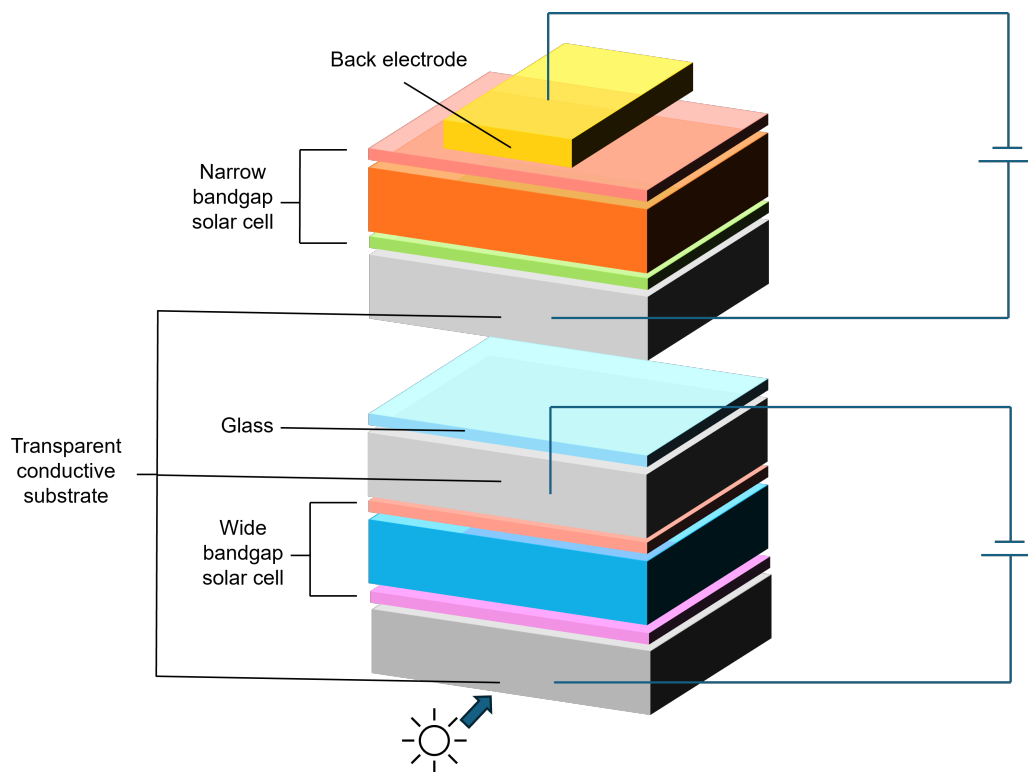


FIGURE 2.4: Schematic of a 4-terminal tandem solar cell.

Alternatively, the two subcells can be optically coupled with each other rather than electrically coupled. This can be achieved by mechanically stacking one cell on top of the other cell to form a 4-terminal tandem structure (refer to Figure 2.4). In this case, the subcells operate independently from one

another, with each cell having a separate set of terminals for the current collection. Transparent conductive contacts are necessary to enable light transmission between subcells. These contacts allow light to pass through from the top cell to the bottom cell, enabling each subcell to absorb its respective portion of the solar spectrum. Since the subcells operate independently, the lack of current matching constraints allows more diversity in the choice of materials with a broader range of bandgaps to form tandem solar cells with high theoretical efficiency. Despite the potential benefits, the fabrication of 4-terminal tandem solar cells presents some practical challenges. The use of extra transparent conductive materials can be costly, making the process less cost-effective and more complicated. Moreover, the involvement of additional transparent conductive layers in the device stack will increase the parasitic absorption, potentially reducing overall device efficiency [10], [16].

In addition, a 3-terminal tandem solar cell is a less-reported but advanced PV architecture in the PSC field [28], designed to overcome key limitations of conventional 2-terminal and 4-terminal tandems. By adding an extra electrical contact to interconnect subcells, a partial decoupling of currents is viable while retaining a monolithic structure. Therefore, the strict requirement for current matching in a 2-terminal tandem and the optical/spectral losses in a 4-terminal tandem can both be effectively relieved.

Multi-junction solar cells can be created by adding more subcells to a tandem system. This approach can lead to even higher efficiencies because it allows for a more precise allocation of photons to materials with optimal bandgaps, thereby minimising energy dissipation through unwanted thermalisation processes. However, while adding more subcells can increase efficiency, it also introduces additional production costs due to the need for extra layers and materials in the solar cell structure. These costs can include more complex fabrication processes, specialised materials, and higher

overall manufacturing expenses. Finding a balance between cost efficiency and power conversion efficiency is crucial to maximising the cost-payback ratio of this technology. This involves optimising the number of subcells and the choice of materials to achieve the desired efficiency gains without incurring prohibitive production costs. Multi-junction solar cells are often used in high-performance applications, such as space missions or concentrated photovoltaics, where the higher efficiency can justify the increased cost [10], [16].

2.2 Perovskite Solar Cell Fabrication Methods

The past decade has seen significant advancements in the device performance and long-term operational stability of PSCs [18], [60]. Alongside these improvements, the research community has developed and optimised a variety of perovskite deposition methods. Here, I mainly introduce the two mainstream perovskite fabrication routes: solution-processing and thermal evaporation (also known as the "dry process"). While other variations, such as inkjet printing [61], spray coating [62], and chemical vapour deposition [63] have been explored, they are less commonly reported in the literature. These methods generally exhibit lower performance compared to solution processing and thermal evaporation and are, therefore, out of the scope of this thesis.

2.2.1 Solution Processing vs Thermal Evaporation

In lab-scale fabrication, solution processing for PSCs is typically carried out using spin coating (as depicted in Figure 2.5). This method involves depositing a solution containing perovskite precursors onto a substrate, which is then spun at high speed to distribute the solution evenly and form a thin film. In the early stages of perovskite research, a one-step deposition method

was commonly employed [64]. In this approach, all precursor materials are dissolved in a single solution and deposited onto the substrate. The substrate is then subjected to thermal annealing to form the perovskite film. However, this method can result in undesirable chemical reactions in the solution, affecting the quality of the perovskite film and the overall device performance [65]. To address these issues, a two-step deposition method was developed [66]. This involves separately dissolving the inorganic precursors (e.g., lead iodide) and organic precursors (e.g., methylammonium iodide) and depositing them sequentially onto the substrate. The process is followed by thermal annealing to form the perovskite film. This alternative approach led to slight improvements in efficiency and gained popularity for a time [67]. However, both one-step and two-step methods were later outperformed by the solvent-engineering method, which remains the most commonly used technique today [38], [68]. In the solvent-engineering method, all precursors are deposited in a single step. An anti-solvent quenching process is introduced, where an anti-solvent is added during or immediately after deposition to promote perovskite crystallisation. This technique leads to the formation of perovskites with improved optoelectronic properties and enhanced device performance [38], [68].

On the other hand, thermal evaporation, also known as the "dry process" for perovskite solar cell fabrication, can take several forms depending on the number of precursor sources and deposition steps involved. The variations include single-source evaporation, sequential evaporation, and multi-source co-evaporation, as illustrated in Figure 2.5). In single-source evaporation, all precursor materials (both inorganic and organic) are mixed together in one crucible [69]. The mixture is then heated up to evaporate in a vacuum chamber. The vapour is then allowed to deposit onto a substrate to form the perovskite film. This method is straightforward but may pose challenges in

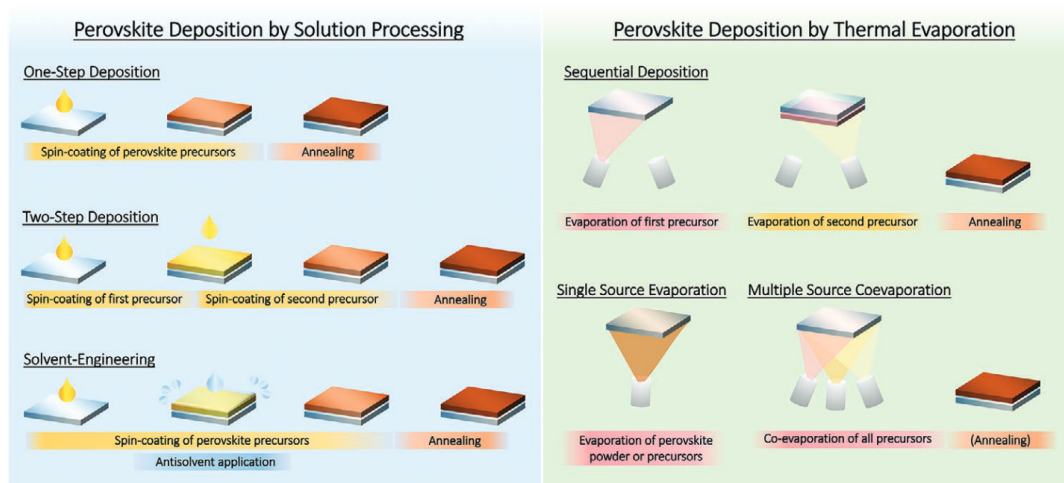


FIGURE 2.5: Schematic illustration of the most common methods for the deposition of perovskite layer by solution-processing and thermal evaporation. The figure is adapted from [29]. CC BY 4.0.

controlling the composition and uniformity of the resulting perovskite film. In sequential evaporation, the inorganic and organic precursors are evaporated separately onto the substrate, followed by thermal annealing to promote the conversion towards a perovskite phase [70]. This approach allows for more precise control over the deposition process, as each type of precursor is deposited individually. Multi-source co-evaporation is the most commonly reported method. In this process, each precursor is placed in an individual crucible, and all precursors are evaporated simultaneously to form the final perovskite phase [71]–[73]. This method allows for precise control over the deposition rates of each precursor, leading to a more uniform and controlled perovskite film. Given the distinct volatility of the organic and inorganic species, multi-source co-evaporation and sequential evaporation are more compatible with the increasing demand for compositional complex perovskites (i.e., mixed cation, mixed halide perovskites), which are sought after for their wider bandgaps in tandem applications [73], [74].

Both solution-processing and thermal evaporation possess their unique edges. Compared to thermal evaporation, a complicated vacuum system is

unnecessary for solution-processing, which significantly simplifies the production process of PSCs. In addition, there remains a big gap for the thermally evaporated PSCs to overcome to catch up with the state-of-the-art efficiency achieved by the solution-processed PSCs [18], [70]. This is mainly due to the numerous additives and passivation molecules available to boost the performance of solution-processed PSCs [75]. In comparison, vapour-depositable additives or passivation molecules are rarely reported in the literature.

On the contrary, thermally evaporated perovskites offer significant advantages for the large-scale production of PSCs, particularly in terms of environmental impact and compatibility with multi-layer structures. As implied by its name, the key advantage of thermal evaporation is that it prevents the use of any toxic solvents [43], which are ubiquitous for the solution processing of perovskites. As a result, the accompanying environmental impacts of toxic solvents, such as reproductive toxicity, carcinogenicity, water contamination, etc., can be effectively mitigated, which is crucial for industrial application [43]. Moreover, it is especially compatible with the deposition of multi-layer structures, e.g. multi-junction PSCs for a few reasons. Firstly, it allows an accurate thickness control of each single layer in multi-junction solar cells to minimise the optical loss and maximise the charge extraction [46]. Secondly, it enables conformal and uniform coating over large areas [47]. Thirdly, the perovskite deposition causes no damage to the underlying layers in tandem devices [76]. In contrast, a compact buffer layer and orthogonal solvent system need to be carefully designed for solution-processed tandem devices [29]. It's also worth highlighting that, unlike solution processing, thermal annealing is not essential for thermally evaporated perovskites, which makes them ideal candidates for flexible optoelectronic applications which require low-temperature processing [77]. However, in

many studies nowadays, annealing is still used to achieve high-quality thermally evaporated perovskites [71]. Given the distinct natures of these two processing methods discussed above, they face different challenges towards commercialisation.

2.2.2 Perovskite Grain Structure

Solution-processed and thermally evaporated perovskites exhibit different crystallisation mechanisms, which can significantly impact the performance and stability of PSCs. After solvent quenching, an intermediate phase forms in the solution processing route due to solvent interactions [78], [79]. Upon thermal annealing, large and continuous grains tend to grow at high temperatures [79]. The larger grain size in solution-processed perovskites tends to result in fewer grain boundaries, which can improve the quality of the perovskite absorber layer and lead to better PSC performance and stability [80]. In contrast, in the thermal evaporation route, the perovskite phase spontaneously forms when the precursor vapour comes into contact with the substrates, which are typically kept at room temperature [79], [81]. Hence, the grain size of evaporated perovskites is much smaller than their solution-processed counterparts [71]. The smaller grain size in thermally evaporated perovskites introduces more grain boundaries on the surface and within the bulk perovskite film. These grain boundaries can affect ion migration within the PSCs and may serve as nucleation centres for defects, which can negatively impact the device performance and longevity [80].

There are three fundamental growth models for thin films deposited by thermal evaporation in vacuum: Volmer-Weber (Island) growth, Frank-van der Merwe (Layer-by-Layer) growth, and Stranski-Krastanov (Layer-plus-Island) growth [82]. The dominant growth mechanism depends on the strength of the adatom-adatom bonds and the substrate-adatom interactions.

Volmer-Weber (Island) growth occurs when the evaporation atoms bond more strongly with each other than to the substrate, or when the surface diffusion is slow. In this case, the atoms/ molecules deposited on the substrates tend to form 3-dimensional islands. This growth mode happens more frequently on substrates with poor wettability or low substrate temperature ($< 50\text{ }^{\circ}\text{C}$). Consequently, high nucleation density creates many small islands that grow independently, leading to polycrystalline films with mixed orientations and small grain size. By contrast, when the adatom-substrate bonds are stronger than the bonds between atoms, or when the surface diffusion is fast, the Frank-van der Merwe (Layer-by-Layer) growth mode will dominate. The atoms or molecules tend to form a complete 2D monolayer before starting to form the next layer, resulting in smooth, layer-by-layer growth. The resultant films often demonstrate strong (100) orientation, large grain size in the order of micrometres, and compact coverage. This mode can be promoted by high substrate temperature, slow deposition rate, or low substrate surface polarity [83]. In addition, the Stranski-Krastanov (Layer-plus-Island) growth mode combines the first two and occurs due to a change in the balance of surface energies after the initial layers are formed. Initially, a few monolayers form in a layer-by-layer fashion, followed by the formation of three-dimensional islands due to strain relief. This mode is preferred on substrates with moderate polarity or with medium deposition rates. The resultant film tends to exhibit a bimodal distribution of grains: large grains with (100) orientation from at the bottom, and smaller grains with random orientation form at the top surface. In the literature, the large, columnar grains with uniaxial orientation enabled by the Frank-van der Merwe model lead to evaporated perovskite solar cells with the best efficiency and stability [83].

The grain structure of perovskite films plays a critical role in the performance and stability of PSCs. Therefore, numerous strategies have been

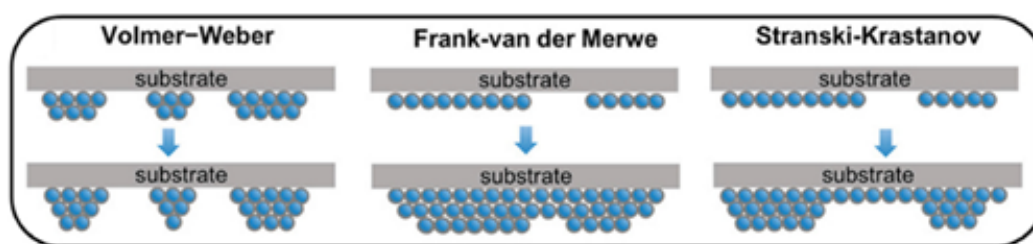


FIGURE 2.6: Schematic illustration of the 3 growth models for thin films by evaporation in vacuum.

developed to modify the microstructure of solution-processed perovskite films, such as hot casting [84], the use of additives [85], and ageing of perovskite precursor solutions [86]. In contrast, the study of microstructure engineering in thermally evaporated perovskites remains less explored and underdeveloped [71]. For example, research by Johnston et al. has shown that the grain size of thermally evaporated methylammonium lead iodide (MAPbI_3) can be controlled from tens of nanometers to microns by varying the substrate temperature [71]. However, this enlargement of grain size did not lead to improved device performance due to the delicate balance between microstructure and stoichiometry in thermally evaporated perovskite films. These findings highlight the complexity of the crystallisation and film formation mechanisms in thermally evaporated perovskites and the need for further investigation into grain structure engineering in these systems. In chapter 5, I will delve into a novel approach for intermediate-phase engineering to control the crystallisation and surface morphology of thermally evaporated perovskites in detail. This investigation aims to address the current gap in understanding and explore potential methods for optimising the grain structure and overall performance of thermally evaporated perovskite films.

2.2.3 Perovskite Compositional Control

One of the most significant advantages of using perovskite materials for PV applications is their tunable bandgaps [33]. This characteristic makes them ideal candidates for constructing tandem solar cells. The tunability of the bandgap is typically achieved by varying the perovskite compositions. In the context of solution processing, an ideal perovskite composition can be readily achieved by precisely measuring the appropriate amounts of each precursor to satisfy the stoichiometry requirement before adding the solvent. This process allows for easy control over the final perovskite material's composition. However, even with this level of control, compositional inhomogeneities are often observed between the surface and the bulk of the solution-processed perovskite material, particularly in mixed-cation and mixed-halide compositions, which are among the most efficient perovskite formulations [87]–[89]. These local compositional heterogeneities in perovskites have been recently recognised as a significant issue because they can facilitate the formation of defects and impact both the performance and stability of the device [87]–[89].

When it comes to thermal evaporation, achieving the desired perovskite compositions involves considering several factors and precise control during the deposition process. For example, in multi-source co-evaporation, the final composition of the perovskite is determined by the deposition rate of each precursor. This process can be complex due to the distinct density, volatility, and throw distance of each precursor material [90], [91]. To achieve the target composition, several rounds of tooling and calibration experiments are typically necessary for each precursor. These experiments are followed by a series of characterisations such as ellipsometry, X-ray diffraction (XRD), scanning electron microscopy (SEM), and UV-Vis absorption spectroscopy to verify the film thickness and perovskite compositions. The cross-talk between adjacent evaporation sources and the thickness monitor also makes the

geometric position an additional factor to consider [92]. Moreover, Meerholz and coworkers found that a thin layer of non-stoichiometric material often forms during the evaporation of the first few nanometers of perovskites due to an induction period needed to passivate the substrate [93]. These layers can hinder charge extraction at the bottom interface and limit the device performance. Finally, as I discussed in section 2.2.2, the limited choice of thermal evaporation-compatible additive molecules has been a significant limitation in improving device performance. Additives can play a crucial role in passivating defects and enhancing stability, and their unavailability for thermal evaporation has constrained progress [75]. Despite these challenges, recent efforts have focused on exploring molecules with the ideal volatility for thermal evaporation [72]. These molecules have the potential to boost device performance significantly, suggesting that this area of research holds great promise for advancing PSCs and other optoelectronic devices.

In addition to the conventional methods of solution processing and thermal evaporation, researchers have explored combining the advantages of both techniques to overcome their respective limitations and improve perovskite solar cell performance. This hybrid approach seeks to leverage the strengths of both methods while mitigating their drawbacks. For example, Baliff and coworkers demonstrated a perovskite-Si tandem solar cell with a certified efficiency exceeding 31% by employing a hybrid two-step deposition process for the perovskite absorber layer [94]. In this approach, inorganic precursors were first conformally coated onto a textured industry-standard silicon bottom cell using thermal evaporation. This step allowed for precise control over the deposition and formation of perovskite layers on the textured structure, minimising the risk of pinholes. In the second step, organic precursors were deposited onto the inorganic layers by spin coating.

A solution-based additive was introduced during this step to enhance crystallisation and reduce interfacial losses, ultimately improving device performance. Moreover, this innovative approach opens a new field of research into the interdiffusion mechanisms between solution-processed organic precursors and thermally evaporated inorganic precursors. Understanding how these precursors convert to the final perovskite phase can provide valuable insights into optimising hybrid fabrication methods for PSCs and potentially other optoelectronic devices.

2.2.4 Device Performance and Stability

While the latest reports show that solar cells with thermally evaporated perovskite absorbers have achieved performance levels comparable to those with solution-processed perovskite absorbers, much of this improvement relies on the use of solution-processed charge transport layers and solution-based passivations [70], [95], [96]. On one hand, these excellent outcomes demonstrate that high-performance thermally evaporated PSCs can be achieved when efficient charge extraction layers and well-passivated interfaces are present. On the other hand, the use of solution-processed layers goes against one of the main motivations for employing thermal evaporation in industrial production—its solvent-free nature. To fully realise the potential of thermally evaporated PSCs, efforts should be focused on developing PSCs with fully evaporated device architectures. This approach would maintain the solvent-free benefits of thermal evaporation, simplifying the production process and reducing the environmental impact.

Operational stability is another key factor in the commercialisation of perovskite PV technology. While solution-processed PSCs have seen considerable advances in their operational lifetimes due to the developments

of novel additives and passivation molecules [60], [79], the stability of thermally evaporated PSCs has received comparatively little attention and less improvement [73], [97], [98]. Surprisingly, there is limited data available to assess the operational stability of thermally evaporated PSCs. Few papers on this topic include stability studies, and those that do often focus on ageing tests conducted in the dark or at room temperature [73], [97], [98]. In contrast, solution-processed PSCs undergo accelerated ageing tests under heat and light stress to identify the weakest links in device stability and to develop strategies to extend device lifetimes. The absence of such comprehensive studies in the field of thermally evaporated perovskites, particularly in fully evaporated PSCs, highlights a gap in the research and a need for focused attention on this topic. To close this gap, in chapter 6, I conduct a comprehensive study comparing the stability of fully evaporated PSCs and solution-processed PSCs under accelerated ageing conditions. Moreover, for the first time, I demonstrate an exceptionally stable fully evaporated perovskite solar cell under harsh heat and light stress. This study aims to provide valuable insights into the operational stability of thermally evaporated PSCs and identify strategies for enhancing their performance and longevity, ultimately contributing to the commercial viability of this technology.

2.3 Perovskite Solar Cell Stability

Over the past decade, the power conversion efficiency of PSCs has become competitive with state-of-the-art single-crystalline silicon solar cells [18]. However, besides high device performance, long-term operational stability is also a critical parameter for assessing the commercial viability of a PV technology. Commercial silicon solar cells are known for their exceptional operational stability, retaining 80% of their initial PCE (T_{80} lifetime) after a few decades of operation [10]. In contrast, the stability of PSCs is still limited and needs

further investigation and improvement. A PSC consists of several layers: a perovskite absorber layer, charge transport layers, and electrodes. These layers collectively contribute to the overall instability of PSCs under external stress such as light, heat, oxygen, and humidity. As a result, various strategies have been developed over the past decade to address stability issues in each layer. In this section, I will review the factors that contribute to PSC instability and discuss methods for mitigating the degradation mechanisms. I will focus specifically on Pb-based WBG PSCs in the p-i-n configuration, as they are more relevant to the main topic of this thesis.

2.3.1 Intrinsic Stability of Perovskite Absorbers

Perovskite materials, due to their salt nature, are highly susceptible to degradation pathways induced by exposure to water and oxygen [99]. Water can infiltrate perovskite structures, forming hydrated intermediate structures. This hydration process may be reversible at an early stage by storing perovskites in dry air for 48 hours. However, as degradation progresses, lead iodide (PbI_2) may accumulate at the grain boundaries of the hydrated perovskite, hindering the reverse conversion and leading to permanent performance loss [100]. In addition, water can weaken the bonds between the organic cation and lead halide through deprotonation or protonate iodide to form volatile hydroiodic acid. Aqueous hydroiodic acid can either evaporate as a gas at room temperature or react with oxygen to form iodine gas and more water [100]–[102]. Both situations result in the irreversible and accelerated decomposition of perovskites.

Compositional tuning has proven effective in enhancing the ambient stability of perovskites. Noh et al. found that by substituting iodide

with bromide in a $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$ perovskite, the Br-induced lattice shrinkage strengthens the organic cation-lead halide bonding and reduces the permeability of moisture through the perovskite [34]. The same principle applies to a mixed-cation system. A methylammonium (MA)-formamidinium (FA) alloyed composition is more resistant to deprotonation by water because of weaker interactions between FA- H_2O relative to MA- H_2O [103]. Similarly, enhanced ambient stability with relative humidity up to 90% has been achieved in both FAPbI_3 -based perovskite films and devices after alloying Cs [104], [105]. In Chapter 4, I demonstrate that methylammonium chloride additive can effectively mitigate the ambient degradation of a 1.8 eV $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ perovskite. This additive improves perovskite crystallinity and suppresses the degradation pathway leading to the formation of δ - CsPbI_3 phase. As a result, the modified perovskites demonstrate more than two times better ambient stability compared to the control [78].

In addition, advances in encapsulation techniques have significantly reduced concerns about humidity and oxygen on perovskite stability. Encapsulated devices have shown negligible performance loss after storage in ambient conditions for up to one year [106]. While ambient-induced stability issues can be readily addressed with encapsulation, challenges related to the stability of PSCs under illumination and high temperatures remain and continue to attract significant attention.

The tunability of the bandgap in perovskite materials opens up significant opportunities for tandem applications. Starting with an archetypal MAPbI_3 perovskite with a bandgap of 1.5-1.6 eV, the bandgap can be increased up to 2.3 eV by substituting iodide with bromide. However, as more bromide contents are incorporated, the perovskite is more prone to undergo light-induced halide segregation. This segregation leads to the perovskite phase separating into iodide-rich and bromide-rich phases. Consequently,

electron-hole pairs migrate into the low-energy iodide-rich region, resulting in a deficit in photovoltage and poor light stability [107], [108]. This voltage deficit, commonly seen in WBG perovskites ($E_g \leq 1.65$ eV) remains a major obstacle to achieving efficient tandem devices.

The exact cause of this behaviour is not yet fully understood, but several hypotheses have been proposed. Some people suggest it is driven by thermodynamic force [109], some suggest it arises from polaron-induced lattice strain [110]. A recent explanation suggests that iodide may be oxidised by photo-generated holes. The discrepancy in mobility between iodide and bromide then leads to halide demixing [111]. This interpretation is supported by Albrecht's work, which demonstrated that an ultrathin self-assembled monolayer (SAM) hole transport layer could enable efficient hole extraction and suppress halide segregation in a 1.68 eV PSC [112]. Moreover, the formation of local halide heterogeneity during the crystallisation of perovskites has been found to act as nucleation centers for further halide segregation under illumination [88]. This mechanism will be discussed in more detail in Chapter 4, where I demonstrate that achieving more homogeneous crystallisation of 1.8 eV perovskite can effectively reduce halide segregation [78]. Additionally, the aforementioned oxygen-induced degradation process of perovskites accelerates under illumination. Superoxide, O_2^- can form after accepting a photoexcited electron. The superoxide may then deprotonate the organic cation, forming water and other volatile organic species, further exacerbating perovskite degradation [113].

For several reasons, the intrinsic thermal stability of perovskite materials is crucial for solar cell applications. The fabrication of the perovskite layer and charge transport layers usually involves a thermal annealing step at or above 100 °C to improve the film quality and get rid of residual solvents [78], [79]. Furthermore, the encapsulation process for commercial solar

cell modules is conducted at elevated temperatures up to 140°C, making it important for the perovskite materials to withstand such conditions [114]. Also, solar cells in hot climates can operate at temperatures as high as 65°C, so the perovskite materials must maintain stability under these conditions [115].

Heat-induced degradation of certain perovskite compositions, such as MAPbI₃, stems from their low enthalpy of formation. This is a significant issue for MA-based perovskites due to the high volatility of the MA⁺ cation [116]. However, this thermal instability associated with MA has been largely addressed by substituting other cations, such as formamidinium (FA), cesium (Cs), or rubidium (Rb) for the MA cation. This substitution leads to new compositions such as FACs, MAFACs, FAMA, and MAFACsRb, which are now commonly used in high-efficiency, stable PSCs [104], [105], [117], [118]. Despite these advances, heat stress can still accelerate undesirable chemical reactions and degradation processes, particularly at the interfaces between perovskites and charge transport layers or electrodes. These interfacial issues will be discussed further in section 2.3.2, as they play a significant role in the overall stability and performance of PSCs.

It is also worth highlighting that the use of volatile solvents, such as DMSO in solution-processed PSCs can have a particularly detrimental effect on their operational stability. Residual DMSO trapped in the perovskite layer can gradually escape over time, leading to the formation of voids and pinholes between the perovskite and charge transport layers. This issue can become more pronounced in large-area devices, resulting in rapid degradation of device performance under light and heat stress [119]. In contrast, thermal evaporation offers natural advantages in the fabrication of stable, large-area devices. The process does not require the use of volatile solvents, eliminating the risk of voids and pinholes caused by residual solvents. This makes

thermal evaporation a promising approach for creating PSCs with improved operational stability and larger-scale applicability. I will present relevant research outcomes that demonstrate the benefits of using thermal evaporation for fabricating stable, large-area PSCs in Chapter 6.

2.3.2 Stability of Charge Transport Layers and Electrodes

In addition to the intrinsic stability of perovskite materials, the long-term stability of PSCs is also significantly influenced by the stability of charge transport layers and electrodes. Any physical or chemical reactions at the perovskite–charge transport layer interface, the charge transport layer–electrode interface, or within the charge transport layers themselves can have a major impact on the overall stability of the device.

Organic hole transport materials are commonly used in PSCs and often require molecular doping to improve the conductivity and the device fill factor. For example, 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenylamine)-9,9'-Spirobifluorene (Spiro-OMeTAD) is a widely used hole transport material in n-i-p structure PSCs and has been a key contributor to record efficiencies in single-junction PSCs over the past decade [95]. However, Spiro-OMeTAD alone exhibits low hole mobility and is typically doped with lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI) and tert-butylpyridine (tBP) to achieve optimal performance. While doping can enhance performance, it often comes at the expense of device stability. Both tBP and lithium ions in Li-TFSI can react with perovskites to form voids and promote perovskite decomposition at relatively low temperatures (80°C) [120].

As for electron transport materials, metal oxides such as zinc oxide, nickel oxide, and tin oxide are popular choices in high-performance devices. Although these materials generally exhibit thermal stability in isolation, they

can react with perovskites and produce undesired byproducts that compromise device stability. For example, zinc oxide is known to deprotonate the MA cation, leading to the formation of methylamine gas and PbI_2 after only 20-min annealing at 100 °C in air [121]. Such reactions can be mitigated by using mixed-cation perovskite compositions (e.g., FACs) with lower acidity, as discussed in previous sections. Nevertheless, the instability of existing charge transport layers has motivated significant research into the development of dopant-free and stable charge transport materials.

The significant contributions of researchers in the field have led to the development of a variety of robust and stable charge transport materials that can be employed to fabricate efficient and stable p-i-n PSCs. In this thesis, I mainly use Poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA), SAM and 2,2',7,7'-Tetra(N,N-di-p-tolyl)amino-9,9-spirobifluorene (Spiro-TTB) as HTLs, and C60 fullerene as electron transport layers. Their good stability has been verified elsewhere [60], [112], [122], [123]. These charge transport materials not only facilitate efficient charge extraction but also serve as buffer layers, potentially mitigating undesirable reactions between the electrodes and perovskites. This buffering effect helps improve the overall stability and longevity of PSCs.

In most high-efficiency PSCs reported to date, metal electrodes such as copper (Cu), silver (Ag), and gold (Au) are frequently used due to their high conductivity, which contributes to high fill factor and improved device performance. However, these metal electrodes can present stability challenges due to unwanted chemical reactions with perovskites at elevated temperatures and under light.

Among all three metals, Cu is the most cost-effective choice. Nevertheless, it readily oxidises in the presence of moisture and oxygen and also

reacts with perovskites to form copper halides, which decreases its conductivity over time [124]. Similarly, silver can also offer good conductivity at a relatively low cost. However, iodide on the perovskite surface can migrate through the charge transport layers in the form of volatile organic species, including HI and MAI. They will then corrode the Ag electrode to form AgI, which is an insulating layer that causes substantial performance loss [125]. By contrast, Au has high diffusivity and can easily diffuse through the charge transport layer at relatively low temperatures (as low as 70 °C), creating shunt paths in the device stack and reducing the fill factor. This process has been shown to be effectively mitigated by placing a chromium oxide interlayer between the charge transport layer and Au electrode to act as a diffusion barrier, preventing gold diffusion and improving device stability [126]. However, the work function mismatch between chromium (Cr) and gold, as well as the high resistance of chromium oxide, can lower the device performance, implying space for further improvement [126]. A multifunctional ytterbium oxide (YbO_x) buffer layer has recently been demonstrated to provide an inert diffusion barrier for harmful species (e.g. I^- , Cs^+ , Rb^+ , and Cu) in both directions while retaining performance and operational stability. This innovative approach has led to a certified PCE of over 25% with a 1.54 eV PSC, and an impressive 20.1% PCE with a 1.77 eV PSC, which features an ideal bandgap for all-perovskite tandem solar cells. Under multiple external stress, the encapsulated YbO_x -based 1.54 eV cell also exhibited an elongated operational lifetime ($T_{85} = 500$ hours) while measuring at maximum power point tracking (MPPT) condition under 1-sun intensity at 85 °C in ambient air (relative humidity = 50%) [127].

An alternative choice to metal electrodes in PSCs is carbon electrodes,

which offer several advantages. Carbon electrodes are chemically inert, reducing the risk of unwanted reactions with perovskite materials and enhancing long-term stability. Furthermore, they are inexpensive to fabricate, making them a cost-effective option for PSCs [128]. Additionally, carbon paste is compatible with blade coating and roll-to-roll coating techniques, which are promising for upscaling PSC production [129]. Recently, Egelhaaf and coworkers presented a fully-printed carbon-electrode PSC with an efficiency of 19.2%, which is close to the performance of fully-printed PSCs with metal electrodes. Furthermore, the carbon-electrode PSC with a hole transport bilayer exhibited a negligible drop in PCE after operating at 65°C, 1-sun intensity for 2,500 hours, making it one of the most stable PSCs reported in the literature [130]. Given these promising results, carbon electrodes appear to be a viable candidate for stable and cost-effective perovskite PV technologies in the coming decade.

Chapter 3

Experimental Techniques

3.1 Device Fabrication

In this thesis, all powders were used as purchased without further purification and weighed in a nitrogen-filled glovebox without exposure to light.

3.1.1 Substrate Preparation

All the PV devices presented in this thesis adopted a p-i-n configuration. They were fabricated on Indium tin oxide-coated glass substrates (ITO, $15 \Omega \text{ cm}^{-2}$, Biotain) or fluorine-doped tin oxide-coated glass substrates (FTO, $15 \Omega \text{ cm}^{-2}$, Biotain). The ITO/FTO substrates were cleaned before use by 15-minute sonication in deionised (DI) water with Decon90 (2 vol%) cleaning detergent, followed by scrubbing with a toothbrush to get rid of stains and dust, before being rinsed and sonicated in DI water, acetone and IPA for 15 minutes sequentially. The substrates were then dried with a nitrogen gun, followed by a UV-ozone treatment. Immediately after the substrate preparation, the substrates were transferred into an N_2 -filled glovebox and the hole transport layer was deposited.

3.1.2 Hole Transport Layers

PTAA

Poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA, Xi'an Polymer Light Technology Corp.) was used as HTL for reference devices in Chapter 4. PTAA was dissolved in toluene (anhydrous, 99.8%, Sigma Aldrich, 1.5 mg mL⁻¹) and stirred overnight. 80 μ L of solution was dispensed onto a substrate statically. The substrate was spun at 6000 rpm (3 seconds ramp time) for 30 seconds and then annealed at 100 °C for 10 minutes.

Self-Assembled Monolayers

For optimised devices in Chapter 4 and solution-processed devices in Chapter 6, SAMs were used as the HTLs. The SAM solutions were prepared by dissolving [2-(9H-Carbazol-9-yl)ethyl]phosphonic acid (2PACz, Tokyo Chemical Industry, Chapter 4), [2-(3,6-Dimethoxy-9H-carbazol-9-yl)ethyl]phosphonic acid (MeO-2PACz, Tokyo Chemical Industry, Chapter 4) or [4-(3,6-dimethyl-9H-carbazol-9-yl)butyl]phosphonic acid (Me-4PACz, Tokyo Chemical Industry, Chapters 4 and 6) into anhydrous ethanol ($\geq 99.9\%$, VWR, 0.3 mg mL⁻¹) and stirred overnight. 100 μ L of SAM solutions were statically spin-coated onto the ITO substrates. After 5 seconds to help the solution spread, the substrate was spun at 3000 rpm (6 seconds ramp time) for 30 seconds, and then annealed at 100 °C for 10 minutes.

Al₂O₃ Nanoparticle Layer

The surface of PTAA and SAMs films were very hydrophobic, hence aluminium oxide nanoparticles (Al₂O₃, < 50 nm particle size, 20 wt.% in isopropanol (IPA, anhydrous, 99.5%, Sigma Aldrich), Sigma Aldrich, 1:150 vol% in IPA) was spin-coated dynamically on top of the HTLs at 2000 rpm for 20 seconds as a wetting agent.

Spiro-TTB

Spiro-TTB (Lumtec, sublimed > 99.9%, LT-N138) was vacuum deposited in a thermal evaporator chamber of the cluster facility to 7 (Chapter 5) or 5 (Chapter 6) nm at 0.1 Å/s. After deposition, the substrates were transferred to the perovskite chamber of the cluster facility for further processing without breaking the vacuum.

A vacuum environment is essential for thermal evaporation for several reasons [29]. Firstly, the presence of gas molecules can collide with evaporated materials, leading to energy loss and omnidirectional evaporation path to the substrates. Consequently, the deposited film can be porous and non-uniform. Meanwhile, some air-sensitive materials can get contaminated or oxidate, resulting in films with low purity. Secondly, vacuum allows materials to evaporate at lower temperatures, which is more cost-effective and environmentally friendly. Lastly, electron beams can ignite arcing or plasma in air, causing damage to the system.

Spiro-TTB solution (100 µL, 5 mg/mL, in CB) was used as HTL for solution-processed WBG perovskites as a preliminary test (Chapter 6). The solution was mixed and stirred overnight before use. The substrate was spun at 5000 rpm for 30 s, and the solution was dropped dynamically onto the substrate 5 seconds after the program started. The film was then annealed at 120 °C for 10 minutes.

3.1.3 Perovskite Absorber Layers

The perovskite materials demonstrated in this thesis were prepared via two deposition routes: solution processing and thermal evaporation. The resultant perovskite films show distinctive crystallographic and optoelectronic properties. I further discuss this topic in Chapter 6.

Solution-Processed Perovskite Absorber Layers

In Chapter 4, I prepared $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ perovskite films by solution processing with anti-solvent quench. Lead iodide (PbI_2 , 99.99%, trace metal basis, Tokyo Chemical Industries), lead bromide (PbBr_2 , > 98+%, Alfa-Aesar), formamidinium iodide (FAI, > 99.99%, Greatcell Solar Materials), and cesium iodide (CsI , 99.9% (metal basis), Alfa-Aesar) were weighed stoichiometrically in an N_2 -filled glovebox to obtain the target perovskite composition ($\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$). To form the precursor solution, a N,N -dimethylformamide (DMF, anhydrous, 98%, Sigma Aldrich): dimethyl sulfoxide (DMSO, anhydrous, 98%, Sigma Aldrich) solvent mixture (4:1 volume ratio) was added to the precursors to achieve a concentration of 1.2 M. To make $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ solutions with different additives, excess molars (0-45 mol%) of lead chloride (PbCl_2 , 99.999%, trace metal basis, Sigma Aldrich), methylamine hydrochloride (MAH, 99.99%, Xi'an Polymer Light Technology Corp.), methylammonium iodide (MAI, 98+%, Sigma Aldrich), or methylammonium bromide (MABr, 98+%, Sigma Aldrich) was added into the precursor as additives. The precursor solutions were agitated until all solids were fully dissolved. 170 μL of perovskite precursor solution was dispensed dynamically onto a UV-Ozone-treated substrate spinning at 1000 rpm. The substrate was accelerated to 5000 rpm over 5 seconds and remained at this speed for 35 seconds. 5 seconds before the end of this process, 325 μL of anisole (anhydrous, 99.7%, Sigma Aldrich) was applied to the spinning substrate as an anti-solvent quench. For devices with no additives (control cells), the perovskite films were then annealed at 100 °C for 30 minutes in an N_2 -filled glovebox. For devices with additives, the substrates were transferred out of the glovebox and annealed at 150 °C for 10 minutes under ambient atmosphere (relative humidity (RH) = 30%). The annealed substrates were allowed to cool down, then transferred back into an N_2 -filled glovebox

and loaded into a thermal evaporator to deposit the subsequent layers.

In Chapter 6, the $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.75}\text{Br}_{0.20}\text{Cl}_{0.05})_3$ perovskite solution was prepared by dissolving the precursor salts into a solvent mixture of N,N-dimethylformamide (DMF, anhydrous, 98%, Sigma Aldrich): dimethyl sulfoxide (DMSO, anhydrous, 98%, Sigma Aldrich) (4:1 volume ratio) to obtain a stoichiometric solution with the desired perovskite composition and concentration (1.45 M). The precursor salts include lead iodide (PbI_2 , 99.99%, trace metal basis, Tokyo Chemical Industries), lead bromide (PbBr_2 , > 98+%, Alfa-Aesar), lead chloride (PbCl_2 , 99.999%, trace metal basis, Sigma Aldrich), formamidinium iodide (FAI, > 99.99%, Greatcell Solar Materials), and cesium iodide (CsI , 99.9% (metal basis), Alfa-Aesar). The precursor solution was stirred at room temperature overnight in an N_2 -filled glovebox. 170 μL of perovskite precursor solution was dispensed dynamically onto a UV-Ozone-treated substrate spinning at 1000 rpm. The substrate was accelerated to 5000 rpm over 5 seconds and remained at this speed for 35 seconds. 5 seconds before the end of this process, 325 μL of anisole (anhydrous, 99.7%, Sigma Aldrich) was applied to the spinning substrate as an anti-solvent quench. The films were annealed inside an N_2 -filled glovebox for 60 min to remove residual solvents.

Evaporated Perovskite Absorber Layers

The evaporated perovskite films presented in Chapter 5 and 6 were fabricated using the perovskite deposition chamber of the national thin-film cluster facility (Figure 3.1) based at the Department of Physics, University of Oxford.

The Angstrom Engineering-made perovskite chamber fabricates the perovskite thin film layer at the ultimate vacuum level by two-step automated processes with a roughing vacuum step followed by a high vacuum



FIGURE 3.1: Photo of the national thin-film cluster facility. Only part of the facility (perovskite deposition chamber and organic chamber) is shown in the photo. Image credit: Angstrom Engineering.

step utilising the combination of an Ebara EV-A10-2 multistage dry vacuum pump and CTI Cryo Torr 8F pump. The chamber is equipped with an Inficon Gemini MPG500 pressure gauge (Pirani and cold cathode) to monitor the real-time vacuum pressure. The venting gas used in the perovskite chamber is grade 5.0 (99.999%) nitrogen (N_2).

Inside the perovskite chamber, eight identical thermal evaporation sources (Luxel branded Radak type II) housing 10 cc crucibles (made of alumina) are laid on the chamber base with individual vapour shields and partition shields protected for cross-talk or cross-contamination (Figure 3.2). All sources are equipped with oil-free compressed dry air-driven shutters that can be controlled via software to open or close. To precisely monitor the rate of the materials evaporated from each Radak II source, water-cooled quartz crystal monitors (QCM) are employed above the sources with shields and shutters to prevent crosstalk.

The QCM sensor measures the mass change per unit area by measuring the change in the resonance frequency of a quartz crystal resonator. The resonance is disturbed by the addition or removal of a small mass due to film deposition. Hence, the film thickness can be monitored by tracking the

change in QCM frequency. The proportional-integral-derivative (PID) control system is a feedback-based control loop mechanism commonly used in industry to manage processes that require continuous control and automatic adjustment. The PID aims to match a process variable with its target value using three methods: the proportional (P) component reacts instantly to the current error size; the integral (I) component considers the cumulative sum of historical errors to address any long-standing steady-state errors, eliminating lingering discrepancies; the derivative (D) component enhances the system stability against rapid shifts via error trend prediction. These three components continuously fine-tune the actuators using voltage/current signals, making the systems self-correcting and less error-prone.

The rotatable stage (0 – 30 RPM) is equipped with a combinatorial shutter design that allows for partial shielding of the substrate as desired from the vapour flux to achieve a high throughput deposition fashion, e.g. thickness and compositional gradient across the substrate. The stage can also be heated up to 400°C with $\pm 2.5^\circ\text{C}$ thanks to the resistive heater design. The SRS RGA (Residual Gas Analyser) 300 is installed on the perovskite deposition chamber to monitor the quality of the vacuum as well as the impurities in the vacuum chamber to make sure it is safe to open the gate valve. Impurities and their thresholds can be set on the Aeres software, and it interlocks the opening of the gate valve so that the minimised impurities can pass to other cluster chambers.

I used commercially available ultra-pure and anhydrous precursor materials for my depositions. The inorganic precursors were ordered from Alfa Aesar and had the following purities for the metal base: PbI_2 (99.999%, metal basis, beads, 044314), PbBr_2 (metal basis, 99.999%, 035703), PbCl_2 (metal basis, 99.999%, 035704), CsCl (metal basis, 99.999%), CsI (metal basis, 99.998%, 035729). FAI (trace elements basis, 99.999%, DN-P10-5N) was ordered from

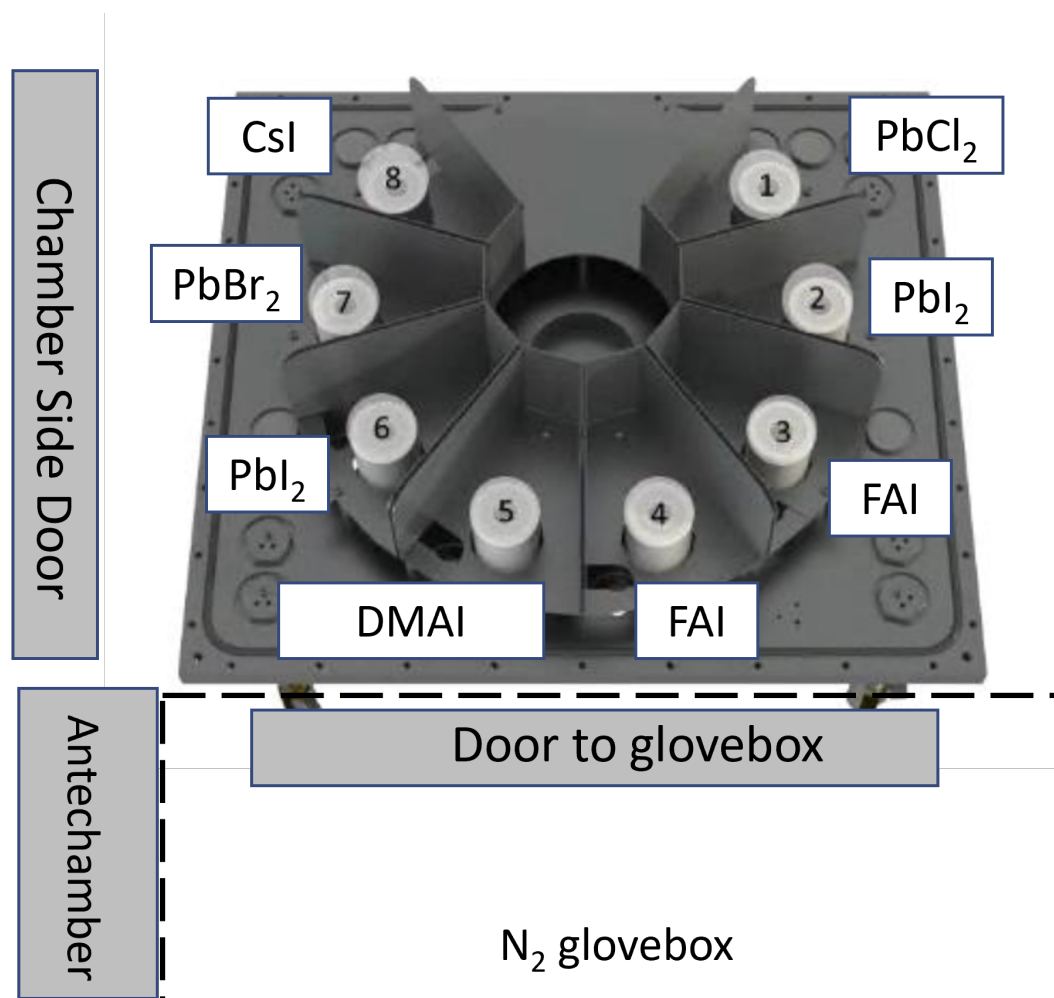


FIGURE 3.2: Source layout inside the perovskite deposition chamber. Two FAI sources were introduced to prevent overheating the precursor materials as discussed in Chapter 5.

Dynamol. Using high-purity precursors reduces the batch-to-batch variation and ensures good reproducibility.

For a typical deposition, the chamber was pumped down to 9×10^{-7} mbar before I started heating the sources. During the deposition of co-evaporated perovskites without DMAI, the pressure was typically around 7×10^{-6} mbar. As for the deposition with DMAI, the pressure could go up to 5×10^{-5} mbar because of the high volatility of DMAI. I found that depositions at low pressure ($< 1 \times 10^{-5}$ mbar) gave us better batch-to-batch reproducibility due to more precise control of perovskite compositions.

In Chapter 5, I co-evaporated FAI, CsI, PbI₂, PbBr₂, PbCl₂ to deposit the control compositions of FA_{0.83}Cs_{0.17}Pb(I_{0.68}Br_{0.27}Cl_{0.05})₃ by accurately controlling the deposition rates of each source with QCMs. For the DMA-modified perovskite compositions, I progressively added excess molars of DMAI (0 %, 40 %, 60 %, 80 %, and 100 %) into the co-evaporation. Since the exact density of DMAI is unknown, I assumed that it had the same density as FAI and calibrated the molar deposition rate of DMAI with respect to FAI. The rates of other sources were kept the same for all depositions. During the evaporation, the pressure always shot up to 5×10^{-5} mbar, especially with a high molar concentration of DMAI sublimated. The source rates were kept constant using QCMs adjacent to the crucibles and PID-loop-control software, with set rates and typical deposition temperatures detailed in Figure 3.3. The control perovskite films were annealed after deposition at 135°C for 30 minutes in an N₂-filled glovebox. The DMA-modified perovskite films were transferred out of the glovebox after deposition and annealed at 150 °C for 40 min, 160 °C for 40 min, or 170 °C for 20 min under an ambient atmosphere (RH = 40 - 50%).

Materials	DMAI	FAI	CsI	PbI ₂	PbBr ₂	PbCl ₂
Set rate (Å/s)	0.08 – 0.4	0.4	0.074	0.295	0.169	0.027
Temperature (°C)	140 - 185	190	435	270	300	335

FIGURE 3.3: Set rate values for the materials vapour deposited for Chapter 5, and the range of temperatures typically reached by the crucibles during deposition

The perovskite deposition chamber was used intensively by internal and external users, and a large amount of organic and inorganic materials could be deposited on all the surfaces of the vacuum chamber. This issue became a greater concern after DMAI was introduced into the system. During deposition, DMAI is known to sublime omnidirectionally and severely

contaminate the chamber because of its high volatility. To reduce contamination from materials resublimated off the walls during a deposition, I regularly bake out all the sources at 400°C and the chamber wall at 150°C, much higher than is reached during film deposition. During deposition, the substrate temperature is typically between 27 - 30 °C.

In Chapter 6, I co-evaporated $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.75}\text{Br}_{0.20}\text{Cl}_{0.05})_3$ perovskites following a protocol optimised from the standard recipe I used to deposit the control perovskite composition in Chapter 5. Details of the updated recipe will be discussed in Chapter 5. More PbBr_2 was substituted with PbI_2 to achieve the target bandgap of 1.67 eV which is ideal for making tandem solar cells with Si bottom cells. The set rates and typical deposition temperatures of each source are detailed in Figure 3.4. To improve the reproducibility of the recipe, I introduced a second FAI source to control the deposition temperature of each single FAI source within the safe regime (below 190 °C). Therefore, undesired thermal degradation and side reactions of FAI were effectively inhibited. In addition, I found that the unstable deposition rate of FAI originated from a volatile coating on the raw materials. Hence, I regularly baked the FAI materials at 80 °C to remove the coating. Consequently, I realised a more stable FAI deposition as well as a more precise perovskite composition control. Moreover, before every deposition, I always topped up the FAI and PbI_2 crucibles to 3 g and 10 g, respectively by adding fresh materials to the remainder of the previous deposition. The tooling factor of these precursor materials which represents the ratio between the actual thickness deposited onto the substrate and the thickness detected by the QCM sensor close to the source was calibrated for a certain mass in the crucible. In this way, I could repetitively obtain the target perovskite compositions. The perovskite films were transferred out of the glovebox after deposition and annealed at 135 °C for 30 min under an ambient atmosphere (RH = 40 - 50%).

To deposit the reference perovskite composition $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.80}\text{Br}_{0.20})_3$ with no PbCl_2 , five precursor sources: two FAI, PbI_2 , CsI, and PbBr_2 were co-evaporated in a perovskite deposition chamber that is integrated as part of the national thin-film cluster facility at Oxford. During the evaporation, the pressure was typically $< 1 \times 10^{-6}$ mbar. The source rates were kept constant using water-cooled gold-plated QCM and PID-loop-control software. The sublimation rates of all the precursors were controlled using QCMs adjacent to the crucible, while the total deposition rate could be monitored using a QCM at the substrate level. The set rates and typical deposition temperatures for two FAI, PbI_2 , CsI, and PbI_2 are 0.2 Å/s (160 °C), 0.2 Å/s (160 °C), 0.397 Å/s (310 °C), 0.074 Å/s (435 °C), and 0.125 Å/s (285 °C), respectively to achieve the target molar ratio and perovskite composition. For the preliminary attempt with various seed layers, 10 nm of PbCl_2 , CsCl or CsPbI_3 were deposited prior to the perovskite deposition. The perovskite film final thickness is 500 nm.

Materials	FAI	FAI	CsI	PbI_2	PbBr_2	PbCl_2
Set rate (Å/s)	0.2	0.2	0.074	0.354	0.125	0.027
Temperature (°C)	170	170	435	300	285	335

FIGURE 3.4: Set rate values for the materials vapour deposited for Chapter 6, and the range of temperatures typically reached by the crucibles during deposition

3.1.4 Electron Transport Layers

In Chapter 4, 30 nm of fullerene-C60 (C60, 99.5%, Sigma Aldrich) was deposited on top of the perovskite active layer via thermal evaporation under vacuum (3×10^{-6} mbar) with no masks applied. After completing the evaporation, 100 µL of bathocuproine (BCP, 98%, Alfa-Aesar) solution (0.5 mg/mL in IPA) was applied onto a substrate spinning at 5000 rpm for 30 seconds followed by annealing at 100 °C for 1 min in an N_2 glovebox to remove any remaining solvent.

In Chapter 5, C60 was vacuum deposited in the organic chamber of the cluster facility to 20 nm at 0.1 Å/s. The rate was controlled using a QCM sensor. Following C60 deposition, without breaking the vacuum, 5 nm of BCP (99.5%, Sigma Aldrich) was deposited in the same chamber at 0.1 Å/s.

In Chapter 6, C60 was vacuum deposited in the organic chamber of the cluster facility to 20 nm at 0.1 Å/s. For devices with BCP buffer layers, 5 nm of BCP (99.5%, Sigma Aldrich) was deposited in the same chamber at 0.1 Å/s without breaking the vacuum. On the other hand, for devices with SnO₂ buffer layers, 20 nm of SnO₂ was deposited via atomic layer deposition (ALD) in the ALD chamber of the cluster facility.

The Picosun-branded model R200 Advanced Plasma ALD chamber is connected and controlled by a main cluster system that allows users to carry out automated sequences to fabricate full PV devices by utilising different mask designs. The ALD system is vacuum-pumped by a two-stage Edwards iXH610 pumping system, and the process pressure is usually maintained at 5 mBs.

The background carrier gas for the ALD system is N₂ (99.9999%). The system also connects to a plasma source that performs as a precursor for deposition, at the National Thin-Film Cluster Facility, selection of Ar (99.999%), O₂ (99.9999%), H₂S (99.999%), and NH₃ (99.999%) supplied by BOC are available. Besides the plasma source, the ALD is also equipped with two room temperature sources for liquid-based precursors (typically de-ionised water and Trimethylaluminum (TMA, Pegasus) are loaded) in Pico 100 containers and 2 heatable sources in Pico 200 (TDMASn, Pegasus) and Pico 300 (InCp, Epivalence) liquid-based precursor containers.

20 nm SnO₂, as a buffer layer of the perovskite PV device in Chapter 6, was grown at the ALD chamber using the combination of the TDMASn

and DI water precursors with 140 pulses. The reactor temperature during pulsing was stabilised at 100 °C while TDMASn was kept at 75 °C.

3.1.5 Electrode Evaporation

A silver (Ag, 99.999%, Kurt J. Lesker Company) or gold (Au, 99.999%, Kurt J. Lesker Company) electrode of 100 nm thickness was thermally evaporated through shadow masks (active area defined as 0.25 cm² or 1 cm²) at an initial rate of 0.2 Å/s (ramped up to 1 Å/s in 20 min) under a vacuum of $< 2 \times 10^{-6}$ mbar in an Edwards Nano36 evaporator or the organic chamber of the cluster facility. For devices used for accelerated stability tests in Chapter 6, a thin layer of Cr (3.5 nm) was deposited before Au to prevent gold diffusion and improve the device stability.

3.1.6 Fully-Evaporated Perovskite-Si Tandem Solar Cell

Sputter system for Indium zinc oxide (IZO) deposition

The sputter system was manufactured by Angstrom Engineering limited with connecting to the cluster system that allows users to carry out automated sequences to fabricate full PV (or other) devices with utilising different mask designs. The NTCF Sputter is capable of depositing up to M2 size substrates with 96.6% uniformity. The sputter is vacuum pumped by a combination of Ebara EV back pump and a Pfeiffer turbo pump to provide a base pressure of 1×10^{-8} mbars. The available carrier gases for the sputter tool are BOC-supplied Ar (99.9999%), N₂ (99.9999%), O₂ (99.9999%), and CF₄ (99.99%). H₂ (99.99%) is also available via a hydrogen generator manufactured by Peak Scientific. All gases are connected and controlled by the MFCs through the cluster software AERES. Indium zinc oxide (In₂O₃)₉₀(ZnO)₁₀, 99.99%) sputter target was supplied by Plasmaterials with bonded to oxygen-free copper backplate to enhance the thermal and electrical conductivity. The

target is mounted on a tilted sputter head, the optimised combination of the high uniformity deposition is Z of 25 mm and sputter target titling angle of 32 degrees. As a critical window/interlayer for the 2nd generation of thin film PV tandem devices, 100 nm IZO was sputtered by the plasma strike using a combination of 18.1 sccm of Ar with 0.3 sccm of O₂. We firstly set 180 seconds of plasma cleaning the target surface without opening the substrate shutter to ensure a stoichiometric and contamination-free IZO sputter process is done on the substrates. During the IZO sputter process (room temperature, 22.3 °C), the substrate rotates at a speed of 10 RPM to obtain a high coating uniformity. The process pressure is set as 3×10^{-3} mbars by controlling the position of the gate valve. The parameters of the sputtering are listed below: actual voltage is 410 V, actual current is 289 mA, and the actual power is 118.4 W, which gives a deposition rate of 1.14 Å/s. The whole sputter process will take 175 seconds, and the substrate will transfer in high vacuum back to the load lock for the user to unload.

Fully-Evaporated Perovskite-Si Tandem Solar Cell

The fully-evaporated perovskite-Si tandem solar cell was prepared on a commercial standard micro-textured Si wafer provided by CEA, France. The device architecture is shown in Figure 6.30. 100 nm of ITO was sputtered on the Si wafer as the recombination layer. A thermal treatment at 180 °C for 3 min in air (relative humidity = 40-50% in the lab) was used to heal the sputter damage on the Si wafer prior to use. After 15 min of UV-Ozone treatment, the Si wafer was loaded into the cluster system to deposit 5 nm of Spiro-TTB under vacuum (1×10^{-7} mbar). Then an 800 nm of 1.67 eV FA_{0.83}Cs_{0.17}Pb(I_{0.75}Br_{0.20}Cl_{0.05})₃ perovskite absorber layer was deposited using the seed-free co-evaporation described above. The perovskite layer thickness was increased to 800 nm to enhance the light absorption and photocurrent. The Si wafer was then transferred outside to do post-annealing at

135 °C for 30 min in air (relative humidity = 40-50% in lab). 20 nm of C60 and 20 nm of ALD SnO₂ were subsequently grown on top of the perovskite, followed by 100 nm of IZO deposited by sputtering as the semi-transparent top contact. Finally, 300 nm and 100 nm of Ag were deposited through an active area metal mask as the front and back metal contacts, respectively, to complete the device. The device active area is 1 cm².

3.2 Characterisation

3.2.1 Optical and Spectroscopic Characterisation

Ultraviolet-visible Absorption Spectroscopy

Reflectance and transmittance spectra were recorded on a Varian Cary 1050 Ultraviolet-visible (UV-Vis) spectrophotometer equipped with an integrating sphere. From these measurements, in combination with the photoactive layer thickness, absorption coefficients were calculated assuming a direct bandgap semiconductor. Separately, absorbance spectra were measured with a Varian Cary 300 Bio UV-Visible spectrophotometer with a 50x50 mm reflective neutral density filter with an optical density of 3.0 (made out of UV-fused silica).

Photoluminescence Quantum Efficiency Measurement

Photoluminescence quantum efficiency (PLQE) measurements were acquired using a custom-built PLQE setup in an integrating sphere. Samples were photoexcited using a 405 nm laser (laser power = 5.86 mW). The PL was collected using a high-resolution monochromator and hybrid photomultiplier detector assembly (PMA Hybrid 40, PicoQuant GmbH). The PLQE were extracted from the photon energy, photon numbers of the excitation and emission obtained from numerical integration using Python.

Steady-State Photoluminescence

A 398 nm diode laser (PicoHarp, LDH-D-C-405M) was used to photo-excite the samples, on a continuous wave setting at an intensity of 5800 mW/cm². The resultant photoluminescence (PL) was collected and coupled into a grating spectrometer (Princeton Instruments, SP-2558), which directed the spectrally dispersed PL onto a silicon iCCD (intensified charge-coupled device, PI-MAX4, Princeton Instruments). The samples were deposited on quartz substrates and mounted in a vacuum cell under low pressure (10⁻² mbar). The steady-state PL measurements and halide segregation characterisation in Chapter 4 were measured and analysed by Dr. Karim Elmestekawy. The in situ PL measurements in Chapter 4 were conducted by Dr. Zhongcheng Yuan and Xinyi Shen on freshly prepared perovskite precursor phases deposited on ITO substrates.

AM1.5 Equivalent Photon Flux

The AM1.5 equivalent intensity is estimated to be the equivalent laser intensity that photogenerates the same density of charge carriers within the film as would be under the AM1.5 solar spectrum. Due to the sharp absorption onset and high values of the absorption coefficient of perovskite films, I expect light penetration through the film to be much shorter than its thickness, and it can be assumed that all incident photons with energies higher than the bandgap to be entirely absorbed. Accordingly, the AM1.5 equivalent intensity would correspond to a laser intensity that results in the same incident photon flux as the AM1.5 solar spectrum from the above-bandgap photons.

The bandgap of the WBG mixed phase perovskite in Chapter 4 was

measured to be at 677 nm from the steady-state PL measurements, and integrating over the spectral photon flux from the AM1.5 solar spectrum, expressed as $AM1.5(\lambda) (hc/\lambda)^{-1} d\lambda$, from $\lambda = 0$ nm to $\lambda = 677$ nm, reveals that there are 1×10^{21} photons per second per meter squared incident on our samples under an AM1.5 solar spectrum.

Therefore, an AM1.5 equivalent intensity corresponds to an intensity of 50 mW/cm^2 from a 398 nm laser with an effective illumination area of $2.97 \times 10^{-4} \text{ cm}^2$, while a 5800 mW/cm^2 laser intensity would correspond to around 115 times an AM1.5 equivalent intensity used for halide segregation characterisation in Chapter 4.

Photoluminescence and Quasi-Fermi Level Splitting Mapping

The spatially resolved data (QFLS maps) were taken using an in-house-built PL measurement setup (Figure 3.5). The setup consists of an LED illumination source, an image sensor and lens (camera) to collect and measure the PL, a longpass filter to prevent stray/reflected light from the excitation source from falling onto the image sensor, and a source meter to bias the sample.

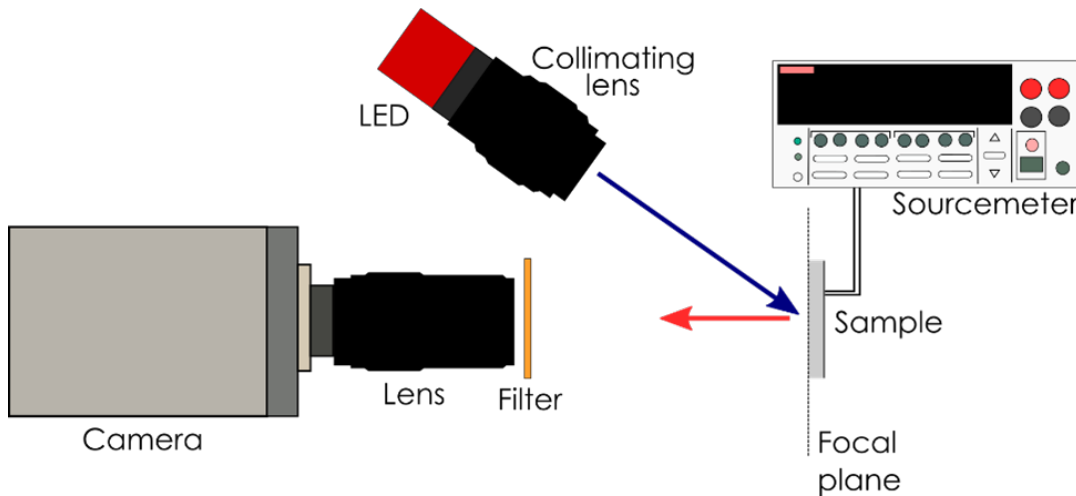


FIGURE 3.5: In-house-built photoluminescence measurement setup for measuring the photoluminescence and quasi-fermi level splitting maps. The figure is adapted from [78], [131]. CC BY 4.0.

The illumination was provided by a ThorLabs M450LP1 LED collimated by a Thorlabs SM2F lens. The emission was at 450 nm, well above the bandgap of the tested samples. The Intensity was controlled by controlling the power supplied to the LED. In order to determine the '1 sun' illumination, the sample was shorted and the LED power was tweaked till the current readout was near the short circuit current measured on a solar simulator. The biasing was done using a Keithley 2400.

The PL was measured using an ANDOR Zyla 4.2, a 'scientific CMOS' or sCMOS sensor. The sensor was cooled to 0 °C. The collection lens was a Kowa LM50XC, a 50 mm lens with an aperture of f2.0. The sample was brought to the focal plane of the lens, and positioned to coincide with the centre of the incident beam. The filter was a Thorlabs FGL515S longpass filter, with a cut-off of 515 nm. Exposure times were varied to obtain a good signal. In the analysis, the measured counts were linearly scaled by exposure time to correct for this.

In order to both correct for beam nonuniformity as well as calculate the PLQY for the QFLS calculation, a white reference was imaged without the filter. This was a barium sulphate plate, which has near unity reflectivity and a Lambertian reflection profile. This gave both a spatial map of the beam that could be used to correct the PL images, as well as the measured counts corresponding to the photon flux from the LED, at some known intensity and exposure time. The

$$\text{PLQE} = \frac{\text{Counts from sample}}{\text{Counts from LED}} \times C, \quad (3.1)$$

on a per-pixel level, where C is a correction factor determined to account for the LED intensity difference between the sample and the ref images

and the Quantum efficiency of the detector and wavelength response of the lens and filter.

The QFLS was determined in line with our previous work [60], [131]. In brief, I calculate the QFLS according to

$$\text{QFLS} = k_B T \ln \left(\text{PLQE} \cdot \frac{J_G}{J_{0,\text{rad}}} \right), \quad (3.2)$$

where k_B is the Boltzmann constant, T is the absolute temperature, PLQE is the photoluminescence quantum efficiency, J_G is the generation current and $J_{0,\text{rad}}$ is the radiative recombination current in the dark. The generation current can be calculated according to

$$J_G = q \int_0^\infty \text{EQE}(\lambda) \varphi_{\text{AM1.5}}(\lambda) d\lambda, \quad (3.3)$$

where q is the elementary charge, EQE is the photovoltaic external quantum efficiency and $\varphi_{\text{AM1.5}}$ is the solar photon flux. In a similar manner, I calculate $J_{0,\text{rad}}$ as

$$J_{0,\text{rad}} = q \int_0^\infty \text{EQE}(\lambda) \varphi_{\text{BB}}(\lambda) d\lambda, \quad (3.4)$$

with φ_{BB} being the blackbody spectrum at room temperature. Following the Shockley-Queisser approach, our calculation estimated a QFLS_{rad} by assuming a step function absorption profile instead of the EQE_{PV} .

From that, the radiative limit of the QFLS (QFLS_{rad}) ($\text{PLQE} = 100\%$) can be calculated with the following equation:

$$\text{QFLS}_{\text{rad}} = k_B T \ln \left(1 + \frac{J_G}{J_{0,\text{rad}}} \right). \quad (3.5)$$

In this case, I approximated J_G to short circuit current J_{SC} and used the room temperature where $T = 298$ K. As such I calculated the QFLS_{rad} of our perovskite absorber as

$$\text{QFLS}_{\text{rad}} = k_B T \ln \left(1 + \frac{J_{\text{SC}}}{J_{0,\text{rad}}} \right), \quad (3.6)$$

where $\text{QFLS}_{\text{rad}} = 1.484$ eV for $E_g = 1.77$ eV or 1.512 eV for $E_g = 1.8$ eV.

Finally, I calculated our QFLS as follows:

$$\text{QFLS} = \text{QFLS}_{\text{rad}} + k_B T \ln (\text{PLQE}). \quad (3.7)$$

The PL and QFLS mappings and analysis in Chapter 4 were done by Akash Dasgupta.

3.2.2 Material Characterisation

X-ray Diffraction

The 1D XRD patterns were obtained with a Panalytical X'Pert Pro X-Ray diffractometer and 2D-XRD patterns using a Rigaku SmartLab X-ray diffractometer and a HyPix-3000 2D hybrid pixel array detector, both with a $\text{CuK}_{\alpha 1}$ (1.54060 Å) source. An Anton Paar DCS-350 heating stage was employed in conjunction with the Rigaku SmartLab diffractometer for relevant in situ annealing measurements. The 2D XRD data in Chapter 4 were collected and analysed by Dr. Philippe Holzhey. The samples were prepared

shortly (< 1 hour) by Xinyi Shen before measurement and measured in ambient conditions.

Ex situ Grazing-incidence wide-angle X-ray scattering (GIWAXS)

The ex situ GIWAXS measurements were conducted using a Rigaku SmartLab diffractometer outfitted with a HyPix-3000 hybrid pixel-array 2D detector and a rotating 3 kW CuK α source operating at 40 kV and 45 mA. X-ray photons with an energy of 8.048 keV, delivered through CBO-f optics, impinged upon an accurately aligned sample surface at grazing incidence angles of 0.5° and 1°. The samples were secured on a 2D-XRD attachment stage incorporating a beam stop to intercept the primary beam, which was positioned 65 mm from the detector. Subsequent to data acquisition, detector images were integrated and resampled into Q-space, then compiled using custom scripts based on the PyFAI and pygix libraries; these same libraries facilitated the extraction of azimuthally integrated one-dimensional profiles. For variable-angle GIWAXS measurements (with incident angles, α_i , ranging from 0.5° to 1°), with 60 min acquisition at each angle. The samples were analyzed under an alternative 2D-XRD aperture slit configuration that incorporated parallel-beam optics, a 0.5° in-plane parallel-slit collimator, a 0.1 mm incident slit, and a 10 mm length-limiting slit at a fixed detector position, with the subsequent data processing performed as described above. The ex-situ GIWAXS data in Chapter 6 were collected and analysed by Fengning Yang. The samples were prepared shortly (< 1 hour) by Xinyi Shen before measurement and measured in ambient conditions.

In situ Grazing-Incidence Wide-Angle X-Ray Scattering

In situ GIWAXS measurements in Chapter 4 were performed and analysed by Dr. Joel Smith at the mySpot beamline at the BESSY II synchrotron. Solutions were prepared according to the methods above, before

blade coating with a film thickness of 20 μm and then immediately transferred into a sealed chamber. Films were then measured while drying, from room temperature to 100 $^{\circ}\text{C}$ controlled with an integrated hotplate and under a flow of N_2 to emulate quenching. The synchrotron beam with an energy of 9 keV ($\lambda = 1.378 \text{ \AA}$) was incident at an angle of 2° , and the diameter of the beam was 100 μm . Scattering was collected in 2 s increments using an Eiger 9M (DECTRIS) hybrid photon counting detector at a distance of 320 mm, with the geometry calibrated using LaB6 as the calibrant. Detector images were then resampled into Q-space and azimuthally integrated using scripts based on the PyFAI and pygix libraries.

In situ GIWAXS measurements in Chapter 6 were conducted and analysed by Fengning Yang at the I07 beamline at Diamond Light Source. Perovskite films were put into a built-in hotplate with a temperature controller to carry out the in-situ thermal annealing process. Throughout the characterisation, a continuous flow of nitrogen gas was maintained to establish an inert atmosphere. A synchrotron X-ray beam with an energy of 10 keV was directed onto the samples at a grazing incidence angle (α_i) of 0.5° . Scattering data were collected using a Pilatus 2M (DECTRIS) hybrid photon counting detector, with the experimental geometry calibrated using Silver Behenate (AgBe) powder as a standard reference. The wet film of the solution process was prepared in the chemical laboratory at Diamond Light Source using a Laurell spin coater within a fume hood. The evaporated film was fabricated in Oxford and transported via a KF (Klein Flange) tube. All the in situ GIWAXS data was acquired during the experiment session SI40188-1. Detector images were then resampled into the Q-space and azimuthally integrated using scripts based on PyFAI and pygix libraries.

Scanning Electron Microscopy

A FEI Quanta 600 FEG Environmental Scanning Electron Microscope was employed to investigate perovskite layer morphology. Accelerating voltages between 4-15 kV were employed for various analyses. The cross-sectional SEM images presented in Chapter 6 were measured by Dr. Shuaifeng Hu.

Nuclear Magnetic Resonance (NMR) Spectroscopy

A two-channel Bruker AVANCE III HD Nanobay 400 MHz instrument running TOPSPIN 3 equipped with a 5 mm z-gradient broadband/fluorine observation probe was used. The signal from residual non-deuterated DMSO solvent was used for reference. The NMR measurements in Chapter 4 were measured by Dr. Benjamin Gallant. The NMR measurements in Chapter 6 were measured by Prof. Nakita Noel. Deuterated ethanol was used to resolve the signals of DMF and DMSO.

Optical Microscopy

Optical microscope images were taken on a Nikon Eclipse LV100ND microscope with Nikon TU Plan Fluor lenses (10x/0.30 A, 20x/0.45 A, 50x/0.60 B, 100x/0.90 A). The images are taken with an attached Nikon Digital Camera D6.10.

Wavelength Dispersive X-Ray Fluorescence

The atomic percentages of the halide and lead atoms in the perovskite thin films were determined using wavelength dispersive X-ray fluorescence (WDXRF). Measurements were performed on a WDXRF with a Rh-tube at room temperature. The angle between the XRF detector and the incident X-ray beam is fixed at 90°. The angle between the normal to the sample surface and the incident X-ray beam was 15°, optimised to reduce self-absorption effects in the XRF signal while minimising the footprint of the X-ray beam. The X-ray beam entered the substrate through the perovskite side. From the XRF,

we identify the elements in the film according to their characteristic fluorescence energy. Atomic percentages were determined using the fundamental parameters method [132]. The WDXRF data in Chapter 4 were measured at Oxford PV Ltd..

Time-of-flight secondary ion mass (ToF-SIMS) spectrometry

Perovskite samples for ToF-SIMS measurements were prepared following the same procedure used for solar cells. Measurements were conducted using a hybrid SIMS instrument (IONTOF M6), which was equipped with a bismuth primary ion source and an O^{2+} sputter source to probe the positive atomic and/or fragment ions. The ToF-SIMS data were acquired over an area of $150 \times 150 \mu m$ using a 30 keV Bi^+ primary ion beam. This was followed by a sputtering process, with each cycle lasting for 3 seconds. During each sputtering cycle, a $400 \times 400 \mu m$ area of the sample was bombarded with 1 keV O_2^+ ion beams in an interlaced mode. The sample holder, containing the samples was sealed in a container filled with argon gas and was transferred into the instrument immediately before testing. The ToF-SIMS data in Chapter 6 was performed and analysed by Lirong Rong.

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. The data presented in Chapter 4 was performed and analysed by Benjamin Gallant.

3.2.3 Characterisation of Solar Cells

Current Density Voltage Measurements

JV and MPPT measurements were measured (2400 series source meter, Keithley Instruments) in ambient air under both light (simulated AM 1.5 irradiance generated by a Wavelabs SINUS-220 simulator) and in the dark. The active area of the solar cell was masked with a black-anodised metal aperture to either 0.25 or 1.00 cm², within a light-tight holder. For each device, the PV metrics were obtained in the following sequence. Firstly, the devices were kept at open-circuit conditions under illumination for 6 seconds until the fluctuations in readings were nearly negligible to obtain the steady-state V_{OC} . Then, a 'reverse' JV scan (from forward bias to short-circuit) and a 'forward' JV scan (from short-circuit to forward bias) were measured both at a scan rate of 245 mV s⁻¹. Subsequently, active MPPT measurements using a gradient descent algorithm were performed for 30 seconds to obtain the η_{MPPT} . Lastly, the devices were kept at short-circuit conditions under illumination for 3 seconds until the fluctuations in readings were nearly negligible to obtain the steady-state J_{SC} . The intensity of the solar simulator was set periodically such that the short-circuit current density from a KG3-filtered Si reference photodiode (Fraunhofer ISE) matched its 1-sun certified value. A local measurement of the intensity before each batch of solar cell measurements was performed by integrating the spectrum obtained from the solar simulator's internal spectrometer. By taking the ratio of this internal intensity measurement to one obtained at the time of calibration, I determined the equivalent irradiance at the time of measurement. For the device data presented in this thesis, this gave values ranged from 0.985-1.005 suns equivalent, which have been applied to the calculation of power conversion efficiencies for each individual measurement.

Pseudo Current Density Voltage characterisation

Pseudo-*JV* characterisation is a technique used to estimate the *JV* behaviour of solar cells without exposing them to full sunlight or performing traditional illuminated *JV* measurements. It leverages dark *JV* measurements combined with light-intensity-dependent open-circuit voltage data to reconstruct a "pseudo" *JV* curve. It avoids light-induced degradation and allows high-throughput screening of devices. Series resistance, shunt resistance, ideality factor and pseudo-FF can be extracted from the characterisation to estimate the device performance under operation without the risk of stability issues.

External Quantum Efficiency

EQE measurements were performed using a custom-built set-up based on a Bruker Vertex 80v Fourier transform interferometer. The solar cells were illuminated with a 250 W quartz-tungsten halogen lamp that was first passed through a monochromator (Princeton Instruments SP2150) with a filter wheel (Princeton Instruments FA2448), then chopped with an optical chopper (Thorlabs MC2000B) at 280Hz, and finally focussed onto the sample with a smaller spot size than the solar cell area (as defined by the metallic top contact). The amplitude of the resulting AC current signal was measured with a lock-in amplifier (Stanford Research Systems SR830) as the voltage dropped across a 50-ohm resistor in series with the solar cell. To determine the EQE, the photocurrent spectrum of the device under test was divided by that of a calibrated Si reference cell (Thorlabs FDS100-CAL) of a known EQE. Device active areas were masked with a black-anodised metal aperture, having an active area of either 0.25 cm² or 1 cm².

Stability Measurements

Chapter 4

In the ambient ageing experiment, unencapsulated perovskite films were aged under dark, ambient conditions (25 °C, 50% relative humidity (RH) in air). The perovskite films were periodically characterised with UV-Vis, XRD, SEM and optical microscopy to monitor the material degradation. The photo and thermal stability measurements were carried out on encapsulated devices in a light-soaking ageing box with full-spectrum, continuous illumination of intensity equivalent to 1-sun. The devices were kept at open-circuit conditions, 65 °C in air (RH = 50%) and periodically moved to the atmosphere to test photovoltaic performance.

Chapter 6

The PSCs for the stability test were sputtered with a thin layer of 300 nm SiO_x with an active area mask to prevent reaction with UV adhesive. The full devices were encapsulated using a cover glass (28.0 mm × 21.5 mm × 1.1 mm) and UV adhesive (AB-341, Eversolar) in a nitrogen-filled glove-box. The adhesive was applied over the whole substrate area, followed by a UV-treatment for 3 min. All the encapsulated devices were aged using an Atlas SUNTEST CPS+ (1,500 W air-cooled Xenon lamp) light-soaking chamber under simulated full-spectrum AM1.5 sunlight with $\sim 78 \text{ mW cm}^{-2}$ irradiance and without applying any UV filters. All the ageing tests performed in this work were conducted at open-circuit conditions. To carry out current-voltage characterisations, the samples were taken out of the chamber and tested at different ageing times, following the measurement protocol as described above. The ageing chamber for storing the encapsulated samples was air-cooled with the temperature controlled at 85 °C (measured using a black standard temperature control unit positioned next to the test cells). During

the ageing period, the relative humidity in the laboratory (at 21°C) was monitored in the range of 50 ~ 60%. The ageing test is in correspondence to ISOS-L-2 ageing protocol.

The perovskite thin films used for photo and thermal stability tests were coated with a 3-5 nm layer of Poly(methyl methacrylate) (PMMA, Sigma Aldrich) to prevent scratches and dust.

Outdoor stability test

The perovskite-Si tandem cells were prepared at Oxford and sent to CEA, France for lamination. The laminated cells were then sent to a test facility that was deployed at Eurac Research in Bolzano, Italy (coordinates: 46°28'31.7"N 11°19'49.7"E) that allows for the measurement of low-TRL perovskite-silicon tandem devices. The samples are installed on a frame with a tilt of 30 degrees and an orientation of 190 degrees from North. The setup was designed to measure electrical parameters of up to 24 small-scale encapsulated photovoltaic cells, with voltages up to 2.0 V and currents up to 100 mA at resolutions of 1 mV and 2 microamperes, respectively (Figure 6.23a). It monitors current, voltage, and power at the MPP using micro-MPPTs from Ljubljana University at a time resolution of 1 minute. PT100 sensors concurrently measure cell temperature at the outer backside. All data is collected using a Python script. In addition to the device measurements, we collect plane-of-array irradiance data using a pyranometer and two crystalline-silicon-based reference cells, and weather data including ambient temperature, relative humidity and precipitation intensity and type. The samples were laminated by Dr. Perrine Carroy. The outdoor stability test was conducted and analysed by Dr. Atse Louwen.

Chapter 4

Chloride-Based Additive Engineering for Efficient and Stable Wide-Bandgap Perovskite Solar Cells

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Xinyi Shen, Benjamin M. Gallant, Philippe Holzhey, Joel A. Smith, Karim A. Elmestekawy, Zhongcheng Yuan, P. V. G. M. Rathnayake, Stefano Bernardi, Akash Dasgupta, Ernestas Kasparavicius, Tadas Malinauskas, Pietro Caprioglio, Oleksandra Shargaieva, Yen-Hung Lin, Melissa M. McCarthy, Eva Unger, Vytautas Getautis, Asaph Widmer-Cooper, Laura M. Herz, Henry J. Snaith, Chloride-Based Additive Engineering for Efficient and Stable Wide-Bandgap Perovskite Solar Cells. *Adv. Mater.* 2023, 35, 2211742.

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4.1 Introduction

Metal halide perovskites have emerged in the past decade as a remarkable class of PV materials. They possess desirable optoelectronic and material properties, such as strong light absorption [26], long charge-carrier diffusion lengths [27], and versatile processability using solution-based manufacturing techniques or ambient temperature vapour phase deposition [28]. A series of breakthroughs have led to PCE rising from 3.8% to nearly 26% for single-junction PSCs in just over a decade [24], [25], [133], [134]. In addition, their adjustable material compositions that result in highly tuneable bandgap (E_g) offer an opportunity to develop multijunction solar cells that can capture a broad spectrum of sunlight while surpassing the efficiency limit of single-junction solar cells calculated based on the principle of detailed balance [135]. Among various types of perovskite tandem cell technologies, recent life cycle assessments suggest that “all-perovskite” tandem cells could have a much lower energy payback time and reduced greenhouse gas emissions, in comparison with Si single junction cells or perovskite-on-silicon tandem solar cells [136], making them a promising prospect for rapid growth, terawatt scale, low-cost, low environmental impact photovoltaics [137].

Although the reported PCE of all-perovskite tandem cells has exceeded 27% [134], [138], [139], there remains plenty of scope for improving the absolute efficiency of the WBG sub-cells, since they often underperform due to severe “photovoltage deficits” (the difference in energy between the band gap of the absorber material and the open-circuit voltage generated) as compared to their narrow-bandgap counterparts [140]. The underlying material issues responsible for mediocre WBG V_{OC} include non-radiative bulk and interfacial losses [141], as well as heterogeneous crystallisation of the mixed-ion perovskites required for wide-bandgaps.[15] In addition, the high Br contents in WBG perovskites make them susceptible to light-induced halide

segregation [142]. The mechanism which causes halide segregation under illumination is not fully understood, however, a number of studies suggest that compositional inhomogeneity and the presence of a small fraction of iodine-rich phases in the fully annealed films, may be central to “seeding” the growth of the iodine-rich domains [87], [88], [110]. Under light stress, mixed-halide perovskites undergo reversible phase segregation into Br- and I-rich phases, as a result of halide migration [142]. The I-rich phase with a narrower bandgap will thus function as a charge-carrier trapping domain [143]. Although these lower-bandgap I-rich phases appear only to have a minor negative influence upon both V_{OC} and charge-carrier mobility [141], [144], they do introduce a radiative bimolecular recombination pathway within the lower-gap domains, which results in current losses [144]. Hence, effective strategies to form low-loss and stable WBG perovskites are still required.

ABX_3 -perovskite can be composed of single cations and single anions, such as $FAPbI_3$ (FA, formamidinium) and $MAPbI_3$ (MA, methylammonium), or mixed ions, such as mixed organic and inorganic cations and mixed halides, such as $FA_yCs_{1-y}Pb(I_xBr_{1-x})_3$. For a range of perovskites, it is a common strategy to employ methylammonium chloride (MACl) as an additive for fabricating high-efficiency PSCs [27], [145], [146]. Indeed, the first report of a perovskite solar cell exceeding 10% efficiency, employed a significant quantity of Cl salts in the precursor composition in the form of $PbCl_2$ [25]. So far, the effect of MACl on improving the crystallisation and optoelectronic quality by forming intermediate phases has been studied for archetypal $MAPbI_3/FAPbI_3$ materials [145], [147], [148]. In $MAPbI_3$, some studies have implicated MACl in influencing the colloidal composition of the precursor solution, resulting in improved morphology and performance [149], [150]. More frequently, there have been reports observing solid-state crystalline intermediates incorporating Cl, such as MA_2PbI_3Cl [151], [152].

Following this, a key principle is the sublimation of excess MACl from the film during thermal annealing, which may proceed via decomposition products of the MACl salt [153]. In a work reported by Kim et al. [145], with excess MACl addition in FAPbI₃ fabrication, the authors anticipated that MA⁻ and Cl⁻ loss during thermal annealing results in FAPbI₃ containing only minimal MA inclusion, and no chloride or chloride-rich phases were observed. In addition, MAPbCl₃ has been added to mixed-cation, mixed-halide perovskites to create a “triple-halide perovskite”, in which the authors demonstrated that both MA and Cl could incorporate into the perovskite lattice [118]. However, the impact of MACl on the precursor phases and crystallisation of the mixed-ion perovskites, such as FA_{0.83}Cs_{0.17}Pb(I_{0.6}Br_{0.4})₃, is yet to be revealed [118], [154]. Here, I report a comprehensive study of the impact of MACl on a mixed-cation mixed-halide perovskite. By investigating MACl-assisted intermediate phase formation, I identify the role of additives using a range of halide salts, including formamidinium chloride (FACl), cesium chloride (CsCl), methylammonium iodide (MAI) and methylammonium bromide (MABr). The MACl-modified perovskite films exhibit suppressed halide segregation and improved ambient stability (25 °C, 50% relative humidity (RH), in air, in the dark) compared to the control perovskites. In conjunction with using a phosphonic acid-based self-assembled monolayer as the HTL, I demonstrate efficient WBG PSCs with a maximum power point-tracked efficiency (η_{mpp}) of 17% and a steady-state V_{OC} of 1.25 V. Additionally, I demonstrate large-area cells (1 cm²) with η_{mpp} as high as 16.1%.

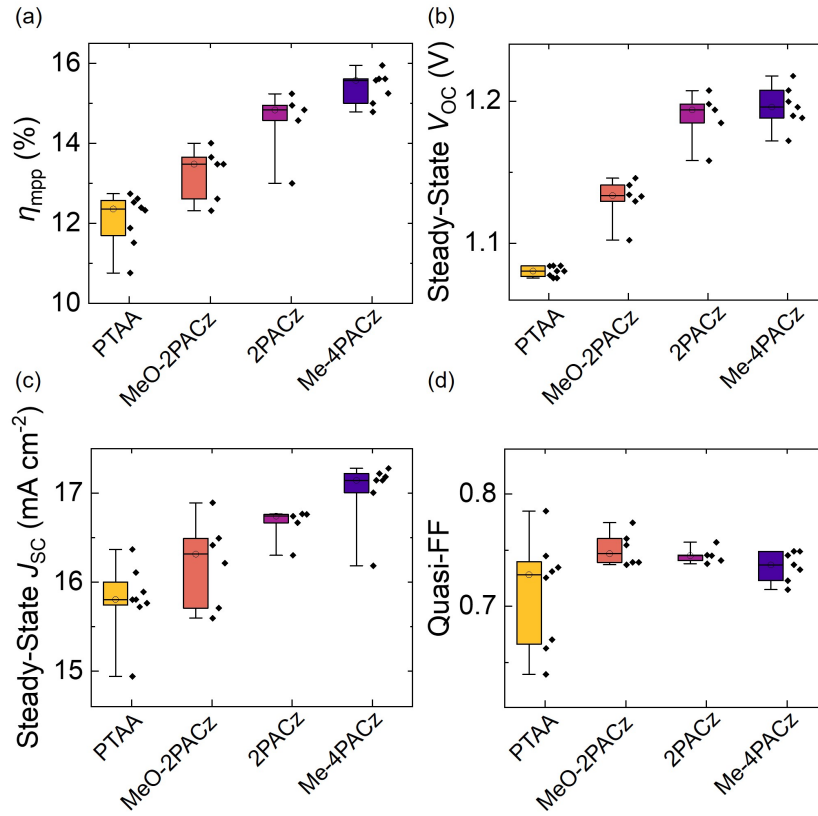


FIGURE 4.1: (a) η_{mpp} , (b) steady-state V_{OC} , (c) steady-state J_{SC} and (d) quasi-FF of $FA_{0.83}Cs_{0.17}Pb(I_{0.6}Br_{0.4})_3$ PSCs employing PTAA, MeO-2PACz, 2PACz and Me-4PACz respectively as the hole transport layer. These devices were fabricated in a single experimental batch. Any pixel with $\eta_{mpp} \leq 75\% \eta_{mpp}$ of the champion device is cut off from the figure.

4.2 Selection of Hole Transport Layer for WBG Perovskite

SAM hole-transport materials have previously been shown to reduce the V_{OC} deficit and suppress halide segregation in p-i-n PSCs via mitigating non-radiative losses and improving hole extraction [112], [155], [156]. I first examined three different SAMs, including 2PACz, MeO-2PACz and Me-4PACz, and PTAA as the HTL for a perovskite solar cell composed of $FA_{0.83}Cs_{0.17}Pb(I_{0.6}Br_{0.4})_3$ ($E_g = 1.77$ eV) in a p-i-n configuration. As I show in Figure 4.1, all three SAMs lead to enhancements in PV performance, especially in V_{OC} and J_{SC} . In Figure 4.2, I present the EQE and integrated J_{SC} of champion cells with different

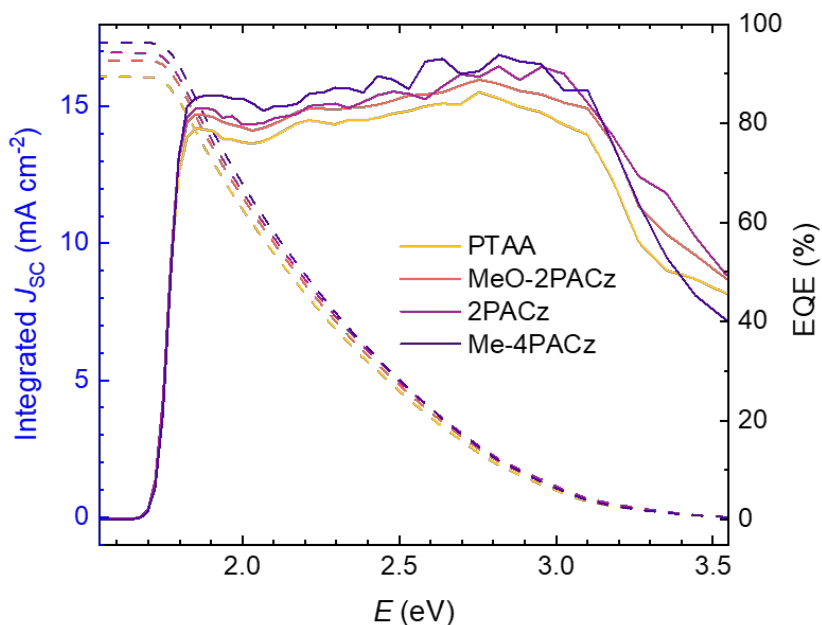


FIGURE 4.2: EQE and integrated J_{SC} of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ PSCs employing PTAA, MeO-2PACz, 2PACz and Me-4PACz respectively as the hole transport layer. These devices were fabricated in a single experimental batch.

HTLs. All the SAMs exhibit higher EQE than PTAA over a wide range (1.8 - 3.0 eV), among which Me-4PACz yields the highest EQE and integrated J_{SC} . Hence, I attribute the performance boost to better charge extraction enabled by the ultrathin HTL [112]. Less interfacial recombination may contribute to the improved V_{OC} . In this work, I selected Me-4PACz as our standard HTL in further investigations because it provided the most substantial device performance boost.

4.3 Impacts of Chloride Additives on WBG Perovskites

Having established Me-4PACz as the HTL of choice for our 1.8 eV PSCs, I now investigate the impact of MACl as an additive across a range of concentrations (0 – 45 mol% excess) upon the formation and performance of

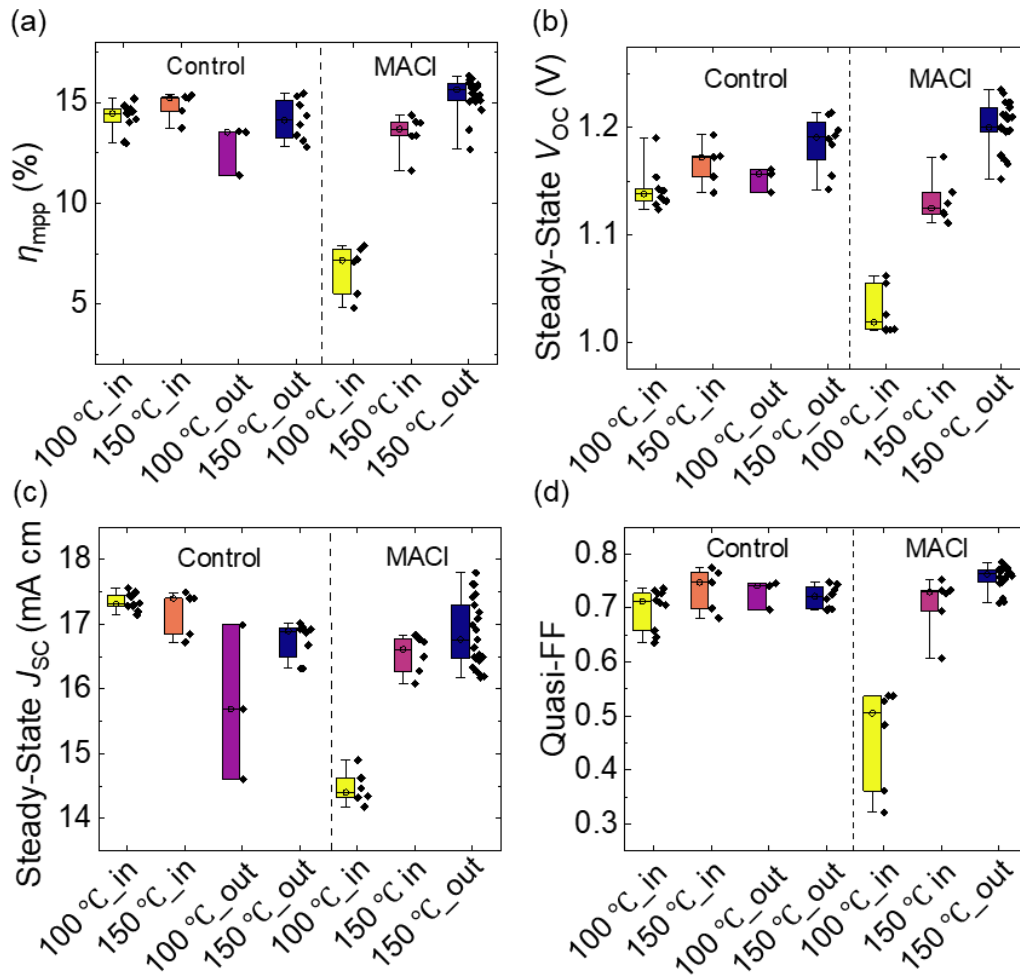


FIGURE 4.3: PV parameters of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ PSCs based on Me-4PACz with no MACl additives (control) or 15 mol% MACl additives annealed at different conditions: (a) η_{mpp} , (b) steady-state V_{oc} , (c) steady-state J_{sc} and (d) quasi-FF. These devices were either annealed in the glovebox (N_2 atmosphere, 'in') or transferred out of the glovebox immediately after deposition and annealed at ambient conditions (RH = 30%, 'out'). The annealing temperature and time were selected between 30 min at 100 °C ('100 °C') or 10 min at 150 °C ('150 °C'). All devices (59 cells) were fabricated in two batches of experiments.

$\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ perovskite films and devices. During the fabrication of MACl-derived perovskite thin films and devices, I found that the photovoltaic performance is more sensitive to annealing temperature, as compared to our control films. As mentioned in previous literature [146], methylammonium chloride (MACl) has been used as a crystallisation aid to improve the film quality and enlarge the grain size of triple-A-cation (FAC-sMA) perovskite films. In this work, I added an extra amount of MACl into

a more complex perovskite composition ($\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$) and optimized the fabrication process of perovskite films (composition, annealing temperature and atmosphere). The involvement of high bromide contents in the precursor will change the crystallisation dynamics of perovskite films [157], which is not elucidated yet.

Figure 4.3 presents the PV parameters achieved by the MACl-free and MACl-modified $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ PSCs which were processed at various annealing conditions. A higher annealing temperature (150 °C) only slightly increased the V_{OC} in the absence of MACl additives, whereas substantial improvements in all the PV parameters could be realised with the aid of MACl. As mentioned in previous literature [145], MACl allowed a higher annealing temperature and improved the perovskite crystallinity. This is consistent with our XRD results (see Figure 4.6). Interestingly, annealing at ambient environment (30% RH in air) in the presence of MACl led to further boosts in the PV parameters compared to annealing in a N_2 -filled glovebox.

In order to decouple which factor accounted for the performance enhancement, I conducted further investigations. As shown in Figure 4.4, by transferring the MACl-doped $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ films out of the glovebox after deposition and annealing the films in a compressed air-filled dry box ($\text{RH} < 1\%$), the PV parameters (especially the V_{OC}) of the devices were improved compared to the films annealed in a N_2 -filled dry box ($\text{RH} < 1\%$). Interestingly, annealing the MACl-modified perovskites at ambient conditions with $\text{RH} = 30\%$ did not reduce the device performance, instead, slightly higher FF and J_{SC} were achieved. This suggests that there is a minimum humidity condition for optimal performance, but that there exists a wide processing window in which such performance can be achieved. However, for the best reproducibility of the process, I employed a controlled RH level (30%) in further experiments. Based on our results shown above, we chose

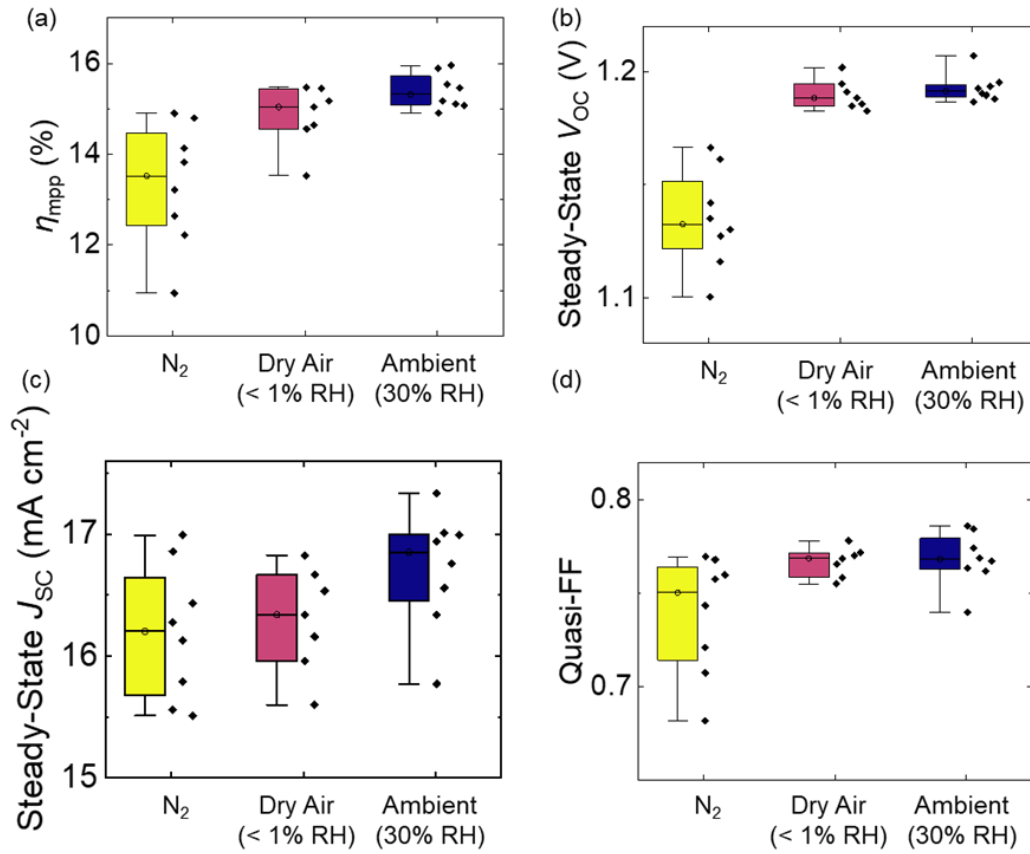


FIGURE 4.4: PV parameters of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ PSCs based on Me-4PACz with 15 mol% MACl additives annealed at different conditions: (a) η_{mpp} , (b) steady-state V_{OC} , (c) steady-state J_{SC} and (d) quasi-FF. The devices were deposited in the glovebox and transferred out to anneal at 150 °C for 10 min in a dry box purged with N_2 (< 1% RH, ' N_2 ') or a dry box purged with compressed air (< 1% RH, 'Dry Air (< 1% RH)'); or at ambient conditions (30% RH, 'Ambient (30% RH)'). All devices (23 cells) were fabricated in one batch.

150 °C as our annealing temperature, and our cells were processed in air with $\sim 30\%$ RH. The requirement for higher annealing temperatures may be due to the requirement to volatilise the majority of the excess MACl during annealing. In a previous work reported by Brenes et al. [158], the humid air treatment on MAPbI_3 perovskite films has been shown to enhance the PL intensity and lifetime, which resulted in reduced V_{OC} loss and improved J_{SC} and PCE of PSC devices, due to reduction of the density of shallow surface states and minimal non-radiative losses. Therefore, the performance boost in our optimised MACl-based cells when annealed in air, as compared to in a nitrogen-filled glove box, may be attributed to such a moisture-activated

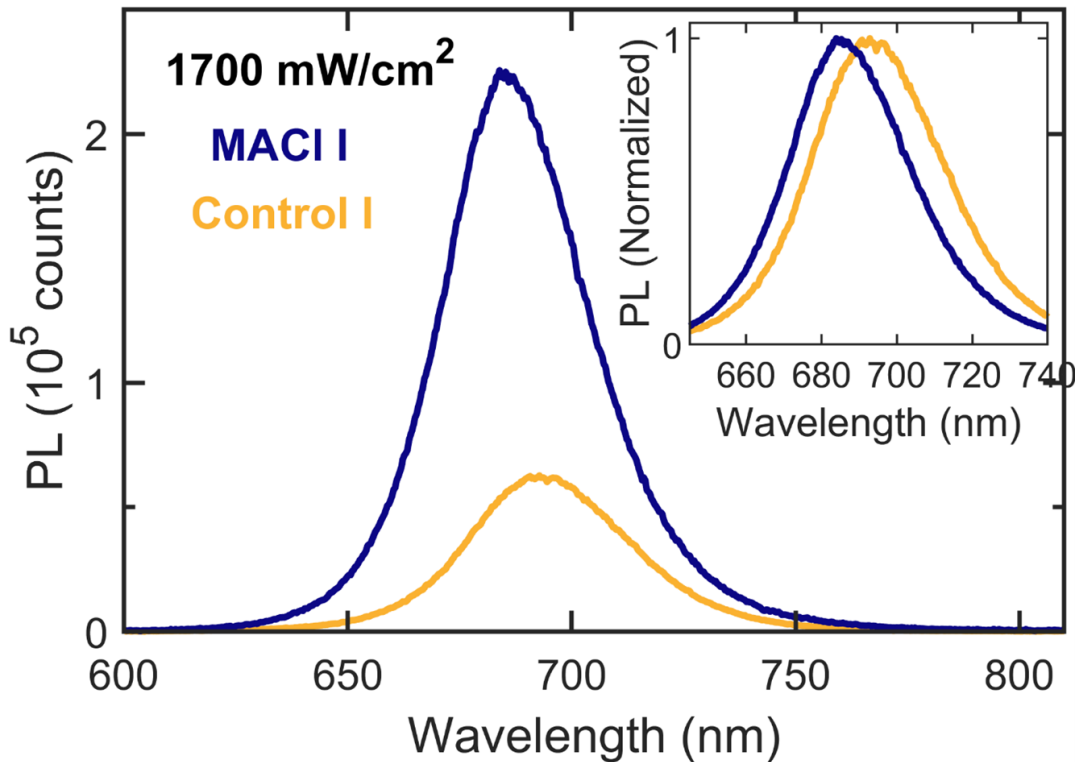


FIGURE 4.5: Steady-state PL spectra of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ perovskite films on quartz with or without 15 mol% MACl additive, namely ‘MACl I’ or ‘Control I’, under continuous illumination equivalent to 29 suns. The excitation wavelength is 398 nm. Inset: normalised PL spectra. Steady-state PL was measured by Karim A. Elmestekawy.

passivation effect as the 15 mol% MACl-processed perovskite film achieves a nearly four-fold increase in PL intensity compared to the control film (Figure 4.5).

To investigate the impact of MACl concentration on the crystallographic properties of perovskite films across the range of additive concentrations, I carried out XRD measurements (Figure 4.6). All perovskite films show characteristic pseudo-cubic diffraction peaks but with different preferred orientations. With 15 mol% or less MACl, the dominant orientation has cubic (110) planes ($2\theta = 20.4^\circ$) aligned parallel to the plane of the substrate. With increasing MACl content there is a pronounced effect on orientation, with reflections corresponding to (100) planes ($2\theta = 14.4^\circ$) growing in

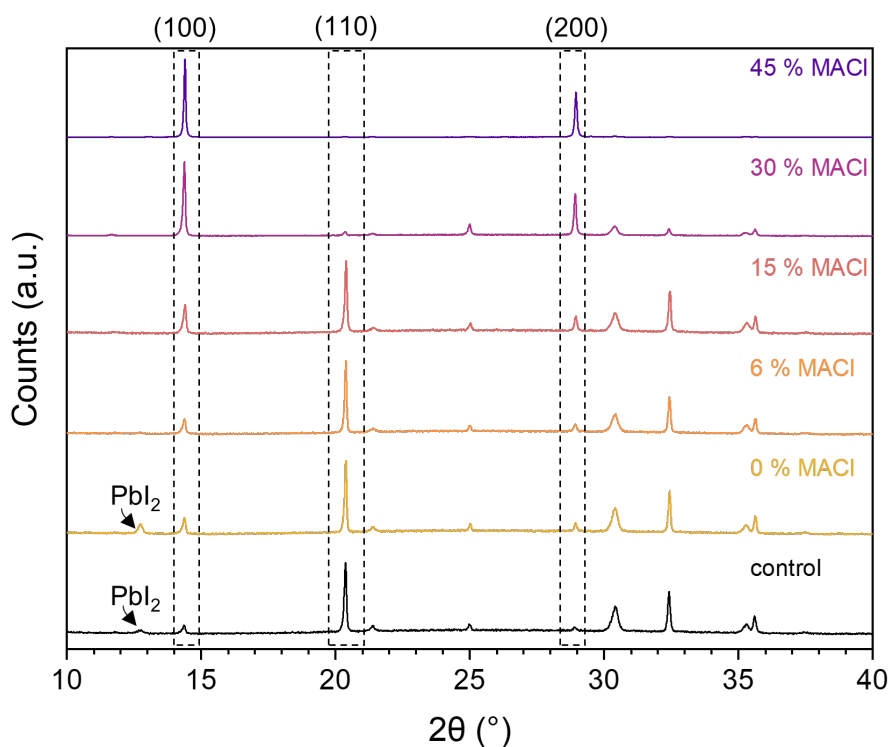


FIGURE 4.6: X-ray diffraction (XRD) patterns of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ as a function of MACl additive concentrations. ‘Control’ contains 0 mol% MACl additive and is annealed at 100 °C in a N_2 -filled glovebox, whereas perovskites fabricated with MACl additive are annealed at 150 °C in air with $\sim 30\%$ RH. ‘0 mol% MACl’ refers to a film without MACl additive but is annealed at 150 °C in air with $\sim 30\%$ RH.

intensity. With 30 mol% MACl and above, films are almost completely oriented to have the (100) plane parallel to the substrate. Notably, though, this apparent shift from uniaxial $\langle 110 \rangle$ orientation to uniaxial $\langle 100 \rangle$ orientation does not lead to an increase in PSC performance (Figure 4.7). This might be explained by our XRD measurements also revealing an increase of undesirable impurity phases above the optimal additive content (Figure 4.8). Use of > 6 mol% MACl additive suppresses lead (II) iodide (PbI_2) formation, the continued addition of MACl additive leads to the gradual growth of non-perovskite 2H (δ -phase) and 4H hexagonal polytype phases in the final material. These polytype phases are photo-inactive, but they can act as charge-blocking layers since they have wider gaps than the bulk ABX_3 3C perovskite

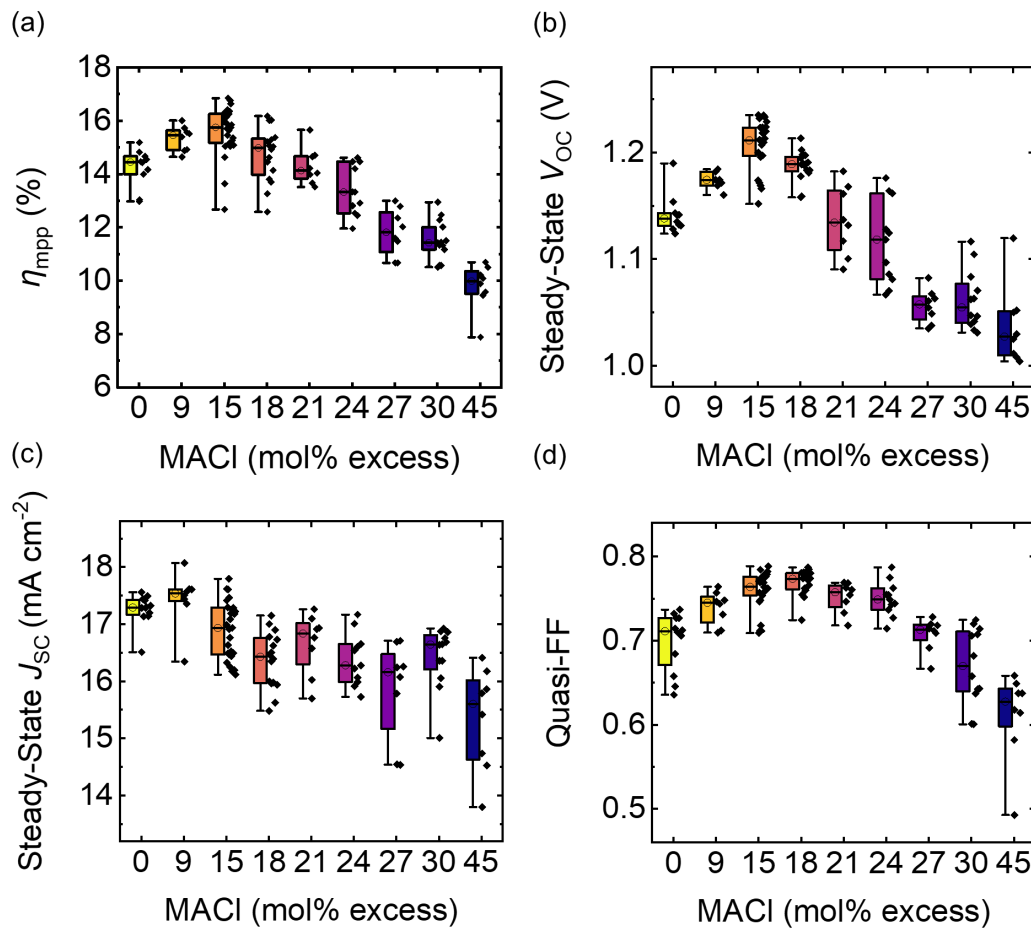


FIGURE 4.7: PV parameters of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ PSCs based on Me-4PACz with a different excess molar ratio of MACl additives (0 - 45 mol%): (a) η_{mpp} , (b) steady-state V_{OC} , (c) steady-state J_{SC} and (d) quasi-FF. These devices (101 cells in total) were fabricated in 3 batches of experiments.

phase (Figure 4.9) [159]. Hence, I postulate the increasing inclusion of poly-type phases as contributing to the drop in all device performance metrics (Figure 4.7). Using top-view SEM, I observed that excess MACl leads to a reduction in “surface wrinkling” (Figure 4.10), a commonly reported feature of high-bromide content perovskite materials cast via anti-solvent quenching [160], particularly at higher solution concentrations.

As reported previously [161], the addition of excess AX-type additives can influence the optical bandgap of perovskites, for example via halide substitution. However, there has been significant debate as to whether Cl can

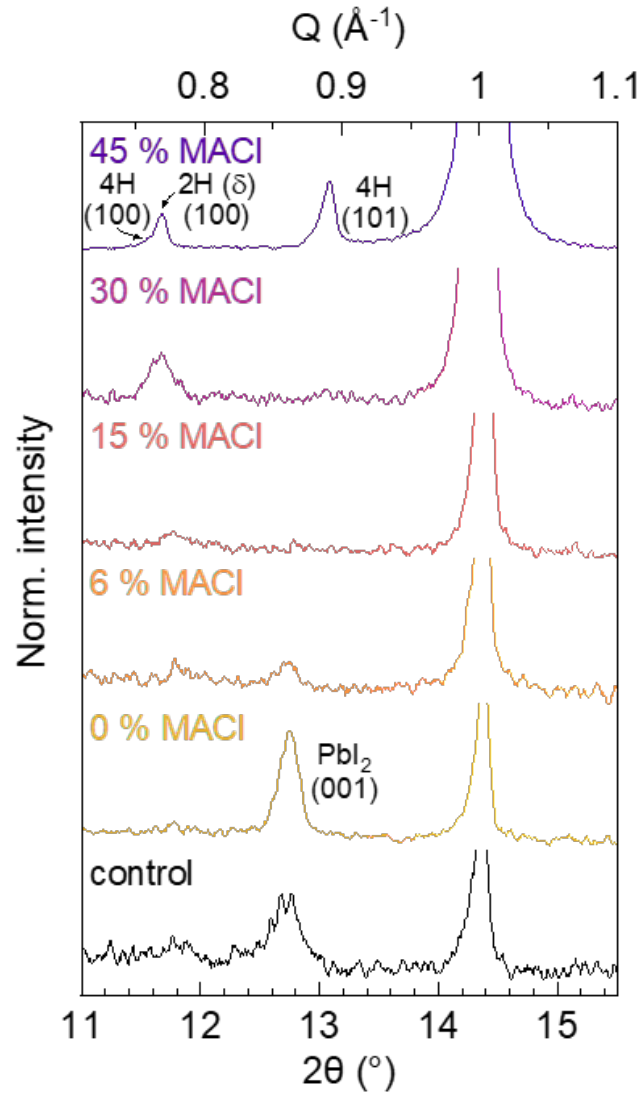


FIGURE 4.8: XRD patterns highlighting trace impurities in $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ perovskite films with various MACl additive concentrations (x) with $0 \leq x \leq 45$ mol%.

be incorporated into an I-rich lead halide perovskite [118], [152], on account of the large difference in ionic radii between iodide and chloride, and the extraction of the additional chloride during post-deposition annealing reported with other fabrication protocols [145], [146]. To investigate the influence of MACl on the optical bandgap of our perovskite composition I conducted Tauc analyses (See Figure 4.11). I observe a modest Tauc bandgap increase from 1.79 eV to 1.81 eV when increasing the excess concentration of MACl from 0 mol% to 45 mol% ($E_g = 1.8$ eV for $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ with 15 mol% MACl), indicating compositional variation in the as-fabricated WBG

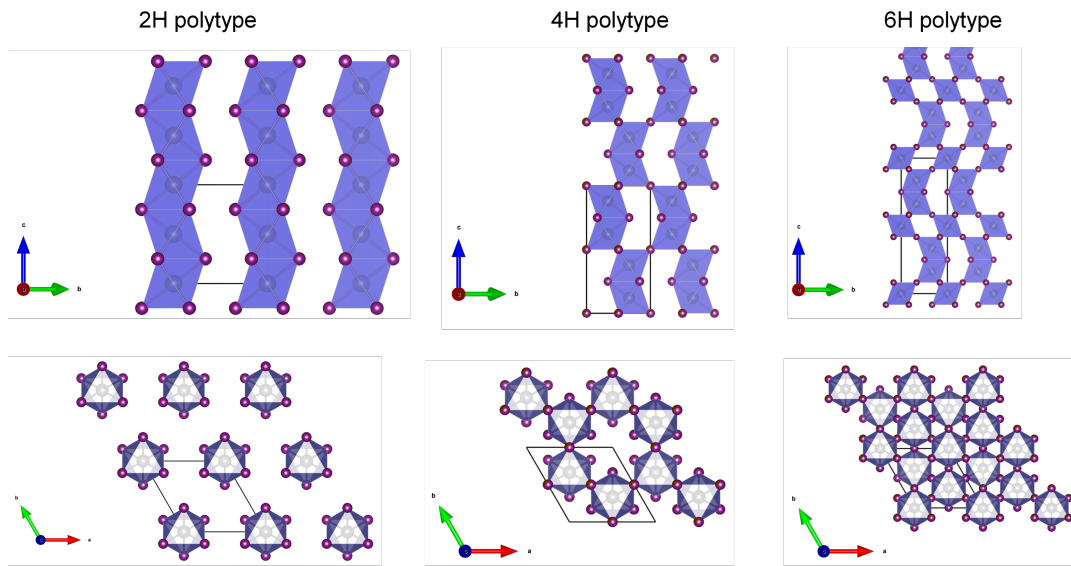
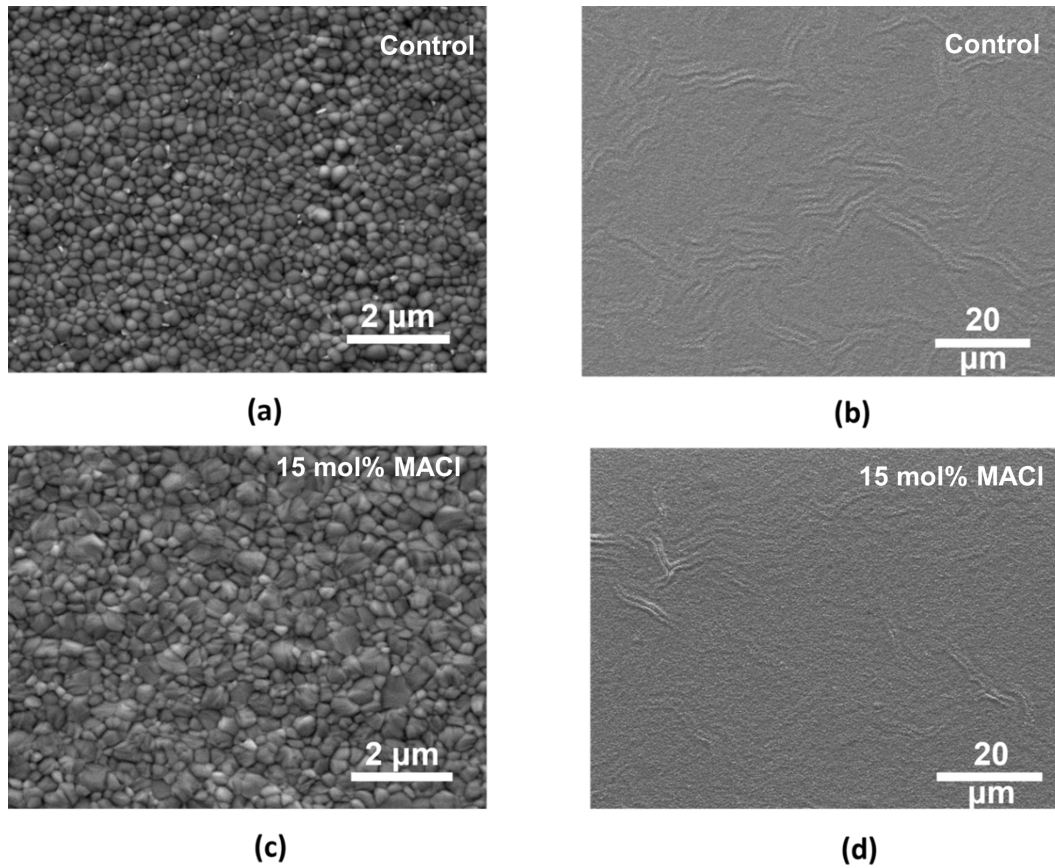


FIGURE 4.9: Crystal diagrams of 2H, 4H and 6H polytypes.

FIGURE 4.10: Top-down SEM images of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ films (a - b) without or (c - d) with 15 mol% MACl additive, namely ‘Control’ or ‘15 mol% MACl’.

perovskite materials. The blue-shift of the optical bandgap is also supported by steady-state PL measurements (See Figure 4.5). In Br-free perovskites, the

addition of MACl typically does not result in a bandgap shift [145], [148]. However, Xu et al. have recently demonstrated that chloride can be incorporated into the perovskite lattice for certain mixed halide compositions [118], with maximum Cl^- inclusion increasing with Br^- content, confirmed by a bandgap widening effect. Since the perovskite A-site cations, FA and Cs are also alloyed, substitution of FA with MA could also result in small indirect changes to the perovskite band structure and bandgap [162].

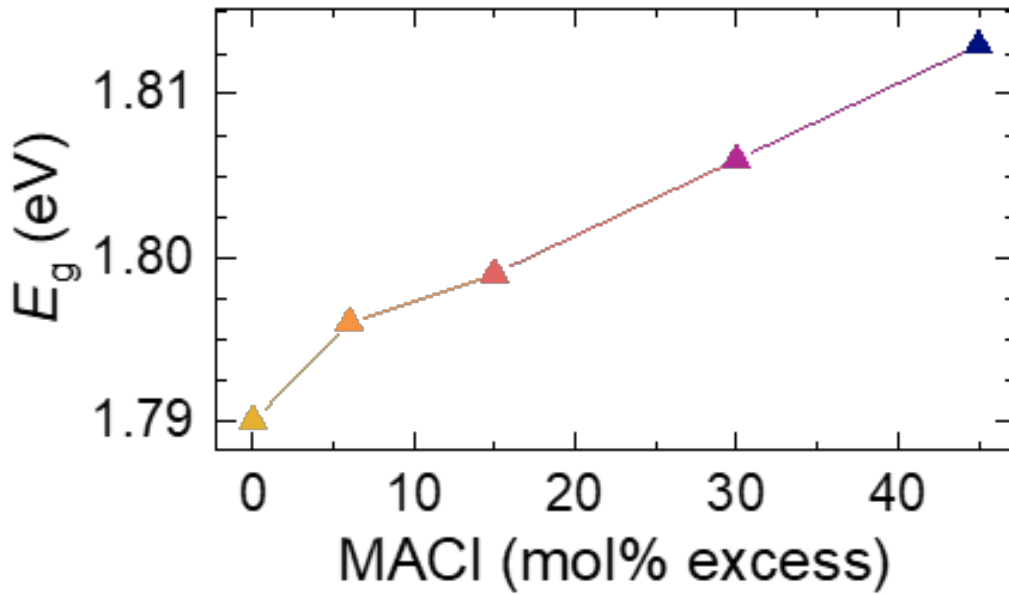


FIGURE 4.11: Optical bandgaps extracted via Tauc analysis based on transmittance and reflectance measurements taken on $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ perovskite films with various MACl additive concentrations (x) with $0 \leq x \leq 45\text{mol}\%$.

To assess how MACl and the other AX additives influence the photovoltaic performance, I fabricated PSCs employing a range of concentrations and additive types (e.g. MACl, FACl, CsCl, MABr etc.). I show the performance of these devices in Figure 4.12 and find that the significant V_{OC} and FF boost achieved with MACl addition is unique to this AX-additive. A possible interpretation is that only the combination of MA^+ and Cl^- is volatile

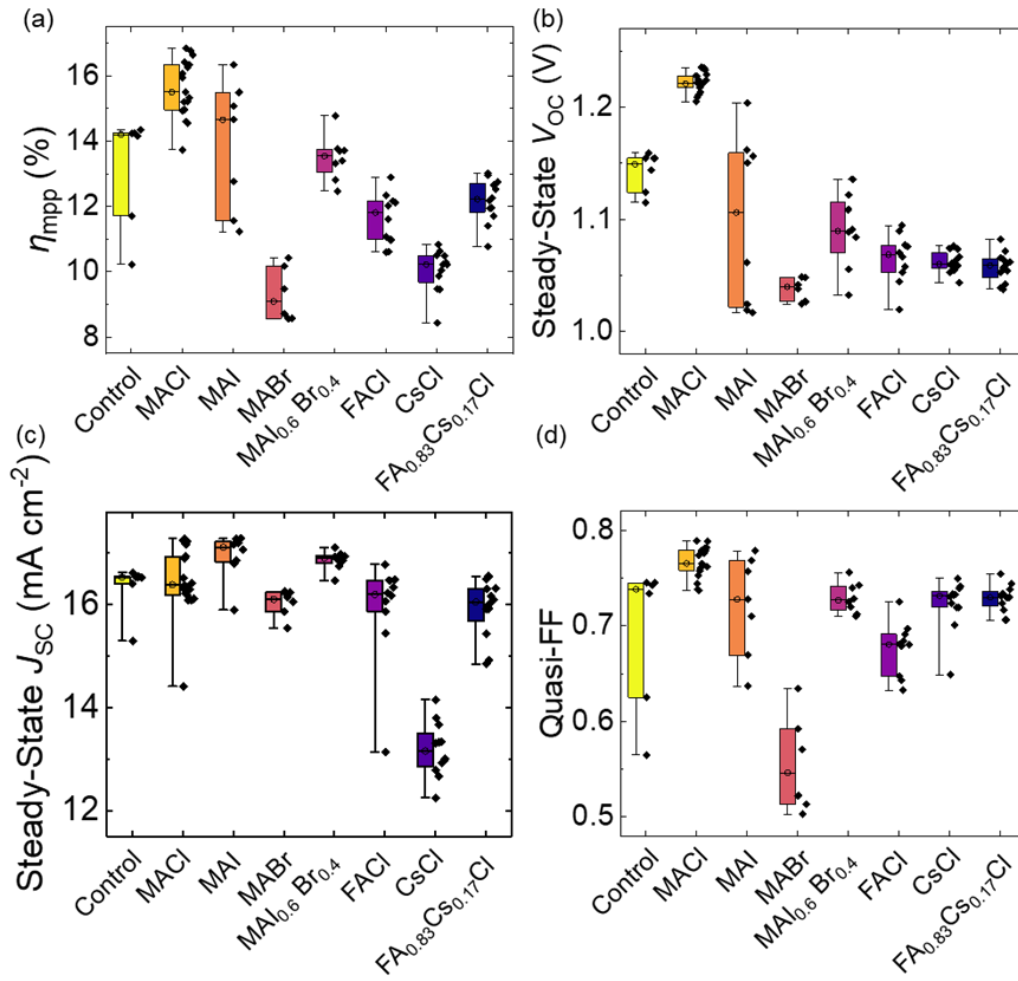


FIGURE 4.12: Statistics of (a) η_{mpp} , (b) steady-state V_{oc} , (c) steady-state J_{sc} and (d) quasi-FF values of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ devices based on Me-4PACz with no additive (control, 6 cells), or with 15 mol% addition of MACl (17 cells), %FACl (7 cells), %CsCl (6 cells), %FA_{0.83}Cs_{0.17}Cl (8 cells), %MAI (10 cells), %MABr (12 cells) or %MA(I_{0.6}Br_{0.4})₃ (12 cells). These cells were fabricated across two batches of experiments.

enough and can be effectively driven out of the final perovskite film upon annealing. With the other additives, excess ions remaining in the perovskite films can cause compositional and bandgap heterogeneity, rendering defect formation which is detrimental to device performance [163]. For the thin-film fabrication, I employ the antisolvent quenching method, where I spin-coat from a DMF:DMSO precursor solution, and drop a certain volume of anisole antisolvent on the film during spin-coating. Prior to thermal annealing, as-cast films are formed in “intermediate phases” distinct from the final

perovskite phase. I observe pronounced additive dependence on the visual appearance of the intermediate phase formed immediately following anti-solvent treatment. Notably, the different colours of the as-cast films suggest substantially different bandgaps and therefore intermediate phases. The evolution of these intermediate phases under storage in a N₂ atmosphere, and after subsequent removal to ambient, is also revealing. In Figure 4.13, I show images at different stages of this “room temperature crystallisation” process, under which conditions the conversion to a perovskite phase is slowed compared to the optimised thermal treatment (150 °C annealing in air). I observe pronounced differences in intermediate behaviour, with the control film transformation proceeding far more quickly than with 15 mol% MACl. In Figure 4.14, I show the evolution in absorbance and corresponding PL spectra of these intermediates. With 15 mol% MACl a higher energy absorbance band emerges, which I interpret as relating to a Pb coordination environment specific to an intermediate phase.

4.4 MACl-Assisted Intermediate Phase Formation

To first determine if Cl-rich perovskite phases are present in as-cast 15 mol% MACl additive perovskite films, I perform in situ XRD measurements during stepwise thermal annealing. I observe reflections from cubic (100)- and (110)-planes which are stronger and shifted to higher angles with MACl added, suggesting a reduction in the lattice parameter of this initial perovskite phase (See Figure 4.15). I interpret this as resulting from Cl- preferentially incorporating into the perovskite crystal lattice at early times, likely due to stronger Pb-Cl bonding. As films are annealed in situ, I observe these reflections shift to smaller angles, consistent with the lattice spacing of the cubic perovskite phase increasing during thermal processing. I interpret this as the gradual

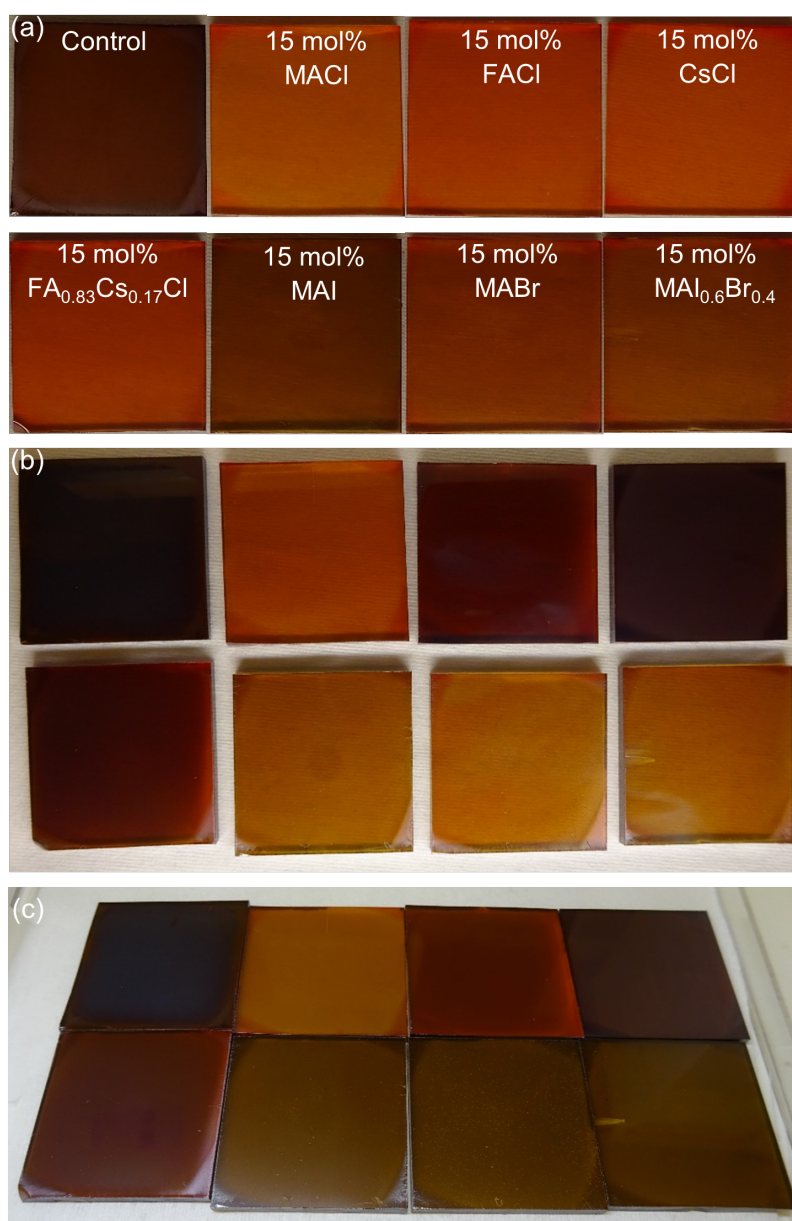


FIGURE 4.13: Photos of the intermediate phases of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ with no additive (Control) or with 15 mol% MACl, FAcI, CsCl, $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Cl}$, MAI, MABr or $\text{MA}(\text{I}_{0.6}\text{Br}_{0.4})_3$ taken (a) immediately after spin coating (b) 30 min stored under N_2 atmosphere and (c) 60 min stored under N_2 atmosphere followed by exposure to air for 5 min.

removal of chloride ions from the perovskite lattice, replaced by larger bromide and iodide ions within growing cubic perovskite domains.

To assess how these as-deposited materials evolve into the final perovskite materials during thermal curing, I performed in situ GIWAXS during a gradual thermal annealing procedure designed to retard the perovskite

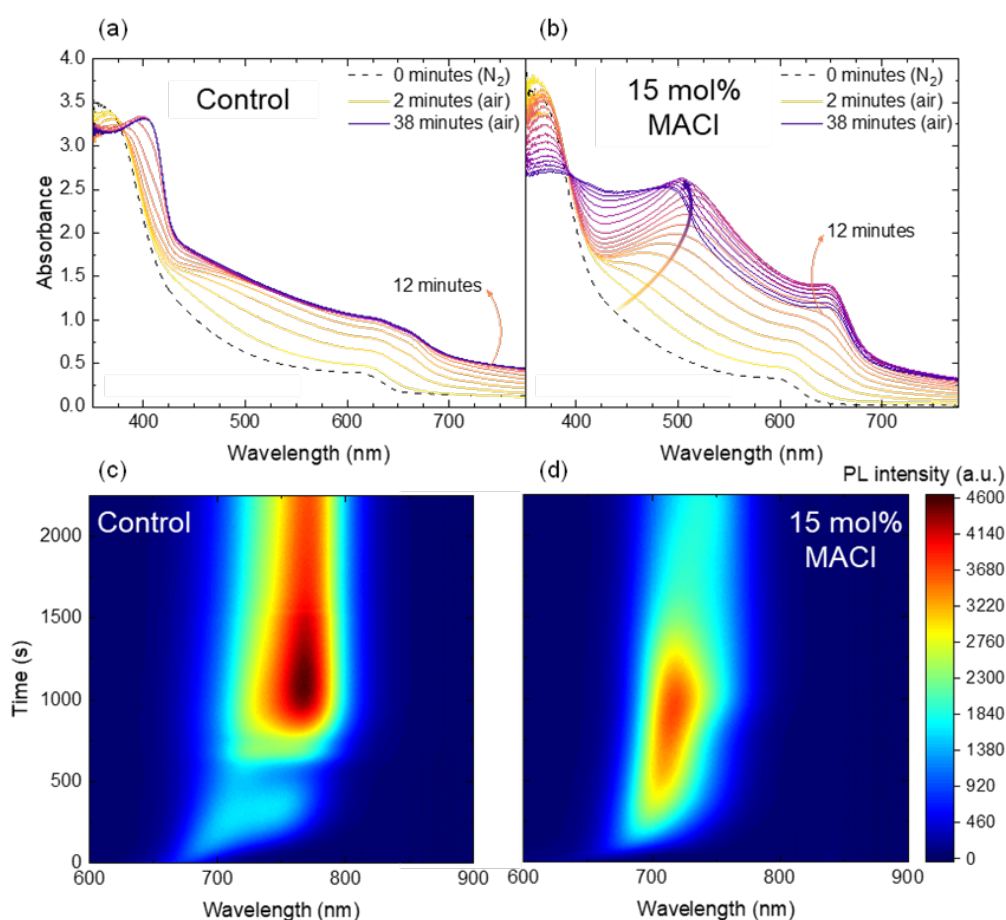


FIGURE 4.14: Evolution of the absorption and PL spectra of the antisolvent-quenched (a and c) $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ films and (b and d) $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ with 15 mol% MACl measured under ambient conditions (25 °C, RH $\sim$ 50% in air), namely ‘Control’ and ‘15 mol% MACl’.

crystallisation pathway. As I show in Figure 4.16a, 2D GIWAXS from the control film at the crystallisation onset appears as weak isotropic scattering rings, consistent with a cubic perovskite phase with no preferential orientation. In contrast, for the 15 mol% MACl film scattering in the perovskite (100) Debye-Scherrer ring is more intense and concentrated along the Q_z direction - (100) planes primarily oriented out-of-plane - with a second weaker orientation at $q = 45^\circ$, as would be expected for (110) orientation (Figure 4.16b). This demonstrates that the initial perovskite nuclei with 15 mol% MACl are highly oriented corner-sharing crystallites, rendering them ideal intermediates for the subsequent growth of cubic perovskite films. Although with 15 mol%

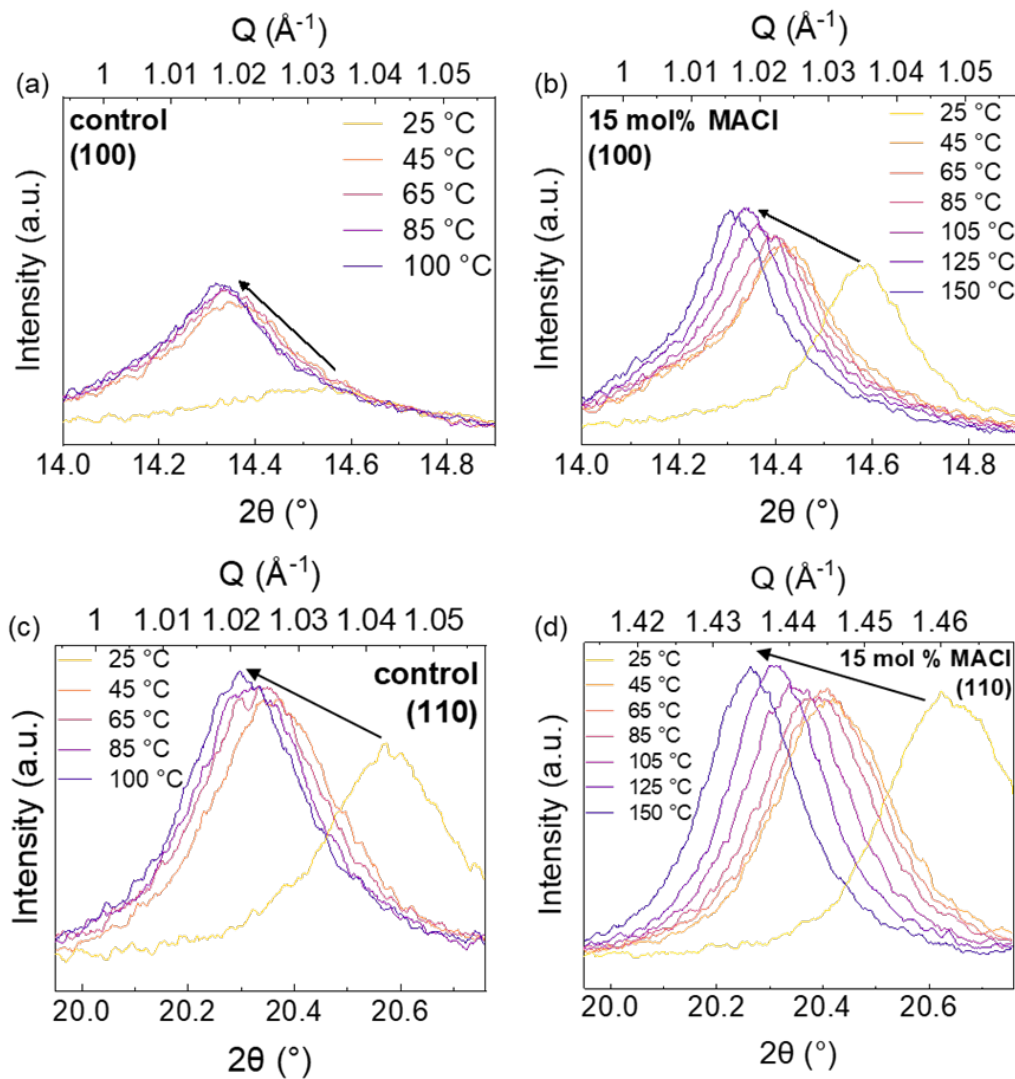


FIGURE 4.15: XRD patterns tracking the evolution of cubic perovskite (100) and (110) reflections during step-wise annealing of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ perovskite films (a - b) with or (c - d) without 15 mol% MACl additive, namely '15 mol% MACl' and 'control'. The temperature range for step-wise annealing is analogous to the device processing conditions (150 °C for MACl-processed film and 100 °C for control film).

In situ 2D XRD was performed by Philippe Holzhey.

MACl these intense crystallites appear earlier than in the control, the evolution to the final perovskite film occurs more slowly in the MACl-modified film. This suggests that MACl addition has retarded the overall crystallisation pathway. The gradual increase in the cubic perovskite lattice parameter upon thermal annealing discussed above is also observed in our GIWAXS measurements.

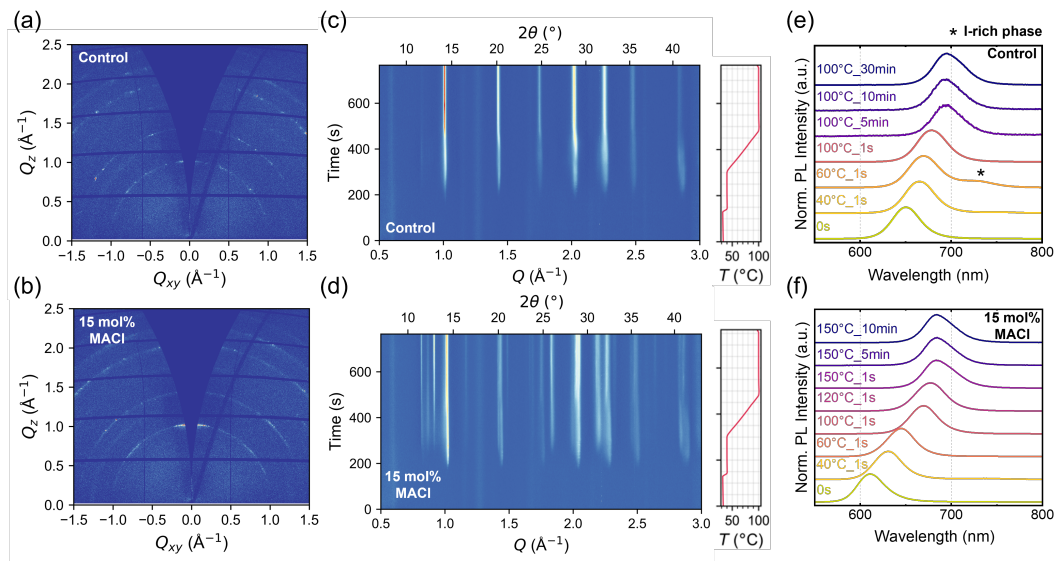


FIGURE 4.16: (a - b) 2D GIWAXS patterns collected at 250 s into the in situ thermal treatment of FA_{0.83}Cs_{0.17}Pb(I_{0.6}Br_{0.4})₃ perovskites without or with 15 mol% MACl additive, denoted as 'Control' and '15 mol% MACl'. (c - d) Time-resolved GIWAXS of FA_{0.83}Cs_{0.17}Pb(I_{0.6}Br_{0.4})₃ perovskites without or with 15 mol% MACl additives as the as-deposited materials crystallise during thermal treatment (temperature changes are shown on the right), denoted as 'Control' and '15 mol% MACl'. The perovskite materials were blade-coated in air and measured in a measurement chamber with low flow of N₂ (accelerating solvent removal analogous to antisolvent treatment). (e - f) Normalised PL spectra of the intermediate phases formed after various thermal treatments on FA_{0.83}Cs_{0.17}Pb(I_{0.6}Br_{0.4})₃ perovskites without or with 15 mol% MACl additive, denoted as 'Control' and '15 mol% MACl'. The full spectra of the region with an asterisk (I-rich phase) can be found in Figure 4.17. 2D GIWAXS and time-resolved GIWAXS were measured and analysed by Joel A. Smith and Oleksandra Shargaieva. In situ PL was measured by Zhongcheng Yuan and Xinyi Shen.

Further, I am able to observe and better understand the hexagonal polytypes that appear as intermediates in the growth of our WBG perovskites. The control film appears to crystallise in the cubic perovskite phase with limited subsequent change in cubic lattice parameter; however, a reflection at 11.7° corresponding to a 2H (δ) phase forms early in the growth process, suggesting this material is an intermediate in the crystallisation of this composition. By contrast, with 15 mol% MACl after the formation of perovskite nuclei, the remaining material crystallises into a number of polytype intermediates with substantial reflections corresponding to both 4H and 6H phases (Figure 4.16c-d). Given these phases are not observed in the final perovskite,

I deduce that these phases are formed from the excess of the super stoichiometric solution composition and act as intermediates in the growth process [159], [164].

The exact nature of this transformation is unclear. However, recent work on mixed-cation mixed-halide lead perovskites has shed light on the importance of controlling both polytype intermediate evolution, and halide homogenisation, and may be insightful. Both Qin et al., and Szostak et al. [164], [165], have demonstrated that in $\text{FA}_{0.83}\text{MA}_{0.17}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$ perovskites, formation of the 6H polytype is entirely suppressed by Cs^+ addition, while expression of the 4H phase is minimal and thus only the 2H polytype is observed. This is consistent with our findings for the MA-free $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ composition used here where only the 2H phase is observed in the as-cast antisolvent quenched films. Qin et al. and Szostak et al. argue that the absence of 4H and 6H polytypes allows for the more straightforward crystallisation of the desirable cubic phase [164], [165]. However, I note that the thermal annealing is just 100 °C in both these works. In our work, I have shown that 100 °C anneal is insufficient to give complete conversion to the perovskite phase when MACl is added in excess. In light of these findings, the role of the annealing appears to be partial removal of Cl from the eventual perovskite and the complete transformation of the 4H and 6H polytypes to the cubic perovskite.

Huang et al., [166] have also recently investigated the crystallisation of more compositionally complex perovskites, including $\text{FA}_{0.7}\text{MA}_{0.2}\text{Cs}_{0.1}\text{Pb}(\text{I}_{0.8}\text{Br}_{0.2})_3$. In their work, the authors employ in situ PL to demonstrate that bromide-rich phases crystallise initially during growth, which are gradually transformed into lower bandgap materials as iodide-bromide homogenisation takes place. I fabricated a series of control and 15 mol% MACl perovskite films and annealed them at different temperatures to

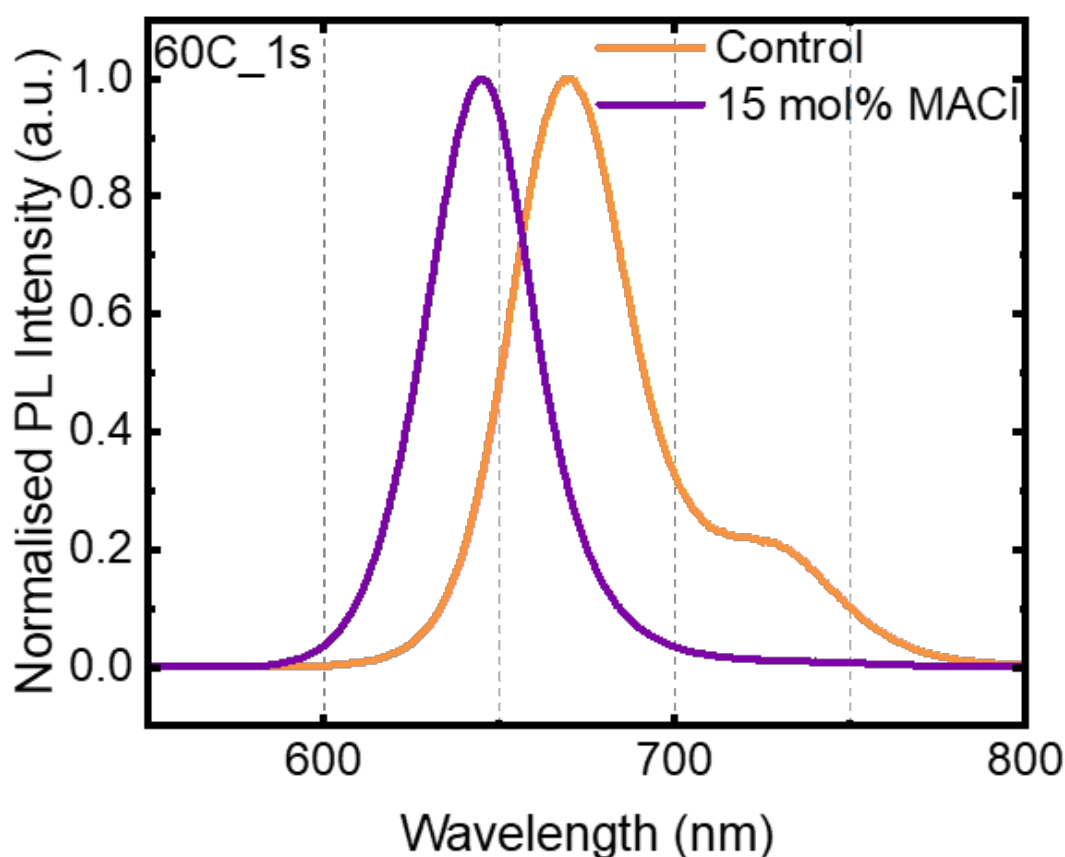


FIGURE 4.17: Normalised PL spectra of intermediates formed for $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ and 15 mol% MACl-processed $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ after 1 seconds of thermal annealing at 60 °C, denoted as ‘Control’ and ‘15 mol% MACl’. In situ PL was measured by Zhongcheng Yuan and Xinyi Shen.

replicate the intermediates presented in the stepwise annealing process used in our GIWAXS measurements. As I show in Figure 4.16e, in the absence of MACl, although the crystallisation of an initial wider-bandgap phase is observed, the rapid transformation towards the final perovskite phase occurs. Interestingly, following a 60 °C anneal, I observe the presence of a lower-energy emission peak at 740 nm (enlarged spectrum shown in Figure 4.17), which I interpret as emission from iodide-rich perovskite regions [107], [159], [167]. With higher temperature annealing, emission at an intermediate bandgap replaces both initial spectral features. The presence of the double emission peak at intermediate annealing temperatures indicates that

at least two discrete phases of iodide-rich and iodide-poor perovskite compositions exist at the early stages of crystallisation, which homogenise into a single mixed-halide phase as annealing progresses. The addition of MACl also leads to the initial formation of a higher-bandgap phase consistent with the nucleation of a chloride-rich phase. Subsequent evolution of this spectral feature to the mixed halide bandgap is more gradual, with no emission at lower energies than that of the final stable phase observed (Figure 4.16f). I thus deduce that crystallising in the presence of MACl leads to a more homogeneous inclusion of halides in the growing phase, following the initial formation of chloride-rich phases. In Figure 4.18, I present the PL images of the control films and the 15 mol% MACl additive films under photoexcitation using a 450 nm continuous-wave laser. I observe more homogeneous PL intensities across the 15 mol% MACl-processed perovskite films and devices compared to the control. Therefore, I confirm that reduced halide heterogeneity in the crystallisation stage leads to the formation of more compositionally homogenous perovskite films.

I thus conclude from our in situ GIWAXS and PL measurements that MACl addition is responsible for retarding and controlling the crystallisation of WBG perovskites. Initial formation of Cl-rich phases, shortly afterwards, a more complex polytype phase mixture induced by MACl additive, leads to a crystallisation regime in which gradual addition of I and Br into the growing cubic perovskite phase is controlled by the need to sequentially replace Cl. The polytypes identified do not appear to vary compositionally as they disappear from the initial as-deposited material, which leads us to suggest that these phases may act as a source for the I and Br that migrate into the initial cubic perovskite phase to replace Cl. Higher annealing temperatures are thus required to drive both conversion from the hexagonal intermediate

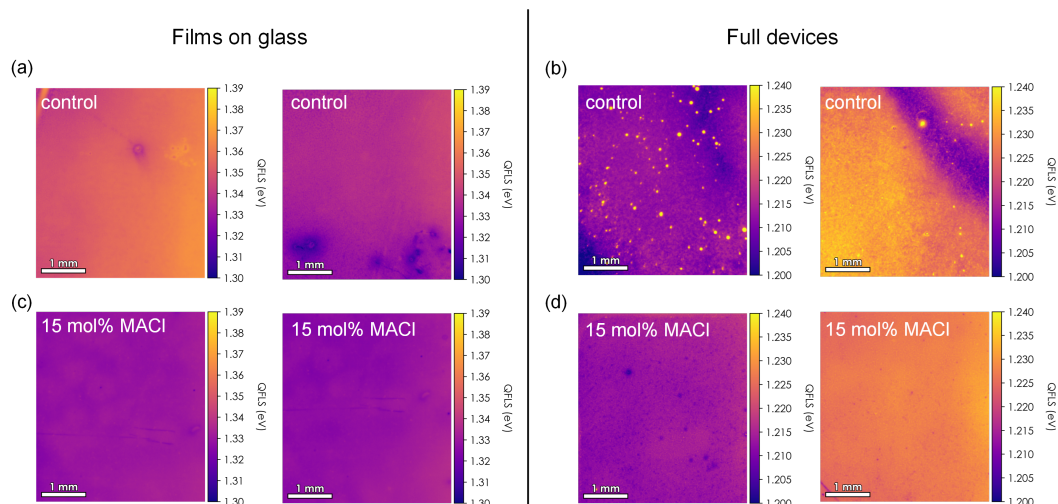


FIGURE 4.18: QFLS maps taken using an in-house-built PL measurement setup on (a) thin films on glass (b) full devices of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ perovskite compositions and (c) thin films on glass (d) full devices of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ with 15 mol% MACl additive, namely ‘control’ and ‘15 mol% MACl’. Me-4PACz and C60 were used as HTL and ETL, respectively, in the full devices. Two films and two pixels were measured for each variable; small variations in the absolute QFLS values between different samples are shown in the graph. A 450 nm laser is used for photoexcitation. PL imaging measurement and QFLS analysis was conducted by Akash Dasgupta.

phases into the cubic phase, and the removal of MA and Cl from the perovskite structure.

From our PL study above, it is apparent that iodine-rich phases are present during the crystallisation of the control films, but are not observable in the MACl-containing films. I, therefore, proceed to investigate if this has an impact on the halide segregation when the perovskite films are exposed to intense illumination. In Figure 4.19, I show steady-state PL measurements to compare the photostability of the control and the 15 mol% MACl-processed perovskite films. The rate and severity of halide segregation are dependent on the density of photo-generated charge carriers within the film [144]. Accordingly, I probed the severity of this segregation by exposing the films to continuous illumination of a 398 nm wavelength optical pump, under an

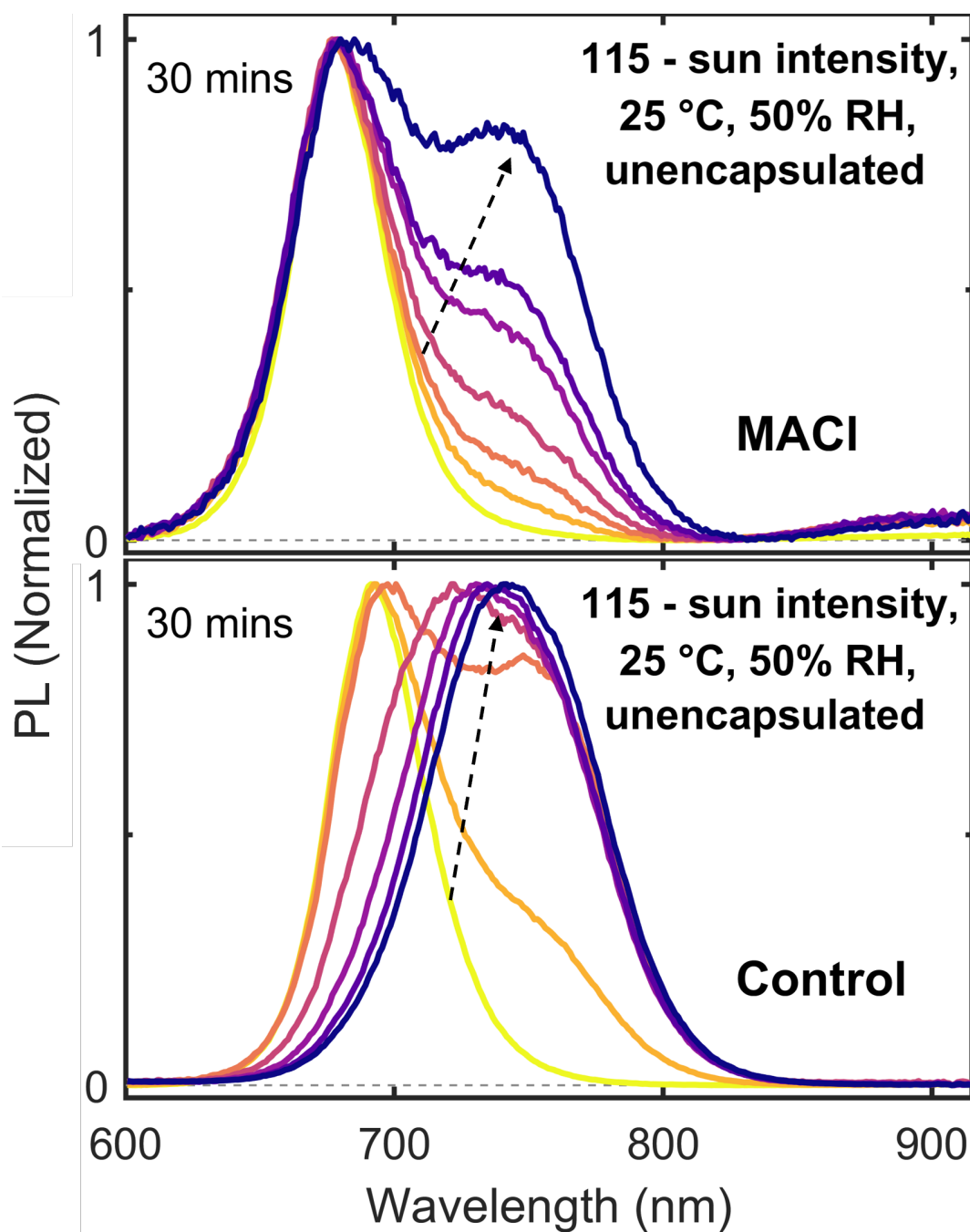


FIGURE 4.19: Normalised steady-state PL in increments of 5 minutes was collected and measured on the $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ films (on quartz) with or without 15 mol% MACl additives for 30 mins, denoted as 'MACI' or 'Control'. The films were exposed to continuous illumination equivalent to around 115 suns to probe the severity of halide segregation. Arrows indicate the evolution of PL spectra with respect to ageing time. Steady-state PL measurement was conducted by Karim A. Elmestekawy.

excitation intensity equivalent to around 115 suns, and collected the PL spectra in increments of 5 minutes. Through this qualitative measurement, I observe a rapid reduction in the PL intensity at 700 nm and concurrently an

Sample Name	Pb (at. %)	I (at. %)	Br (at. %)	Cl (at. %)	I:Br:Cl ratio (%)
Control Sample 1	3.151	6.345	3.756	0	62.8:37.2:0
Control Sample 2	3.124	6.322	3.754	0	62.7:37.3:0
MACl Sample 1	3.108	6.196	3.702	0.084	62.1:37.1:0.8
MACl Sample 2	3.097	6.229	3.691	0.083	62.3:36.9:0.8

FIGURE 4.20: The atomic percentages (at. %) of the halide and the lead atoms in the $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ perovskite films with or without 15 mol% MACl, namely 'Control' and 'MACl' determined with WDXRF measurement. Two samples were measured for each condition. All the samples were deposited on ITO substrates, and the measured atomic percentage values have been corrected with a calibrated standard (blank ITO substrate). The I: Br: Cl ratio is calculated from the at. % of each halide. WDXRF was measured by Oxford Photovoltaic Ltd..

increase in the PL intensity at 760 nm within the first 10 minutes in the control film. I interpret this as the separation of the mixed-halide phase (700 nm) into an iodide-rich (760 nm) and bromide-rich phase under illumination. The intensity of the collected PL centred around the mixed phase progressively weakens, likely originating from charge carriers funnelling into the iodine-rich phase [107]. In comparison, the 15 mol% MACl-processed perovskite film shows a much slower reduction in the PL amplitude of the mixed-phase and a slower evolution of the iodide-rich PL peak compared to the case of the control film, indicating a noticeably suppressed halide segregation. It is noteworthy that I measured the rate of halide segregation under 115-sun intensity instead of 1-sun, which is a highly accelerated stability test. Halide segregation is driven by photoexcited carrier density, which scales linearly with the

light intensity [107]. Hence, at high light intensity, the perovskite undergoes significantly more rapid ion migration. In addition, substantial heat generated under 115-sun will further promote segregation kinetically. Moreover, higher carrier density at 115-sun saturates traps and alters the dominant recombination pathway to Auger recombination compared to trap-assisted recombination at 1-sun, leading to faster degradation [168]. Hence, the segregation rate cannot be linearly extrapolated to 1-sun conditions; the halide segregation in the MACl-modified perovskites is likely to be exponentially slower than the control under less harsh conditions (1-sun) instead. I propose two possible factors contributing to the reduced halide segregation in the MACl-modified perovskite films. Firstly, the suppression of I-rich phases during the crystallisation of the MACl-modified perovskites leads to a reduction in regions of halide heterogeneity in the processed materials (See Figure 4.18), which subsequently act as nucleation centres for further halide demixing under illumination [87], [88], [110]. Secondly, I have confirmed the presence of a trace amount of chloride (around 0.8 at.% with respect to the total amount of halides) in our MACl-modified perovskites by Wavelength Dispersive X-Ray Fluorescence (WDXRF) measurement (Figure 4.20). This is also consistent with the bandgap widening effect induced by MACl as discussed in 4.3. In the control perovskites, no Cl was detected. Alloying of chloride into mixed-halide perovskite has been shown to increase the entropy of mixing due to the presence of three different halide species, and resultantly increase the activation energy of phase segregation to make the homogeneously mixed phase more favourable [169].

4.5 Improved Device Performance

The more controlled crystallisation of perovskite films with the MACl additive also translates to an enhancement in photovoltaic device performance. I

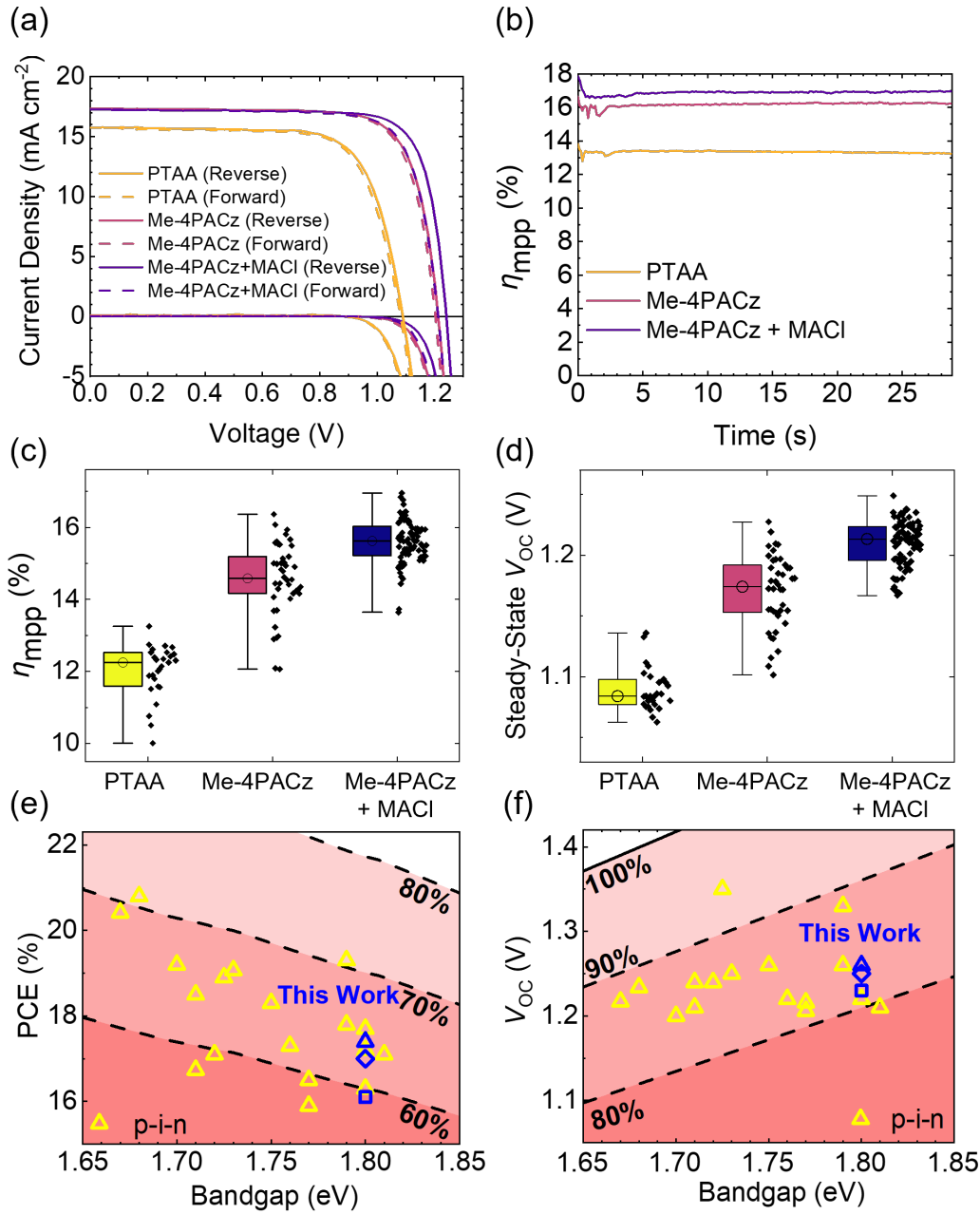


FIGURE 4.21: (a - b) JV scans and η_{mpp} of the champion cells ($FA_{0.83}Cs_{0.17}Pb(I_{0.6}Br_{0.4})_3$ on PTAA or Me-4PACz and $FA_{0.83}Cs_{0.17}Pb(I_{0.6}Br_{0.4})_3$ with 15 mol% MACl on Me-4PACz). (c - d) Statistical analysis of the η_{mpp} and steady-state V_{oc} of 27 PTAA, 42 Me-4PACz and 84 Me-4PACz + 15 mol% MACl PSCs fabricated in 8 batches of experiments. Any pixels with η_{mpp} 75% η_{mpp} of the champion device are shown in the statistical analysis (153 out of 168, = 91% yield). (e - f) Summary of high-efficiency p-i-n PSCs reported in the literature (PCE and V_{oc}) with various bandgaps (1.65 eV - 1.85 eV) compared to the detailed balance limit of single-junction solar cells (black lines). All the data points are extracted from the reverse JV scans reported in literature.[170] Blue triangle: reverse scan PCE and V_{oc} of our 0.25 cm² champion cell, blue diamond and blue square: η_{mpp} and steady-state V_{oc} of our 0.25 cm² and 1 cm² champion cell.

fabricated and characterised PSCs in a p-i-n configuration (TCO glass/PTAA or SAMs/ Al_2O_3 nanoparticles/perovskite/ C60 /BCP/Ag or Au). A 0.25 cm^2 champion cell ($\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ with 15 mol% MACl) with PV parameters $\eta_{\text{mpp}} = 17.0\%$, steady-state $V_{\text{OC}} = 1.25\text{ V}$, steady-state $J_{\text{SC}} = 17.2\text{ mA cm}^{-2}$ and nearly negligible hysteresis is achieved (Figure 4.21a). In addition, I demonstrate a large-area cell (1 cm^2) with $16.1\% \eta_{\text{mpp}}$. The detailed PV metrics of champion PSCs of MACl-processed perovskites and control can be found in Figure 4.22. Maximum power point (MPP) tracking under one-sun illumination further confirms that the MACl-processed device is stable under short-term operation (Figure 4.21b). A statistical analysis of 153 solar cells (27 of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ control on PTAA, 42 of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ on Me-4PACz, and 84 of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ with 15 mol% MACl on Me-4PACz) fabricated across 8 batches of experiments shows that MACl-processed devices have a less scattered distribution in η_{mpp} and steady-state V_{OC} compared to the control devices, implying better reproducibility (Figure 4.21c-d). The MACl-processed champion device performance is among the highest η_{mpp} , and steady-state V_{OC} reported with a 1.8 eV perovskite composition so far (Figure 4.21e-f).

To confirm that the V_{OC} improvement comes from a reduction of non-radiative losses, I perform PLQE measurement and QFLS calculations for neat perovskite films and “half-stacks”, presented in Figure 4.23. In comparison to the control films, I determined higher QFLS for the MACl-treated perovskite films on glass, increasing from 1.30 eV to 1.34 eV, respectively, indicating a reduction of non-radiative recombination in the isolated perovskite films. Moreover, I observe a concomitant increase in the PLQE and estimated QFLS, for MACl-treated perovskite films integrated into half-stacks with both the ETL and HTL. I infer this to indicate a reduction of interfacial recombination and non-radiative losses, upon MACl treatment, at both the

Devices	Scan Direction	V_{OC} (V)	J_{SC} (mA cm ⁻²)	FF	PCE (%)
PTAA	Reverse	1.07	17.3	0.74	13.8
	Forward	1.06	17.3	0.73	13.5
	Steady-State	1.07	16.5	0.75	13.3
Me-4PACz	Reverse	1.23	17.4	0.78	16.6
	Forward	1.21	17.4	0.77	16.1
	Steady-State	1.22	17.3	0.78	16.3
Me-4PACz + 15 mol% MACl	Reverse	1.25	17.2	0.80	17.4
	Forward	1.22	17.2	0.78	16.6
	Steady-State	1.25	17.2	0.78	17.0

FIGURE 4.22: Device performance of the optimised PSCs. PV metrics are extracted from the J-V scan and maximum power point tracking of the champion cells (FA_{0.83}CS_{0.17}Pb(I_{0.6}Br_{0.4})₃ on PTAA or Me-4PACz and FA_{0.83}CS_{0.17}Pb(I_{0.6}Br_{0.4})₃ + 15 mol% MACl on Me-4PACz).

ETL and HTL interfaces, consistent with our V_{OC} improvement. I do observe, however, a mismatch between the internal QFLS and external open-circuit voltage (40 meV) of our optimised devices, which is consistent with previous work using perovskites of similar bandgap and the same ETL [122], [171]. This phenomenon has been associated with energetic misalignment between 1.8 eV perovskite and C60 [122].

4.6 Long-Term Stability Test

Stability testing under enhanced environmental stressing conditions (e.g. high temperature, humidity, illumination) is important to find failures and understand the degradation of PSCs [172]. Perovskite thin films in the absence of “protective” charge extraction layers are particularly sensitive to atmospheric humidity. I deliberately expose “bare” perovskite films to ambient

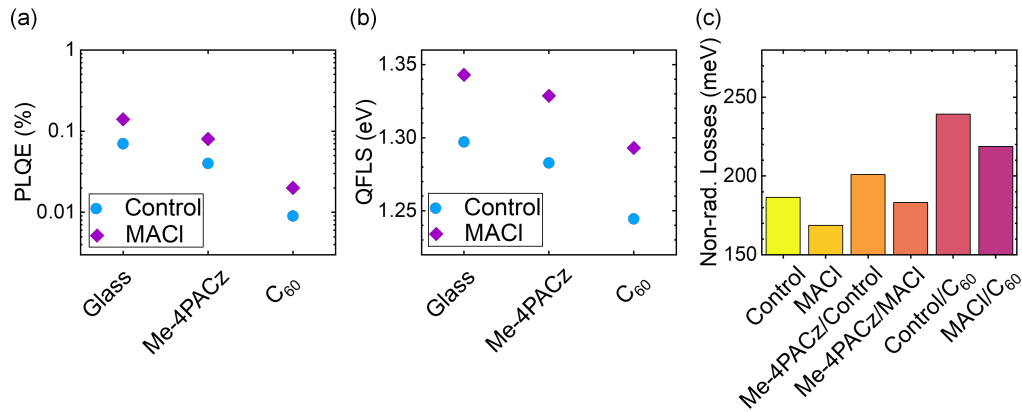


FIGURE 4.23: (a) Photoluminescence quantum efficiency (PLQE) for bare perovskite thin-films on glass substrates, a device half-stack ITO/Me-4PACz/Al₂O₃/perovskite and glass/perovskite/C60 for control and 15 mol% MACl-modified samples, namely ‘MACl’ and ‘Control’. (b) The quasi-Fermi level splitting (QFLS) of the same samples calculated from the PLQE presented in (a). (c) Non-radiative energy losses with respect to the theoretical radiative limit of perovskite absorbers of the same samples calculated from the QFLS presented in (b).

air (25 °C, 50% RH) in the dark and characterise their optical and morphological changes with SEM, XRD, UV-Vis absorption spectroscopy and optical microscopy. In Figure 4.24a, I show SEM images of the control and 15 mol% MACl-processed perovskite films ageing for 17 days. The two materials show markedly different degradation behaviour. In particular, I observe the formation of large (order of 10 μm) platelet features in our control perovskite, which are entirely absent from the perovskite with 15 mol% MACl added. EDX confirms that these regions are rich in Cs (Figure 4.25), which is also in accordance with recent results of ToF-SIMS 2D measurements of aged WBG perovskite in ambient conditions [79]. Corresponding XRD patterns of the two materials (Figure 4.26) show the evolution of the non-perovskite $\delta\text{-CsPbI}_3$ phase ($2\theta = 10.0, 10.1, 13.3, 17.9^\circ$), reported, for example, by Straus et al. [173], who links its formation to the presence of moisture. By contrast, SEM imaging of our MACl-additive perovskite shows the formation of a phase that appears concurrently with pinhole formation. Our XRD measurements correlate the appearance of this phase with 2H $\delta\text{-FAPbI}_3$ ($2\theta =$

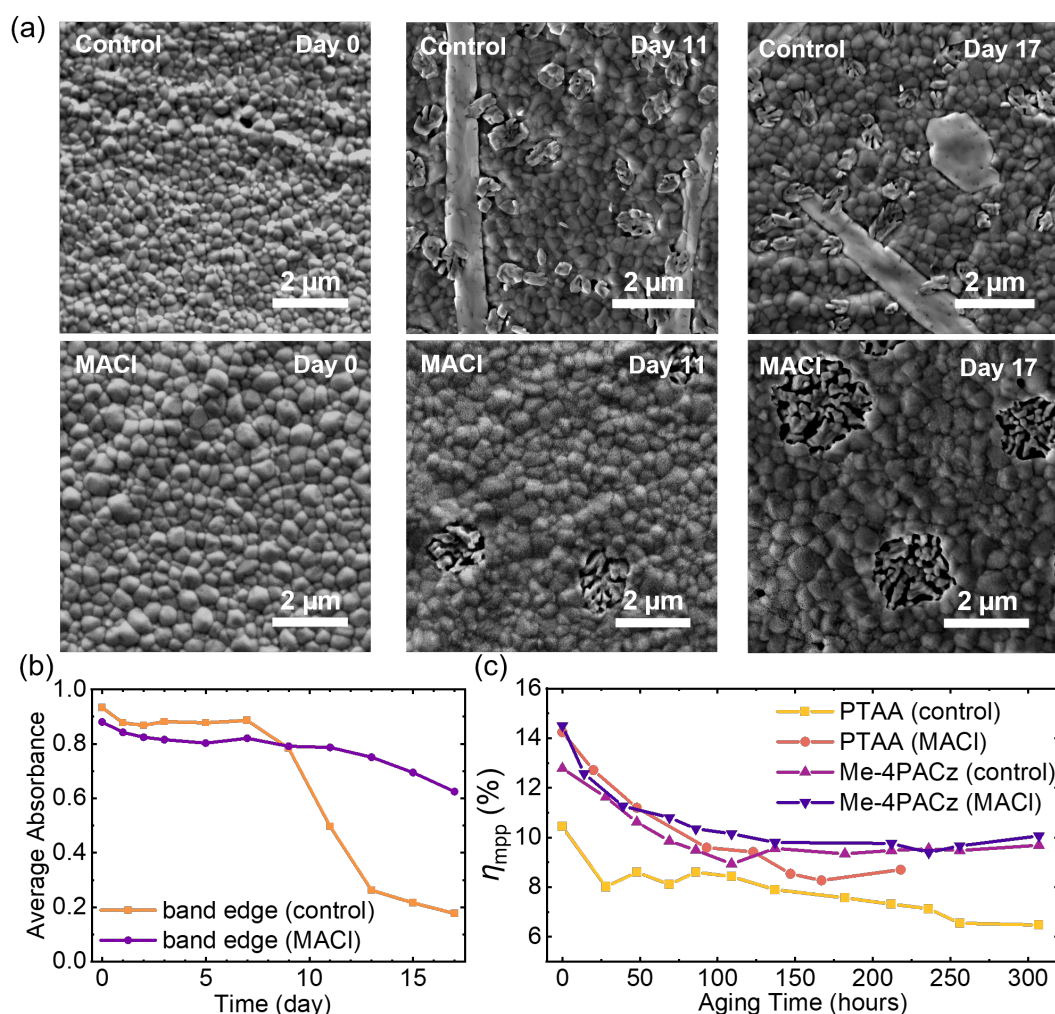


FIGURE 4.24: (a) SEM images of unencapsulated $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ perovskite films with or without 15 mol% MACl additives, denoted as ‘MACl’ or ‘Control’, measured before and after ageing at dark, ambient conditions (25 °C, 50% RH) for 17 days. (b) Evolution of the absorbance spectra of the perovskite films in (a) over 17 days. The average absorbance refers to the integrated area per nm under the absorbance spectra near the band edge (650 – 655 nm). Two samples of each variable were aged and measured. The data points shown in the graph are averaged between two samples. (c) Long-term stability measurements (η_{mpp} reported here are the median of 8-12 devices of each variable from the same batch) of PSCs based on control or 15 mol% MACl-modified perovskites with PTAA or Me-4PACz as the HTL. All the devices were encapsulated and aged under 1-sun illumination, at open-circuit condition, 65 °C, in air for over 300 hours.

11.7°) formation. A higher density of similar features appears in the control perovskite also, although these are typically smaller (0.5 μm). The XRD patterns of the aged control confirm that this is also 2H δ -FAPbI₃. Interestingly, I can also reveal the δ -CsPbI₃ phases form as transparent needle-like features

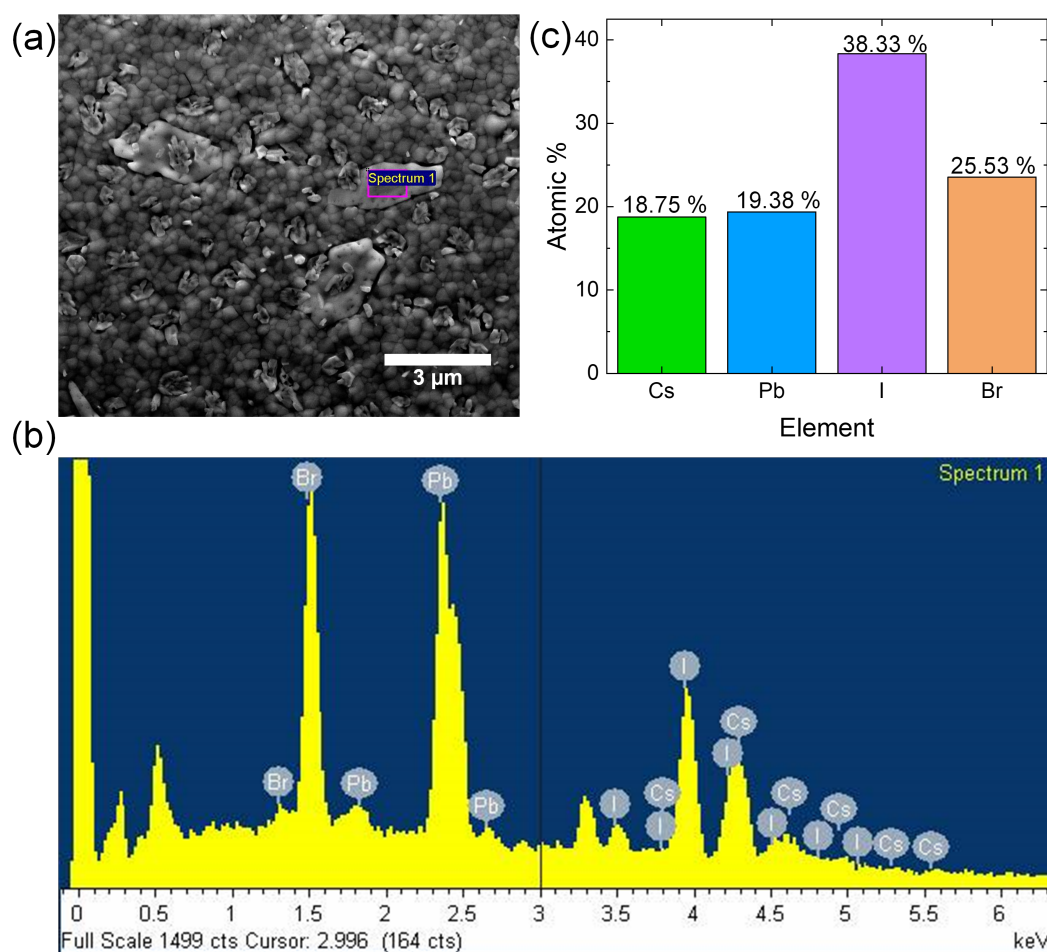


FIGURE 4.25: Summary of EDX on platelets forming in degradation of control perovskite (Figure 4.26a). (a) SEM image of the area of interest, showing region from which EDX spectrum is collected. (b) EDX spectrum, with automatic assignment of emission features applied by INCA software. (c) Chart showing atomic composition extracted from EDX spectrum (extracted using INCA software). The assignment highlights that platelet regions are Cs-rich compared to the overall perovskite composition. SEM and EDX were measured by Benjamin M. Gallant.

with an optical microscope with sizes of a few mm (Figure 4.27).

Degradation of the photoactive perovskite phase results in a reduction in absorbance at the band edge, and can thus also be studied via UV-Vis spectroscopy. In Figure 4.24b, I present the evolution of the absorbance at the band edge of the control and 15 mol% MACl additive perovskite films over 17 days. A sharp drop in the absorbance is observed at the band edge in the control films between Day 7 and 13. I interpret this as a near-total loss of the photoactive phase in the thin film. In addition, the evolution of absorbance

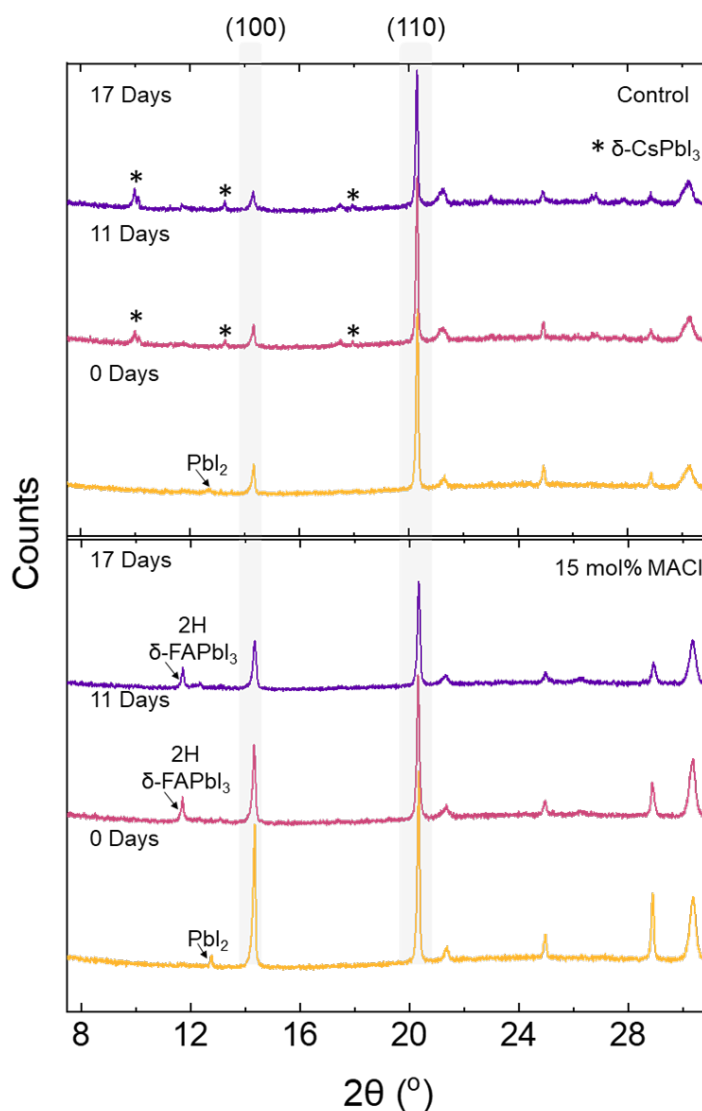


FIGURE 4.26: Evolution of the XRD patterns of unencapsulated $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ films without or with 15 mol% MACl additives (denoted as 'Control' and '15 mol% MACl'), stored at dark, ambient conditions (25 °C, 50% RH in air) for 17 days.

features in the control film at 400 nm and 530 nm, which are not observed in the MACl-additive materials, may correspond to the formation of non-perovskite phases [174], [175]. In contrast, I witness a substantially slower drop in the absorbance of the perovskite films with 15 mol% MACl additive, suggesting a significantly slower degradation of the MACl-processed perovskite composition [176]. More homogeneous perovskite films have been previously shown to have improved ambient stability. In our case, the MACl additive not only promotes the growth of homogeneous perovskite films (See

Figure 4.18), but also completely suppresses the formation of δ -CsPbI₃ phases in the presence of air and humidity, thus slowing down perovskite degradation in ambient conditions.

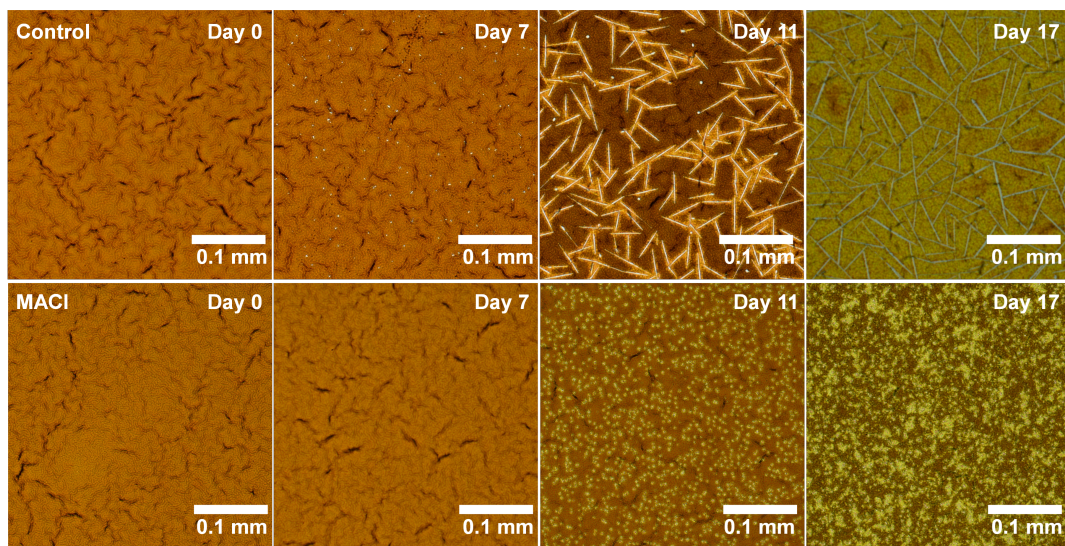


FIGURE 4.27: Photos of unencapsulated $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ films without or with 15 mol% MACl additives (denoted as ‘Control’ and ‘15 mol% MACl’) stored at dark, ambient conditions (25 °C, 50% RH in air) for 17 days. Photos shown here were taken with an optical microscope on Day 0, Day 7, Day 9, Day 11 and Day 17.

Light and heat stress is currently the most challenging ISOS condition for PSCs to survive. Poor stability under the combination of light and temperature of WBG PSCs remains as the bottleneck for tandem applicability. Hence, I proceed to investigate if the enhanced ambient stability of MACl-treated perovskite translates into more stable PV devices by ageing encapsulated devices under the ISOS L-2 procedure (65 °C, 1-sun illumination, under open-circuit condition), in air over 300 hours [177]. The positive observation is that neither the SAM hole transport layer nor the MACl treatment adversely affects the stability of our solar cells with the MACl-treated Me-4PACz cells showing the highest efficiency after 300 hours. However, the most stable cells in our study still degraded to 70% of their initial efficiency over this ageing time window, indicating that stability remains a key challenge for 1.8 eV PSCs. Under these ageing conditions, the 15 mol%

MACl additive PSCs on Me-4PACz demonstrate comparable photo and thermal stability of the η_{mpp} to the control devices (Figure 4.24c). I do observe a higher and more stable V_{OC} in the MACl-processed PSCs (Figure 4.28b). This could be attributed to the suppression of both non-radiative recombination and halide segregation in the MACl-processed perovskite films [141], [178]. Additionally, the MACl-treated cells always deliver somewhat higher PCE and V_{OC} over the entire ageing period, indicating that the enhanced properties are sustained, even during prolonged thermal ageing. Although these treated cells are not significantly more stable under these accelerated ageing conditions, I have confirmed that they are at least as stable as the less efficient control devices. Thus, I can conclude that the MACl-treated devices remain more efficient than the controls over the entire ageing period.

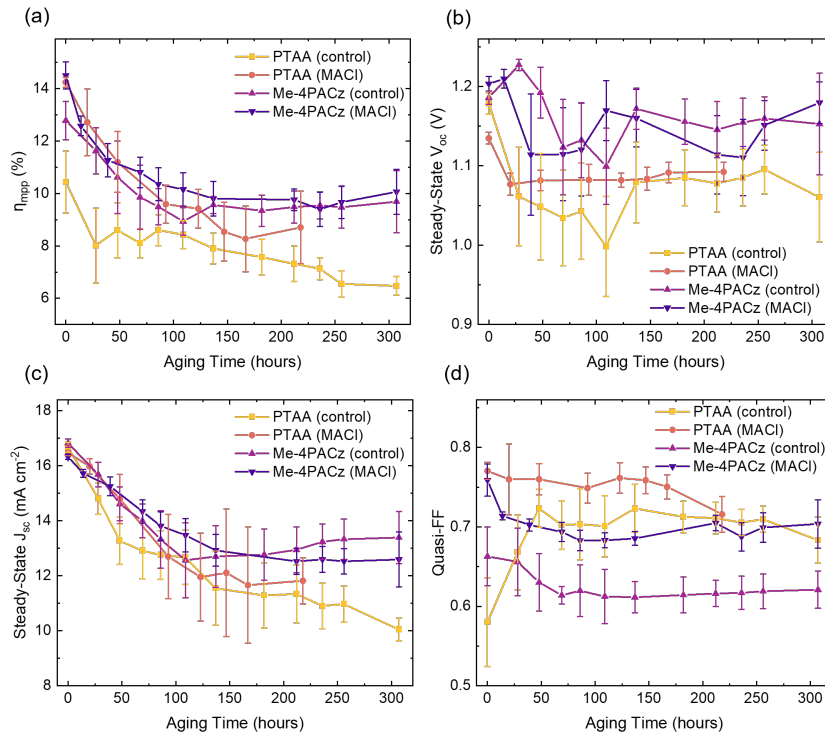


FIGURE 4.28: Long-term photo and thermal stability measurements of control or 15 mol% MACl additive PSCs based on PTAA or Me-4PACz: (a) η_{mpp} , (b) steady-state V_{OC} , (c) steady-state J_{SC} and (d) quasi-FF. All the devices were encapsulated and aged under 1-sun illumination, at open-circuit condition, 65 °C in ambient air ($\sim 40\%$ RH) over 300 hours. Medians and standard median deviations of 40 devices (10 devices for each variable) are shown in the graph.

4.7 Conclusion

In summary, I have demonstrated an effective method to simultaneously improve the efficiency and ambient stability of 1.8 eV WBG PSCs based on $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$. Combining MACl additive and a SAM HTL, PSCs with 17% η_{mpp} and 1.25 V steady-state V_{OC} (16.1% η_{mpp} for 1 cm² cell) were achieved. Additionally, I provide mechanistic insight into the role MACl plays in guiding the intermediate-controlled crystallisation pathway of these compositionally complex WBG perovskites. The formation of a chloride-rich intermediate phase directs the crystallisation of a 1.8 eV perovskite material with improved halide homogeneity and demonstrates reduced halide segregation under light. I believe these results will help significantly in the successful advancement of all-perovskite tandem technologies in the future.

Chapter 5

Intermediate Phase-Assisted Growth of Co-evaporated Wide-Bandgap Perovskites

5.1 Introduction

Thermal evaporation has been considered to be a promising technique for the large-scale production of PSCs [29]. In contrast to solution-processing which is most commonly used in lab-scale research [38], [41], [179], evaporation is more easily upscalable because of conformal coating on large-area substrates [42], and more accurate thickness control [42]. More importantly, it's particularly compatible with the fabrication of multi-junction PSCs because it allows depositing perovskite films without damaging the underlying layers of tandem devices [46]. In addition, evaporation avoids the use of any toxic solvents [45], such as DMF and DMSO. Hence, it can be more environmentally friendly and cost-effective in the long run.

However, after over one decade of development, evaporated PSCs still underperform compared to their solution-processed counterparts, especially for WBG perovskites which are most relevant to tandem applications

[73], [97], [98]. The small grain size of evaporated perovskites has been considered as one of the major limiting factors for their poor device performance [180], [181]. The presence of more grain boundaries in the perovskite films can act as nucleation centres for the formation of more defects which is detrimental to device efficiency and stability [182]. As discussed in section 2.2, an intermediate phase that spontaneously forms in solution-processed perovskites due to solvent interaction is a key stage that determines the final crystallographic properties and morphology of perovskite films [78], [79]. A diversity of additives have been designed to modify the intermediate phase and lead to perovskite films with large grain sizes and better optoelectronic properties [78], [79]. In contrast, evaporated perovskite precursors immediately form the final perovskite cubic phase upon reaching the substrates [29]. Since the crystallisation occurs at room temperature (25 °C), smaller grains tend to form [71]. The absence of an intermediate phase in the crystallisation process of evaporated perovskites posed additional difficulty in modulating their crystallographic properties and morphology [29]. Consequently, many fewer additive engineering studies have been reported for evaporated perovskites in recent years [72], thus slowing down the development of evaporated PSCs. In a recent work published by Snaith and co-workers, Dimethylammonium (DMA)-based additive has been found to effectively promote the formation of intermediate phases in solution-processed WBG perovskites and significantly enlarge the grain size to a few micrometres [79]. As a result, the modified PSCs demonstrated boosted efficiency and operational stability. This work inspired us to investigate whether DMA-based additives can be used to induce an intermediate phase in co-evaporated WBG perovskites and realise beneficial impacts on perovskite film quality.

In this work, I experimentally proved that an intermediate phase with

distinctive bandgap (E_g), surface morphology, and XRD patterns to the cubic perovskite phase, can be formed by incorporating an excess amount of dimethylammonium iodide (DMAI) additive into co-evaporated $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.68}\text{Br}_{0.27}\text{Cl}_{0.05})_3$ perovskites ($E_g = 1.7$ eV). This DMAI-assisted crystallisation route can substantially increase the grain size of the final perovskite films from around 300 - 400 nm to up to 2 μm with a pinhole-free morphology. The maximum power point tracked efficiency of the best DMAI-modified cell is 11.7%, which is comparable to the control cell. Furthermore, I identified the limitations of using DMA-containing additives in an evaporation system. Their high volatility led to poor reproducibility between different batches. The use of DMAI also caused serious contamination in the chamber, which affected the subsequent experiments. Therefore, I ceased using DMAI in our lab after completing the essential exploration. Overall, I provided a successful proof of concept in demonstrating the benefits of employing intermediate-phase engineering to control the crystallographical properties and surface morphology of co-evaporated perovskites. Moreover, I also provided some perspective for the selection and development of alternative additive materials for intermediate-phase engineering for evaporated perovskites. Materials with similar size to DMA and binding energy with Pb, but lower volatility and a more controllable evaporation pattern than DMAI can be a promising candidate to proceed with. Nevertheless, this topic is out of the scope of this work, hence, it won't be discussed in detail in this chapter.

5.2 DMAI-Induced Intermediate Phase Formation In Co-evaporated Perovskites

Dimethylammonium chloride (DMAcI) has previously been shown as an effective crystallisation mediator [79]. The addition of an excess amount of

DMACl into solution-processed WBG perovskites promoted the formation of an intermediate phase during the crystallisation and in turn helped with the growth of large crystalline grains as well as improved PSC efficiency and operational stability under heat and light stress [79]. Here, I first examined whether a DMA-containing molecule, Dimethylammonium iodide (DMAI), could also induce the formation of an intermediate phase in a co-evaporated WBG perovskite ($\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.68}\text{Br}_{0.27}\text{Cl}_{0.05})_3$) to regulate the final perovskite properties. DMAI was chosen instead of DMACl because it gave a more controllable evaporation pattern, less cross-talk between adjacent sources, as well as a more stable evaporation rate during preliminary tests.

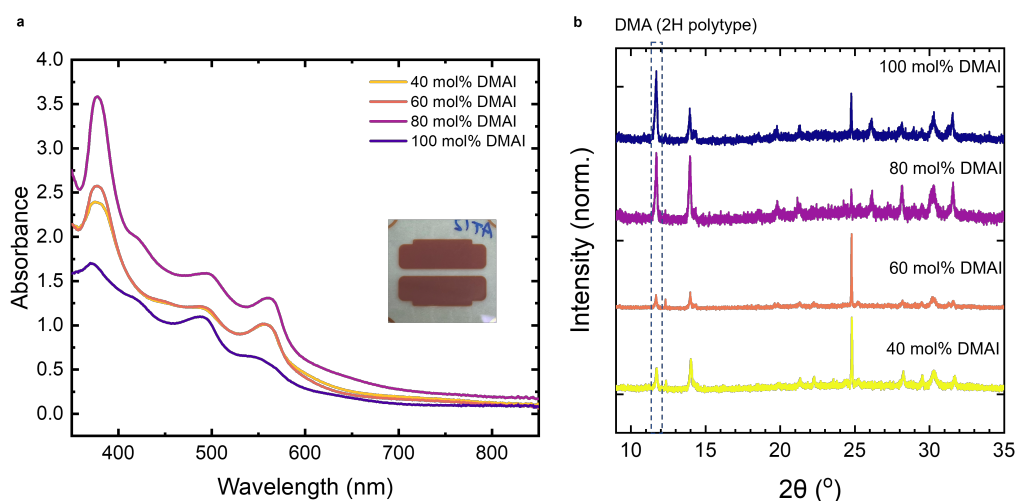


FIGURE 5.1: The (a) absorption spectra and (b) XRD patterns of the intermediate phases formed in DMA-modified co-evaporated $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.68}\text{Br}_{0.27}\text{Cl}_{0.05})_3$ perovskite materials with different excess molar ratio of DMAI additives (40 - 100 mol%). Inset: photo of the intermediate phase.

In previous work, a high concentration (≥ 35 mol%) of DMACl additive has been found to be more beneficial for the final perovskite film quality [79]. Therefore, in this work, I started with testing a range of high DMAI concentrations (excess molar ratio = 40 - 100 mol%) in co-evaporated $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.68}\text{Br}_{0.27}\text{Cl}_{0.05})_3$ perovskite materials. The spontaneously formed materials demonstrated a visually distinctive colour (orange, see inset photo

in Figure 5.1a) to a black perovskite cubic phase prior to thermal post-treatment. I then characterised the material's optical and crystallographic properties with UV-Vis absorption and XRD measurements, respectively. In the absorption spectra (Figure 5.1a), I observed no band edge at the predicted bandgap (1.7 eV) of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.68}\text{Br}_{0.27}\text{Cl}_{0.05})_3$ perovskites at any DMAI concentration, suggesting no cubic perovskite phase presenting in the DMAI-modified materials. Alternatively, additional high-energy absorption peaks were found within the low wavelength regions below 600 nm. Our XRD results correlated these peaks to the non-perovskite hexagonal polytypes, reported, for example, by Mcmeekin et al [78], [79]. (Figure 5.1b). The peak at $2\theta = 11.7^\circ$, with intensity increasing with the DMAI concentration, can be assigned as DMA-containing 2H polytypes, which is a well-known intermediate phase in DMA-modified perovskites [79]. In addition, our top-view SEM images of the DMAI-modified materials showed that the surface morphology was dominated by needle-shaped platelets, which were likely to be the DMA-containing intermediate phase rather than perovskite crystalline grains (Figure 5.2). Based on these results, I can confirm that I have successfully altered the crystallisation route of the co-evaporated $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.68}\text{Br}_{0.27}\text{Cl}_{0.05})_3$ perovskites with DMAI additive from the direct formation of cubic perovskite phases to a DMA-containing intermediate phase.

5.3 Impacts of Intermediate Phase-Assisted Crystal Growth

The formation of an intermediate phase retarded the overall crystallisation of the final perovskite film and created an additional processing window to precisely tune the conversion to the cubic perovskite phase [78], [145], [154]. Thermal annealing has been found to play a critical role in determining the

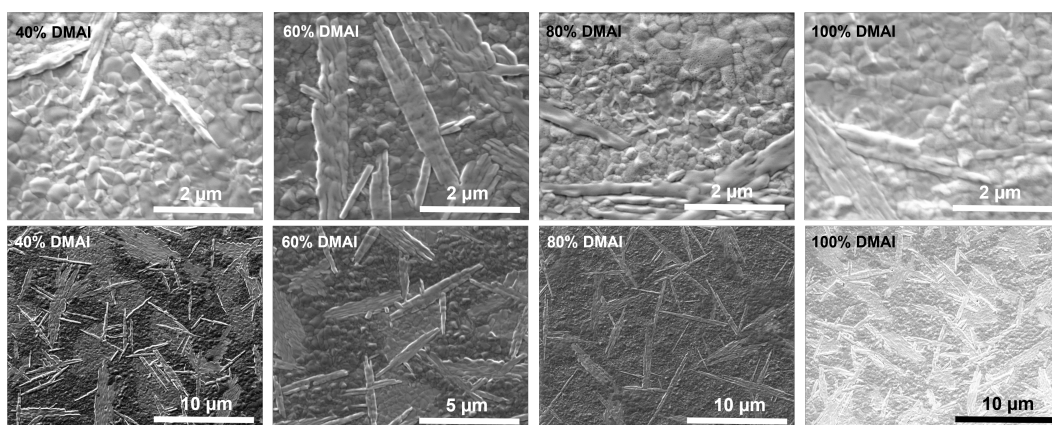


FIGURE 5.2: Top-view scanning electron microscopy (SEM) of the intermediate phases formed in DMA-modified co-evaporated $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.68}\text{Br}_{0.27}\text{Cl}_{0.05})_3$ perovskite materials with different excess molar ratio of DMAI additives (40 - 100 mol%).

perovskite crystal quality [183]. In this section, I screened a series of annealing conditions (e.g., temperature and time) and DMAI molar ratios to find the optimal processing conditions that gave rise to the best perovskite film quality.

As discussed in Chapter 4, ambient annealing is beneficial in reducing shallow defects on perovskite surfaces and minimising non-radiative recombination [78], [158]. Hence, I annealed all the perovskite films presented in this work in ambient air at a relative humidity of 40-50%. Previous literature mentioned that a high annealing temperature (180 °C) was essential to remove any excess DMA from the DMA-containing intermediate phase and promote the transformation towards the final perovskite phase [79]. Here, I chose 170 °C and a relatively short annealing time (20 min) as a starting point. I present the XRD spectra and top-view SEM images of the co-evaporated $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.68}\text{Br}_{0.27}\text{Cl}_{0.05})_3$ perovskite materials converted from DMA-containing intermediate phases with different DMAI concentrations (40 - 100 mol%) after annealing at 170 °C for 20 min in air in Figure 5.3 and 5.4, respectively. Noticeable differences between the XRD spectra of the DMA-modified perovskite material before and after annealing treatment (Figure 5.1 and 5.3)

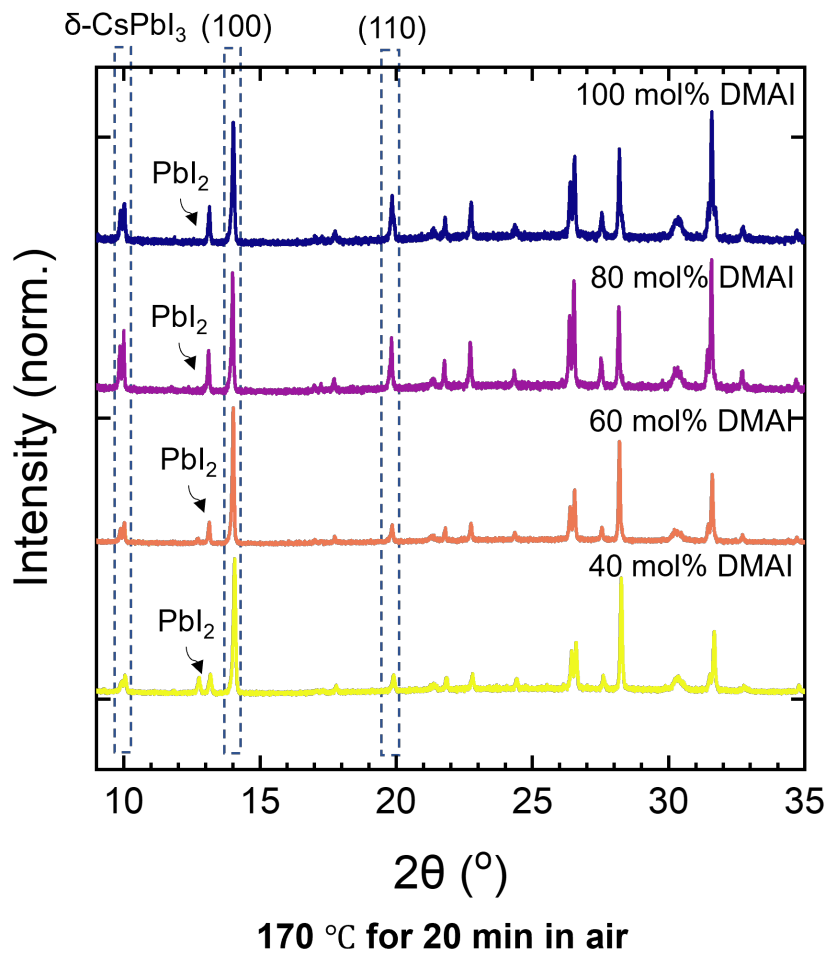


FIGURE 5.3: XRD spectra of the co-evaporated $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.68}\text{Br}_{0.27}\text{Cl}_{0.05})_3$ perovskite materials converted from DMA-containing intermediate phases with different excess molar ratio of DMAI additives (40 - 100 mol%) after annealing at 170 °C for 20 min in air.

were the disappearance of the peak at $2\theta = 11.7^\circ$ (DMA-containing polytypes) and an increase in the intensities of the peaks at $2\theta = 14.1$ and 20.1° . This could be interpreted as a complete conversion from the DMA-containing intermediate phase to the final perovskite cubic phase driven by heat. However, I also observed additional diffraction peaks corresponding to the non-perovskite δ -CsPbI₃ phase ($2\theta = 10.0, 10.1, 13.3, 17.9^\circ$) and PbI₂ phase in all DMAI concentrations [173], [184], [185], suggesting perovskite degradation. This could also be confirmed by the pinholes, cracks, and pointy features on

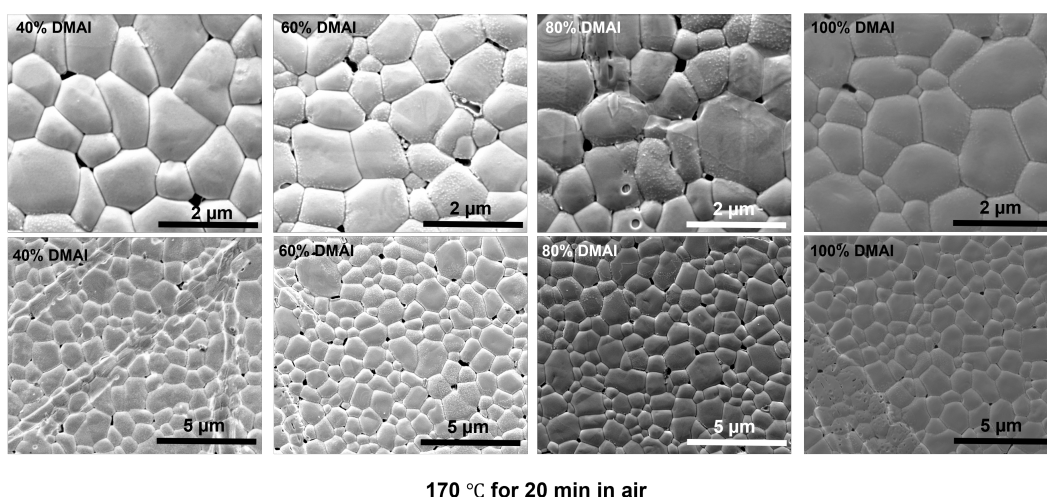


FIGURE 5.4: Top-view SEM images of the co-evaporated perovskite materials shown in Figure 5.3.

the crystal grains, and the needle-shaped features in the SEM images (Figure 5.4). To prevent the undesired degradation of perovskite materials, I examined lower annealing temperatures (160 °C and 150 °C) with an extended annealing time (40 min).

In Figure 5.5, I demonstrate and compare the XRD spectra of co-evaporated perovskites with different DMAI concentrations (40 - 100 mol%) after annealing. Among all the test conditions, 40 mol% of DMAI in conjunction with annealing at 150 °C for 40 min in the air led to the formation of the most phase-pure, highly crystalline perovskite, whilst impurity phases existed in all other conditions. Hence, I concluded that 40 mol% of DMAI molar ratio and annealing at 150 °C for 40 min in the air, were the optimal processing conditions for the best crystallographic properties of DMA-modified co-evaporated $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.68}\text{Br}_{0.27}\text{Cl}_{0.05})_3$ perovskites.

After establishing an optimal annealing condition for the DMA-modified co-evaporated $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.68}\text{Br}_{0.27}\text{Cl}_{0.05})_3$ perovskites, I then investigated the impacts of the DMAI-induced intermediate phase-assisted crystal growth on the surface morphology and optical properties of the perovskite films. As

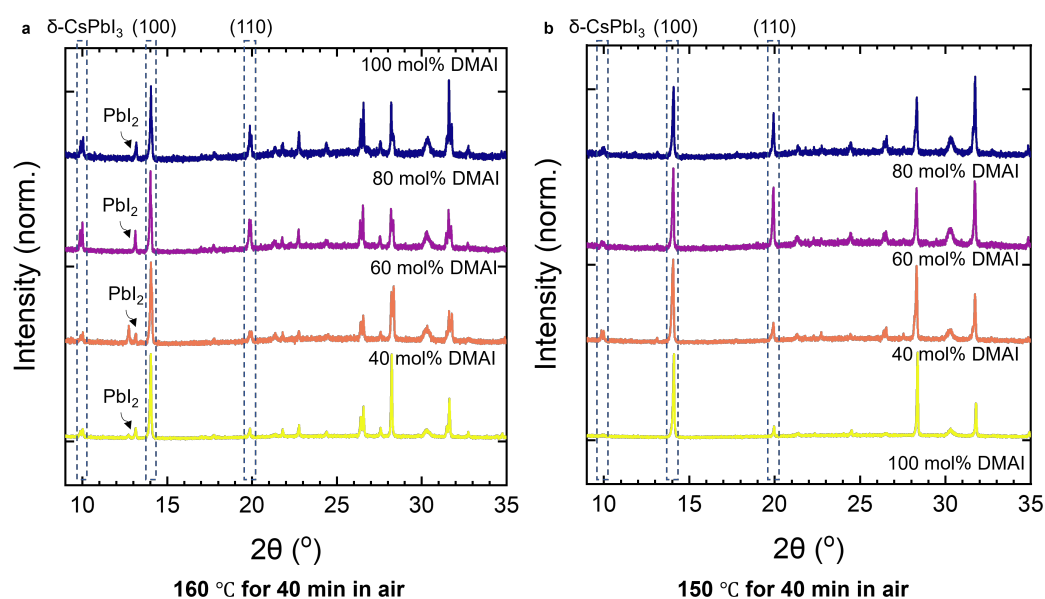


FIGURE 5.5: XRD spectra of the co-evaporated $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.68}\text{Br}_{0.27}\text{Cl}_{0.05})_3$ perovskite materials converted from DMAI-containing intermediate phases with different excess molar ratio of DMAI additives (40 - 100 mol%) after annealing at (a) 160 °C for 40 min in air and (b) 150 °C for 40 min in air.

shown in Figure 5.6, the control perovskite had a tiny grain size of 100 - 200 nm. In contrast, the DMAI-modified perovskites showed significantly improved grain sizes in the order of a few micrometres. Therefore, I postulate that there is potentially lower defect density on the perovskite surface due to fewer grain boundaries as nucleation centres [80].

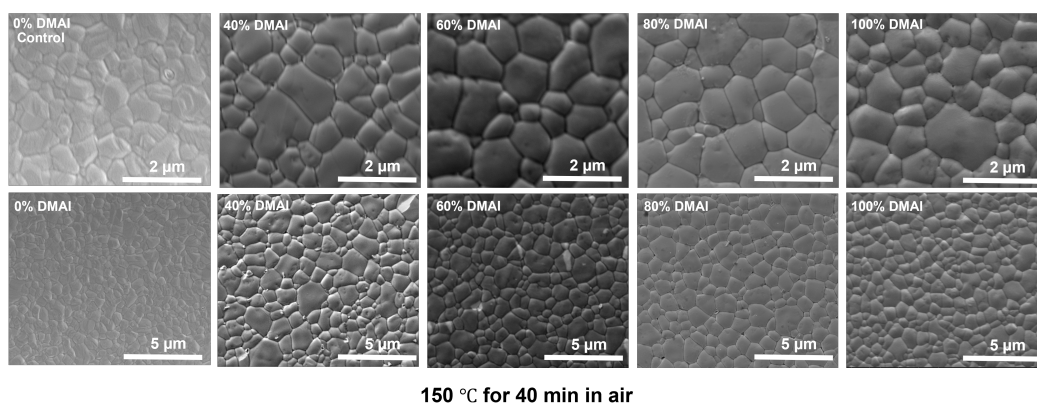


FIGURE 5.6: Top-view SEM images of the co-evaporated $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.68}\text{Br}_{0.27}\text{Cl}_{0.05})_3$ perovskite materials converted from DMAI-containing intermediate phases with different excess molar ratio of DMAI additives (40 - 100 mol%) after annealing at 150 °C for 40 min in air. The control sample with no DMAI additive was annealed at 135 °C for 30 min in air.

Moreover, I found that the absorption spectra of the final co-evaporated perovskites showed a strong dependence on the DMAI molar ratios (Figure 5.7). In general, there was a red shift in the material bandgap upon annealing at all the DMAI molar ratios. This corresponded to the conversion from the DMA-containing intermediate phase to the cubic perovskite phase. Interestingly, after annealing, the intermediate phases initially containing more DMAI experienced more bandgap narrowing. This could be attributed to the lower boiling points of DMABr and DMACl relative to DMAI [186]. The excess DMA species preferentially left the lattices in the form of DMABr and DMACl [78], [79], leading to more reduction in the material bandgap. The absence of extra peaks in the low wavelength region (below 600 nm) in the absorption spectra of the perovskite phase with 40 mol% DMAI additive further confirmed its higher phase purity compared to other molar ratios, which is consistent with the XRD results in Figure 5.5b.

As I have discussed in section 2.2.2, the final DMA-modified perovskite is likely formed via the Frank-van der Merwe growth model, as indicated by the large grain size and smooth surface morphology. More importantly, a high annealing temperature is found critical for the transformation from the intermediate phase towards the final perovskite phase, which is also a key factor that promotes the Frank-van der Merwe growth mode. In comparison, the intermediate phase formed during evaporation is likely grown via the Volmer-Weber growth mode due to the strong binding force between DMA and Pb [79], consistent with the small grain size and high surface roughness I observe in Figure 5.2. Even though it remains ambiguous to reveal the exact composition of the intermediate phase, based on the absorption spectra and XRD patterns shown in Figure 5.1, I postulate that the as-formed intermediate phase via the DMA-assisted route is likely a DMA-containing 2H polytype (non-cubic) phase with low crystallinity (low peak intensity)

and poor phase purity (various impurity phases). Given that the band edge is strongly blue-shifted with respect to the post-annealed perovskite phase, the intermediate phase is likely to be more Br/Cl-rich compared to the final perovskite composition. Upon annealing, a halide exchange process (Br/Cl replaced with I) along with volatilisation of DMA renders a slow recrystallisation process [78], [79], similar to what I presented in Chapter 4, facilitating the formation of high-quality perovskites through the Frank-van der Merwe growth mode.

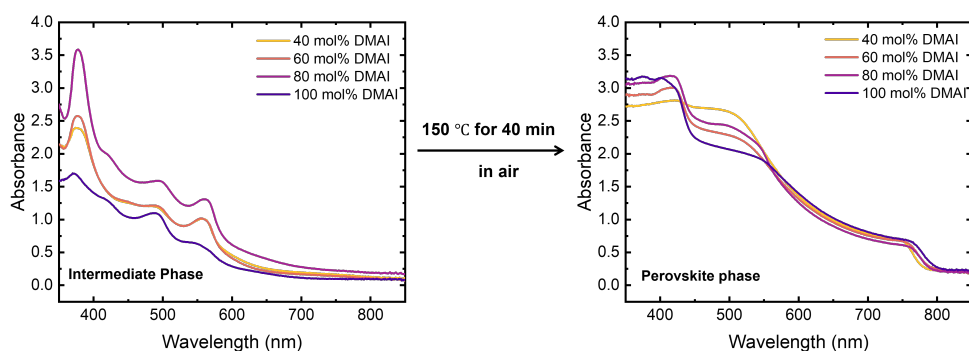


FIGURE 5.7: Evolution of the absorption spectra from the DMA-containing intermediate phases with different excess molar ratio of DMAI additives (40 - 100 mol%) to the final $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.68}\text{Br}_{0.27}\text{Cl}_{0.05})_3$ perovskite phases after annealing at 150 °C for 40 min in air.

5.4 Device Performance

To study whether the improved crystallographic properties and grain size of the DMAI-modified co-evaporated perovskites translated to better solar cell performances, I fabricated and measured PSCs in an inverted (p-i-n) configuration: TCO glass/Spiro-TTB/perovskite/C60/BCP/Au (see Figure 5.8). It's worth highlighting that thermal evaporation was used to deposit all the layers in the device stack to address their biggest advantage for industrial production compared to solution processing: no use for toxic solvents.

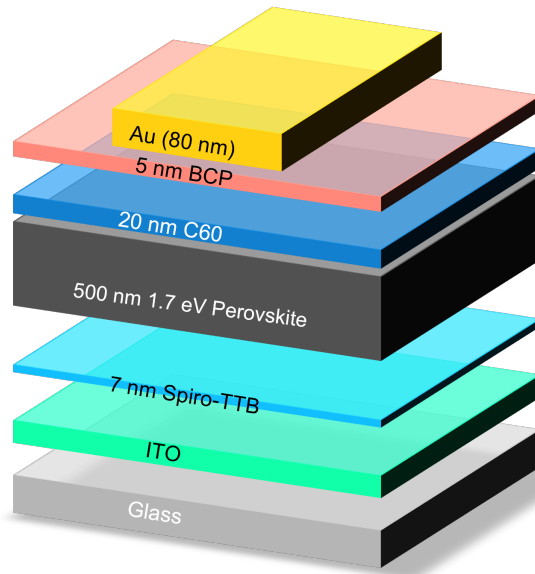
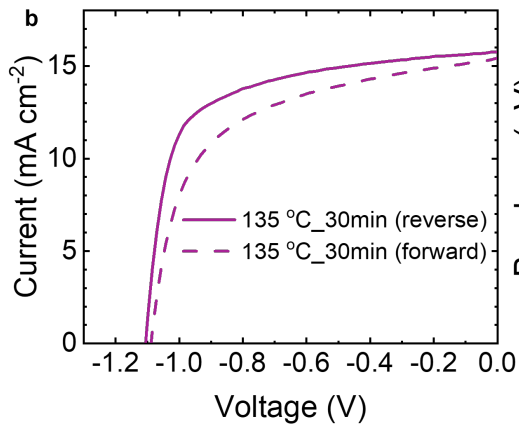


FIGURE 5.8: Device architecture of DMAI-modified fully evaporated perovskite solar cell.

a

Annealing conditions	Scan Direction	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	η_{mpp} (%)
No anneal	Steady-State	1.13	12.9	0.65	8.6
100 °C_30min	Steady-State	1.15	13.1	0.58	7.9
135 °C_30min	Steady-State	1.10	15.3	0.68	11.4
150 °C_30min	Steady-State	1.06	15.2	0.51	9.6

b



c

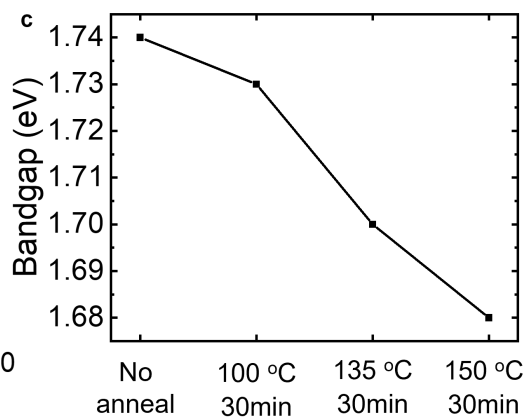


FIGURE 5.9: (a) PV metrics of the fully evaporated $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.68}\text{Br}_{0.27}\text{Cl}_{0.05})_3$ PSCs fabricated with different annealing conditions. η_{mpp} was measured under 1-sun illumination for 30 s. (b) J/V characteristics of the champion control cell based on $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.68}\text{Br}_{0.27}\text{Cl}_{0.05})_3$ perovskite annealed at 135 °C for 30 min in air. (c) PV bandgaps of the fully evaporated cells are shown in (a).

The photovoltaic metrics and bandgaps of the fully evaporated reference $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.68}\text{Br}_{0.27}\text{Cl}_{0.05})_3$ PSCs fabricated with different annealing conditions are presented in Figure 5.9. The highest maximum power point tracked efficiency ($\eta_{\text{mpp}} = 11.4\%$) was achieved by annealing the perovskite film at 135°C for 30 min in air. Under the same condition, I also obtained the target PV bandgap of 1.7 eV, which is ideal for perovskite-Si tandem cells (Figure 5.9c). The PV bandgap extracted from the inflection point of the 1st derivative of EQE became narrower when annealing the perovskites at higher temperatures, suggesting the gradual removal of chloride ions from the films. Moreover, I witnessed a drop in the steady-state V_{OC} , which nearly followed the same trend as the reduction in the PV bandgaps.

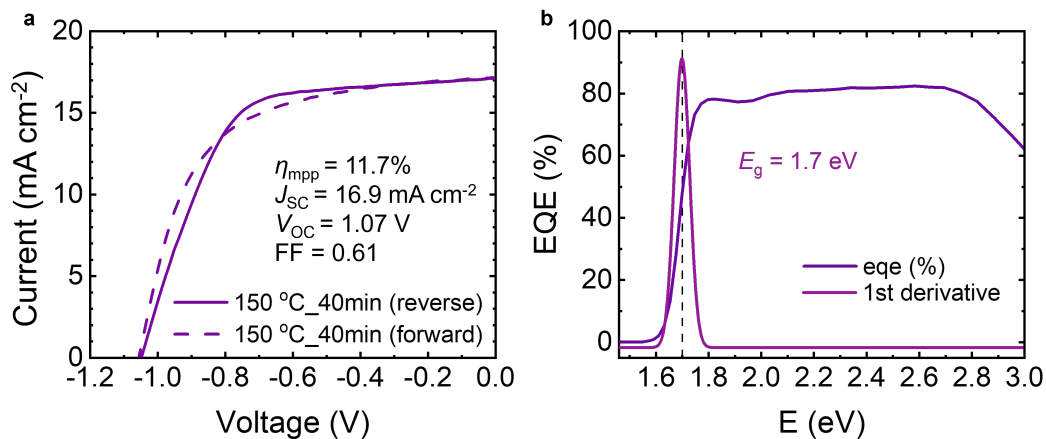


FIGURE 5.10: (a) J/V characteristics of the fully evaporated champion DMAI-modified $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.68}\text{Br}_{0.27}\text{Cl}_{0.05})_3$ PSCs. The maximum power point tracked efficiency (η_{mpp}) was measured under 1-sun illumination for 30 s. (b) PV bandgaps of the fully evaporated champion cells shown in (a).

The champion PSC based on $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.68}\text{Br}_{0.27}\text{Cl}_{0.05})_3$ with DMAI modification was achieved with 40 mol% excess of DMAI additive and annealing at 150°C for 40 min in air. A 0.25 cm^2 cell reached $\eta_{\text{mpp}} = 11.7\%$, steady-state $V_{\text{OC}} = 1.07 \text{ V}$, steady-state $J_{\text{SC}} = 16.9 \text{ mA cm}^{-2}$, and FF = 0.61, which are comparable to the control cell (Figure 5.10a). A target PV bandgap of 1.7 eV was also achieved (Figure 5.10b).

I noticed that both the control and DMAI-modified cells showed generally low PV parameters and suffered from large hysteresis. In addition, I experienced reproducibility issues and high shunting rates from batch to batch. The material stability was also quite poor, and the fresh perovskite films turned yellow after 2 days of storage under N₂. The non-optimised control cell could have hindered us from revealing the real impacts of DMAI-induced intermediate-phase engineering on the device performance of fully evaporated PSCs. However, due to the contamination issues associated with the use of DMAI (details discussed in section 5.5, I had to stop its use in the evaporation systems, and no more investigations could be carried out on this topic.

Based on the lessons learnt from this project, I have carried out a few rounds of optimisations and developed the reference cell recipe towards higher reproducibility and improved device efficiency and operational stability. Firstly, a thinner spiro-TTB layer was found to be beneficial in reducing the hysteresis and FF loss because of better charge extraction. Secondly, the FAI deposition temperature I initially used was too high. Undesired thermal-induced degradation and side reactions of FAI materials contaminated the perovskite films and chamber, leading to poor performance and stability [187]. I resolved this issue by introducing a second FAI source into my standard recipe to keep the deposition temperature of each single FAI source within the safe regime (< 190 °C). Thirdly, the FAI deposition rate tended to fluctuate vigorously during deposition which resulted in perovskite compositional heterogeneity. I later identified that this was caused by a volatile coating on the FAI raw materials. A pre-baking of the FAI material before use could get rid of the volatile materials and guarantee a more stable deposition rate and a more precise perovskite composition. Lastly, the reproducibility issue was addressed by establishing a standard operating protocol

for the perovskite evaporation chamber. Since then, I have always topped up the precursor materials to a certain mass level before each deposition and calibrated the tooling factor of each material according to the fixed loaded mass in the crucible. I also replaced the QCM sensor that monitored the film thickness after completing each deposition. With these measurements implemented, I have successfully realised high-performance fully evaporated WBG PSCs with efficiency and stability comparable to the state-of-the-art solution-processed PCs. The outcomes will be presented in detail in Chapter 6.

5.5 Limitations of DMAI and Outlooks

In this work, I identify several problems associated with the evaporation of DMAI in vacuum systems. Firstly, DMAI has high volatility, leading to similar issues experienced with MAI deposition [90]. While an ideal vapour-depositable material requires a predictable evaporation pattern (nearly a cone shape) to allow a homogeneous, conformal deposition across the whole substrate, DMAI vapour has a non-uniform distribution within the evaporation chamber, resulting in an unstable deposition rate and severe cross-talk with adjacent sources. Consequently, it's hard to get the target perovskite composition and reproduce the same composition from batch to batch. In addition, the DMA-containing species have strong adhesion to the wall of the evaporation chamber and the cryo pumps. The remaining species continuously degas over a long period. It not only contaminates the subsequent experiments that use different perovskite compositions, but also causes issues with pumping down the chamber to vacuum. To avoid causing undesired contamination to the evaporation system, I decided to stop the use of DMAI. However, I believe that intermediate phase-assisted crystallisation can be a great addition to the toolkit for better control of the crystallographic properties and

grain structure of co-evaporated perovskites. Therefore, I encourage explorations on materials with similar molecular size to DMA and similar binding energy with Pb, but lower volatility and more controllable evaporation pattern than DMAI. They may be promising alternatives to DMA-containing species, paving a pathway to improve the device performance and stability of co-evaporated PSCs to catch up with their solution-processed counterparts. However, this topic is beyond the scope of this work.

5.6 Conclusion

In this project, I demonstrated a DMAI-assisted crystallisation route, which led to the formation of intermediate phases in co-evaporated perovskites, thus significantly enlarging the grain sizes of the final perovskite materials. This strategy offered a novel technique to manipulate the crystallographic properties and surface morphology of co-evaporated perovskite materials towards better film quality and improved device performance. However, the introduction of vapour-phase DMAI into the evaporation chamber also caused long-lasting contaminations, deteriorating the reproducibility and compositional homogeneity. DMA-containing species could accumulate in the evaporation chamber and contaminate the following experiments. Degassing of the remaining DMA materials continuously increased the chamber pressure and caused problems with pumping down the evaporation chamber to vacuum. Additionally, the cross-talk of DMA with other adjacent sources made the final perovskite composition hard to control. Therefore, in addition to highlighting the beneficial impacts and great potential of employing intermediate phase-assisted crystallisation into co-evaporated perovskites, I also pointed out the impracticality of using DMA-containing materials in an evaporation system due to their high volatility and severe contamination of

the evaporation chamber. Finally, I call for further investigations on alternative additives with more ideal physical and chemical properties than DMA-containing materials. They may shed light on closing the performance and stability gaps between the evaporated and solution-processed PSCs.

Chapter 6

Facet Engineering Enables Stable Wide-Bandgap Perovskites Via Seed-Free Co-evaporation

6.1 Abstract

Vacuum thermal evaporation is an industrial standard for scalable, solvent-free manufacturing, enabling uniform films on complex substrates. Yet, evaporated PSCs lag solution-based counterparts in efficiency and stability, owing to limited crystal-growth control, requiring improved approaches. Here, I report a seed-free co-evaporation fabrication route for depositing high-quality methylammonium-free, mixed-cation, mixed-halide 1.67-eV WBG perovskites. By introducing an additional PbCl_2 co-evaporation source and optimising the annealing conditions, I promote the formation of WBG perovskites with a pronounced (100) face-up orientation whilst delivering the first certified fully evaporated cells delivering efficiencies up to 19.3% (certified at 18.3% on 0.25 cm^2) and 18.5% on 1 cm^2 . These cells retain their initial performance over 10,000 h of storage and maintain 80% of their peak efficiency after 1,080 h under the ISOS-L-2 protocol using simulated sunlight. I further show that our

co-evaporated perovskite-Si tandem devices achieve excellent field-lifetime stability, maintaining $\sim 80\%$ of their initial performance over eight months of continuous operation.

6.2 Introduction

Organic-inorganic lead halide perovskites have redefined the limits of solution-processed PVs, achieving certified PCEs of 27.0% in single-junction cells and 34.6% in perovskite-Si tandems [18], [39]. Their low-temperature processability [188] and bandgap tunability [33] position them as ideal candidates for next-generation applications, from lightweight flexible modules [36], [37] to ultrahigh-efficiency tandem architectures [38]–[41]. Yet, the dominant solution-based fabrication methods that are responsible for most record-breaking devices, face fundamental scalability bottlenecks, including solvent toxicity [43], batch-to-batch variability [189], and incompatibility with textured substrates critical for tandem light trapping [190].

Vacuum thermal evaporation (VTE), a solvent-free, industry-proven deposition technique widely used in organic light-emitting diode displays and inorganic thin-film solar manufacturing [22], [191], offers a compelling pathway to overcome these limitations. Its inherent compatibility with large-area, conformal coatings on arbitrary geometries makes it uniquely suited for perovskite-Si tandem cells [47]. Unlike the solution-processed counterparts that are typically formed of a mixture of needed precursors [79], [192], [193], the VTE co-deposition of perovskite layers heavily relies on the fine-control of each thermal source [83]. Two hurdles that pose a significant challenge to forming homogeneous perovskite layers are the deposition of low boiling point materials, such as methylammonium (MA) or formamidinium (FA) iodides [90], and the control of stoichiometry for needed bandgaps in

targeted PV applications [91]. Therefore, translating this potential into high-performance evaporated “baseline” perovskite PV devices will be crucial for establishing industrially compatible VTE manufacturing paradigms and requires tremendous efforts on crystallisation control [194], halide segregation mitigation [195], and grain orientation engineering to render high operational stability for a perovskite absorber [41], [79].

Here, I demonstrate a multi-source co-evaporation strategy that decouples stoichiometric precision from crystallisation kinetics, enabling phase-stable, methylammonium-free WBG perovskites of a 1.67-eV bandgap with dominant (100) face-up-oriented facets. By independently tuning five thermal sources, I achieve certified PCEs of 19.3% (18.3% certified, 0.25 cm²) and 18.5% (1 cm²) for fully evaporated WBG cells. These cells retained 100% initial efficiency after 10,000 hours of storage. Under the highly stringent ISOS-L-2 protocol (85°C, full-spectrum simulated sunlight illumination, open circuit), our devices maintain 80% PCE after 1,080 h, rivalling state-of-the-art solution-processed counterparts [196]–[199]. Critically, I integrate these advances into perovskite-Si tandem cells that achieve exceptional field-lifetime stability, retaining ~80% of initial performance after 8 months of continuous operation, representing a milestone toward industrial adoption of perovskite-based tandem photovoltaics.

6.3 Facet engineering of seed-free co-evaporated mixed-cation mixed-anion perovskites

Compared to dual-source deposited MAPbI₃ or FAPbI₃, there are only a handful of reports on evaporated WBG perovskites [74], [96]–[98], [200]. One effective approach is to employ “seeded” layers to guide the crystal growth and improve perovskite film quality during VTE. In particular, depositing a thin

layer of CsCl facilitates improved crystallisation kinetics, reduces unwanted polymorphs, and enhances the final grain orientation [96]. This seeded layer acts as a template, promoting the formation of desired crystal orientations or phases in the subsequently deposited perovskite layer. Our early approach attempted to replicate the use of seed layers in our co-evaporation process to form MA-free, mixed-cation, mixed-halide ~ 1.67 -eV WBG perovskites suitable for perovskite-Si tandems [96]. Figure 6.1 shows the schematic of our co-evaporation system with multiple VTE sources available for precursors. I first deposited 10-nm seed layers of CsCl, PbCl₂, and CsPbCl₃, separately for examining how they affect the growth of a 500-nm WBG perovskite of FA_{0.83}Cs_{0.17}Pb(I_{0.80}Br_{0.2})₃, which was subsequently deposited, after seeded layers, by adjusting the deposition rate of each precursor, i.e., FAI, CsI, PbI₂, and PbBr₂, based on their molecular weight and density (see Methods). For seed-free co-evaporation, 5 VTE sources were used for co-evaporating FAI,

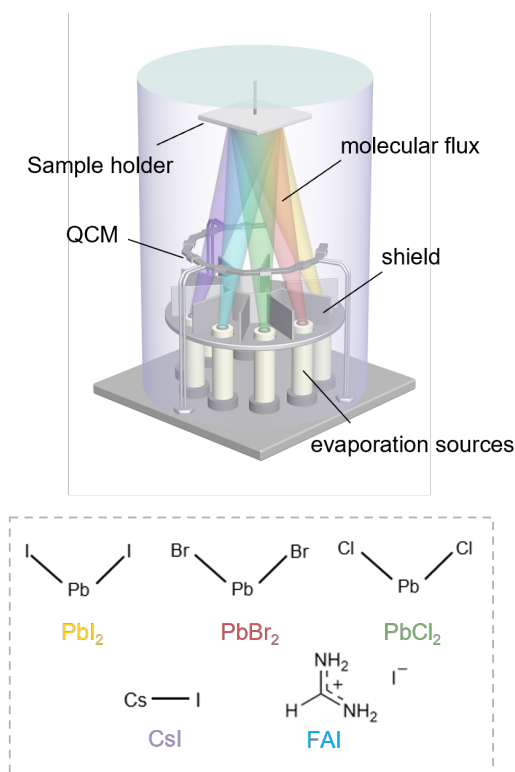


FIGURE 6.1: Schematic of a co-evaporation system with multiple VTE sources available for separate precursors.

CsI, PbI₂, PbBr₂, and PbCl₂ to form a FACs-based triple halide perovskite of FA_{0.83}Cs_{0.17}Pb(I_{0.75}Br_{0.2}Cl_{0.05})₃, following the same deposition protocols as how I grew a 500-nm WBG perovskite on various seeded layers.

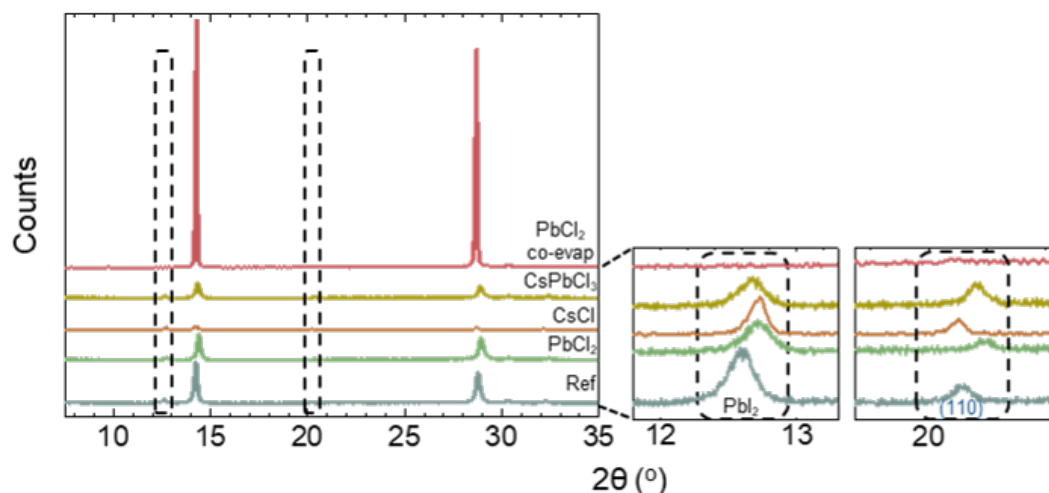


FIGURE 6.2: XRD patterns of 500-nm of co-evaporated perovskite films of FA_{0.83}Cs_{0.17}Pb(I_{0.80}Br_{0.20})₃ (Ref), with 10 nm seed layers of CsCl, PbCl₂, and CsPbCl₃ separately, to compare with a seed-free FA_{0.83}Cs_{0.17}Pb(I_{0.75}Br_{0.20}Cl_{0.05})₃ co-evaporated perovskite. Certain diffraction angles are enlarged to show the PbI₂ and (110) impurity phases.

Johnston and co-workers demonstrated that the partial substitution of 20 mol% PbI₂ for PbCl₂ in co-evaporated FA_{0.83}Cs_{0.17}PbI₃ PSCs effectively passivated defects and improved optoelectronic properties.[72] However, the concurrently formed undesirable CsPbCl₃ impurity phase at high PbCl₂ ratio (> 20%) is detrimental to material stability [72], [78]. Perovskites with high Br ratios have exhibited a stronger ability to incorporate Cl contents [78], [118]. Hence, I introduced only 5 mol% of PbCl₂ into our seed-free co-evaporation, and optimised the deposition rate of each precursor and the post-annealing conditions to realise WBG perovskites with high crystallinity, phase purity and desirable facet orientation. The corresponding XRD patterns are shown in Figure 6.2. I observe a preferential orientation along the (100) planes (2θ = 14.2-14.4°) in all the co-evaporated perovskite films which is likely due to the slow crystallisation rate at low temperature in the evaporation chamber [79],

[81]. A subtle shift of the (100) peak to higher reflection angles upon introducing Cl-containing seed layers or co-evaporated sources indicates a reduction in the lattice parameter due to Cl incorporation.[78] Furthermore, I identify the presence of PbI_2 impurity phases ($2\theta = 12.6\text{-}12.8^\circ$) only in the reference and seeded-layer-assisted perovskite materials (Figure 6.2). PbI_2 is photo-unstable and usually associates with non-stoichiometric perovskite composition which can cause device stability issues [184], [185]. Various impurity phases are also observed in a recent work studying seeded-layer-assisted co-evaporated WBG perovskites [96]. Typically for seeded layer approaches, a non-stoichiometric perovskite composition (e.g. $(\text{FA}_{0.94}\text{Cs}_{0.20}\text{Pb}(\text{I}_{0.94}\text{Br}_{0.11}))_3$) is a prerequisite to form a final composition close to a targeted bandgap due to the fact that excess metal/organic cations and halides introduced by the seed layer could migrate into the final material and influence the bandgaps [96]. However, the bandgap of the perovskite deposited onto a seed layer cannot be straightforwardly controlled in an “in-situ” fashion, hence potentially introducing inhomogeneity in the final perovskite composition. Similarly, WBG perovskites prepared via molten alloy dual source co-evaporation or hybrid deposition need extra effort to achieve a certain material bandgap [74], [94]. By contrast, our seed-free co-evaporation with PbCl_2 leads to the formation of phase-pure, bandgap-tuneable perovskites. A fine tuning of the material bandgaps from ~ 1.65 to 1.72 eV, which is a series of ideal bandgaps for perovskite-Si tandems, with a step size of ~ 0.01 eV, is demonstrated in Figure 6.3.

In addition, the WBG perovskites grown by seed-free co-evaporation with PbCl_2 shows highly oriented, uniaxial domains along the (100) planes with the complete disappearance of the (110) peak ($2\theta = 20.2\text{-}20.4^\circ$) which is observed in other deposition protocols (Figure 6.2). Lastly, the full width at half maximum (FWHM) of the (100) peak is narrowed by a factor of two

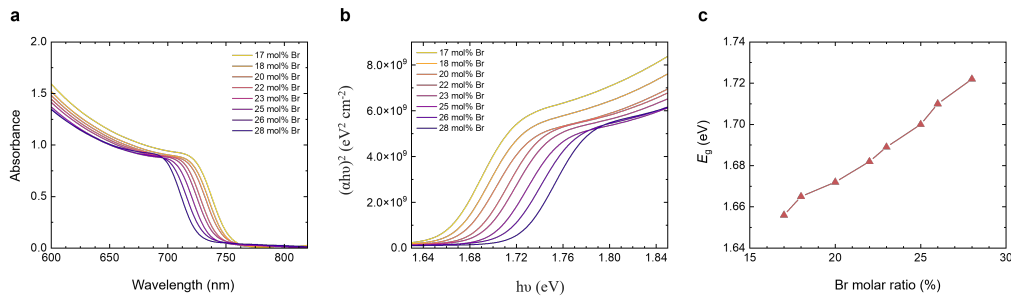


FIGURE 6.3: (a) UV-Vis absorbance spectra and the corresponding (b) Tauc analysis of seed-free co-evaporated perovskites with compositions of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.95-x}\text{Br}_x\text{Cl}_{0.05})_3$, with a range of Br molar ratio (x) with $17 \leq x \leq 28$ mol%. (c) Optical bandgaps (E_g) of the corresponding perovskites with various Br molar ratios shown in (a).

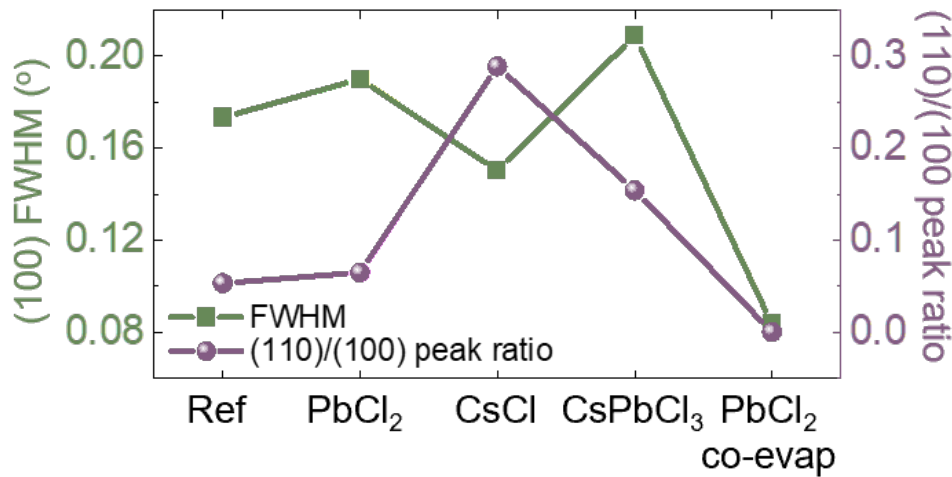


FIGURE 6.4: Full width at half-maximum (FWHM) (green square, green line, left axis) and (110)/(100) peak ratios (purple sphere, purple line, right axis) of the corresponding 500-nm co-evaporated perovskite films shown in Figure 6.2.

compared to other deposition protocols, indicative of improved crystallinity (Figure 6.4).

To link the crystallographic properties and the device performance of co-evaporated WBG PSCs, I fabricated fully-evaporated devices in positive-intrinsic-negative (p-i-n) configuration with the architecture shown in Figure 6.5a. While other devices suffer from substantial hysteresis and s-kinked

behaviour, the seed-free co-evaporation with PbCl_2 delivers the highest device efficiency (Figure 6.5b). Therefore, it was selected for further optimisation and investigation. Hereafter, the perovskite composition is always $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.75}\text{Br}_{0.2}\text{Cl}_{0.05})_3$ unless I specify otherwise.

Thermal annealing is a crucial post-treatment for growing high-quality perovskite films with high crystallinity [183]. I adopted an ambient annealing procedure (135 °C in air, relative humidity 40-50%) which has been shown beneficial for solution-processed WBG perovskites due to a humid-air activated passivation effect and screened different annealing times (0-30 mins) for the optimised co-evaporated WBG perovskites [78], [158]. I present the corresponding XRD patterns in Figure 6.6a. Before annealing, the perovskite material readily adopts a uniaxial (100) orientation. Upon thermal treatment, I observe no change in the orientation preference and a continuous increase of 29 times of magnitude ($\times 29$) in the number of counts and a reduction in

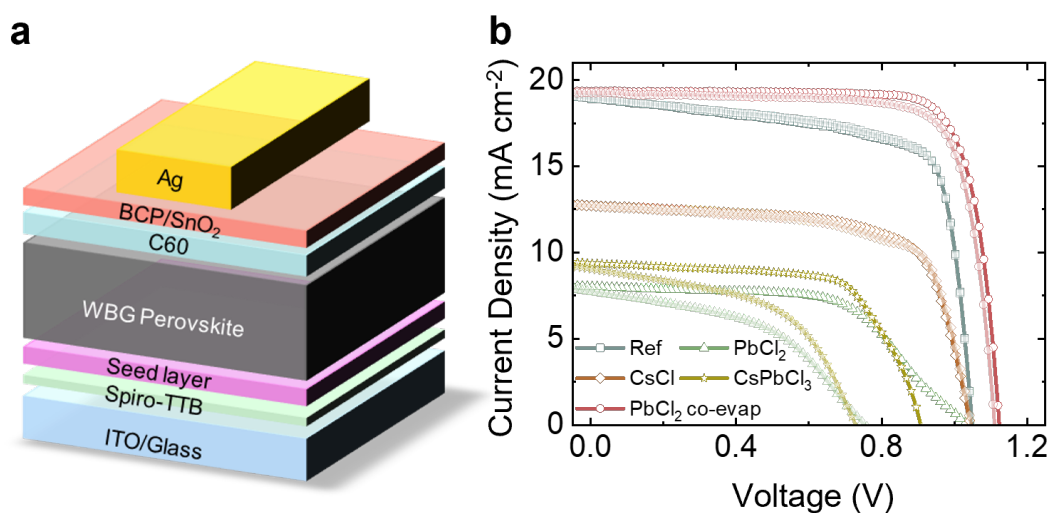


FIGURE 6.5: (a) Schematic of device architecture for a fully-evaporated WBG PSCs. The absorber layers are the corresponding 500-nm co-evaporated perovskite films shown in Figure 6.2. (b) *JV* characteristics of fully-evaporated WBG PSCs using the device architecture shown in (a). The absorber layers are the corresponding 500-nm co-evaporated perovskite films shown in Figure 6.2.

the FWHM by a factor of 2 for films annealed for 30 min, suggesting improved crystal quality. Surprisingly, following the XRD measurements, I immediately observed pinhole formation and decolouration of the perovskite films with short annealing times (< 10 min), indicative of material degradation (Figure 6.6b). The poor ambient stability is likely associated with low perovskite crystallinity because the evaporated perovskites with longer annealing times show larger grain sizes and better surface morphology in the SEM images as well as improved ambient stability (Figure 6.6b) [201].

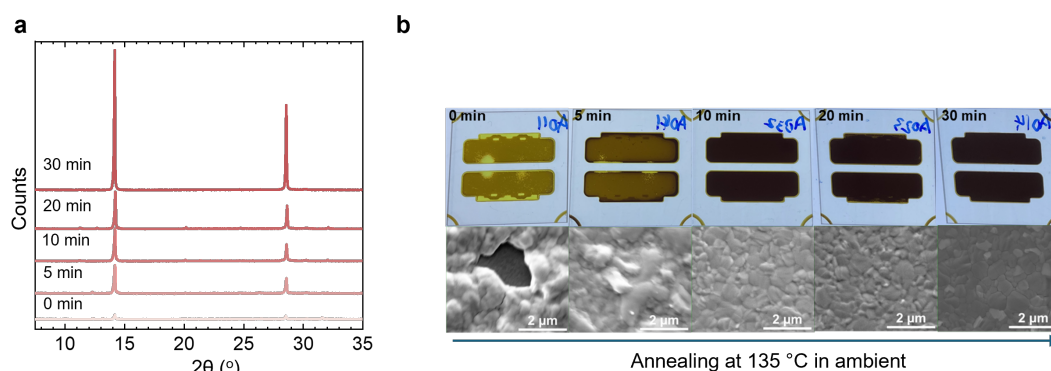


FIGURE 6.6: (a) XRD patterns of 500-nm of seed-free, co-evaporated $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.75}\text{Br}_{0.20}\text{Cl}_{0.05})_3$ perovskite films which were annealed at 135 °C in air (relative humidity in lab 40-50%), for 0 – 30 min. (b) Photos and top-view SEM images of the corresponding films shown in (a), taken immediately after the XRD measurements.

To assess how the crystallographic properties of co-evaporated WBG perovskites evolve during annealing, I performed in situ GIWAXS measurements on freshly prepared as-deposited evaporated perovskite materials. The temperature of the heating stage was slowly ramped to 135 °C in air (relative humidity 40-50%), which is analogous to the annealing conditions for device fabrication, while tracking the real-time evolution of the GIWAXS patterns upon annealing. In the evaporated perovskites, I identify (100) scattering rings with intensity significantly enhanced after annealing (Figure 6.7), leading to the formation of highly oriented, highly crystalline perovskite materials. The final perovskites adopted a face-up orientation where the

(100) planes lay along the out-of-plane direction perpendicular to the substrate (Figure 6.8 and 6.9c). I hypothesise that the face-up orientation already formed in the pre-annealed evaporated perovskites, which then acted as an ideal template for the subsequent growth of highly oriented, phase-pure, high-quality WBG perovskites.

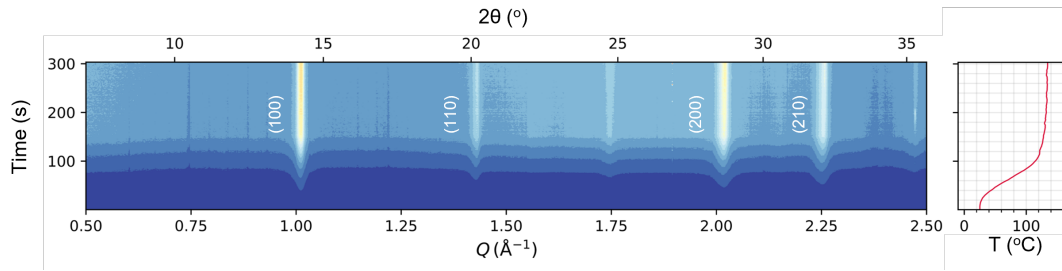


FIGURE 6.7: Time resolved GIWAXS pattern for the in situ annealing of an as-deposited co-evaporated perovskite material at 135 °C in air (relative humidity in lab 40-50%), which resembled the device fabrication condition. The in situ GIWAXS measurements were performed by Fengning Yang.

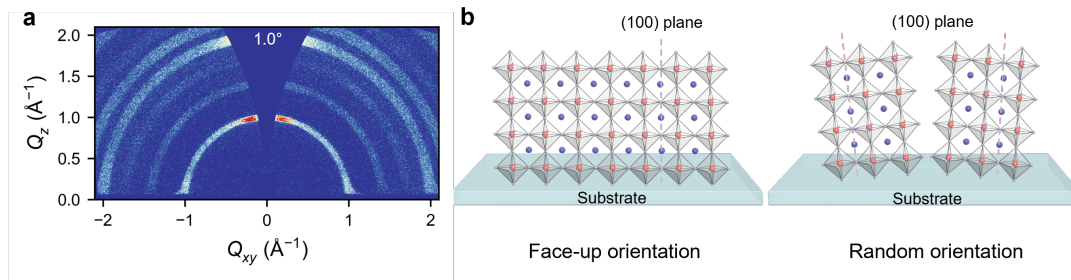


FIGURE 6.8: (a) Ex situ 2D GIWAXS intensity mapping from an incident angle of 1.0° for a post-annealed co-evaporated perovskite film of 500-nm. The ex-situ GIWAXS measurements were performed by Fengning Yang. (b) A schematic illustration comparison between the face-up and random orientations with respect to the ITO substrate.

On the other hand, I also investigated the crystallisation process of a solution-processed perovskite of the same composition. The pre-annealed perovskite adopted a more omnidirectional, random orientation with poor crystallinity which did not improve by thermal treatment (Figure 6.9 and

6.8b). Various intermediate phase engineering has been developed to promote the formation of (100) facets along the out-of-plane direction (face-up orientation) in WBG perovskites to suppress non-radiative recombination and improve material stability [41], [79]. Our optimised seed-free co-evaporation provides a new route for facet engineering to realise highly ordered, face-up-oriented WBG perovskites.

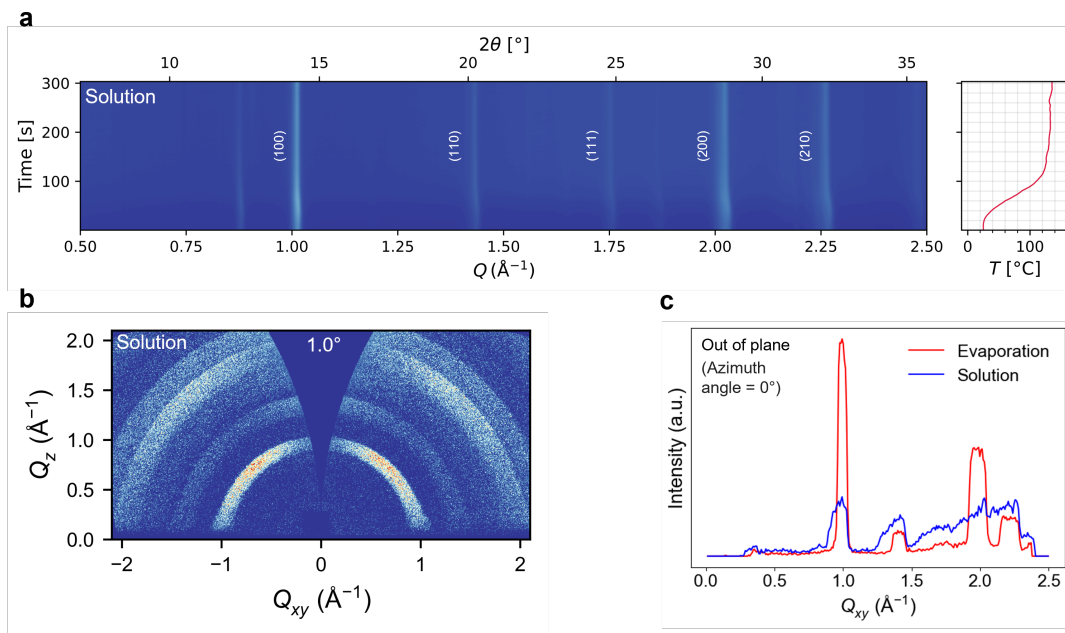


FIGURE 6.9: (a) Time resolved GIWAXS pattern for the in situ annealing of an as-deposited solution-processed perovskite material at 135 °C in air (relative humidity in lab 40-50%), which resembled the device fabrication condition. (b) Ex-situ 2D GIWAXS intensity mapping from an incident angle of 1.0° for a post-annealed solution-processed perovskite film of 500 nm. (c) Line cuts along the out-of-plane direction (Azimuthal angle = 0°) of the ex-situ 2D GIWAXS intensity mappings shown in (b) and Figure 6.8a. The in situ and ex-situ GIWAXS measurements were performed by Fengning Yang.

The perovskite film morphology is also governed by the facet orientation as shown in the top-view and cross-sectional SEM images (Figure 6.10 and 6.11). The face-up orientation of the evaporated perovskites substantially reduces the surface roughness compared to the solution-processed perovskites (Figure 6.10). This feature allows the growth of smooth and compact top layers (e.g. charge transport layers and electrodes) (Figure 6.11), which

may benefit the device performance and long-term stability by offering better protection for the underneath layers [127], [202]. Furthermore, the evaporated perovskites demonstrate more continuous aggregated grain domains in the vertical direction with much fewer cracks, indicating fewer aggregated grain boundaries present within the bulk absorber material for defect formation (Figure 6.11) [80].

Based on the uniaxial crystal orientation, large columnar grains and smooth surface morphology, our seed-free co-evaporation with PbCl_2 seems to promote the perovskite thin film growth via the Frank-van der Merwe growth model. In comparison, the perovskite films deposited on seed layers demonstrate less orientation preference and poorer phase purity, indicating Volmer-Weber or Stranski-Krastanov growth modes [83]. Although it is impractical to characterise the impacts of PbCl_2 on modulating the crystallisation within the evaporation chamber, a possible role of PbCl_2 is to enhance the bonding between the Spiro-TTB substrate and the perovskite precursor molecules, thus altering the preferential growth model to the Frank-van der Merwe mode. A previous work demonstrated that a PbCl_2 seed layer allowed the transformation into denser and pinhole-free MAPbBr_3 films upon dripping of MABr solution on TiO_2 substrates compared with PbI_2 and PbBr_2 seed layers [203]. This implies potentially better adhesion of PbCl_2 with the HTL. In addition, the smaller ionic radius of Cl^- vs I^-/Br^- facilitates deeper penetration into organic species such as Spiro-TTB [203]. Hence, a stronger electrostatic interaction also promotes layer-by-layer growth of my seed-free evaporated perovskites. Moreover, despite of I did not intentionally deposit a seed layer in my seed-free route, an ultra-thin layer of PbCl_2 that initially formed on the substrate due to its stronger binding ability during the early stage of evaporation may spontaneously act as a template/seed

layer to guide the subsequent growth of face-up oriented, highly pure, homogeneous perovskite films via the Frank-van der Merwe mode. The poor quality of perovskite films grown on 10 nm of PbI_2 seed layer might be attributed to non-optimal seed layer thickness or annealing conditions.

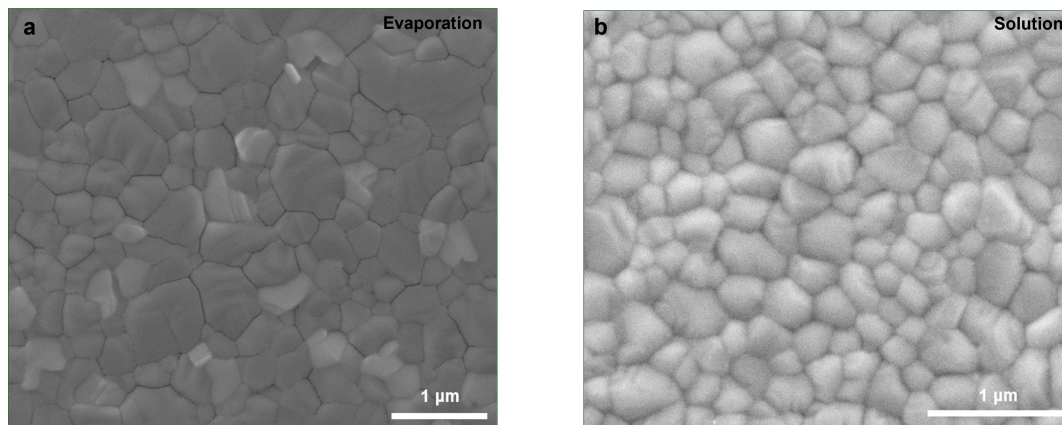


FIGURE 6.10: Top-view SEM images of the evaporated (a) and solution-processed (b) perovskite thin films.

6.4 Ageing of co-evaporated WBG perovskites

Given that the evaporated perovskite film is more oriented and highly crystalline in contrast to solution-processed WBG perovskites, I proceeded to study whether this had a positive impact on the intrinsic perovskite material stability when they were exposed to extreme ageing conditions. Perovskite thin films in the absence of “protective” charge-extraction layers and encapsulations are particularly sensitive to light, heat, and atmospheric humidity [78], [204], [205]. I deliberately aged “bare” perovskite films under the ISOS-L-2 procedure (ISOS: International Summit on Organic Photovoltaic Stability, 85 °C, 0.78-sun, full spectrum illumination, under open-circuit (OC) condition) [172], in air (relative humidity in lab = 50~60%) and tracked the evolution of their morphological and optical properties with optical microscope, XRD, and UV–Vis absorption spectroscopy. A thin layer (< 10 nm) of PMMA was deposited on the films to protect them from dust and scratches.

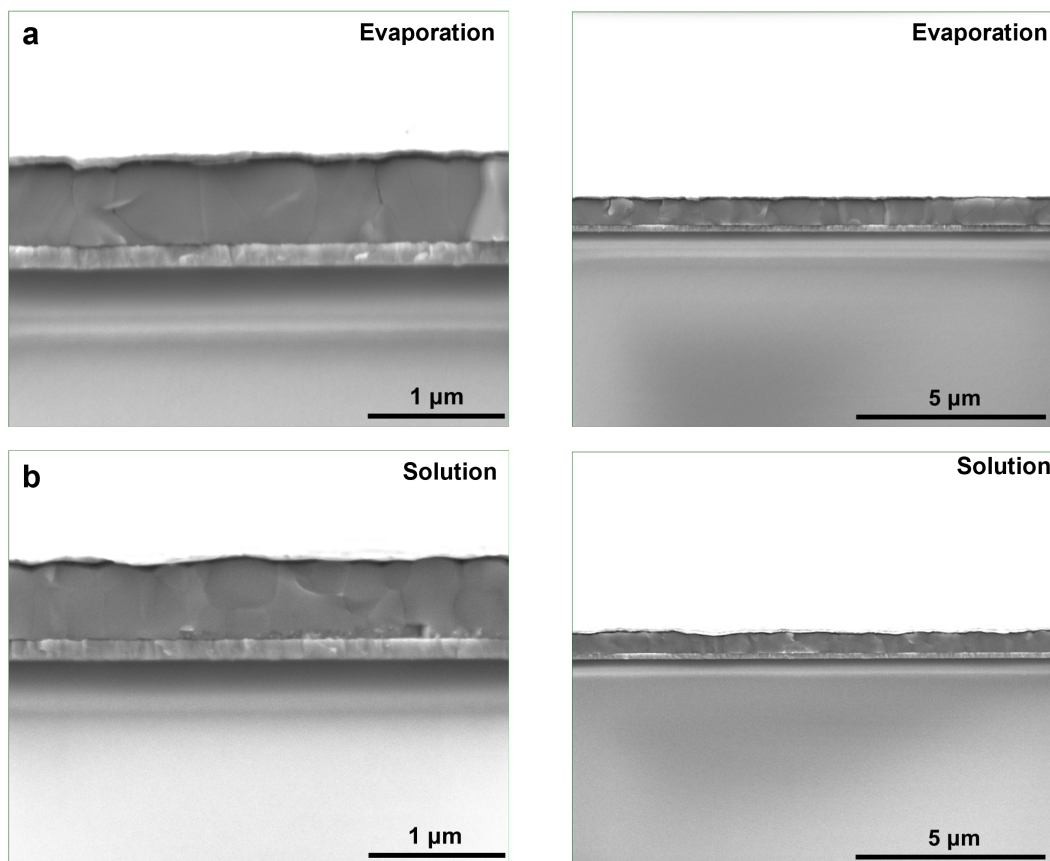


FIGURE 6.11: Cross-sectional SEM images of evaporated (a) and solution-processed (b) PSCs, with atomic layer deposited SnO_2 buffer layer, same as the device architecture shown in Figure 6.5a. The cross-sectional SEM images were measured by Shuaifeng Hu.

In Figure 6.12a, I present the optical microscopic images for the evaporated and solution-processed perovskite films ageing for 196 hours. The fresh films already showed strikingly different surface morphology. In particular, I observed intense “surface wrinkling” on the solution-processed perovskite film. Recently, wrinkles in WBG perovskites have been associated with local halide heterogeneity that accelerates light-induced degradation and halide segregation.[163] Such a feature was completely absent in the evaporated perovskites, implying better compositional homogeneity and photostability.

I observed the formation of pinholes in the solution-processed film after 48 hours of ageing, followed by complete decolourisation after 96 hours, indicating the complete degradation of the photoactive perovskite phase. By

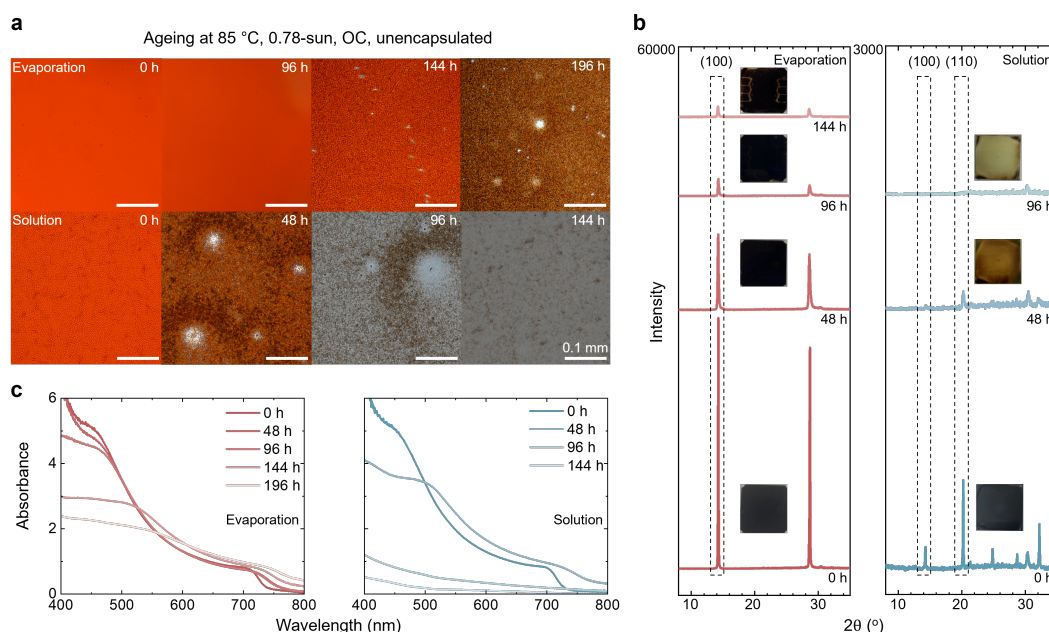


FIGURE 6.12: (a) Optical microscopic images of unencapsulated evaporated and solution-processed perovskite films, aged under ISOS-L-2 protocol (0.78-sun full-spectrum simulated sunlight, 85 °C, ambient air with relative humidity in the laboratory 50~60%). A thin layer of PMMA was deposited on the films to protect them from dust and scratches. Photos shown here were taken with an optical microscope with 20x magnification rate. The scale bar is 0.1 mm for all the images. Evolution of the XRD patterns (b) and the absorbance spectra (c) of the corresponding perovskite films shown in (a). Inset: Photos of the perovskite films taken during ageing. The XRD patterns (b) in log scale are shown in Figure 6.13 to reveal any impurity phases formed during ageing.

contrast, the degradation of the evaporated perovskite became visible after 196 hours, which was nearly 4-times slower than the solution-processed perovskite. In Figure 6.12b and Figure 6.13, I present the XRD patterns of the corresponding aged perovskite films. The reduction in the intensity of perovskite cubic phases in the solution-processed film is substantially faster than the evaporated one, confirming that the evaporated perovskite is more phase-stable under light and heat stress. In the fresh solution-processed perovskite, a trace amount of PbI_2 readily formed ($2\theta = 12.7^\circ$), whereas a similar feature was only observed in the evaporated perovskite after 144 hours of ageing. From the latter, I also observe minor impurity peaks corresponding to Pb-rich secondary phases at $2\theta = 14.8^\circ$ and 29.6° [206], which were absent

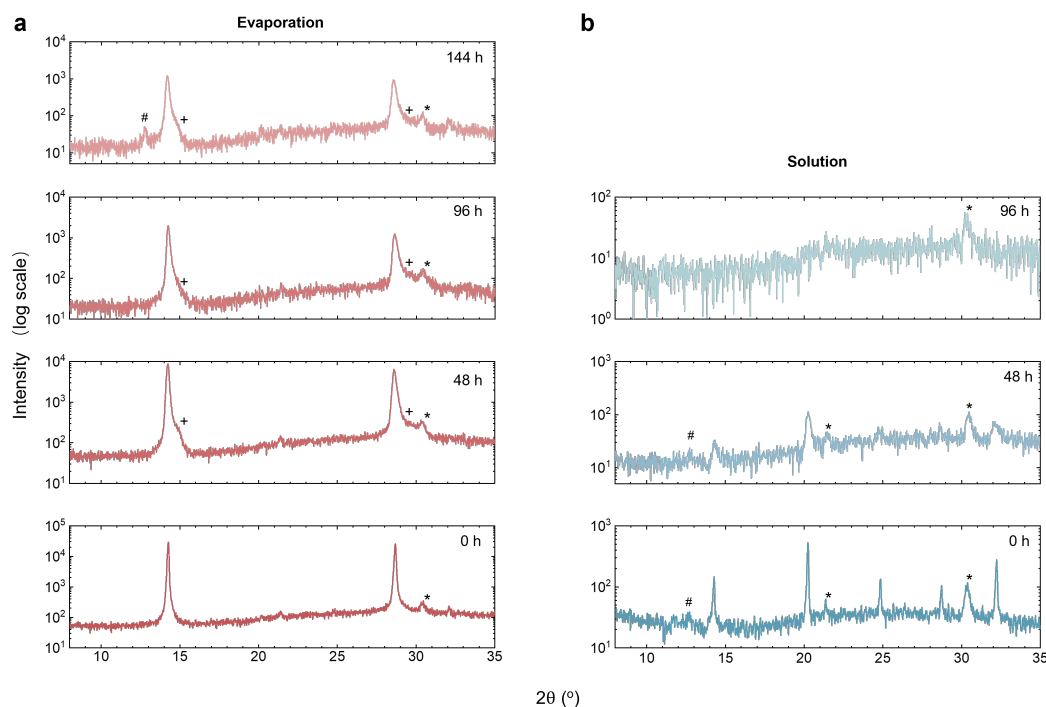


FIGURE 6.13: Evolution of the XRD patterns of unencapsulated evaporated (a) and solution-processed (b) perovskite films as shown in Figure 6.12b, aged under ISOS-L-2 protocol (0.78-sun full-spectrum simulated sunlight, 85 °C, ambient air with relative humidity in the laboratory 50~60%). The XRD data are plotted on a log scale to show impurities: PbI_2 (#), Pb-rich secondary phases (+). The peaks due to ITO are marked with *.

in solution-processed perovskites (Figure 6.13), suggesting different material degradation pathways existed in these perovskites. I note that despite having these Pb-rich phases, PV devices based on evaporated perovskites were operational much longer than their solution-grown counterparts, as described later in this article. Absorbance at the band edge of the photoactive perovskite material can also be used to track the rate of material degradation. In Figure 6.12c, I present the evolution of the absorbance spectra of the corresponding perovskite films shown in Figure 6.12a. A sharp drop in the absorbance at the band edge was observed in the solution-processed film between 48 and 96 hours. I interpret this as a near-total loss of the photoactive phase in the film. In comparison, the drop in the absorbance of the evaporated film was much slower, suggesting a suppressed degradation of the

perovskite composition [176], consistent with the morphological and crystallographic characterisation.

I demonstrated that the outstanding intrinsic stability of evaporated perovskites is closely relevant to the face-up orientation of (100) facets, as the (100) facet has been reported to be the most stable facet in perovskite crystals because it has the most bonded atoms.[207] Furthermore, it has better thermal transfer than the (110) facet [179]. Hence, having such facets exposed to the external environment is beneficial for the long-term stability of materials and devices under extreme conditions [208]. In addition, Liu and McMeekin have recently demonstrated that solution-processed WBG perovskites with face-up oriented (100) facets are more stable than the randomly oriented (110) and (100) facets [41], [79]. It is worth noting that the surface properties (e.g. morphology [208], [209], defect density [209], [210], defect types [209], [211]) of perovskite thin films are determined by the exposed facet orientation. Zhou and co-workers reported that (100) facet orientation could facilitate charge carrier transport across the absorber material and enhance the device performance [212]. Such well-defined facet orientation in our optimised evaporated perovskites also sheds light on facet-specific passivation and modifications to further boost the device efficiency and stability, whilst the study of facet engineering on solution-processed perovskite films is largely hindered by their complex nature and rough surface morphology [208].

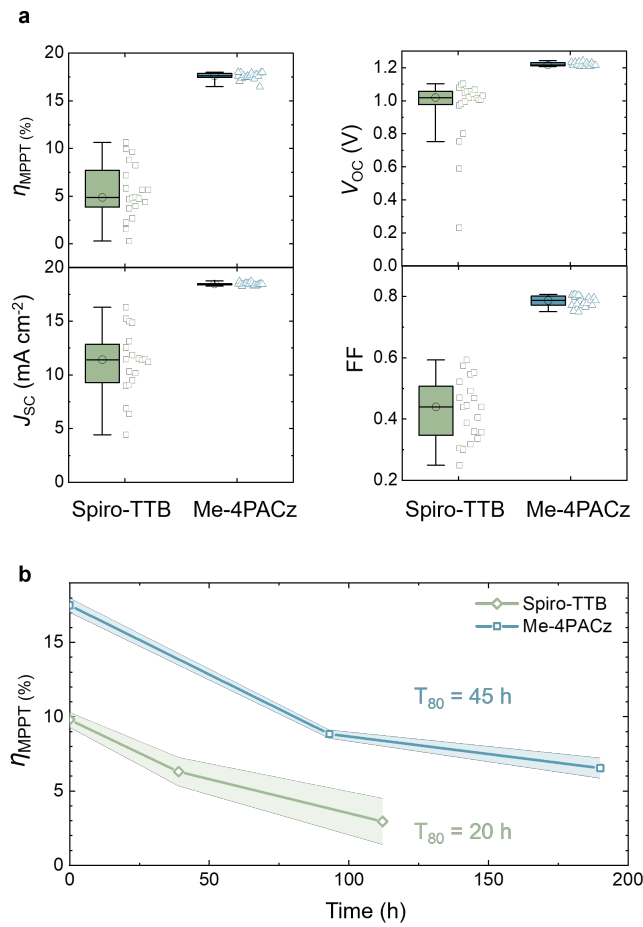


FIGURE 6.14: (a) PV performance of solution-processed WBG PSCs, with solution-processed Spiro-TTB or Me-4PACz as the HTLs (20 cells for Spiro-TTB and 20 cells for Me-4PACz), and C60 and ALD SnO₂ as the ETLs. (b) Evolution of the medians of η_{MPPT} (with the corresponding standard deviations as error bands) of encapsulated solution-processed WBG PSCs, with solution-processed Spiro-TTB or Me-4PACz as the HTLs (4 cells for Spiro-TTB and 4 cells for Me-4PACz), and C60 and ALD SnO₂ as the ETLs, aged under the ISOS-L-2 ageing protocol: OC condition, full-spectrum simulated sunlight, at 85 °C, in ambient air with relative humidity in the laboratory at 50~60%. The T_{80} of the cells on spiro-TTB and Me-4PACz are 20 h and 45 h, respectively. Cr/Au electrodes were used in cells for stability tests instead of Ag.

6.5 Performance and operational stability of co-evaporated WBG perovskite PV cells

To assess the performance of the facet-engineered seed-free co-evaporated WBG perovskites in complete solar cells, I fabricated a p-i-n device configuration as shown in Figure 6.5a using evaporated Spiro-TTB and C60 and BCP

or ALD SnO_2 , as the HTL and ETL, respectively, following a solvent-free fabrication route (Methods). While keeping all the ETLs the same, I also fabricated solution-processed PSCs of the same composition based on Me-4PACz to compare the device performance and stability. In our preliminary test, I compared solution-processed perovskites deposited on solution-processed spiro-TTB vs Me-4PACz. The latter showed better efficiency and stability (Figure 6.14). Therefore, I selected Me-4PACz as the HTL for solution-processed perovskites.

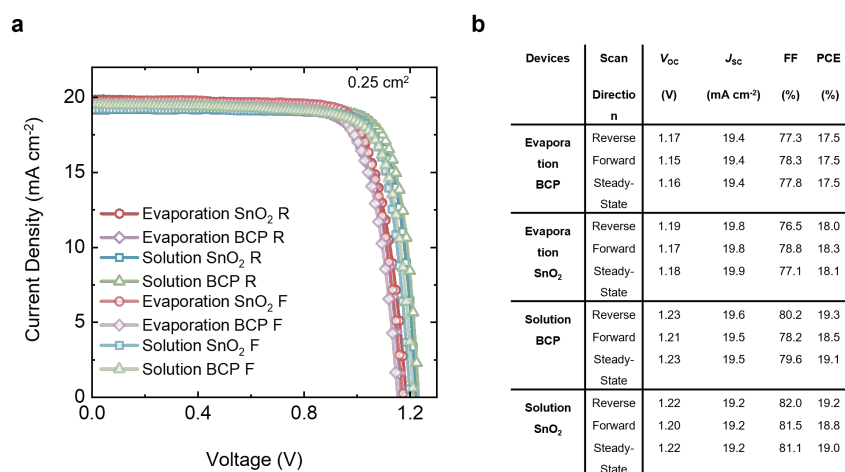


FIGURE 6.15: (a) JV characteristics of the representative evaporated and solution-processed PSCs with an aperture size of 0.25 cm^2 , with either ALD SnO_2 or evaporated BCP buffer layers. R: reverse scan. F: forward scan. Anti-reflective foils were applied on the glass side of the cells to minimise the optical loss. Detailed PV metrics are shown in (b).

The representative JV characteristics obtained from the evaporated and solution-processed PV cells are shown in Figure 6.15a. The full PV parameters are shown in Figure 6.15b. The evaporated cells with SnO_2 buffer layer, with an aperture area of 0.25 cm^2 , exhibit a steady-state V_{OC} up to 1.19 V, and much less hysteresis compared to the solution-processed cells. The EQE-derived PV bandgaps for the evaporated ($E_g = 1.67 \text{ eV}$) and solution-processed ($E_g = 1.69 \text{ eV}$) PSCs are ideal for making perovskite-Si tandems (Figure 6.16). The slightly wider bandgap of the solution-processed PSC is likely due to a higher Cl- ratio remaining in the absorber layer as evidenced

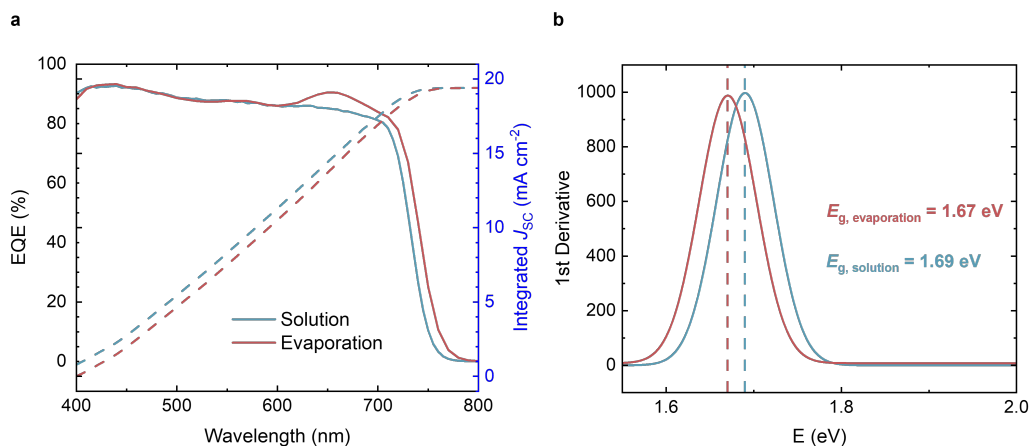


FIGURE 6.16: (a) EQE spectra (left axis) and the corresponding integrated J_{sc} (integration of the product of EQE and AM 1.5G spectrum) (right axis) of the representative evaporated or solution-processed PSCs with an aperture size of 0.25 cm², with ALD SnO₂ buffer layer. (b) PV bandgap extracted from the inflection point of the onset of the EQE shown in (a).

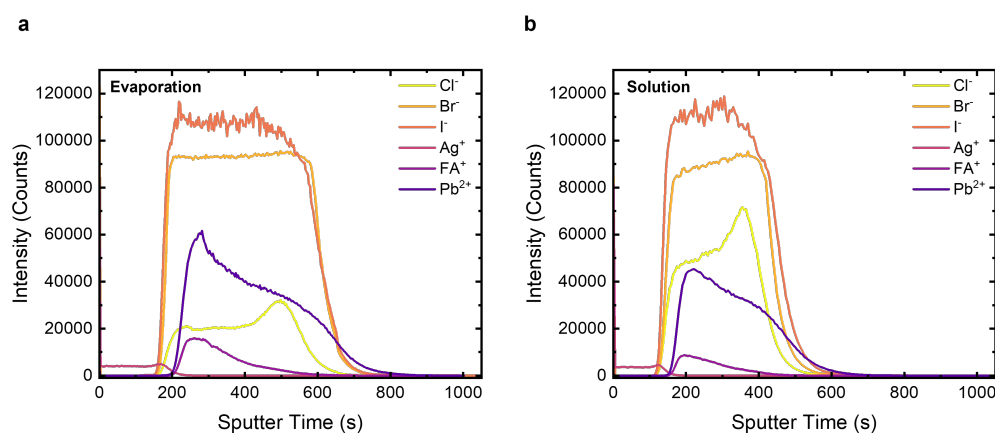


FIGURE 6.17: ToF-SIMS depth profiles of the evaporated (a) and solution-processed (b) PSCs, measured in positive and negative polarity. The device architecture of the evaporated cell is ITO/Spiro-TTB/perovskite/C60/SnO₂/Ag. The device architecture of the solution-processed cell is ITO/Me-4PACz/perovskite/C60/SnO₂/Ag. Except Me-4PACz, which is solution-processed, all the other charge transport layers are evaporated. The ToF-SIMS measurements were performed by Lirong Rong.

by the ToF-SIMS measurement on full devices (Figure 6.17). The JV characteristics and the corresponding 30-second maximum power point tracking efficiency (η_{MPPT}) for the champion evaporated PSCs with SnO₂ buffer layer ($\eta_{MPPT} = 19.3\%$, certified as 18.35% (Figure 6.18 and 6.19)) are shown in Figure 6.20. This is the only certified fully evaporated PSC reported to date. I also fabricated 1-cm² evaporated cells (Figure 6.21 and 6.22) with efficiency

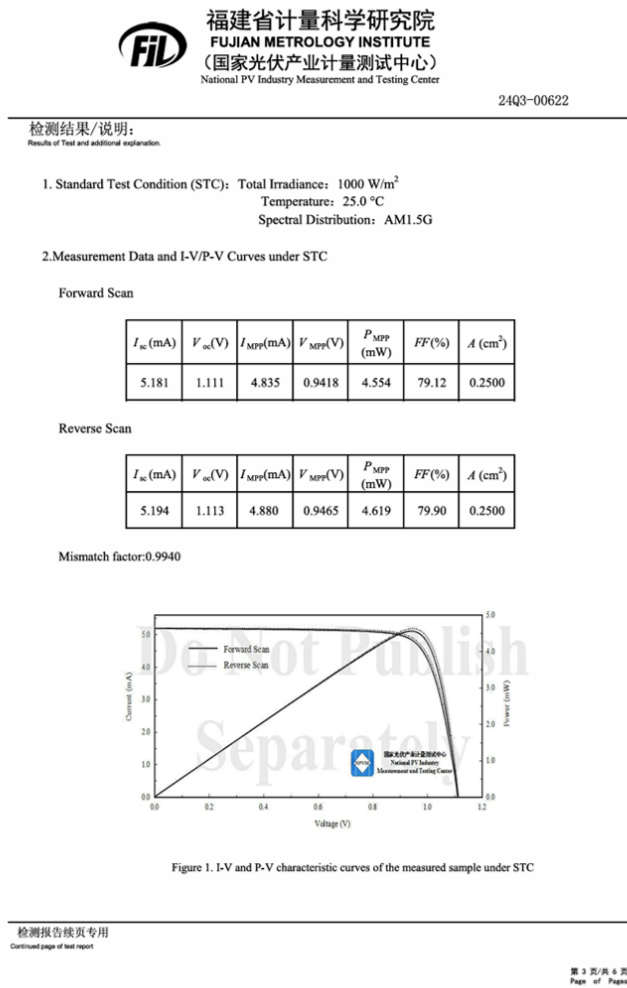


FIGURE 6.18: The certificate of a representative evaporated 1.67-eV perovskite solar cell with SnO₂ buffer layer (*JV* characterization). The report is issued by NPVM (Chinese national PV industry measurement and testing center). The aperture area is 0.25 cm² measured by NPVM. The report includes the optical aperture area, *JV*, MPPT, and EQE measurements.

($\eta_{\text{MPPT}} = 18.5\%$) similar to that seen in 0.25-cm² small-area cells with a minimum performance deficit when enlarging the cell area, indicating that the evaporated perovskite film is highly uniform and promising for large-area deposition. To the best of our knowledge, the η_{MPPT} I achieve on both small area and large area are among the highest efficiencies reported up-to-date for methylammonium-free (MA-free) fully-evaporated PSCs with a PV bandgap as high as 1.67 eV [74], [97], [98], [117], [170], [213]–[215].

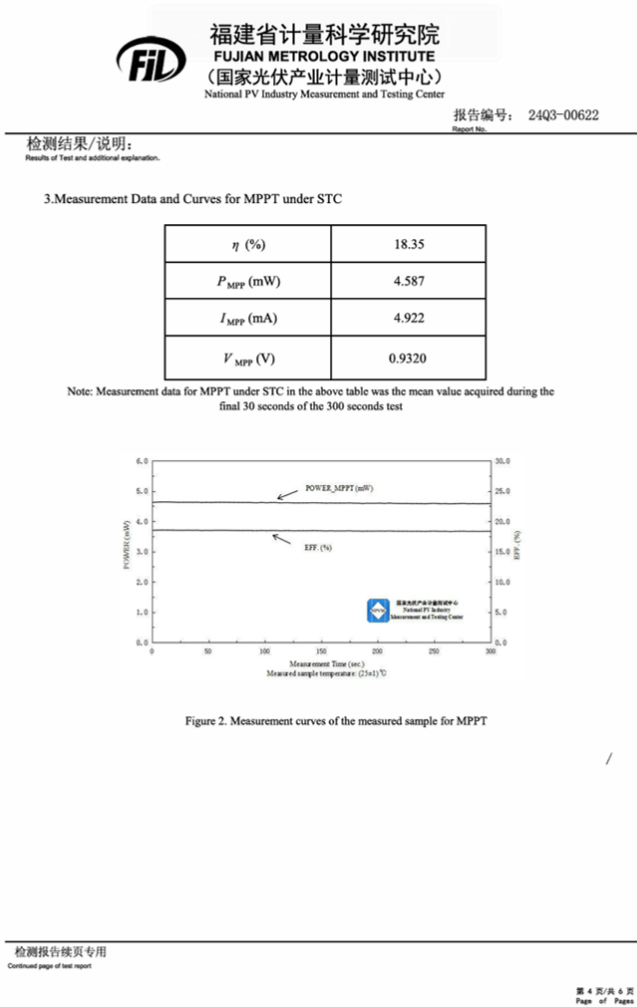


FIGURE 6.19: The certificate of a representative evaporated 1.67-eV perovskite solar cell with SnO₂ buffer layer (*JV* characterization). The report is issued by NPVM (Chinese national PV industry measurement and testing center). The aperture area is 0.25 cm² measured by NPVM. The report includes the optical aperture area, *JV*, MPPT, and EQE measurements.

In Figure 6.23, I present the shelf lifetime of 28 evaporated PSCs with SnO₂ buffer layer, fabricated from the same batch. I stored these unencapsulated cells under ISOS-D-1 conditions (ambient temperature, dark) and measured them periodically under full-spectrum sunlight in ambient conditions (relative humidity = 50 - 60%). These cells demonstrate an exceptionally long shelf lifetime with nearly no loss in efficiency after 1 year of storage. Notably, several cells maintain their peak performance ($\eta_{MPPT} \sim 18\%$) for over

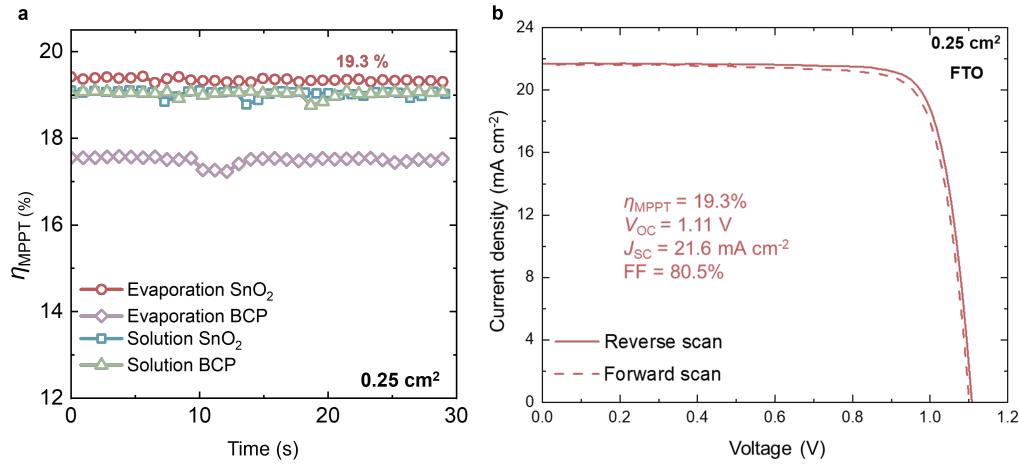


FIGURE 6.20: (a) The η_{MPPT} for 30 seconds of the representative evaporated or solution-processed PSCs with an aperture size of 0.25 cm^2 . (b) JV characteristics of a representative evaporated perovskite solar cell with ALD SnO_2 buffer layer, deposited on FTO substrate with anti-reflective foil applied to minimise the optical loss. The aperture size is 0.25 cm^2 . The corresponding MPPT data is presented in (a).

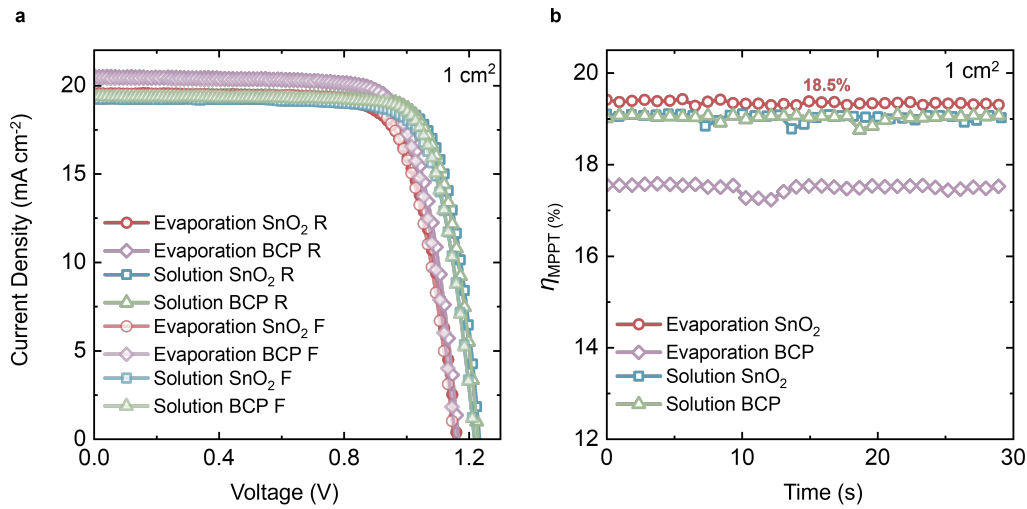


FIGURE 6.21: JV characteristics (a) and 30 s of MPPT tracking (b) of the representative evaporated or solution-processed PSCs with an aperture size of 1 cm^2 , with either ALD SnO_2 or evaporated BCP buffer layer. R: reverse scan, F: forward scan. The cells shown in this figure have anti-reflective foils applied on the glass side to reduce the optical loss.

10000 hours ($T_{100} > 10000 \text{ h}$) (Figure 6.23a). In the corresponding JV characteristics of these cells (Figure 6.24), I find that the freshly made cells suffered from shunting behaviour which spontaneously recovered over time, leading to a boost in J_{SC} and FF over the first 2 weeks of storage. I postulate that

1 cm ² cells					
Devices	Scan	V_{oc}	J_{sc}	FF	PCE
	Direction	(V)	(mA cm ⁻²)	(%)	(%)
Evaporation BCP	Reverse	1.16	19.6	74.5	16.9
	Forward	1.15	19.5	75.8	17.1
	Steady-State	1.16	19.5	74.7	16.9
Evaporation SnO ₂	Reverse	1.17	20.5	76.0	18.2
	Forward	1.16	20.5	77.6	18.1
	Steady-State	1.16	20.5	76.1	18.1
Solution BCP	Reverse	1.23	19.4	79.2	18.9
	Forward	1.22	19.4	78.8	18.6
	Steady-State	1.23	19.4	78.8	18.8
Solution SnO ₂	Reverse	1.23	19.2	79.6	18.9
	Forward	1.22	19.2	77.2	18.1
	Steady-State	1.23	19.3	78.4	18.6

FIGURE 6.22: PV metrics of representative 1-cm² evaporated and solution-processed 1.67-eV PSCs shown in Figure 6.21a.

the shunting issue was caused by a misalignment between the metal shadow mask and the device active area. Silver deposited outside the active area created a direct contact between the electrode and the perovskite absorber layer. The shunting issue became less severe as the silver oxidised and became insulated over time. The shunting issue has been resolved when I fabricated cells with Cr/Au electrodes and different metal shadow masks (Figure 6.25).

Light and heat stress are the most challenging conditions for PSCs to survive in real operation [216], [217]. Poor stability of WBG PSCs under the combination of light and heat remains as the bottleneck for tandem applicability. However, the operational stability of WBG PSCs under harsh conditions is rarely reported. In most cases, the device stability was tested under heat or light separately rather than combined, which were much milder than the ISOS-L-2 conditions [216], [217]. Moreover, the reported operational lifetime of evaporated PSCs is much shorter relative to the solution-processed counterparts [74], [97]. To test the operational stability of our WBG PSCs

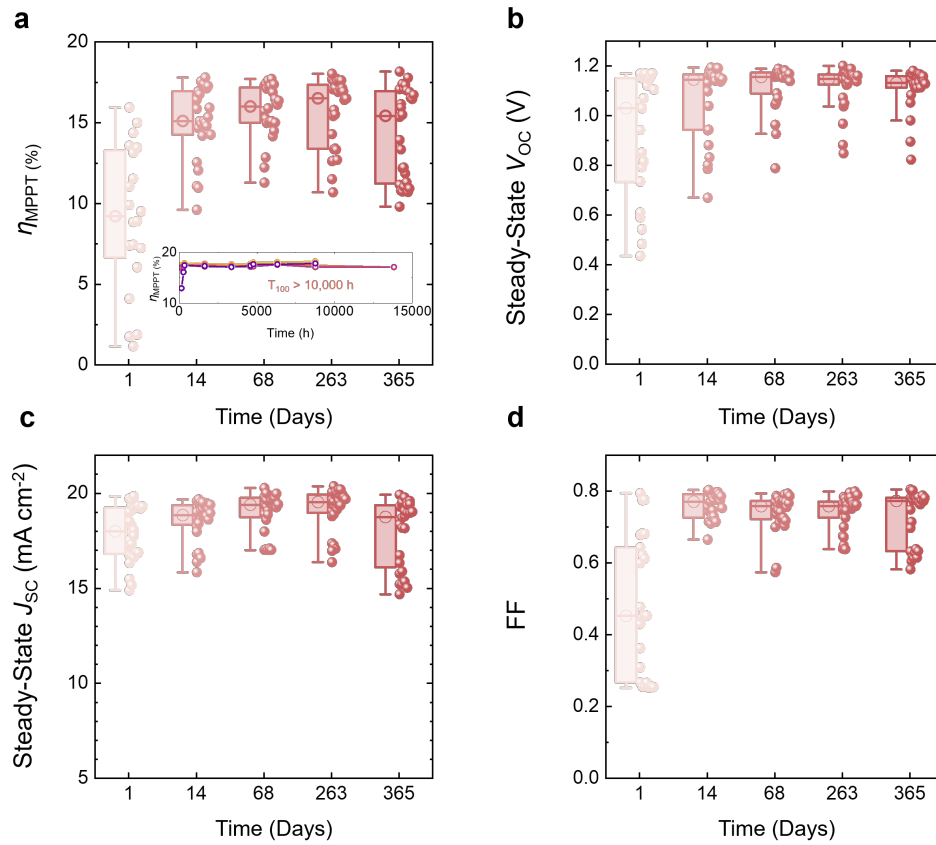


FIGURE 6.23: The shelf lifetime of one batch of evaporated PSCs (28 cells in total) with ALD SnO_2 buffer layer. The unencapsulated cells were aged under ISOS-D-1 protocol (ambient temperature, dark, OC) and measured periodically in ambient conditions (relative humidity = 50-60%). Inset: Shelf lifetime of several representative cells with $T_{100} > 10,000$ hours. The PV parameters include η_{MPPT} (a), steady-state V_{OC} (b), steady-state J_{SC} (c), and FF (d).

fabricated via seed-free co-evaporation, I encapsulated and aged evaporated and solution-processed cells under the ISOS-L-2 protocol: full-spectrum simulated sunlight (0.78 sun, Xenon lamp ageing box), 85 °C, OC condition, in ambient air (relative humidity in the laboratory at 50~60%) (Figure 6.26). The devices were taken out of the ageing chamber, allowed to cool to room temperature and characterised under 1-sun simulated sunlight at various time intervals.

The median η_{MPPT} of the cells, along with the standard deviations,

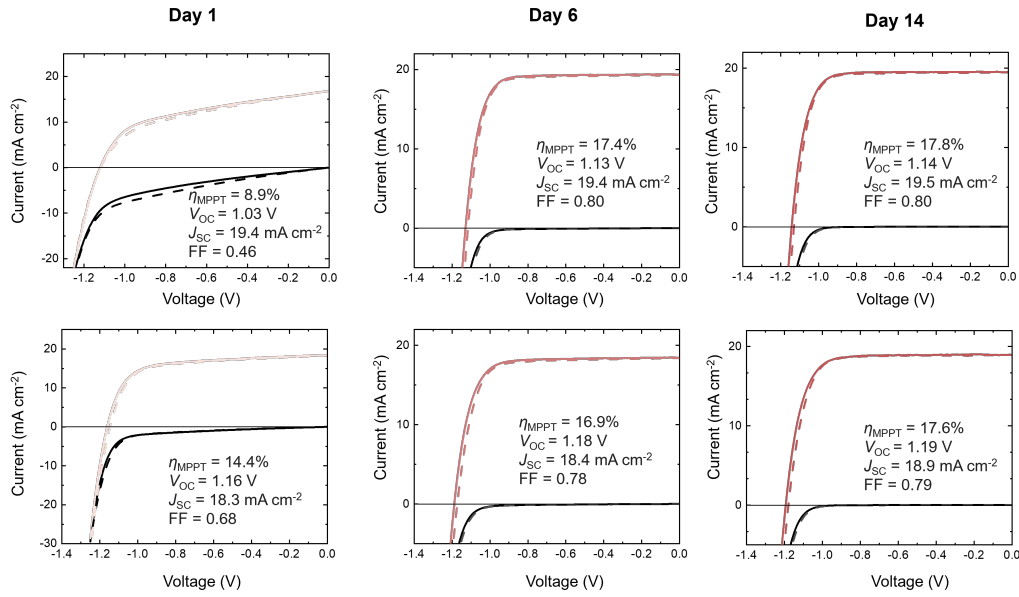


FIGURE 6.24: Evolution of the JV characteristics of two representative evaporated PSCs shown in Figure 6.23a after the first 14 days of ageing under ISOS-D-1 protocol (dark, ambient temperature). The device performance was measured periodically in ambient conditions (relative humidity = 50-60%).

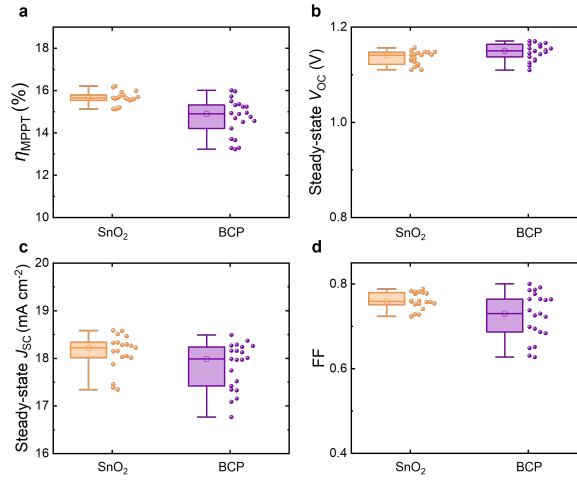


FIGURE 6.25: Statistical analysis of one batch of evaporated PSCs (19 SnO₂ cells, 21 BCP cells), with an atomic layer deposited SnO₂ or evaporated BCP buffer layer. Cr/Au was used as the electrodes. The unencapsulated cells were freshly made and measured in ambient conditions (relative humidity = 50-60%). The PV parameters include η_{MPPT} (a), steady-state V_{OC} (b), steady-state J_{SC} (c), and FF (d).

are plotted in Figure 6.27a, whilst the evolution of the corresponding PV performance parameters: V_{OC} , J_{SC} , and FF are shown in Figure 6.28. Our evaporated PSCs retained 80% of peak performance (T_{80}) after approximately 840

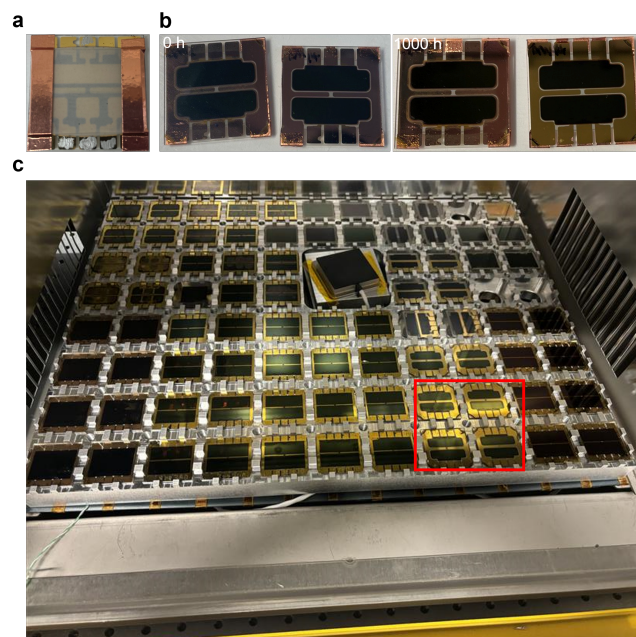


FIGURE 6.26: (a) Photos of the front side of the evaporated cells after encapsulation with epoxy sealant. Cr/Au electrodes are used instead of Ag for stability test. (b) Photos of the back side of the evaporated cells before and after 1000 hours ageing under ISOS-L-2 protocol. Copper tape and silver paste were applied to help maintain electrical contact over the ageing period. (c) Photos of the encapsulated cells in the ATLAS ageing box with simulated sunlight (0.78 sun) and heating stage (85 °C). Cells marked in red square are the seed-free co-evaporated cells.

and 330 hours for the SnO_2 -based and BCP-based devices, respectively, representing outstanding stability for mixed-cation, mixed-halide WBG PSCs. Of particular note, our champion evaporated device (aperture area = 0.25 cm^2) with SnO_2 reached a T_{80} over 1080 hours ($T_{80,\text{Champ}} = 1080$ h) with no observable change in perovskite appearance (Figure 6.27b and 6.26b). A similar level of stability ($T_{80,\text{Champ}} = 900$ h) has been realised on a large-area champion device (aperture area = 1 cm^2). On the contrary, the solution-processed cells only achieved a $T_{80} < 80$ hours. No additional passivation or additives were introduced to improve the stability of solution-processed cells because I want to reveal and compare the intrinsic stability of the co-evaporated and solution-processed cells [60], [218]. Light intensity, spectrum, and temperature have significant impacts on the PSC performance and stability [219]. It is critical to mimic the real solar spectrum in indoor

stability measurements to provide a reliable prediction for the field lifetime of PSCs [219]. Hence, I employed full-spectrum simulated sunlight with no UV filter for all of our stability tests (Figure 6.29). Intriguingly, this work is among the best stability reported to date for WBG (1.65-1.72 eV) PSCs with no passivation [39], [117], [119], [196], [197], [199], [220]. Notably, this is for the first time that a fully evaporated mixed-cation, mixed-halide WBG PSC achieves a similar level of operational stability (T_{80} over 1000 hours) under ISOS-L-2 protocol with state-of-the-art solution-processed PSCs [39], [117], [119], [196], [197], [199], [220]. Given the exceptionally harsh ageing conditions I adopted: full-spectrum illumination, elevated temperature, OC conditions, our results show a substantial advancement towards high-performing, stable fully-evaporated WBG PSCs, which are ideal candidates for tandem applications.

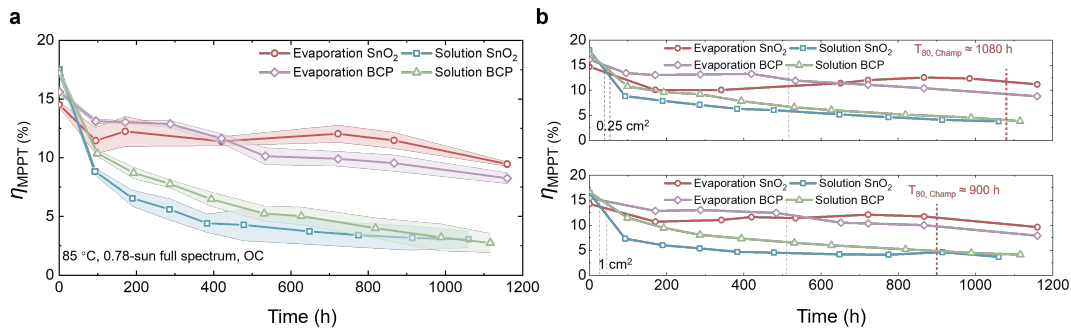


FIGURE 6.27: (a) Evolution of the median η_{MPPPT} (with the corresponding standard deviations as error bands) of encapsulated evaporated and solution-processed PSCs with an aperture size of 0.25 cm^2 or 1 cm^2 , with either ALD SnO_2 or evaporated BCP buffer layers (including five evaporation SnO_2 , six evaporation BCP, eight solution SnO_2 , and eight solution BCP cells), aged under the ISOS-L-2 protocol (OC, full-spectrum simulated sunlight, 85°C , in ambient air with relative humidity in the laboratory at 50-60%). η_{MPPPT} was tracked for 30 seconds for each cell at different ageing stages. (b) Evolution of η_{MPPPT} for individual champion cells used and recorded for (a). The dashed lines indicate the time taken to reach 80% of their initial η_{MPPPT} ($T_{80, \text{Champ}}$). For the champion evaporated cell, the $T_{80, \text{Champ}}$ is approximately 1,080 hours.

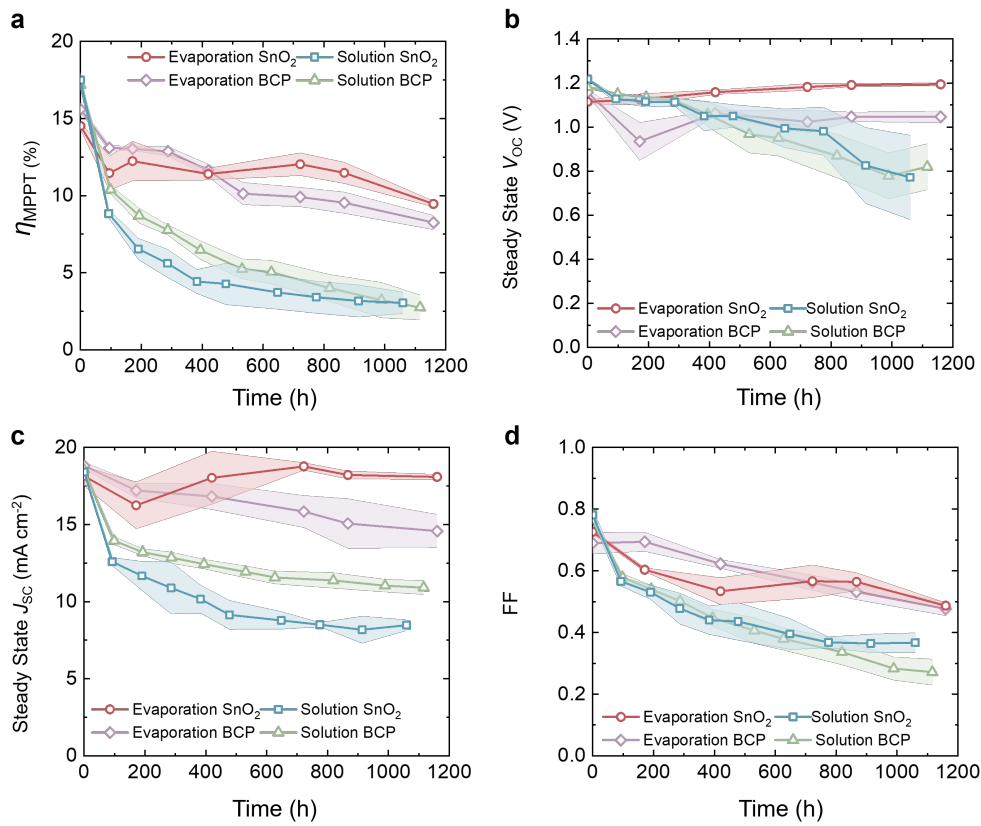


FIGURE 6.28: Evolution of the medians of η_{MPPT} (a), steady-state V_{OC} (b), steady-state J_{SC} (c), and FF (d), with the corresponding standard deviations as the error bars, of encapsulated evaporated or solution-processed PSCs with an aperture size of 0.25 cm² or 1 cm², with either ALD SnO₂ or evaporated BCP buffer layers (including six evaporation BCP, five evaporation SnO₂, eight solution BCP and eight solution SnO₂ cells) aged under ISOS-L-2 protocol: OC condition, full-spectrum simulated sunlight, at 85 °C, in ambient air with relative humidity in the laboratory at 50~60%.

6.6 Evaporated Perovskite-Silicon Tandem Solar Cells

Furthermore, I have verified the compatibility of our seed-free co-evaporated WBG perovskites on industrial standard Si wafers with micro-scale textured structure (Figure 6.30). As shown in Figure 6.31, a homogeneous, compact crystal structure with continuous aggregated grains can be formed on micro-textured Si wafers, suggesting their great promise for making operationally stable perovskite-Si tandems. The cell achieved a η_{MPPT} up to 23%, which should be further optimised by reducing the V_{OC} deficit. After lamination, I implemented our fully-evaporated perovskite-Si tandems into an outdoor field test in Italy (Figure 6.32a). This is the first time a fully-evaporated

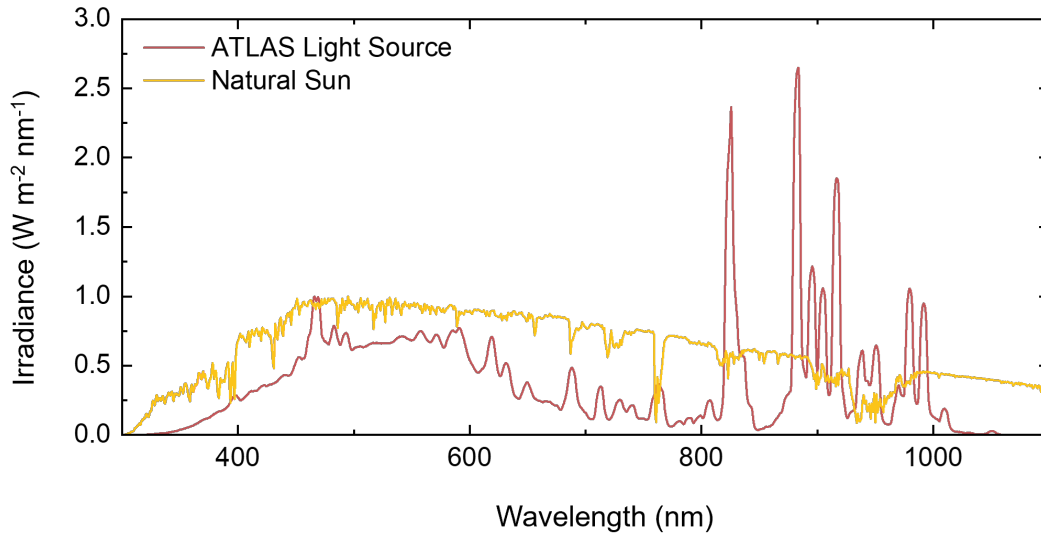


FIGURE 6.29: The full spectra of simulated sunlight used for ISOS-L-2 ageing study carried out at University of Oxford. The comparison between simulated solar spectra and natural sun spectra is shown. No UV filter was used in all the ageing tests.

perovskite-Si tandem has been tracked under continuous operation at MPPT under outdoor conditions. During the first 3 months of ageing from August to October, where the sunlight and ambient temperature were the highest among the whole year, the evaporated tandem showed an exceptional stability on par with a reference commercial heterojunction (HJT) Si cell, with a negligible loss in the temperature-corrected performance ratio (PR_{tc}) (Figure 6.32b). The PR_{tc} shows how well the device performs compared to standard testing conditions, by comparing actual outdoor yield with the reference yield expected from its rated power (P_{stc}), solar irradiance, and cell temperature. The bands around PR_{tc} indicate the 10% to 90% percentile range weighted by power. After 8 months of operation, the evaporated tandem still maintained $\sim 80\%$ of their initial PR_{tc} , suggesting that the excellent stability of our single-junction fully evaporated WBG PSC is readily transferrable to perovskite-Si tandems. Moreover, I plot the variation in daily average cell temperature weighted by power ($T_{cell,wt}$, left axis) and the daily sum of global plane-of-array irradiance (G_{POA} , right axis) over the entire ageing period (Figure 6.32b). Intriguingly, I found a clear correlation between the G_{POA}

and PR_{tc} for both the reference HJT cell and the co-evaporated perovskite-Si tandem. For the HJT device, the fluctuation in PR_{tc} seems to be mostly caused by days being either cloudy or clear, with negligible loss in the overall power output. In contrast, the variation in PR_{tc} for the co-evaporated perovskite-Si tandem mimics the continuously slow decay in G_{POA} from Autumn to winter, and early signs of recovery of PR_{tc} as spring approaches, implying a stronger reliance of the power output of co-evaporated perovskite-Si tandems on the sun irradiance intensity than the commercial HJT Si cells. This correlation is out of the scope of this work and will be investigated in more detail in a follow-up work. At the time of submitting this article, the outdoor testing is still continuing.

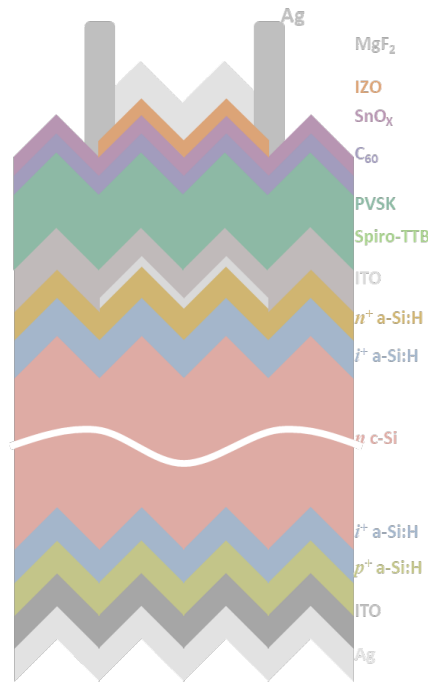


FIGURE 6.30: Device architecture of fully evaporated perovskite-Si tandem solar cell based on micro-textured industrial-standard HJT Si wafer.

On the contrary, volatile solvent residues, such as DMF and DMSO trapped in solution-processed perovskites could lead to device stability issues under light and heat, which becomes more severe in the fabrication of large-area PSCs [119]. I indeed found signals corresponding to these solvent

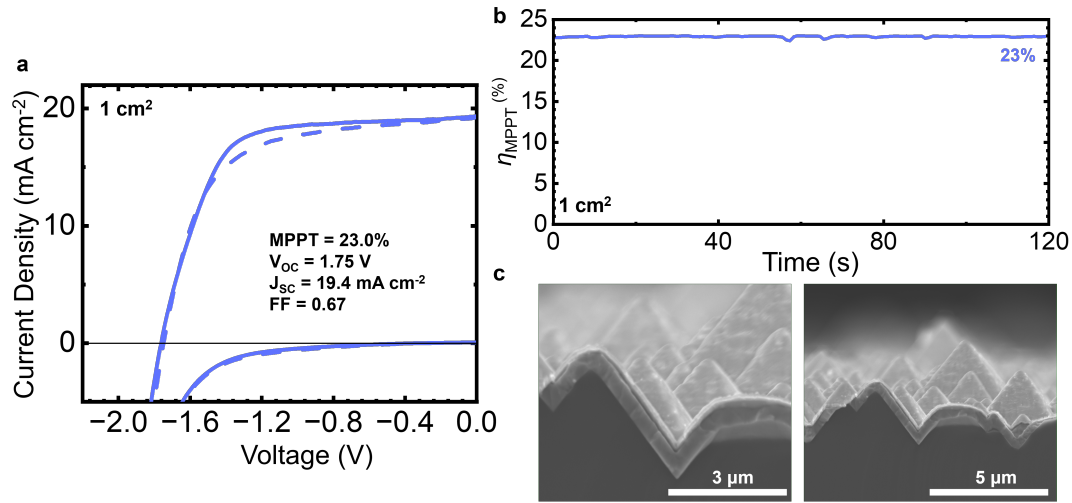


FIGURE 6.31: (a) J/V characteristics and (b) maximum power point tracked efficiency (η_{MPPT}) of a 1 cm^2 representative fully evaporated perovskite-Si tandem solar cell based on micro-textured industrial-standard Si wafer. (c) Cross-sectional SEM of the corresponding tandem cell.

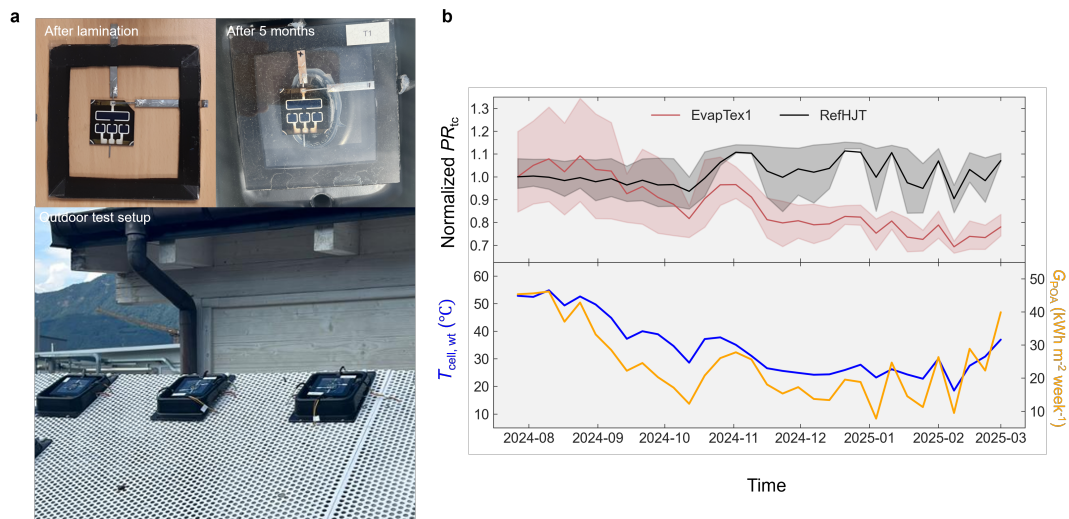


FIGURE 6.32: (a) Photos of a laminated fully-evaporated perovskite-Si tandem before and after 5 months of continuous operation at MPPT under outdoor ageing conditions in Italy. (b) Top panel: Evolution of the normalised temperature-corrected performance ratio (PR_{tc}) for a laminated fully-evaporated perovskite-Si tandem (EvapTex1) and a reference heterojunction Si (RefHJT) cell under outdoor ageing conditions over 8 months. The error bands around PR_{tc} indicate the 10% to 90% percentile range weighted by power. Bottom panel: The daily average cell temperature, weighted by power ($T_{cell,wt}$, left axis) and the daily sum of global plane-of-array irradiance (G_{POA} , right axis). The cells were laminated by Perrine Carroy. The outdoor stability was measured by Atse Louwen.

residues in ^1H liquid NMR spectra of our solution-processed perovskite materials (Figure 6.33). Thus, these solvent residues could also contribute to the

instability of our solution-processed devices.

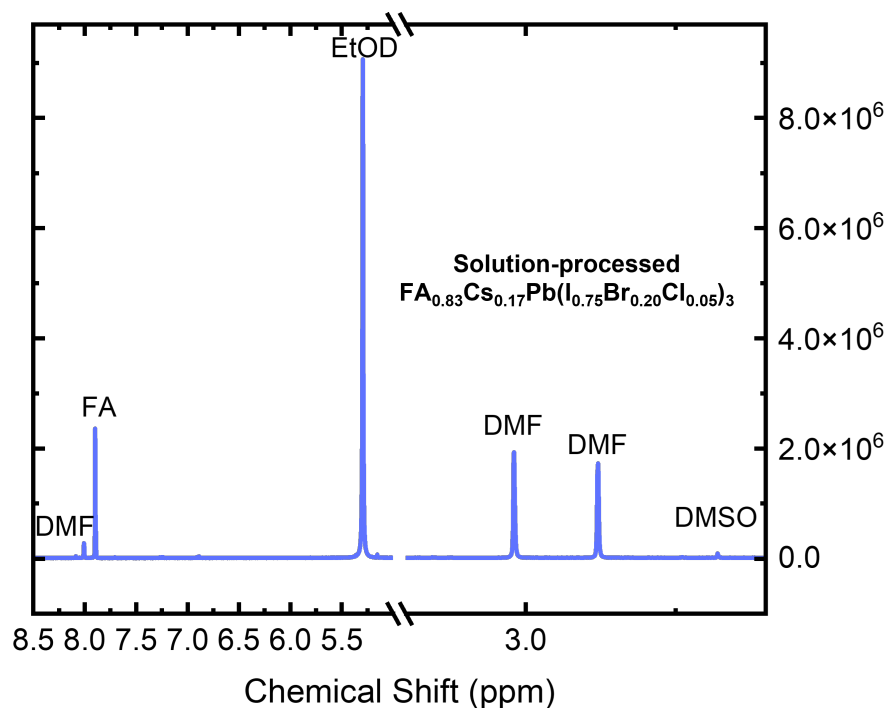


FIGURE 6.33: ^1H liquid NMR spectra of solution-processed perovskite materials. The perovskite materials were fabricated by spin coating with 4:1 v% DMF:DMSO and solvent-quenched by anisole. Spectra are obtained by dissolving material from ca. 90 cm^2 of perovskite thin film material (ca. 600 nm thickness) in deuterated ethanol (EtOD). Spectra are referenced to EtOD signal (not shown). The NMR characterisation was conducted and analysed by Nakita Noel.

6.7 Conclusion and Outlooks

Our findings demonstrate that facet-engineered seed-free co-evaporation provides an effective strategy to grow WBG (1.67 eV) perovskites with high crystallinity, face-up orientation, high phase purity and homogeneity. The improved material quality leads to exceptional material and device operational stability under stringent heat and light stress. Notably, the facet-engineered seed-free co-evaporated WBG PSCs achieve excellent long-term stability on par with state-of-the-art solution-processed solar cells. More importantly, I demonstrate fully evaporated perovskite-Si tandems with robust operational longevity under real outdoor test conditions, highlighting the great promise of realising efficient, durable perovskite PV technologies via a solvent-free fabrication protocol.

In addition to high efficiency and operational stability, high throughput is also a preliminary requirement for a commercial technology. In this chapter, I am using relatively slow deposition rates (total rate $\sim 1 \text{ \AA/s}$) for my perovskite deposition to maintain the good film quality, which translates to 2.5 hours of duration for depositing 800 nm of perovskites for making tandem cells. However, such a long manufacturing process is far below the standard for high-throughput production [42]. Ideally, industrially viable deposition rates for perovskite absorber layers should be equal to or above 1000 nm/min [42]. Examples of successful and scalable thin-film manufacturing can be found in the established thin film industry (e.g., CdTe or copper indium gallium selenide (CIGS) PV, and organic light-emitting diodes (OLED)), which is exclusively based on vapor-based techniques [221]–[223]. Therefore, exploring strategies to deposit perovskite films at high deposition rates ($> 17 \text{ nm/s}$) without sacrificing the optoelectronic properties requires great attention from the communities to bridge the gap between lab-scale research and industry production.

Chapter 7

Conclusions and Outlooks

Metal halide perovskite-based tandem solar cells comprising materials with complementary bandgaps offer a promising approach to circumvent the theoretical efficiency limit of single-junction solar cells. To realise efficient, stable perovskite tandem solar cells, developing high-performance, operationally stable WBG PSCs is essential and attracts great research interest.

The research presented in this thesis demonstrates a range of effective strategies to improve the power output and operational lifetime of WBG PSCs which have ideal bandgaps (1.65 - 1.8 eV) coupled with crystalline Si or narrow-bandgap perovskites for tandem applications. The scope of this thesis is not restricted to solution-processed perovskites which have pioneered the exceptional rise in efficiencies of PSCs in the past decade, but also extends to exploring approaches to optimise evaporated perovskites which hold unique advantages for more environmentally friendly, solvent-free, large-area fabrication of PSCs.

In Chapter 4, I screened a range of chloride additives in a solution-processed 1.8 eV perovskite solar cell to manipulate the perovskite crystallisation pathway. I found that by adding 15 mol% of excess MA₂Cl additive, the

resultant perovskite film became highly crystalline, phase pure, and homogeneous. In turn, the MACl-modified perovskites demonstrated suppressed halide segregation and improved ambient stability. I attributed the improved crystallographic and optoelectronic properties to the MACl-assisted crystallisation route. The MACl additive facilitated the growth of a chloride-rich intermediate phase that directed the crystallisation of the desired cubic perovskite phase and induced more effective halide homogenisation. Combining MACl with a Me-4PACz HTL, I achieved a V_{OC} of 1.25 V and a η_{mpp} of 17.0%. The improved understanding of how chloride additives affect the crystallisation of mixed-cation mixed-halide perovskites could help the design of more effective crystallisation mediators that lead to advancements of perovskite tandem technologies in the future.

In Chapter 5, I demonstrated a novel approach to manipulate the final crystallographic properties and morphology of co-evaporated perovskites. For the first time, I provided experimental evidence for the formation of an intermediate phase induced by DMAI additives during co-evaporation. The modified perovskite films reached grain sizes in the order of a few micrometres. The improved grain structure indicated that intermediate phase-assisted crystallisation could be a great addition to the toolbox for passivating evaporated perovskites. However, I also found that the use of DMAI led to severe contamination in the evaporation chamber. Hence, I encourage explorations of alternative materials to DMAI. The ideal candidate should also fit into the perovskite crystal lattice and have a controllable evaporation pattern.

In Chapter 6, I comprehensively investigated the optoelectronic and crystallographic properties of evaporated and solution-processed 1.67-eV perovskites. I found that the evaporated perovskites had exceptional intrinsic

stability under heat and light due to high crystallinity, (100)-dominant face-up orientation, vertically homogeneous grains, and the solvent-free deposition method. Intriguingly, fully evaporated PSCs also demonstrated excellent device performance and longevity. The 0.25 cm² champion cell reached a η_{MPPT} of 19.3% (certified as 18.35%) and the most stable cell retained 80% of its peak performance after 1080 hours of ageing under ISOS-L-2 protocol (85 °C, 1-sun illumination, under open-circuit condition). We also highlighted that improved orientation and homogeneity of fully evaporated solar cells played a critical role in mitigating the device performance decay during ageing. This was the most stable fully evaporated 1.67-eV solar cells reported to date, implying their potential to advance highly durable and efficient perovskite PV technologies. Furthermore, I demonstrate a fully-evaporated perovskite-Si tandem solar cell on an industrial standard fully textured Si wafer with a η_{MPPT} of 23% with compact coverage. Notably, the evaporated perovskite-Si tandems exhibited exceptional outdoor stability, maintaining ~80% of their initial performance after 8 months of continuous operation at the maximum power point tracking condition.

Reducing the V_{OC} loss is particularly critical for realising high efficiency in tandem solar cells because the major gain of multi-junction solar cell structures arises from an increase in V_{OC} . Although I have made some progress in boosting the efficiency of evaporated PSCs, they still suffer from much more severe V_{OC} deficits compared to their solution-processed counterparts due to a lack of defect passivation techniques compatible with thermal evaporation. Hence, an interesting future research direction could be exploring vapour-depositable passivation molecules to reduce the defect density and non-radiative recombination loss in evaporated perovskites. A recent work published by our group offers a promising route to explore.[60]

Another interesting topic would be the exploration of alternative additives to DMAI for co-evaporated perovskites. This involves the design, synthesis and testing of novel materials in an evaporation system. To prevent direct contamination of the evaporation chamber, the simulation might help predict the chemical structure and physical properties of potential candidates.

Finally, I only present a prototype of fully-evaporated perovskite-Si tandem solar cells in this thesis. There remains plenty of space for further improving the device performance and stability. Optical modelling could be a powerful tool to predict the optimal layer thickness of the charge transport layers and recombination layers to minimise the parasitic absorption. I have demonstrated the exceptional stability of evaporated PSCs. On top of that, the indoor and outdoor operational stability of evaporated tandem solar cells would be a valuable set of data to collect. Research in this direction could help evaluate the limitations of indoor ageing tests compared to real operational conditions of commercial PV products. Therefore, a more reasonable stability measurement protocol can be designed to link the research in the lab with the industry.

In this thesis, I demonstrate a series of effective strategies to overcome the key bottlenecks (poor efficiency and operational stability of WBG perovskites) for the commercialisation of perovskite tandem solar cells via crystallisation control. In addition to revealing the key role of a widely used MAI additive in modulating the crystallisation of solution-processed WBG perovskites, I provide valuable guidelines for the design of additive engineering for the perovskite research community. Then I take one step further to move from a lab-scale favoured solution process to a more industry-relevant, scalable manufacturing technique, thermal evaporation. My findings about the DMA-assisted intermediate phase engineering of co-evaporated

WBG perovskites broaden the toolkit available for in situ crystallisation control of evaporated perovskites, bridging a critical gap that causes the long-lasting efficiency deficit between evaporated PSCs and their solution-processed counterparts. Most importantly, I successfully demonstrated the first fully evaporated WBG PSC with efficiency and stability on par with the state-of-the-art solution-processed PSCs, verifying the great potential of realising efficient and stable PSCs with an industry-compatible manufacturing process.

Although I significantly boost the performance and longevity of evaporated WBG PSCs and tandems, the co-evaporation route is still constrained by slow deposition rates, hence low throughput. In order to make this manufacturing route economically competitive, we need to develop novel methods to reduce the processing time while maintaining the high film quality. In addition, the replacement of expensive and non-renewable raw materials should also attract more attention from the community. Co-evaporation may not be the ultimate solution to the large-scale production of PSCs. We should never stop learning new lessons from other fields, like how perovskite solar cells flourish on the shoulders of dye-sensitised solar cells.

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