University of Groningen

Organic-inorganic hybrid perovskites

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DOI:
[10.33612/diss.95664256](https://doi.org/10.33612/diss.95664256)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2019

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Adjokatse, S. (2019). *Organic-inorganic hybrid perovskites: photophysics, thin film fabrication and solar cells*. [Thesis fully internal (DIV), University of Groningen]. Rijksuniversiteit Groningen.
<https://doi.org/10.33612/diss.95664256>

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Organic-Inorganic Hybrid Perovskites

Photophysics, Thin Film Fabrication and Solar Cells

Sampson Adjokatse

university of
 groningen

faculty of science
 and engineering

zernike institute for
 advanced materials

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Photophysics, Thin Film Fabrication and Solar Cells

Sampson Adjokatse

PhD thesis

University of Groningen, The Netherlands

Zernike Institute PhD thesis series 2019-23

ISSN: 1570-1530

ISBN: 978-94-034-1905-3 (printed version)

ISBN: 978-94-034-1904-6 (electronic version)

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Nederlandse Organisatie
 voor Wetenschappelijk Onderzoek

The research described in this thesis was performed in the research group Photophysics & OptoElectronics of the Zernike Institute of Advanced Materials at the University of Groningen, The Netherlands. The work was funded by the Netherlands Organisation for Scientific Research, NWO (Graduate Programme 2013, No. 022.005.006).

Cover design: Sampson Adjokatse

Printing: Ridderprint | www.ridderprint.nl

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Organic-Inorganic Hybrid Perovskites

Photophysics, Thin Film Fabrication and Solar Cells

Proefschrift

ter verkrijging van de graad van doctor aan de
Rijksuniversiteit Groningen
op gezag van de rector magnificus prof. dr. C. Wijmenga
en volgens besluit van het College voor Promoties.

De openbare verdediging zal plaatsvinden op

vrijdag 20 september 2019 om 12.45 uur

door

Sampson Adjokatse

geboren op 14 december 1980
te Accra, Ghana

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CHAPTER 1

Introduction

Abstract

This introductory chapter provides a general overview of organic-inorganic hybrid perovskites and their application in solar cell fabrication. First, a short history and the crystal structure of perovskites is described, followed by outlining the notable achievements of perovskites solar cells. Additionally, the exceptional optoelectronic properties of this class of materials and the standard solar cell characterization techniques are described. Furthermore, the perovskite solar cell working principle and the key factors guiding and/or affecting the development of this technology are highlighted. Finally, an outline of the thesis is provided.

Optoelectronic devices such as photovoltaics (PV) cells, light-emitting diodes (LEDs), lasers and sensors play very important roles in all aspects of human endeavors from everyday life to the most advanced scientific activity. Their applications are so wide-ranging that it will be very difficult to imagine a modern society without them. In fact, they have proven to be able to address urgent challenges relating to energy saving and greenhouse gas emissions, communication, general lighting and display applications.^[1] For instance, as the worldwide energy demand increases and the fossil-fuel supply steadily declines, PV cells are considered major alternative candidates since they can provide practically, everlasting electrical power at low operational cost, which is virtually nonpolluting. Similarly, LEDs have multitude and pervasive applications such as in room lighting (bulbs), new displays and sensors, while their high switching rates are useful in advanced communications technology. Lasers are applied in optical-fiber communication, optical disk drivers, laser printers, barcode scanners, laser surgery and skin treatments, cutting and welding materials. Optical sensors are also applied across a wide range of industries such as in automotive, medical, appliance, aerospace and defense, industrial and commercial transportation.

The state-of-the-art of these optoelectronic devices and the explosive growth of their industry have been enabled by the incredible investment of time, money and intellectual effort in the development of novel materials and the required processing that is essential for their fabrication. Although it is often the product design or the software of these devices which steal the limelight in marketing, the unassuming heroes or the basis for the optoelectronic devices are the materials used in manufacturing these devices. Through the development of materials science, a variety of optoelectronic materials have been developed since the invention of the first practical silicon solar cell and the first demonstration of visible-spectrum LEDs based on gallium arsenide phosphide (GaAsP) over five decades ago.^[2,3] This has led to the evolution of various PV and light-emission technologies based on inorganic semiconductors, organic molecules, polymers, quantum-dots and most recently, hybrid perovskites. Indeed, the continuous growth and evolution in the technologies based on these materials present exciting opportunities for the investigation and development of new or modification of existing optoelectronic materials and devices for enhanced functionalities. This thesis is devoted to the study of organic-inorganic halide perovskite photophysical properties, film fabrication and solar cells. In the following I will simply refer to them as halide perovskites.

1.1. Brief history and Crystal Structure of Perovskites

Perovskites constitute a very important class of materials within the field of materials science, physics, chemistry and engineering. The name perovskite originally refers to the oxide calcium titanate (CaTiO_3) mineral which was discovered by the German mineralogist Gustav Rose in 1839 and named in honor of the Russian mineralogist Lev Alekseevich Perovski (1792 - 1856).^[4,5]

Figure 1.1: Crystal structure of cubic perovskites with generic chemical formula ABX_3 . The A position is occupied by organic or inorganic cations whereas the B position is occupied by metal cations and anions occupy the X position. (a) and (b) are the schematic representation of the crystal structure in a simple cubic unit cell and in a supercell consisting of a network of 8 corner-sharing BX_6 -octahedra.

The crystal structure of CaTiO_3 is parent to many important compounds. The structure of this family of oxide was first described by Victor Goldschmidt in 1926 in his work on tolerance factors and thereafter, the name perovskite structure became a generic name for all compounds with the general formula, ABX_3 where the A and B sites usually accommodate inorganic cations of various valency and ionic radius and the X site accommodates anions (usually, oxygen or halogens). The crystal structure of perovskites as depicted in Figure 1.1(a), has the A cation at the corners of the cubic unit cell with the B cations at the body-centered position and the X anions occupying the face-centered positions. In other words, the ideal ABX_3 perovskite structure has cubic closed-packed AX_3 layers with the B-site

cations located in the octahedral interstitial sites to form the three-dimensional (3D) network of corner-sharing BX_6 -octahedra as shown in Figure 1.1(b). The structural stability and probable structure of this class of compounds as described by Goldschmidt is determined by the tolerance factor (t) and octahedral factor (μ). The tolerance factor t is defined as

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

where r_A , r_B , and r_X are the ionic radii of A, B and X site ions, respectively and the octahedral factor μ is defined by the ratio, r_B/r_X which assesses whether the B-site cation can fit within the octahedral holes of the X-site anion sublattice. The “A” cation is usually larger than the “B” cation. Ideally, perovskites crystallize into the primitive simple cubic lattice structure in the high-temperature phase without any deformation, corresponding to $t = 1$. However, small deviation from $t = 1$ as a result of changes in the ionic radii of the constituent elements leads to structural distortion in the form of buckling of the BX_6 -octahedra with consequential influence on the physical properties of the material such as in its electronic, optical, magnetic, and dielectric properties.

Empirically, the tolerance factor for most 3D perovskites is $0.8 < t < 1.0$ and the octahedral factor is $0.44 < \mu < 0.90$. By description, these factors impose a strict constraint on the ABX_3 structure in terms of the ionic size of the constituent elements. For example, for a halide perovskite with a high symmetry cubic structure (i.e. $t = 1$), if the largest values for r_B and r_X [i.e. Shannon ionic radii of lead ($r_{\text{Pb}} = 1.19 \text{ \AA}$) and iodine ($r_{\text{I}} = 2.20 \text{ \AA}$)]^[6] are considered in the calculation of the size of the A-site cation, then the largest ionic radius is limited to $\sim 2.6 \text{ \AA}$ for a traditional BX_3 framework. This implies that, the fitting of a larger cation than $2.6 \text{ \AA}$ at the A-site can lead to the disruption of the 3D network (i.e. $t > 1$), lifting the size restriction imposed by the tolerance factor and forming lower-dimensional structures. Additionally, the valency of the ions also restricts the choice of the space-filling elements. For instant, in order to fully fill all the ionic sites in a given 3D halide perovskite, if the “A” cation is monovalent, then the “B” cation must be divalent.

As mentioned above, the lifting of the ionic size restriction imposed by the tolerance factor results in the formation of lower-dimensional derivatives of the perovskite structure which is mainly described in terms of the connectivity of the corner-sharing BX_6 octahedral. This remarkable structural flexibility and tunability

(a) $\langle 100 \rangle$ -orientation (b) $\langle 110 \rangle$ -orientation (c) $\langle 111 \rangle$ -orientation

Figure 1.2: Schematic representation of the derivatives of the lower-dimensional perovskite structures cut from the 3D perovskite along different directions. (a) The $\langle 100 \rangle$ -oriented, (b) $\langle 110 \rangle$ -oriented, and (c) $\langle 111 \rangle$ -oriented families of layered perovskites for $n = 1, 2$ and 3 octahedral layers. The figure is adapted from Ref.^[9]

of the dimensionality from 3D to 0D octahedral clusters provides rich pathways for preparing interesting materials with tunable physical properties. One of the notable lower-dimensional perovskite derivatives is the 2D layered (Ruddlesden-Popper phase) perovskite structure, named after S. N. Ruddlesden and P. Popper who first synthesized and described the structure in 1957.^[7,8] The structure is composed of 2D perovskite-like slabs interleaved with cations that are too large to fit the A-site cage. There are different subgroups of this 2D layered perovskite structure which are obtained from the 3D structure by cutting layers along specific crystallographic

directions such as the $\langle 100 \rangle$ -, $\langle 110 \rangle$ - and $\langle 111 \rangle$ -orientations. The specific orientation of the resultant inorganic frameworks are influenced by the choice of the A cation(s) and the reaction stoichiometry.^[9] The $\langle 100 \rangle$ -oriented perovskite family is the most common and has a general formula given by $(\text{RNH}_3)\text{A}_{n-1}\text{B}_n\text{X}_{3n+1}$ (or $\text{A}_{n+1}\text{B}_n\text{X}_{3n+1}$), where R is an organic functional group and n is the number of the layers of the octahedral in the perovskite-like slab. For $n = 1$, the Ruddlesden-Popper (RP) phase is made solely of a cation that is too large to fit in the A-site while $n = \infty$ represents the 3D perovskite structure with cation(s) that rightly fits in the A-site (Figure 1.1). In principle it is also possible to have systems with $n = 2, 3, 4$, etc., for which the RP phase is then composed of a mixture of large (those that do not fit the A-site) and small (those that fit the A-site) cations in the right proportions.

The $\langle 110 \rangle$ -oriented perovskite family has the formula, $\text{A}'_2\text{A}_m\text{B}_m\text{X}_{3m+2}$ and yields both 1D ($m = 1$) and 2D layered ($m > 1$) members, while, the $\langle 111 \rangle$ -oriented subgroup has the formula, $\text{A}'_2\text{A}_{q-1}\text{B}_q\text{X}_{3q+3}$ and yields the 0D isolated cluster ($q = 1$) and the 2D layered ($q > 1$) members.^[9] The schematic representation of these lower dimensional 2D perovskite structures with n -inorganic octahedral layers are illustrated in Figure 1.2.

1.2. Halide Perovskites and Milestones in Solar Cell Application

Until recently, the most technologically interesting and extensively studied class of perovskites was the oxide perovskites with the formula, ABO_3 . Typical examples are BaTiO_3 , PbTiO_3 , BiFeO_3 , SrTiO_3 , LiNbO_3 etc. These fully inorganic perovskites exhibit a vast number of interesting functional properties, such as catalytic activity, good insulating properties, superconductivity, ferroelectricity, piezoelectricity, thermoelectricity, colossal magnetoresistance, multiferroicity, and so on.^[10,11] Hence, these materials are used in microelectronics and telecommunication. Despite their numerous functional properties, most of these oxide perovskites show poor semiconducting properties. For this reason, they are never considered to be interesting for PV and optoelectronic applications in general. However, a fraction of them referred to as the ferroelectric oxide perovskites have been shown to demonstrate photovoltaic effect as a result of ferroelectric polarization.^[12–16]

Like oxide perovskites, halide perovskites have been known for over a century with the earliest reports on them dating back to the late 19th century, with a couple of articles from 1884.^[17,18] Depending on whether the A-site cation is an inorganic or organic species, two sub-families of halide perovskites are created and referred to as the all-inorganic halide perovskite and organic-inorganic halide perovskites (hybrid perovskites), respectively. Hybrid perovskites combine the advantageous properties characterizing crystalline inorganic solids with those of the organic molecules. The first report on the photoconductivity of these halide perovskites was reported for the all-inorganic CsPbX_3 system in 1958.^[19] However, the application and investigation of halide perovskites in thin-film transistors and light-emitting diodes (LEDs) was first reported decades after by Mitzi and co-workers in 1995 and 2001, respectively.^[20,21] At the time, the authors observed that the LEDs exhibited photovoltaic properties and therefore they anticipated their use in solar cells. However, due to the Pb toxicity and the non-robustness of the Sn-based materials, the halide perovskites were not investigated in solar cells at that time.

Figure 1.3: Device structure evolution of halide perovskite solar cells. **(a)** Dye-sensitized solar cell device structure employing perovskite as the sensitizing absorber. **(b,c)** The device structures with mesoporous conducting TiO_2 (b) and non-conducting Al_2O_3 scaffolds (c). **(d)** Planar heterojunction solar cell device structure without a mesoporous layer.

The first known report on the application and investigation of halide perovskites, specifically, organic-inorganic halide perovskites in solar cells was by Miyasaka and co-workers.^[22,23] Their work was motivated by the quest to replace the organic dye in dye-sensitized solar cells (DSSC) with a more advanced material which could absorb strongly over a broad wavelength range than the conventional

dyes and which also could combine the absorption characteristics with efficient charge-transport properties. Their device structure was composed of a mesoporous TiO_2 layer which was sensitized with nanocrystalline methylammonium lead tribromide ($\text{CH}_3\text{NH}_3\text{PbBr}_3$, abbreviated as MAPbBr_3 where $\text{CH}_3\text{NH}_3^+ = \text{MA}^+$) perovskite absorber. A lithium halide-containing electrolyte solution was used as the hole-transporting medium, allowing for positive contact. The device structure is illustrated in Figure 1.3(a). Their preliminary result yielded a power conversion efficiency (PCE) of 2.2% and was first communicated at the 210th Electrochemical Society Meeting in Mexico in 2006.^[22] The efficiency was increased to 3.8% in 2009 by replacing the bromine with iodine.^[23] There was however, a huge challenge posed by the liquid electrolyte as a result of the dissolution of the perovskite absorber into it, rendering the devices very unstable and with very short time functionality. To improve the stability, they attempted the use of polypyrrole-based conductive polymer composite with carbon as a solid-state hole-transporting material (HTM) in place of the liquid electrolyte but obtained a PCE lower than 1%.^[24] Two years later, Park and co-workers optimized the titania surface and the deposition method of the perovskite sensitizer on thinner TiO_2 films, recording an efficiency of 6.5% in 2011.^[25]

The key advancement that brought the revolution of the halide perovskites is the development of a solid-state perovskite solar cell (PSC). The liquid electrolyte in the previously reported devices was replaced with a solid-state hole conductor (HTM). The first efficient HTM employed in solid-state perovskite solar cells is the organic p-type material called 2,2',7,7'-tetrakis-(*N,N*-di-*p*-methoxyphenylamine)9,9'-spirofluorene (Spiro-OMeTAD). The breakthrough was reported almost simultaneously by two independent collaborating groups. Both reported a great improvement in the device stability and an enhanced efficiency. Park, Gratzel and colleagues were the first to report a PCE of 9.7% based on the exact device structure as the DSSC, except for the absorber being methylammonium lead iodide (MAPbI_3) and the replacement of the liquid electrolyte with Spiro-OMeTAD (Figure 1.3(b)).^[26] The TiO_2 layer acted as the electron selective layer while the Spiro-OMeTAD acted as the hole selective layer. Snaith, Miyasaka and co-workers employed Spiro-OMeTAD in their devices but with a different device architecture, reported an enhanced open-circuit voltage (V_{oc}), resulting in an efficiency of 10.9%.^[27] Their device architecture was composed of a non-conducting mesoporous Al_2O_3 scaffold which replaced the conducting nanoporous TiO_2 layer and the MAPbI_3 absorber was replaced with mixed-halide $\text{MAPbI}_{3-x}\text{Cl}_x$ perovskite

(Figure 1.3c). The high device performance recorded despite the use of a non-conducting alumina scaffold suggested that the perovskite absorber also acts as an electron transporter. Subsequently, Etgar *et al.* also demonstrated good hole-transport properties in a simple two-component TiO_2 -MAPbI₃ solar cell with 5.5% efficiency but lower V_{oc} .^[28] These discoveries elucidated the ambipolar charge transport capabilities of the MAPbI₃ and of the other hybrid perovskite materials studied and paved the way for the planar device architecture as shown in Figure 1.3(d).^[29–31] These early remarkable developments have led to a paradigm shift in the study of perovskites and their application in solar cells. It has also widened the field for further exploration to understand the fundamental properties of this class of materials and improve the solar cells towards commercialization. This quest has triggered the so-called “perovskite fever”.^[32,33] Although the earlier predominant application of hybrid perovskites has been in single-junction solar cells, the renewed research interest and the perovskite fever has also led to the expansion of the field to include applications in a variety of other technologies such as in light-emitting diodes (LEDs),^[34] light-emitting field-effect transistors,^[35] lasers^[36], sensors^[37,38], etc.

1.3. Exceptional Optoelectronic Properties of Halide Perovskite Materials

Given the increasing variety of materials and optoelectronic applications of halide perovskites, understanding the fundamental material properties influencing the exceptional optoelectronic performances is crucial for improving and designing new advanced applications. The most relevant of these properties are the optical and the electrical ones.

Halide perovskites exhibit very interesting optical properties which is necessary to fully understand to exploit optoelectronic devices. The color (bandgap) tunability is one of these optical characteristics. The standard perovskite absorber, MAPbI₃ has a direct bandgap of 1.55 eV corresponding to an absorption onset of 800 nm, making it a very good light absorber over the visible region. Attempts to further extend the absorption to longer wavelengths has led to the tuning of the bandgap through tailoring of the chemical composition (i.e. varying and/or mixing of cations and/or halogens).^[43] Attempts to increase the band gap led to the use of nanostructuring and quantum confinement.^[43] A considerable number of reports have demonstrated that the emission wavelengths are tunable from the ultraviolet

Figure 1.4: Optical and electronic properties of halide perovskite materials. **(a)** An illustration of a typical compositional band gap tuning ranging from 405 nm (CsPbCl_3) to 700 nm (CsPbI_3) for colloidal CsPbX_3 (X = Cl, Br, I) solutions under UV lamp.^[39] **(b)** Representative photoluminescence (PL) spectra of the colloidal samples in (a) which are extended towards the MA(Sn/Pb)I_3 perovskite systems.^[40,41] **(c)** Absorption coefficient of perovskites compared to other solar cell absorbers.^[32] **(d)** Electronic band structure (left diagram) showing the CBM and VBM of MAPbI_3 and its total and partial density of states (DOS) (right diagram).^[42]

to the near-infrared spectral regions (390 – 1050 nm).^[44–50] An illustration of a typical compositional band gap tuning ranging from 405 nm (CsPbCl_3) to 700 nm (CsPbI_3) for colloidal CsPbX_3 (X = Cl, Br, I) and MA(Sn/Pb)I_3 solutions under an UV lamp is shown in Figure 1.4(a), and the representative photoluminescence (PL) spectra of the same colloidal samples are shown in Figure 1.4(b). Importantly, absorption measurements and calculations show that these materials have direct bandgaps.^[51,52] Additionally, halide perovskites exhibit substantially high optical

absorption coefficients (10^4 to 10^5 cm^{-1}), comparable to the one of the best solar cell absorbers such as GaAs, CIGS etc. (Figure 1.4(c)).^[25,53] These high values are attributed to the orbital configuration of the valence band maximum (VBM) and the conduction band minimum (CBM). As demonstrated for MAPbI₃ by first-principles calculation (density functional theory, DFT), the VBM is dominated by strong coupling between the metal Pb *s* and halide I *p* antibonding orbital characters and the CBM is dominated by metal Pb *p* orbital character, resulting in *p-p* electronic transitions (Figure 1.4(d)).^[42,54] The high absorption coefficient enables very efficient light absorption and therefore allows for only a thin layer of the material to absorb the incident light almost entirely.

Another interesting characteristic of these materials is their defect-tolerance. Like the absorption coefficient, the defects are also associated with the coupling of the orbitals at the valence and conduction band edges. Specifically, for MAPbI₃ the defects are attributed to the strong Pb *s* – I *p* antibonding coupling, weak Pb *p* – I *p* coupling and the material's ionic characteristics. The strong *s* – *p* antibonding coupling lowers the VBM close to the I *p* orbital while the weak *p* – *p* coupling fixes the CBM close to the Pb *p* orbital. Thus, defects formed by the removal of an ion such as I results in the creation of a defect state between the Pb *p* orbital level and the CBM while a defect created by Pb²⁺ vacancy results in the creation of a defect state between the I *p* orbital level and the VBM. These defects have been demonstrated to generate trap states that reside within the bands (VB or CB) or exist as shallow traps near the band edges. Hence, carriers trapped in these shallow defect states can easily be detrapped to contribute to current generation.^[54–56] Given that this class of materials is fabricated by low-temperature solution processes, quantitatively, their defect density is small when compared with other polycrystalline inorganic solar cell absorbers. For example, the defect density in halide perovskite single crystals grown by simple solution-processed methods is estimated to be in the order of $\sim 10^{10}$ cm^{-3} while that for the polycrystals is estimated to be in the order of $\sim 10^{15} - 10^{17}$ cm^{-3} .^[57–60] This high defect-tolerance property has led to suppressed recombination and high photovoltages exceeding 1.2 V in PSCs for materials with bandgap energy of 1.55 – 1.6 eV.^[61]

Furthermore, halide perovskites exhibit outstanding charge transport properties which are defined in terms of carrier mobility, carrier diffusion length and lifetime of the photogenerated species. The carriers are directly photoexcited, or are generated from excitons which have binding energy much smaller than K_{BT} .^[62,63] Electronic band structure calculation revealed that the bands at the VBM and CBM

have a similar dispersion, resulting in similar effective masses for both electrons and holes which are small in value of $0.18 - 0.35m_0$.^[54,64] This contributes to the ambipolar properties with carrier mobility exceeding $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for polycrystalline films and $100 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for single crystals. The defect-tolerant nature of halide perovskites also has strong influence on the carrier diffusion lengths and lifetimes. Large diffusion lengths ranging from $1 \text{ }\mu\text{m}$ in polycrystalline films to over $100 \text{ }\mu\text{m}$ in single crystals have been measured.^[65–69] Carrier lifetimes in excess of $1 \text{ }\mu\text{s}$ have been measured from photoluminescence decays.^[70]

Figure 1.5: Typical equivalent circuits and current density-voltage (J-V) curves of a solar cell diode. **(a)** Illustration of the equivalent circuit of an ideal diode. **(b)** Equivalent circuit of an ideal diode with a current source. **(c)** Equivalent circuit of a non-ideal diode with the inclusion of parasitic resistances and current source. **(d)** Typical dark J-V curve of a perovskite solar cell on a semi-logarithmic scale with three distinctive regimes corresponding shunt resistance, ideality factor and series resistance. **(e)** Typical dark (black dotted line) and illuminated (red dotted line) J-V curves of a perovskite solar cell on a linear scale, featuring the figures of merit of a solar cell.

1.4. Solar Cell Characterization

The solar cell's ability to convert an incident photon energy into electrical energy is determined by measuring its electrical current (I) as a function of externally applied voltage (V) both in the dark and under illumination. This is referred to as the current-voltage (I - V) characteristics of the solar cell. The I - V curve is the superposition of the I - V curve of the solar cell diode in the dark and the light-generated current. Figure 1.5(a) and 1.5(b) depicts the equivalent models of the ideal solar cell diode in the dark and under illumination conditions, respectively. Similarly, Figure 1.5(c) shows the non-ideal solar cell with the inclusion of the most common parasitic resistances: series resistance (R_S) and shunt resistance (R_{SH}).

Practically, the power output of the device strongly depends on the size of the device active area (A), hence, the current is normalized by the area (i.e. $J = I/A$, where J is the current density) in order to remove the area dependence. The device performance is determined by the behaviour or shape of the J - V curve. Figure 1.5(d) shows a typical dark J - V curve of a solar cell on a semi-logarithmic scale with a diode-like behaviour. The linear representation of the dark J - V curve is also shown in Figure 1.5(e) with the black dotted line. The current density corresponding to this ideal solar cell diode in the dark is defined by the ideal Shockley diode equation:

$$J = J_0 \left[\exp \frac{qV}{nkT} - 1 \right] \quad (1.2)$$

where J_0 is the saturation current density, q is the elementary charge, n is an ideality factor and k is the Boltzmann constant. As shown in Figure 1.5(d), the curve has three distinctive regimes, namely, shunt resistance regime, exponential behaviour regime and series resistance regime. The negligible current at reverse bias and at small forward bias is due to finite shunt resistance. At large forward bias, the current increases exponentially until it becomes limited by the series resistance. By examining these three regimes, diode related parameters such as leakage current, ideality factor and saturation current can be extracted and be used to evaluate the solar cell behaviour and performance. In order to achieve high performing device, the shunt resistance must be as large as possible while the series resistance must be as small as possible. Under illumination, an additional photocurrent (J_{PH}) contribution is added and the above equation becomes:

$$J = J_0 \left[\exp \frac{qV}{nkT} - 1 \right] - J_{PH} \quad (1.3)$$

leading to the downward shift of the J - V curve into the fourth quadrant as shown in Figure 1.5(e) with the red dotted line. For real devices with shunt (R_{SH}) and series resistances (R_S), the Shockley diode equation is modified to give:

$$J = J_0 \left[\exp \frac{q(V+JR_S)}{nkT} - 1 \right] - J_{PH} - \frac{V+JR_S}{R_{SH}} \quad (1.4)$$

Importantly, the device power output in the fourth quadrant corresponds to the voltage between zero and the open circuit voltage (V_{oc}). Thus, the V_{oc} is the maximum photovoltage that the device can produce under illumination and corresponds to the voltage where the current under illumination is zero. When shunt resistance (R_{SH}) is infinite, the V_{oc} can be obtained by rearranging the equation (1.4) to give:

$$V_{oc} = \frac{nkT}{q} \ln \left(\frac{J_{PH}}{J_0} + 1 \right) \approx \frac{nkT}{q} \ln \left(\frac{J_{PH}}{J_0} \right) \quad (1.5)$$

The maximum photocurrent the device generates under illumination at zero potential difference between the anode and the cathode is the short circuit current density (J_{SC}) and depends on the density of photons incident on the solar cell, the total absorbance of the device, the overlap of the absorption with the solar spectrum and the amount of charge carriers lost to recombination before extraction. Therefore, J_{SC} represents the number of extractable photogenerated carriers. Another significant device parameter is the fill factor (FF) which is a measure of the quality of the J - V characteristics and depends on the point on J - V curve where the maximum power can be generated. This point is called the maximum power point (MPP), hence, the FF is defined as the ratio of the maximum power (P_{MPP}) and the product of J_{SC} and V_{OC} . Mathematically, the FF is defined as:

$$FF = \frac{J_{MPP} \times V_{MPP}}{J_{SC} \times V_{OC}} \quad (1.6)$$

where V_{MPP} and J_{MPP} are the voltage and current density at the maximum power point (MPP) respectively. The power conversion efficiency for the solar cell is therefore defined as:

$$PCE = \frac{P_{MPP}}{P_{in}} = \frac{J_{SC} \times V_{OC} \times FF}{P_{in}} \quad (1.7)$$

where P_{in} is the power input. The strong interdependence between the parameters in the numerator suggests that high efficiency can only be reached by joint optimization of V_{OC} , J_{SC} and FF .

Another important characterization parameter that validates the J - V measurement and describes the device's capability of converting the incident photons into extractable photocurrent is the external quantum efficiency (EQE). It is defined as the ratio of the extracted electrons to the number of photons incident on the solar cell. Using a monochromatic light source, the current of the device can be measured at specific wavelengths (λ) from which the EQE (λ) can be estimated using the relation below:

$$EQE(\lambda) = \frac{\text{extracted electrons}}{\text{Incident photons } (P_i)} = \frac{hc}{q\lambda} \frac{J(\lambda)}{P_i(\lambda)} \quad (1.8)$$

where h is Planck's constant, c is speed of light, q is elementary charge, and P_i is the incident monochromatic light intensity. A typical EQE spectrum for the perovskite solar cell is shown in Figure 1.6. Additionally, the short circuit current can be calculated from the above EQE relation by integrating the current over the entire spectrum of the device. The calculated current (J_{CALC}) which should be equivalent to the J_{SC} obtained from the J - V measurement is given by:

$$J_{CALC} = \int \frac{q\lambda}{hc} EQE(\lambda) P_i(\lambda) \delta(\lambda) \quad (1.9)$$

Figure 1.6: Typical EQE spectrum of a perovskite solar cell, measured under short circuit conditions.

1.5. Metal Halide Perovskite Solar Cells

As described above, the power conversion efficiency (PCE) of a solar cell is determined by three figures of merit, namely, the short-circuit current-density (J_{SC}), the open-circuit voltage (V_{OC}) and the fill factor (FF), all of which require maximization in order to have high-performing devices. The journey from the initial reported perovskite solar cell efficiency of 3.8% in 2009 to the current record efficiency of 24.2%^[71] has been guided by a number of key innovations and developments that can be classified under (i) material processing and engineering, (ii) device architecture engineering, (iii) contact and interface engineering, and (iv) fundamental photophysical and theoretical studies.^[56,72] These developments which are described here have been precipitated by attempts to improve the solar cell efficiency (i.e. maximize the figures of merit), enhance device stability, reduce potential cost and ultimately, push the perovskite PV technology towards commercialization.

1.5.1. General Working Mechanism of Perovskite Solar Cells

The understanding of the fundamental working principle of PSCs has evolved over the period from the presumed DSSC working principle to the present solid-state concept. In the dye-sensitized geometry, the perovskites are not required to have good carrier transport as the device performance is mainly determined by the interfacial properties. The discovery that the electrons and holes are transportable through the perovskite film without the need for any semiconducting scaffold as is required in the case of DSSC has significantly impacted the fundamental understanding and the progress in performance of PSCs.^[27] The present widely accepted working principle of the PSC is based on the n-i-p or p-i-n device configuration concepts, where the perovskite absorber functions as an intrinsic semiconductor (i), sandwiched between an electron-selective (n) and hole-selective (p) contact. The most common n-i-p structure is composed of TiO_2 (compact or mesoporous layer) as the n-type contact and Spiro-OMeTAD as the p-type contact (i.e. FTO/TiO_2 (n)/perovskite (i)/Spiro-OMeTAD (p)/Au), while the most common p-i-n structure has PEDOT:PSS as the p-type contact and the fullerene derivative, [6,6]-phenyl- C_{61} -butyric acid methyl ester (PCBM) as the n-type contact (i.e. ITO/PEDOT:PSS (p)/perovskite (i)/PCBM (n)/Al).

The photovoltaic mechanisms involve charge carrier generation, diffusion and extraction at the charge-selective contacts. As depicted in the schematic of Figure 1.7, the desirable processes involve the photoexcitation of the perovskite after absorbing light of wavelength matching with its band gap (1), electron transfer to the ETM (2) and hole transfer to the HTM (3). The undesirable processes involve: non radiative charge trapping^[73,74] and radiative recombination of photogenerated species (4), back charge transfer at the interfaces of the ETM and the HTM with the perovskite (5,6) and between the ETM and the HTM (7) as a result of pinholes. The intrinsic radiative recombination (4), the trap assisted recombination, and the charge accumulation and surface recombination at the electrodes (5) – (7) significantly affect the V_{oc} , and hence, limit the performance of the device. To achieve high V_{oc} , these undesirable processes must operate on a much slower timescales than the charge generation and extraction (1) – (3) or must be suppressed. These undesirable processes can be reduced by engineering the perovskite absorber, the interfaces and contact electrodes as discussed below.

Figure 1.7: Schematic diagram of the charge-transfer processes in perovskite thin film solar cell. The green solid lines represent the desirable processes while the red dashed lines represent the undesirable processes.

1.5.2. Perovskite Material Processing and Engineering

The development and engineering of the perovskite materials can be analyzed from the perspective of the film deposition methods and compositional engineering. Thin film quality, in general, plays a crucial role in the performance of the solar

cells since it is directly linked to the photocurrent and photovoltage. Hence, the first and foremost research activity in the early developments of PSCs was on the fabrication of high-quality perovskite films with appropriate morphology, uniformity, phase purity and crystallinity. Notably, the first perovskite solar cells were fabricated using the one-step solution deposition method. This method involved the direct deposition by spin-coating of the perovskite solution containing the precursors, a mixture of lead halide (PbX_2) and an organic halide ($\text{CH}_3\text{NH}_3\text{X}$) ($\text{X} = \text{Cl}, \text{Br}$ or I) dissolved in a common solvent such as dimethylformamide (DMF), dimethyl sulfoxide (DMSO) or gamma-butyrolactone (GBL).^[23] Subsequently, other film deposition techniques such as doctor-blade coating,^[75] inkjet printing,^[76] etc., were also employed. However, the one-step deposition method produces films with large and often difficult to control morphological variations, which results in poor reproducibility and device performance. To gain better control of the crystal formation and growth, the sequential (two-step) deposition method was developed. This technique consists of the deposition of a PbI_2 seed layer that is converted to perovskite by exposing it to a solution of $\text{CH}_3\text{NH}_3\text{I}$ in isopropanol. Although this approach improved the device reproducibility and efficiency at the time, it has two major drawbacks.^[77] The first is the incomplete perovskite conversion and the other is the trade-off between perovskite grain size and surface smoothness which limits the device performance. Attempts to find the best deposition approach led to the development of the dual-source high-vacuum evaporation^[30] and vapor-assisted solution deposition^[78] methods, but the efficiencies were limited to the range of 12 to 15%. To overcome the issues associated with the above methods, especially the one-step and sequential deposition methods, engineering strategies were developed to improve the crystallinity and morphological uniformity of the perovskite films in order to push the device efficiency beyond 15%. These strategies include incorporation of solvent additives,^[79] judicious selection of solvent mixtures,^[80,81] anti-solvent treatment,^[80] solvent annealing,^[82] hotcasting,^[83] etc., thereby achieving efficiencies in the range of 18 to 20%. Figure 1.8 illustrates some of the most common perovskite thin film preparation methods. For all these deposition processes, the grain nucleation and growth are unique to the processing conditions.

The efficiency and stability of the perovskite solar cells have also benefited greatly from the compositional engineering of the active material. As described earlier, for hybrid halide perovskites, the A component is usually a monovalent organic cation [typically methylammonium ($\text{CH}_3\text{NH}_3^+ = \text{MA}^+$) or formamidinium

Figure 1.8: Schematic diagrams of perovskite film deposition methods. **(a)** Single-step solution deposition method. **(b)** Sequential solution deposition method. **(c)** Vapor-assisted solution deposition method. **(d)** Thermal vapor deposition method.^[30] **(e)** Single-step solution deposition method with anti-solvent process engineering.

($\text{HC}(\text{NH}_2)_2^+ = \text{FA}^+$), an atomic cation (typically Cs^+) or a mixture thereof, the B component is often a divalent metal cation (usually Pb^{2+} , Sn^{2+} or a mixture thereof) and the X component is a halide anion (typically Cl^- , I^- , Br^- or a mixture thereof) [23,27,48,49,77,84–86]. Since the 3D perovskite formability is determined by the tolerance factor (t), it gives room for different ion replacements and combinations as long as the tolerance factor is within the $0.8 < t < 1$ range. The initial standard composition for the PSCs has been MAPbI_3 perovskite.^[23] However, due to instability issues and the limitation on the light absorption window, the MA^+ has been replaced with FA^+ and shown to improve the thermal stability and extend the absorption edge from 790 to 840nm and consequently, enhancing the photocurrent (J_{sc}) of devices.^[49] The replacement of MA^+ with Cs^+ on the other hand lowered the absorption onset to 720 nm.^[49] Despite the promising potential of FAPbI_3 , it is found to be structurally unstable under ambient conditions. Importantly, although the A cations do not contribute directly to the electronic band structure, they play significant role in providing structural stability and indirectly influence the bandgap of the material. Attempts to stabilize the perovskite structure led to the mixture of cations at the A position. For instance, the mixed-cation perovskite

Table 1.1: Effective ionic radii organic molecular cations and Shannon ionic radii of inorganic cations as well as the effective ionic radii of common X-site anions used in halide perovskite materials. Adapted from ref^[56,93]. Copyright 2015 Springer Vienna.

Cation (A-site)	Effective ionic radius (pm)	Metal ion (B-site)	Effective ionic radius (pm)	Anion (X-site)	Effective ionic radius (pm)
Ammonium (NH ₄) ⁺	146	Pb ²⁺	119	F ⁻	129
Methylammonium [CH ₃ NH ₃] ⁺ , (MA ⁺)	217	Sn ²⁺	110	Cl ⁻	181
Formamidinium [CH(NH ₂) ₂] ⁺ , (FA ⁺)	253	Ge ²⁺	73	Br ⁻	196
Hydrazinium, [NH ₃ NH ₂] ⁺	217	Mg ²⁺	72	I ⁻	220
Azetidinium [(CH ₂) ₃ NH ₂] ⁺	250	Ca ²⁺	100		
Hydroxylammonium [NH ₃ OH] ⁺	216	Sr ²⁺	118		
Imidazolium [C ₃ N ₂ H ₅] ⁺	258	Ba ²⁺	135		
Ethylammonium [(CH ₃ CH ₂)NH ₃] ⁺	274	Cu ²⁺	73		
Dimethylammonium [(CH ₃) ₂ NH ₂] ⁺	272	Fe ²⁺	78		
Guanidinium [(NH ₂) ₃ C] ⁺	278	Pd ²⁺	86		
Tetramethylammonium [(CH ₃) ₄ N] ⁺	292	Eu ²⁺	117		
Thiazolium [C ₃ H ₄ NS] ⁺	320	Bi ³⁺	103		
3-pyrrolinium [NC ₄ H ₈] ⁺	272	Sb ³⁺	76		
Tropylum [C ₇ H ₇] ⁺	333				
K ⁺	164				
Rb ⁺	172				
Cs ⁺	188				

based on the (FA/MA)PbI₃ system resulted in enhanced phase stability, increased light harvesting and carrier lifetime.^[44] A much pronounced structural stability was also achieved by mixing both the A-site cations and the X-site anions, forming the (FA/MA)Pb(I/Br)₃ system. Several other combinations involving triple or quadruple A-cation mixtures and B-cation mixtures have been studied.^[47,87,88] A list of A-, B-, and X-site ions that are or can be used in different combinations to form perovskite structures are given in Table 1.1 with their ionic radii. Interestingly,

besides the first certified PCE, all the National Renewable Energy Laboratory (NREL) certified PSC records are based on the mixed perovskite composition, either mixed cations or anions or both.^[89] Furthermore, the most recent approach in stabilizing perovskites is the mixed-dimensionality strategy which involves the mixing of 2D structures with 3D structures.^[90–92] Over all, it has been shown that compositional engineering of the perovskite material has several significant advantages such as higher device performance, increased stability, enhanced carrier charge transport, broad band-gap tunability, grain boundary passivation and reduction of J - V hysteresis.^[56,89]

1.5.3. Device Architecture Engineering

The advent of the solid-state PSC began the device architectural evolution which has been instrumental in the remarkable achievements to date. The device structures evolved from the typical DSSC structure which is composed of several-micron thick mesoporous TiO_2 layer that is sensitized with the absorber material (hybrid perovskite) and capped with the hole conductor layer (Figure 1.3(a)).^[23] The mesoporous semiconducting TiO_2 layer served as an electron selective/transport material (ETM) and also as a large surface scaffold to induce nucleation in the perovskite material. The amount of absorber in this device structure is usually very low and as a result, the hole conductor material penetrates to fill the remaining pores in order to form a continuous morphology to aid effective charge separation and collection. The low amount of absorber material also limits its light absorption efficiency. As mentioned in the previous section, the demonstration of ambipolar charge transport capabilities of the perovskite absorbers and the long-range balanced electron and hole diffusion observed, showed that the perovskites have broader potentials than just being used as sensitizers.^[27,28,64,70] This understanding prompted the design and evolution of new device geometries with thicker perovskite films as active layer, as illustrated in Figure 1.3(b-d). The thickness of the mesoporous titania/alumina scaffold was also reduced to few hundreds of nanometers such that the mesoporous layer is fully infiltrated and capped by a thicker layer of the perovskite absorber (Figure 1.3(b-c)). Notably, the conductivity of the perovskite absorber improved significantly due to the increased amount of material that infiltrates and covers the pores, forming a continuous and uniform film. This understanding paved the way to the simplification of the device structure thereby designing the planar device geometry as shown in Figure 1.3(d). Subsequently, a large variety of device architectures

emerged, most of which consisted of the intrinsic perovskite semiconductor layer (i) being sandwiched between an electron-selective (n) and hole-selective (p) layer. This evolution of device structures has been accompanied by significant improvement in power conversion efficiency and/or stability.

All the device structures can be categorized into two primary structures depending on which charge-selective contact or electrode is encountered first by the incident light. In the original device configuration, the electron-selective material (n) or the cathode encounters the incident light first and therefore is referred to as the conventional n-i-p geometry. Therefore, geometries in which the hole-selective material (p) or the anode encounters the incident light first are referred to as the inverted p-i-n geometries. These geometries can either be classified as mesoscopic or planar structures depending on whether they are composed of a mesoporous layer or not as shown in Figure 1.9.

Figure 1.9: Schematic diagrams of the most common perovskite solar cells. **(a,b)** The conventional n-i-p device architectures in the (a) mesoscopic and (b) planar device geometries. **(c,d)** The inverted p-i-n device architectures in the (c) mesoscopic and (d) planar device geometries.

1.5.4. Contact and Interface Engineering

The charge-selective contacts, i.e., the electron transporting material and hole transporting material serve various roles in boosting the stability and efficiency of the devices. They act as physical and energetic barrier between the photoanode (photocathode) and the perovskite layer to block hole (electron) transfer to the photoanode (photocathode). They also facilitate the charge extraction, influence the open circuit voltage (V_{oc}) by determining the splitting of the quasi Fermi-energy

levels of the perovskite, and prevent the degradation at the perovskite-metal electrode interfaces.^[94]

The most common device geometry for PSCs utilizes TiO₂ (compact and mesoporous layer) as the ETM and Spiro-OMeTAD as the HTM. TiO₂ is usually sintered at high temperatures (> 400 °C) which makes it incompatible with flexible substrates and perovskite-based tandem devices.^[95] TiO₂ has been found to have two critical drawbacks, the first is the intrinsic low mobility and creation of deep defect traps under UV light, which results in charge accumulation, recombination losses and severe *J-V* hysteresis. This has led to the introduction of other oxides such as Al₂O₃.^[27] Similarly, Spiro-OMeTAD has been the most widely used HTM in the fabrication of high-efficiency PSCs. Like TiO₂, Spiro-OMeTAD has several drawbacks including low hole mobility, complex purification process which makes it expensive, low solubility, etc. The drawbacks of these charge-selective electrodes and the quest to enhance device stability and efficiency, reduce manufacturing cost, improve interfacial imperfection and reduce charge recombination at the perovskite-electrode interfaces have led to the development of several different charge-transport materials and interfacial buffer layers. It has also resulted in doping of the ETM and HTM. For instance, n-type doping of TiO₂ with dopants such as Sn, Nb or Mg was used to match the conduction band (CB) edge of the TiO₂ with that of the perovskite absorber, leading to enhanced electron injection, suppressed recombination, and significantly improved the *V*_{oc} of the devices.^[96–98]

As mentioned above, a vast number of ETMs and HTMs have been incorporated in the PSCs. Some of these are newly developed and others evolved from the organic PV technology. The most commonly used ETMs other than TiO₂ and Al₂O₃ are SnO₂,^[99,100] ZnO^[101,102] and ZrO₂^[103,104] which have been applied to either improve charge extraction and/or stabilize the device. Most of the top-performing PSCs with PCEs above 20% are based on TiO₂ and SnO₂ ETMs with SnO₂ yielding the most stable devices.^[87,95,99] Fullerene derivatives like PCBM and fulleropyrrolidine with a triethylene glycol monoethyl ether side chain (PTEG-1) are examples of some of the organic ETMs that are used in PSCs.^[105]

For the HTMs, the commonly used materials can be categorized into three groups: small molecules [typically, Spiro-OMeTAD doped with 4-tert-butylpyridine (t-BP) and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI)], conductive organic polymers [e.g. poly(triarylamine) (PTAA), poly(3-

hexythiophene-2,5-diyl) (P3HT), (poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS), PCP-Na,^[106] etc.] and inorganic materials such as CuSCN,^[107,108] CuI^[109], NiO,^[110,111] etc. However., the top-performing PSCs with PCEs above 20% are normally based on Spiro-OMeTAD and PTAA.^[86,87] Since most of these organic transport layers have low mobilities and improper band alignment, their transport properties and energy levels are usually enhanced via doping engineering.

Besides contact engineering, interface and surface engineering or passivation has been one of the most efficient strategies employed to significantly stabilize and directly improve the V_{oc} and indirectly also the FF of the PSCs.^[112,113] For the n-i-p (p-i-n) geometry, the interfaces and surfaces are: (i) the interface between the transparent conductive oxide or the bottom electrode and the ETM (HTM); (ii) the interface between the ETM (HTM) and the perovskite; (iii) the surface of the perovskite and grain boundaries; (iv) the interface between the perovskite and the HTM (ETM); (v) the interface between the HTM (ETM) and the top electrode, and (vi) the surface of the top electrode.^[112] Depending on the device geometry or processing order, these interfaces are completely different. For example, the kind of interface present between the ETM and the perovskite depends on whether the ETM or the perovskite is the bottom layer.

A lot has been done to passivate these interfaces and surfaces either by chemical or physical processes, depending on the kind of defects (point defect or surface and grain boundary charge traps) present. While the physical processes involved the isolation of the functional layers from each other or from the external environment using buffer interlayers, the chemical processes mainly involved the use of acid-base adducts to treat the surfaces or grain boundaries in order to reduce the defect traps which are mostly under-coordinated ions. UV ozone, O_2 plasma and functional materials like graphene, polyethylenimine (PEI), and polyethylenimine ethoxylated (PEIE) have been used for this purpose.^[99] To modify the ETL/perovskite interface, electronic coupling and chemical binding have been taken into consideration and based on these, materials like fullerene C_{60} and its derivatives, organic self-assembled monolayers (SAMs), and various inorganic interlayers have been successfully employed to reduce traps and recombination.^[114–117] Surface modification of for example TiO_2 has been achieved via chlorine-capping of the TiO_2 colloidal nanocrystals from which the TiO_2 -Cl layer is found to mitigate interfacial recombination and improve interface binding and device performance.^[95] To passivate the perovskite surface and grain boundaries, one of

the strategies used is self-passivation or the so-called nonstoichiometric approach. For this, excess PbI_2 or MAI is used to improve the crystallinity, grain sizes and also, adjust the electronic properties at the grain boundaries and in the bulk of the perovskite film.^[118–121] Other strategies for the grain boundary passivation include the use of bifunctional organic molecules, halide salts or additives of Br^- , Cl^- , I^- , O^{2-} , etc.^[122–124] In addition to the grain boundary passivation agents, additives such as PCBM and its derivatives, Lewis bases, organic materials with hydrophobic groups, and atmospheric oxygen have been found to effectively passivate the defect traps.^[73,74,125–127] In addition, since the most commonly used metal electrodes (i.e. Au, Ag, Al) are known to diffuse through the transport layers and even to the perovskite layer, few reports have demonstrated the passivation of the perovskite/HTM interface using MoOx , Al_2O_3 or ultrathin layer of Ni to achieve substantial increase in device performance and stability.^[128–130]

1.6. Outline of thesis

Although tremendous work has been done to develop the perovskite field to the present state, further understanding is needed to improve these materials and the optoelectronic devices if the goal of commercialization of the perovskite photovoltaic technology is to be achieved. Thus, the work presented in this thesis contributes to the understanding of the photophysics and opto-electronic properties of these materials and their application in solar cells. The thesis has four chapters besides the introduction, each focusing on different aspects of the material and device physics. Chapter 2 to 4 is on Pb-based perovskites while chapter 5 is on Sn-based perovskite. Chapter 2 focuses on defect passivation in the presence of atmospheric air, chapter 3 is on the scalable fabrication of high-quality thin films while chapter 4 investigates the role of device architecture on device performance. In chapter 5, the effect of strontium insertion on the physical and photophysics of the Sn-based material is examined. The overview of each chapter is given below:

Chapter 2: Single crystals of methylammonium lead tribromide (MAPbBr_3) were synthesized and characterized using photoluminescence spectroscopy. The surface recombination rate (or surface trap state density) in the single crystals have been demonstrated to be fully and reversibly controlled by the physisorption of oxygen and water molecules, leading to a modulation of the photoluminescence intensity by over two orders of magnitude. An unusually low surface recombination velocity (SRV) of 4 cm/s (corresponding to a surface trap state density of 10^8 cm^{-2}) have

been recorded in this material, which is the lowest value ever reported for hybrid perovskites. In addition, a consistent modulation of the transport properties in single crystal devices is evidenced. These findings highlight the importance of environmental conditions on the investigation and fabrication of high quality, perovskite-based devices, and offer a new potential application of these materials for detecting oxygen and water vapor.

Chapter 3: 2D 2-phenylethylammonium lead iodide (PEA_2PbI_4) thin films deposited by scalable doctor-blade coating technique are used as a growth template to fabricate high-quality 3D FAPbI_3 perovskite thin films, which are obtained by organic cation exchange. The structural, morphological and optical properties of these converted 3D FAPbI_3 perovskite films are compared to the directly deposited 3D FAPbI_3 films. The comparison showed that the converted FAPbI_3 thin films are compact, smooth, highly oriented and exhibit better structural stability than the directly deposited 3D films. These results not only underscore the importance of the employed deposition techniques in the formation of highly crystalline and stable perovskite thin films but also reveal a strategy to easily obtain very compact perovskite layers using doctor-blade coating.

Chapter 4: The role of the device architecture (i.e. conventional planar n-i-p versus inverted planar p-i-n structure) and the charge-selective interlayer on the photophysical properties of the perovskite absorber and device performance are explored. $\text{FA}_{0.85}\text{MA}_{0.15}\text{PbBr}_{0.45}\text{I}_{2.55}$ (MA = methylammonium, FA = formamidinium) is employed as the perovskite absorber and chloride-capped TiO_2 colloidal nanocrystals ($\text{TiO}_2\text{-Cl}$) and PEDOT:PSS are used as the close-to-the-substrate layers in the conventional and inverted structures, respectively. Extremely different device performances are demonstrated by the two structures. The device with $\text{TiO}_2\text{-Cl}$ displayed a champion PCE of 19.9%, while that with PEDOT:PSS yielded about 15% efficiency. The photophysical and electrical investigations indicated that the $\text{TiO}_2\text{-Cl}$ /perovskite interface has lower number of traps which underlines the importance of interfaces for achieving highly performing perovskite solar cells.

Chapter 5: The influence of strontium (Sr) doping into solution-processed formamidinium tin iodide (FASnI_3) perovskite thin films is investigated. The addition of the Sr^{2+} dopant to the host perovskite is shown to drastically change the morphology of the material but has no significant effect on the structural phase for doping concentrations lower than 10%. Using PL spectroscopy, it is observed that

for doping contents below 15%, the film is heterogeneously doped and strontium predominantly resides at the surface of the film. Above 15% of Sr, the bulk of the material is significantly doped. These results show that Sr doping into FASnI_3 perovskite can be a route for the attainment of new perovskites with interesting physical properties.

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CHAPTER 2

Ultrahigh Sensitivity of Methylammonium Lead Tribromide Perovskite Single Crystals to Environmental Gases

Abstract

One of the limiting factors to high device performance in photovoltaics is the presence of surface traps. Hence, the understanding and control of carrier recombination at the surface of organic-inorganic hybrid perovskites is critical for the design and optimization of devices with this material as the active layer. Here, we demonstrate that the surface recombination rate (or surface trap state density) in methylammonium lead tribromide (MAPbBr₃) single crystals can be fully and reversibly controlled by the physisorption of oxygen and water molecules, leading to a modulation of the photoluminescence intensity by over two orders of magnitude. We report an unusually low surface recombination velocity (SRV) of 4 cm s⁻¹ (corresponding to a surface trap state density of 10⁸ cm⁻²) in this material, which is the lowest value ever reported for hybrid perovskites. In addition, a consistent modulation of the transport properties in single crystal devices is evidenced. Our findings highlight the importance of environmental conditions on the investigation and fabrication of high-quality perovskite-based devices and offer a new potential application of these materials for detecting oxygen and water vapor.

This chapter is based on the publication:

H.-H Fang, **S. Adjokatse**, H. Wei, J. Yang, G. R. Blake, J. Huang, J. Even, and M.A. Loi, *Science Advances*, **2016**, 2(7), e1600534.

2.1. INTRODUCTION

Like other more traditional semiconductors, the stability and performance of hybrid perovskite devices are strongly dependent on the defect states and on the film morphology, which have a great effect on the carrier lifetime.^[1–4] Great effort has been devoted to produce large-grained perovskite films, improving their crystalline quality.^[5–7] In single crystals of MAPbI₃ and MAPbBr₃, carrier diffusion lengths over one hundred micrometers and bulk trap state densities of the order of 10⁹ to 10¹⁰ per cubic centimeter have been demonstrated.^[8,9] Surface recombination represents an important loss of carriers, and often plays a decisive role in determining the optoelectronic properties of semiconductors, where interfaces between different materials are crucial for the device functioning. A low surface recombination rate is a pre-requisite for approaching the thermodynamic efficiency limits for solar cells and for devising other efficient optoelectronic devices. Thus, understanding and controlling the recombination of carriers at the surface of perovskite crystals is critically important for designing and optimizing devices.

Recently, several studies have shown that the interaction between hybrid perovskite materials and their environment has a significant impact not only on the perovskite morphology or photostability but also on the optoelectronic properties.^[10–13] For instance, Grancini and coworkers reported that moisture and possibly oxygen molecules can cause perovskite lattice strain and a shift in the PL spectrum.^[14] Tian and co-workers showed a PL yield enhancement in oxygen, attributed to a photochemical reaction located both at the surface and in the bulk of MAPbI₃.^[12] Similarly, Müller *et al.* found that water infiltration into MAPbI₃ films increases its ionic conductivity.^[13] However, the interaction mechanism is only partially understood and subject to debate. In polycrystalline thin films, the intrinsic response of the optoelectronic properties to the environment may be shielded by the microstructure quality and non-crystalline domains. On the other hand, in single crystals, grain boundaries and non-crystalline domains are absent, making them the ideal platform to probe the intrinsic material properties as well as the surface recombination, hence providing insight into the mechanisms for improving perovskite polycrystalline thin film solar cells.

Here, we investigate the optical properties of methylammonium lead tribromide (MAPbBr₃) single crystals by single-photon and two-photon excitation and demonstrate an unusually low surface recombination velocity (SRV) of 4 cm s⁻¹ in these crystals. The SRV can be modulated by the physisorption of O₂ and H₂O

molecules. Thus, we reveal that the photophysical properties of MAPbBr₃ single crystals are ultrasensitive to their environment. Moreover, the tunability of the photophysical and charge transport properties of the MAPbBr₃ single crystals is fully and quantitatively reversible. This phenomenon could therefore be exploited for the development of sensitive perovskite-based gas detectors.

2.2. EXPERIMENTAL DETAILS

Materials

All reagents were purchased from commercial vendors and used as received. Test gases [N₂, He, Ar, CO₂, and a mixture of O₂ (20%) and He (80%)] were obtained from Linde Gas. Other reagents used were lead bromide (PbBr₂) (>98%; Sigma-Aldrich), methylamine hydrobromide (>98.0%; Alfa Aesar, TCI), *N,N'*-dimethylformamide (DMF) (>99.8%; Alfa Aesar), and dichloromethane (DCM) (99.7%; Alfa Aesar).

Growth of MAPbBr₃ single crystals

MAPbBr₃ single crystals were prepared from solution by inverse temperature crystallization (ITC) or antisolvent vapour-assisted crystallization (AVC). In the ITC method, lead bromide (PbBr₂) and methylamine hydrobromide (MABr) with a molar ratio of 1:1 were dissolved in DMF to form a solution and the MAPbBr₃ crystals were slowly crystallized at 60 °C. In the AVC method, PbBr₂ and MABr were dissolved in 5 mL DMF solution in a 20 ml vial with a molar ratio of 1:1. The vial was sealed with a punched aluminum foil to allow for DCM to slowly diffuse into the vial. With the vial stored in an atmosphere of DCM, the MAPbBr₃ single crystals slowly grew, reaching a size of a few millimeters after several days.

Optical measurement

PL measurements were performed by exciting the samples with the second harmonic (400 nm) of a mode-locked Ti:Sapphire laser (Mira 900, Coherent). The laser power was adjusted using neutral density filters. The excitation beam was spatially limited by an iris and focused with a 150 mm focal length lens. Fluorescence was collected into a spectrometer with a 50 lines/mm grating and recorded with an Image EM CCD camera from Hamamatsu. The spectra were

corrected for the spectral response of the set up. Time-resolved traces were recorded with a Hamamatsu streak camera working in single sweep mode. The excitation source was the same mode-locked femtosecond laser with a repetition rate of 76 MHz; a pulse picker was inserted into the optical path to decrease the repetition rate of the laser pulses when needed. For the two-photon excited photoluminescence measurement, the fundamental laser pulse from the mode-locked Ti:Sapphire laser was used, and the power density was adjusted by neutral density filters to be $18.5 \mu\text{J cm}^{-2}$.

Charge-transport Measurement.

Electrical contacts were prepared by depositing gold on the largest natural facet of a MAPbBr_3 crystal, in a coplanar configuration. We used a gold microwire as a shadow mask before depositing the gold electrodes. A Keithley 2400 source meter was used for electrical characterization. For the photoconductivity measurements, the top surface of the crystal was illuminated at normal incidence using a laser diode with a wavelength of 405 nm.

2.3. RESULTS AND DISCUSSION

Photoluminescence Modulation Effect in Crystals

The MAPbBr_3 single crystals were prepared from solution by inverse temperature crystallization (ITC) and anti-solvent vapour-assisted crystallization (AVC) methods. The inset of Figure 2.1(A) shows an image of a MAPbBr_3 single crystal with dimensions of $\sim 5 \times 3 \times 1.7 \text{ mm}^3$ grown by the inverse temperature crystallization method. The crystal adopts the cubic $Pm\bar{3}m$ space group at room temperature. Figure 2.1(A) presents the $hk0$ reciprocal lattice plane reconstructed from raw single crystal X-ray diffraction data collected at 295 K. The sharp spots show the high quality of the crystals. A powder diffraction pattern was collected at room temperature (see Appendix A, Figure 2.6) with peaks at 14.92° , 21.11° , 30.07° , 33.71° , 37.11° , 43.05° and 45.77° . Conversion of the peak positions to inter-planar spacings shows that these peaks correspond to the (100), (110), (200), (210), (211), (220), and (300) planes, respectively.

Under ambient conditions, the excitation of the crystal with a 400 nm wavelength femtosecond laser (76 MHz repetition rate) results in strong yellow-

green fluorescence. The corresponding emission peak is located at 556 nm [Figure 2.1(B)], very close to the absorption onset (2.23 eV) as revealed by the photoluminescence excitation spectrum (see Appendix A, Figure 2.7). The crystals show superior photostability under the same ambient conditions; the PL intensity remain constant even after more than 3.5 hours of continuous optical pumping (see Appendix A, Figure 2.8). However, we found that the PL intensity of the MAPbBr₃ crystal can be modulated when the crystals are exposed to different environments. For instance, when the atmospheric pressure is changed, the PL intensity also changes instantaneously. The PL intensity is reduced by more than two orders of magnitude when the sample chamber is evacuated from atmospheric pressure to 1.3×10^{-4} mbar, as shown in Figure 2.1(B). The correlation between the emission intensity and the controlled pressure is clearly seen when the gas pressure is further reduced to 10^{-4} mbar (see Appendix A, Figure 2.9). It is noticeable that the PL intensity reverts to its original magnitude when the chamber is refilled with air to ambient pressure, clearly showing the reversibility of these “deactivation” and “activation” processes.

Figure 2.1(C) shows the reversible variation of the PL intensity with the chamber pressure. The PL intensity decreases to 10 % within 120 s (160 s - 280 s) when the chamber is evacuated. It further decreases slowly to 0.4% of the initial intensity in air after about 1750 s in vacuum. The observed PL modulation effect in the crystals is very high, thus, macroscopically visible. Figure 2.1(D) shows the normalized PL spectra corresponding to various times in the PL intensity plot in Figure 2.1(C), where it is evident that the PL in vacuum is only slightly blue-shifted compared with that in air. The increased surface recombination in vacuum leads to a lower fraction of photogenerated carriers to diffuse toward the interior of the crystal, and therefore in this case, the PL is less affected by reabsorption. We note that the PL modulation effect is observed in both crystals prepared by ITC (Figure 2.1) and AVC methods (see Appendix A, Figure 2.10) as well as in crystals cleaved inside a N₂ filled glove box (see Appendix A, Figure 2.11).

To understand how the presence of air affects the PL, we investigated the dynamics of photoexcitation in the MAPbBr₃ single crystals in different environments [Figure 2.1(E) and 2.1(F)]. Under an excitation power density of $0.71 \mu\text{J cm}^{-2}$ (400 nm wavelength), the decay time of the crystal measured in air shows an initial fast component with lifetime of $\tau_1 \approx 59$ ns (77.2 %) and a slower component with a lifetime of $\tau_2 \approx 818$ ns (22.8 %) [Figure 2.1(G)]. The underlying mechanism for the extremely long carrier lifetime in the hybrid perovskite is not

fully understood. Recently, Rashba spin–orbit coupling has been proposed as one of the possible explanations.^[15]

Figure 2.1: X-ray diffraction pattern and optical properties of MAPbBr₃ single crystals. (A) *hk0* reciprocal lattice plane reconstructed from MAPbBr₃ single crystal X-ray diffraction data at room temperature. Inset: Image of one of the measured crystals grown from solution. (B) Photoluminescence spectra in vacuum and in air (the PL intensity in vacuum is two orders of magnitude lower than in air). (C) Variation in photoluminescence peak intensity of MAPbBr₃ crystals in air - vacuum - air environment. (D) Normalized photoluminescence spectra at different times in (C). (E and F) Two-dimensional pseudo-color plots of time-resolved photoluminescence spectra taken in air and vacuum with an excitation power density of 0.71 μJ cm⁻². (G) Decay of the photoluminescence at a wavelength of 560 nm in air and vacuum.

In vacuum, the PL lifetime of the MAPbBr₃ single crystals is much shorter [Figure 2.1(G)] and its determination is limited by the instrumental resolution in this configuration. A lifetime of 22 ns is measured using a shorter time window (see Appendix A, Figure 2.12). Similar to our observations for steady-state PL, the time-resolved PL reverts to its initial behaviour a few minutes after the chamber is refilled with air. This ability to ‘reset’ the darkening as effect of air exposure suggests that the gas molecules are physisorbed rather than chemisorbed on the crystal surface.

Physisorption of Gas Molecules

To determine which gas molecules are responsible for the observed optical behaviour and to assess the influence of atmospheric gas adsorption on the crystal surface, the PL intensity variation was monitored in different gas environments. Optical spectroscopic measurements were performed in the following atmospheres: moist air, dry N_2 , He, CO_2 , a mixture of O_2 (20 %) and He (80 %), moist N_2 , moist O_2 and vacuum. Before each gas exposure and measurement, the sample chamber containing the crystal was evacuated to a pressure from 10^{-4} to 10^{-5} mbar and left in vacuum for about 30 min before filling the chamber with the test gas. In the case of the measurements performed in vacuum, the crystal with the 400 nm excitation laser beam incident was left in the chamber for an additional 30 min. In each of the measurements, the laser with a pulse repetition rate of 1.4 MHz was kept at a constant fluence of $0.71 \mu J cm^{-2}$. The PL of the sample was monitored every 10 seconds.

Figure 2.2: Effect of exposure to different gaseous environments on the PL intensity of MAPbBr₃ single crystals. (A) PL intensity as a function of time in vacuum, dry N_2 , dry CO_2 and dry Ar. (B) PL intensity as a function of time on exposure to air, dry O_2 and moist N_2 . In each panel, the blue shaded area indicates vacuum. The crystal was excited at 400 nm with excitation power of $0.71 \mu J cm^{-2}$.

The PL intensity variation as a function of time for the single crystal under illumination in different gas atmospheres is shown in Figure 2.2. Exposure of the crystal to dry N₂, CO₂ or Ar [Figure 2.2(A)] has no influence on the PL intensity. However, the PL intensity increases rapidly in the presence of air, dry O₂ and moist N₂, as shown in Figure 2.2(B). It is worth noting that the most rapid and intense PL enhancement is observed in the air-exposed crystal, whereas the PL intensity recovers much more slowly when in dry O₂ and moist N₂. These data clearly indicate that the PL enhancement is due to O₂ and H₂O molecules. Moreover, the presence of a combination of oxygen and water molecules further promotes the activation process to a level that is very similar to that observed in air (see Appendix A, Figure 2.13). All these intensity variations in different gases occur with essentially no difference in the wavelength and shape of the emission peak (a spread of about 5 nm in the peak wavelength can be seen in the normalized PL spectra reported in Appendix A, Figure 2.14). The measurements reported here are highly reproducible and independent of the sample history. Thus, the effect of gas exposure can be reset when the chamber is evacuated. This also implies that the interaction between the defect sites and the gas molecules is weak (they are physisorbed) but dictates the optical emission of the material.

Bulk and Surface Optical Properties of Single Crystals

The results reported in the previous section demonstrate that O₂ and H₂O molecules passivate the charge traps in MAPbBr₃ single crystals. However, it is unclear where the traps are located; whether at the crystal surface or in the bulk of the crystal. To selectively probe the bulk properties of our crystals, an 800 nm femtosecond laser was used to excite the crystal with photon energy below the bandgap energy. Figure 2.3(A) shows the time resolved PL under excitation at 800 nm with a photocarrier density of around $1.9 \times 10^{13} \text{ cm}^{-3}$. Under two-photon excitation, the laser can penetrate deep into the bulk and excite the interior region of the crystal [see inset of Figure 2.3(B)]. Therefore, the bulk properties can be measured in this way, neglecting the contributions from the surface.^[16] The steady state emission peak wavelength is slightly redshifted (566 nm) compared to the emission when the crystal is excited with at 400 nm (556 nm). The lifetimes extracted from the time-resolved PL curves as shown in Figure 2.3(B) are $\tau_1 = 34 \text{ ns}$ and $\tau_2 = 4.5 \text{ }\mu\text{s}$. Figure 2.3(C) shows the two-photon excited PL spectra in vacuum and in ambient air. Unlike in the 400 nm laser excitation experiment, the PL intensity difference is

much smaller under two-photon excitation. The PL intensity variation under two-photon excitation is within the uncertainty of the measurement (see Appendix A, Figure 2.15). The fact that the optical properties of the bulk of the crystal are less affected by O_2 and H_2O molecules allows us to conclude that the majority of the trap states passivated by O_2 and H_2O are localized near the crystal surface.

Figure 2.3: Two-photon excited fluorescence in MAPbBr₃ crystal and single-photon excited optical properties of a cleaved crystal surface. (A) 2D pseudo-colour plot of two-photon (800 nm) excited TRPL measured in air. (B) TRPL dynamics [extracted from measurement reported in (A)]; the fit gives lifetimes of $\tau_1 = 34$ ns and $\tau_2 = 4.5$ μ s. Inset: Image of MAPbBr₃ crystal under two-photon excitation (TPE). (C) TPE PL spectra measured in air and vacuum. (D) 2D pseudo-colour plot of TRPL of a freshly cleaved crystal in air; under single-photon excitation (400 nm). The emission peak wavelength as a function of time is indicated by the red line. (E) Calculated photocarrier density profile at various times under single-photon excitation (SPE). Inset: Image of MAPbBr₃ crystal under SPE. (F) Calculated PL spectra at various times after excitation.

Under the single-photon excitation, the penetration depth of the laser in the crystal is only ~ 150 nm.^[17] Thus, only optical properties in the near-surface region

up to the penetration depth are probed. Therefore, the photocarrier recombination is observed to be strongly affected by the surface properties. Figure 2.3(D) shows a 2D pseudo-colour plot of the time-resolved PL of a crystal freshly cleaved in air, where a red line indicates the variation of the wavelength of the emission peak as a function of time. The PL peak is red-shifted from 546 nm to 560 nm in about 25 ns. This behaviour contrasts with what is observed for two-photon excitation, where the emission peak wavelength remains unchanged with time. Similar behaviour was recently reported by Yamada *et al.* for MAPbI₃ crystals, where they suggested that the redshift originates from the diffusion of photoexcited carriers from the surface to the interior of the crystal.^[18] To verify this, we calculated the photocarrier distribution and simulated the PL spectrum at various times after single-photon excitation (see Appendix A, Figure 2.16 for details). Figure 2.3(E) presents the calculated photocarrier density profiles as a function of distance from the crystal surface. While the carrier density near the surface decreases with time, the bulk carrier density increases due to the long carrier diffusion length. The calculated PL spectrum [Figure 2.3(F)] correctly reproduces the experimental results, confirming that the redshift originates from carrier diffusion.

Low Surface Recombination Velocity (SRV) in Hybrid Perovskites

The time evolution of the density of carriers after their generation is governed by their diffusion and recombination. Recombination mechanisms include Shockley–Read–Hall processes, radiative recombination, Auger recombination as well as surface and/or interface recombination; all these mechanisms contribute directly or indirectly to the observed PL recombination dynamics. Although there are several different recombination channels, it is possible to classify them into two categories: bulk recombination and surface recombination, as illustrated in Figure 2.4(A). The effective lifetime of the carriers, which can be obtained from TRPL, is described as the sum of the recombination rates: $1/\tau = 1/\tau_b + 1/\tau_s$, where τ_b is the bulk recombination lifetime and τ_s is the surface recombination lifetime.

The bulk recombination lifetime τ_b can be determined from the TRPL measured by two-photon excitation. Our analysis in the previous section suggests that the two-photon excitation corresponds to a low injection regime (the estimated photocarrier density is $1.9 \times 10^{13} \text{ cm}^{-3}$). It is noted that the carrier lifetime is not significantly affected by reabsorption and reemission effect; measurements performed in transmission and reflection geometry give rise to similar results. The

bulk recombination rate is estimated to be $1/\tau_b = 2.2 \times 10^{-5} \text{ s}^{-1}$ using the lifetime of $4.5 \text{ } \mu\text{s}$ measured by two-photon excitation. Furthermore, using single-photon excitation (see previous section), the effect of surface states in the single crystals can be quantified by extracting the SRV (S) using the following equation.^[19]

$$\frac{1}{\tau_s} = \frac{2\alpha^2 D}{1 + \sqrt{1 + 8\alpha^2 D^2 / S^2}}$$

where α is the absorption coefficient at the excitation wavelength and $D = \mu kT/q$ is the carrier diffusion coefficient. This expression is applicable if the sample thickness d is much larger than the optical penetration depth α^{-1} , which is the case for the single-photon excitation study on our crystals. With the above expression, an $S = 4 \text{ cm s}^{-1}$ is obtained for crystals with pristine surface, giving a carrier mobility of $\mu = 206 \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$, comparable to the value measured with the time of flight (ToF) method.^[20] Also, an effective lifetime of $2.3 \text{ } \mu\text{s}$ (see Appendix A, Figure 2.17) is measured when a low excitation fluence of 10 nJ cm^{-2} is used. The above general expression reduces to $1/\tau_s = \alpha S / \sqrt{2}$ for small S values, showing that the result is robust toward variation of the charge carrier mobility. An SRV (S) = 2.9 cm s^{-1} is obtained if $1/\tau_s = \alpha S$ is used as proposed by Ahrenkiel and Dashdorj.^[21] This is the lowest SRV value ever reported for hybrid perovskites (3 orders of magnitude lower than previously reported values).^[22] It is also much lower than the SRV values for detector grade semiconducting crystals such as Silicon ($2 \times 10^4 \text{ cm s}^{-1}$) and Germanium (1300 cm s^{-1}).^[23] It is noteworthy that the surfaces of these MAPbBr₃ crystals are not intentionally passivated.

The SRV can be described using the equation $S = \sigma v_{th} N_t$,^[24] where $v_{th} \approx 3.7 \times 10^7 \text{ cm s}^{-1}$ is the carrier thermal velocity, $\sigma \approx 10^{-15} \text{ cm}^2$ is a typical recombination surface cross-section in semiconductors, and N_t is the number of recombination centers per square centimeter. Under these assumptions, we deduce the surface density of electronic defects to be less than 10^8 cm^{-2} . As discussed above, the PL lifetime is shortened to 22 ns when the sample is exposed to vacuum. Under this condition, the calculated SRV increases to $S = 890 \text{ cm s}^{-1}$, corresponding to a surface density of defect states of $2.4 \times 10^{10} \text{ cm}^{-2}$, which is two-orders of magnitude higher than that in air. The effective PL lifetimes for large crystals are plotted with different carrier diffusion coefficients, D and bulk lifetimes, τ_b in Figure 2.4(B). We found that the single-photon excitation PL lifetime in bulk crystals is mainly limited by the SRV and thus, by the density of surface trap states. When the SRV

varies from 1 cm s^{-1} to 10^4 cm s^{-1} , the PL lifetime also varies from microseconds to nanoseconds. This further indicates that perovskite materials may have great potential for detecting oxygen and water vapors.

Figure 2.4: Effect of surface recombination on the optical properties of MAPbBr₃ crystals. (A) Schematic showing photoexcitation and deep levels within the forbidden gap in proximity to the surface. (B) Photoluminescence lifetime in bulk single crystals as a function of surface recombination velocity for various carrier diffusion coefficients and bulk lifetimes. (C) Photoluminescence lifetime in polycrystalline thin films or small crystals for various surface recombination velocities.

One of the most attractive features of hybrid perovskites is their ability to form very good polycrystalline thin films by low temperature solution processes for cheap mass production of solar cells. Precise knowledge of the surface recombination effect in polycrystalline thin films as well as in colloidal perovskite nanocrystals is therefore of high interest for the improvement of perovskite devices. Here, we assumed that surface traps at the thin film grain boundary and/or at the nanocrystal surface are of the same nature as the ones in the single crystals. Given that grain boundaries and the surfaces of each grain have the same concentration of recombination centers per unit area, the PL lifetime as a function of the grain size in the film or nanocrystal can be described by the equation^[22]

$$\frac{1}{\tau_s} = \frac{1}{\tau_b} + \frac{2}{\frac{d}{S} + \frac{1}{D} \left(\frac{d}{\pi}\right)^2}$$

where d is the size of the grain in the film or nanocrystal, S is the surface recombination velocity and D is the carrier diffusion coefficient. This expression is applicable if the sample thickness d is small such that the carriers can easily diffuse from one surface to the opposite surface, which is the case for single-photon excitation studies on thin films. Figure 2.4(C) displays the PL lifetime as a function of grain size at different SRVs. In contrast to bulk crystals, the grain size plays a major role [Figure 2.4(B)] and previous equation). For small grain size d , the effective PL lifetime approaches the bulk recombination lifetime. This occurs only if the surface of the perovskite material is well passivated, so that the surface state density is much lower than that of the bulk defect states. In the case where the thin film has the same bulk recombination lifetime as the single crystal and the grain size is about 1 μm , the SRV would be less than 1 cm s^{-1} , corresponding to a surface trap density of $3.7 \times 10^7 \text{ cm}^{-2}$.

Electronic Properties of Single Crystals

To directly evaluate how the electronic properties are modulated by the interaction between ambient gas molecules and the defect sites, we proceeded to investigate the charge-transport properties of MAPbBr₃ single crystal devices in vacuum and air. For this purpose, we fabricated devices by evaporating Au electrodes (40 nm) on the single crystals with channel length of 120 μm , as illustrated in Figure 2.5(A-C). Figure 2.5(D) shows the measured current as a function of applied bias with and without illumination (405 nm) both in air and vacuum. At an applied bias of

1.5 V, the current obtained in vacuum is about 40 nA and increases to 50 nA after air-exposure. A similar but larger effect is observed in the presence of the illumination; the current increases from 10 μ A in vacuum to 24 μ A in air. The current variation is reversible when the device is re-measured under vacuum. It is important to note that the change in photocurrent is much larger than that of the dark current. The current in the crystal can be expressed as: $I = I_b + I_s$, where I_b is the bulk contribution and I_s is the current near the surface. Due to the short penetration depth of the incoming 405 nm light beam, most of the photogenerated carriers are located close to the surface rather than in the bulk. We indeed observed that the photocurrent is easily modulated by exposing the crystal surface to air or vacuum, confirming that the surface trap sites play an important role in determining the optoelectronic properties of MAPbBr₃ single crystals.

Figure 2.5: Electronic properties of MAPbBr₃ single crystal (SC) devices. (A) Structure of the SC device for I-V measurement. (B) Side-view and (C) top-view of a SC device. (D) Current-voltage curves of the MAPbBr₃ SC device under laser illumination in air and in vacuum. (E) Dark-current of the MAPbBr₃ SC device in air and vacuum.

The oxygen and water molecules have been shown to effectively modulate the optoelectronic properties of MAPbBr₃ single crystals. Recently, Tian *et al.* reported that trapping sites in MAPbI₃ can be deactivated by a photochemical reaction involving oxygen and causing a nonreversible PL enhancement.^[25] It should be emphasized that the interaction between gases and perovskites is strongly dependent on both the chemical nature of the material and the local composition. The PL modulation in MAPbBr₃ single crystals is fast and fully reversible, thus it is reasonable to assume that it is because of physical processes (physisorptions) rather than photochemical reaction. Meanwhile, the MAPbBr₃ crystals show high photostability under ambient condition (see Appendix A, Figure 2.8), in contrast to MAPbI₃.^[26] In a recent study combining experiments and modelling, it has been shown that electrons are trapped by Pb²⁺ cations in MAPbBr₃ and related compounds.^[27] Loss of bromide at the surface of the perovskite leads to vacancy sites, and to undercoordination of the Pb ion, resulting in a net positive charge at the crystal surface. It then creates favourable conditions for coordination with electron-rich molecules such as Lewis bases, for example, thiophenes.^[28] Such defects have been observed in low-temperature scanning tunneling microscopy studies of MAPbBr₃ crystals.^[29] Thus, a possible reason for the observed PL modulation effect is that the reversible physisorption of O₂ and H₂O acts as a kind of “molecular gating” that donates electron density to the Pb²⁺ cation. This helps to effectively neutralize the excess positive charges and therefore to drastically modulate the surface recombination rate in MAPbBr₃ single crystals.

2.4. CONCLUSION

In summary, we have synthesized MAPbBr₃ single crystals with an extremely low surface recombination rate. The measured SRV rate is so far the lowest reported in hybrid metal halides perovskites. We have observed that the PL properties of the crystals can be drastically modulated by exposing them to different gases. In this way, the surface state density can be controlled, and the process is fully reversible. These results have important implications for the design and fabrication of future devices under different environmental conditions. In particular, the large variation in the photoluminescence intensity and lifetime observed in the present study could provide a basis for the application of hybrid perovskites as gas detectors. Therefore, our results not only shed light on the defect physics of hybrid perovskites but also offer a new route toward tailoring their physical properties by defect engineering.

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APPENDIX A

This appendix includes supplementary information that supports the main results discussed in this chapter.

Figure 2.6. Powder X-ray diffraction pattern of crushed MAPbBr₃ crystals.

Figure 2.7. Photoluminescence excitation (PLE) spectrum and photoluminescence (PL) of a MAPbBr₃ single crystal measured at room temperature in ambient air.

Figure 2.8. Photoluminescence intensity as a function of illumination time at room temperature in ambient air. The excitation power is $0.71 \mu\text{J cm}^{-2}$.

Figure 2.9. Photoluminescence spectra taken at different vacuum levels. The excitation power is $0.71 \mu\text{J cm}^{-2}$.

Figure 2.10. Photoluminescence spectra of crystals prepared by the antisolvent vapour-assisted crystallization (AVC) technique in vacuum and air. The excitation wavelength is 400 nm and the excitation power is $0.71 \mu\text{J cm}^{-2}$.

Figure 2.11. (a) Photoluminescence spectra from a freshly cleaved crystal prepared by the ITC technique in vacuum and air under excitation at 400 nm. (b) Decay of the photoluminescence in vacuum and air. The excitation power is $0.71 \mu\text{J cm}^{-2}$.

Figure 2.12. Time resolved photoluminescence decay in vacuum (1.6×10^{-4} mBar) from a crystal grown by inverse temperature crystallization.

Figure 2.13. Photoluminescence intensity variation **(a)** from an atmosphere of moist oxygen to vacuum and then to air; **(b)** from an atmosphere of dry oxygen to vacuum and then to air; **(c)** from an atmosphere of moist nitrogen to vacuum and then to air.

Figure 2.14. Normalized photoluminescence spectra in different gases under 400 nm excitation.

Figure 2.15. PL intensity as a function of time in air under two-photon excitation (800 nm).

Figure 2.16. Calculated photocarrier distribution at $t = 0$ under single-photon (green) and two-photon (red) excitation conditions. In the two-photon condition, the laser power is about 0.123 GW, and the two-photon absorption coefficient is adopted from ref A. The absorption coefficient of around 72000 cm^{-1} at 400 nm is adopted from ref B. ref A^[31], ref B^[17].

Figure 2.17. Time-resolved photoluminescence decay of a crystal prepared by the ITC technique under 400 nm excitation. The fitted lifetimes are $\tau_1 = 0.08 \text{ } \mu\text{s}$ and $\tau_2 = 2.5 \text{ } \mu\text{s}$. The excitation power is $10 \text{ } \mu\text{J cm}^{-2}$.

Comparison of single-photon and two-photon absorption in MAPbBr₃ single crystals

In single-photon pumping, the absorption is governed by the well-known Lambert-Beer law. Thus, the photoexcited carrier distribution is:

$$n(x) \propto I(x) = I_0 \exp(-\alpha x) \quad (2.1)$$

where I is the intensity of the incident light beam propagating along the x -axis, x is the distance from the crystal surface, and α is the one-photon absorption coefficient.

In two-photon excitation, the absorption is proportional to a quadratic function of the laser intensity; where linear absorption is ignored, the penetration of the excitation is:^[30]

$$\frac{dI}{dx} = -\beta I^2 \quad (2.2)$$

In this expression, I is the intensity of the incident light beam propagating along the x -axis, and β is the two-photon absorption coefficient. Thus, the photocarrier distribution at $t = 0$ is:

$$n(x) \propto I(x) = \frac{I_0}{1 + \beta I_0 x} \quad (2.3)$$

Surface recombination velocity in single crystals

In order to extract the surface recombination velocity from the time-resolved PL, we used a simple one-dimensional diffusion model to describe the spatial and temporal behavior of the photogenerated carriers. The evolution of the carrier concentration $n(x, t)$ is assumed to be governed by the diffusion equation,^[32]

$$\frac{\delta n(x, t)}{\delta t} = D \frac{\partial^2 n(x, t)}{\partial^2 x} - \frac{n(x, t)}{\tau} + G, (x \geq 0) \quad (2.4)$$

and boundary conditions

$$n(0, t) = \frac{D}{S} \frac{\delta n(x, t)}{\delta x}, (on \ x = 0) \quad (2.5)$$

The initial carrier distribution deposited by pulse laser is given by

$$n(x, 0) = n_0 e^{-\alpha x}, \quad (2.6)$$

where x is the distance from the surface, t is the delay time, D is the ambipolar diffusion constant, and α is the absorption coefficient at the excitation wavelength.

The solution to equation (4) is the Fourier integral:

$$n(x, t) = e^{-\frac{t}{\tau}} \int_0^\infty e^{-k^2 D t} A(k) \left(\cos kx + \frac{S}{\alpha D} \sin kx \right) dk, \quad (2.7)$$

$$\text{where } A(k) = \frac{2n_0(\alpha + S/D)k^2}{\pi(a^2 + k^2)(\frac{S^2}{D^2} + k^2)}, \quad (2.8)$$

The effective lifetime can be determined by solving the continuity equation for the carrier concentration profile, leading to the following expression:^[18]

$$\frac{1}{\tau} = \frac{1}{\tau_b} + \frac{2\alpha^2 D}{1 + \sqrt{1 + 8\alpha^2 D^2 / S^2}}, \quad (2.9)$$

Numerical simulation of photocarrier distribution and PL spectrum

The photocarrier distribution in a single crystal is calculated by the carrier diffusion equation above. D is the diffusion coefficient and is related to the photocarrier mobility μ . According to the Einstein relation, $D = \mu kT/q$. In the calculation $S = 4 \text{ cm s}^{-1}$ is used. The initial photocarrier distribution is $n(x) = n_0 \exp(-\alpha x)$.

The normalized, time-dependent PL intensity from the crystal is written in terms of an integral:

$$I_\lambda(t) = \int_0^\infty n(x, t)^2 \exp(-\alpha_\lambda x) dx \quad (2.10)$$

where $n(x, t)$ is the photocarrier distribution at time t and α_λ is the absorption coefficient at wavelength, λ .

CHAPTER 3

Scalable Fabrication of High-Quality Crystalline and Stable FAPbI₃ Thin Films by Combining Doctor-Blade Coating and Cation Exchange Reaction

Abstract

Formamidinium lead iodide (FAPbI₃) is one of the most extensively studied perovskite materials due to its narrow band gap and high absorption coefficient, which makes it highly suitable for optoelectronic applications. Deposition from a solution containing both lead iodide (PbI₂) and formamidinium iodide (FAI) or by sequential deposition of PbI₂ and FAI usually leads to the formation of films with poor morphology and unstable crystal structure that readily crystallizes into two different polymorphs: the photoinactive yellow phase and the photoactive black phase. In this work, two-dimensional (2D) 2-phenylethylammonium lead iodide (PEA₂PbI₄) thin films are deposited by a scalable doctor-blade coating technique and used as a growth template for the fabrication of high-quality 3D FAPbI₃ perovskite thin films, which are obtained by organic cation exchange. We report the structural, morphological and optical properties of these converted 3D FAPbI₃ perovskite films and compare them to the directly deposited 3D FAPbI₃ films. The converted FAPbI₃ thin films are compact, smooth, highly oriented and exhibit better structural stability in comparison to the directly deposited 3D films. These results do not only underscore the importance of the employed deposition techniques in the formation of highly crystalline and stable perovskite thin films, but also reveal a strategy to easily obtain very compact perovskite layers using doctor-blade coating.

This chapter is based on the publication:

S. Adjokatse, H.-H. Fang, H. Duim and M.A. Loi, *Nanoscale*, **2019, 11, 5989-5997.**

3.1. INTRODUCTION

One of the key factors that have been central to the demonstrated device performances is the perovskite film quality. This includes the morphology, crystallinity and phase purity. In the last years, the most used deposition method has been the one-step solution processing technique, which involves the direct deposition of the solution containing the perovskite precursors, typically a lead halide (PbX_2 , $\text{X} = \text{I}^-, \text{Br}^-, \text{Cl}^-$) and a methylammonium halide (MAX) or a formamidinium halide (FAX).^[1,2] This technique results in the formation of thin films with poor surface coverage, large surface roughness and often unreacted PbX_2 residues, with negative consequences for performance and stability of devices.^[3] To enhance the perovskite film quality, deposition techniques such as two-step sequential deposition, vapor-assisted deposition, and thermal vapor deposition techniques have been developed.^[4–8] Other techniques such as solvent engineering^[9–11], solvent additives^[12] or temperature-assisted rapid nucleation^[13] and process engineering methods like the anti-solvent treatment,^[14] solvent annealing^[15] and hot-casting^[16] have all been advanced in order to control the film morphology and its quality in general.

An important problem is that the quality of films deposited by these techniques depends highly on the material composition and the solvent used, which is one of the main reasons for the large proliferation of deposition techniques. For instance, while high-quality perovskite films of methylammonium lead iodide (MAPbI_3) have been formed using most of the above-mentioned advanced processing techniques, only the sequential deposition method has given satisfactory formamidinium lead iodide (FAPbI_3) thin films.^[17–21]

FAPbI_3 is a highly interesting material because of its band gap (~ 1.48 eV) and its enhanced thermal stability compared to the widely used MAPbI_3 . However, the ionic radius and symmetry of the FA^+ cation makes FAPbI_3 perovskite structurally unstable, as it can readily crystallize into two different polymorphs at room temperature: the undesired photoinactive “yellow” δ -phase ($\delta\text{-FAPbI}_3$) and the desired photoactive “black” α -phase ($\alpha\text{-FAPbI}_3$).^[21,22] Thus, new strategies are required to fabricate and upscale high-quality FAPbI_3 thin films with improved morphology and structural stability,

which could lead to enhanced optoelectronic properties, both in terms of performances and stability.

Recently, an avalanche of new processing techniques has been employed to control and grow high-quality perovskite thin films and also to tune their composition. One of such techniques is the incorporation of dopants such as Cs to structurally stabilize FAPbI₃ as demonstrated by Zhu and co-workers.^[23] An alternative technique is the ion exchange reaction, which is a well-known method for engineering material composition, creating alloys or obtaining controlled doping.^[24] MAPbI₃ thin films with high surface coverage, smoothness and crystallinity have been successfully fabricated using various starting materials as thin film growth templates.^[25–28] Similarly, using HPbI₃, NH₄PbI₃,^[29] MAPbI₃^[30] etc., as growth templates, various groups have demonstrated the fabrication of phase-pure α -FAPbI₃ thin films with enhanced film quality. Eperon *et al.*, have also successfully demonstrated the exchange of the B-site metal cation by partial or full substitution of tin (Sn) in formamidinium tin iodide (FASnI₃) with lead (Pb).^[31] Jen and co-workers recently used 2D perovskite, namely, phenylethylammonium lead bromide (PEA₂PbBr₄) as growth template, demonstrating highly oriented, high-quality 3D methylammonium lead bromide (MAPbBr₃) thin films.^[32]

At this point, it is important to underline, that all these techniques are based on a spin coating step and are difficult or impossible to scale up, which is a bottleneck towards the commercial exploitation of hybrid perovskites in technology. Given the need for solution-based thin film deposition techniques that are simple, low-cost and compatible with industrial-scale fabrication, here, we demonstrate an industrially relevant deposition pathway, giving rise to high quality hybrid perovskite thin films. This deposition pathway combines the advantages of doctor-blade coating and the ion exchange reaction method to fabricate high-quality phase-pure α -FAPbI₃ perovskite thin films that are structurally stable and highly crystalline. Phenylethylammonium lead iodide (PEA₂PbI₄) perovskite thin films are doctor-blade coated and fully converted to α -FAPbI₃ by immersing the 2D layer in a FAI solution. The choice of PEA₂PbI₄ as our starting material is based on its good film formability on different substrates even when deposited using different deposition techniques, including scalable blade coating. For comparison, one-step doctor-blade coated FAPbI₃ thin films are

also investigated. The structural, morphological and optical characterization shows that the converted thin films exhibit unprecedented film quality, with preferential crystallographic orientation and enhanced ambient stability compared to the one-step deposited films. These results underline the immense potential of the combined blueprint of the scalable doctor-blade coating and ion exchange reaction technique in the growth of stable and high-quality perovskite thin films.

3.2. EXPERIMENTAL DETAILS

Materials and solution preparation

The perovskite precursors: lead (II) iodide (PbI_2) (99.99%), 2-phenylethylammonium iodide ($\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3\text{I}$, PEAI) (>98%) and formamidinium hydroiodide (FAI) (>98%) were purchased from TCI EUROPE N.V and were used as received. *N,N'*-dimethylformamide (DMF) (99.8%) was acquired from Sigma-Aldrich and dimethyl sulfoxide (DMSO) (99.9%) from Alfa Aesar.

The 2D PEA_2PbI_4 perovskite precursor solution was prepared by dissolving PEAI and PbI_2 at a molar ratio of 2:1 in a mixed solvent of DMF and DMSO at a volume ratio of 4:1 to form a solution of 0.5 M. The 3D FAPbI_3 perovskite precursor solution was prepared by dissolving FAI and PbI_2 at a molar ratio of 1:1 also in a mixed solvent of DMF and DMSO at a volume ratio of 4:1 to form a solution of 1 M. The solutions were stirred for at least 3 hours at room temperature before deposition. The organic precursor solution was prepared by dissolving FAI in isopropyl alcohol (IPA) to form a solution with a concentration of 20 mg mL^{-1} .

Perovskite film fabrication

The films were fabricated on glass substrates, which were ultrasonically cleaned in detergent solution, deionized water, acetone and isopropanol, sequentially. After drying them in an oven at 140 °C for about 10 min, they were treated with ultraviolet ozone (UV-O_3) plasma for 20 min and then transferred into a nitrogen-filled glovebox immediately for the film deposition.

The perovskite growth process involved the transformation of pure 2D perovskite, PEA_2PbI_4 to the desired 3D FAPbI_3 perovskite thin film by the ion exchange method. The 2D films were fabricated using spin coating and doctor-blade coating techniques. The spin coated 2D samples were fabricated using a two-step spin program with anti-solvent treatment. The spin program was set at 1000 rpm for 10 s and 4000 rpm for 30 s. The anti-solvent (chlorobenzene) was dropped onto the film at about 10 s prior to the end of the spinning. The films were immediately annealed at 100 °C for 10 min. For the doctor blade coating process, the precursor solution was dropped onto the substrate and swept linearly with a metal blade as depicted in Figure 3.1. The optimized 2D films were blade coated onto glass substrates held at 80°C by spreading the precursor solution with the blade at a speed of 10 mm s⁻¹. The gap between the glass substrate and the blade was fixed at 400 μm. The films were immediately annealed at 100 °C for 10 min. The optimized reference 3D FAPbI_3 perovskite film was also blade coated at a temperature of 90°C with a blade speed of 40 mm s⁻¹ and a fixed gap of 400 μm. The film was annealed at 160°C for at least 30 min. To convert the 2D perovskite into 3D, the 2D film was dipped into 20 mg mL⁻¹ FAI in IPA solution for ~3 min, rinsed in IPA for ~ 30s in order to wash away dangling PEA^+ ions on the surface of the film and subsequently dried by spinning. No further annealing was required to drive the 3D conversion to full completion.

Morphological Characterization

The scanning electron microscopy (SEM) images were obtained using the FEI Nova Nano SEM 650 with an accelerating voltage of 2~10 kV for the secondary electron images and ~10 kV for the backscattered electron images. The Atomic force microscopy (AFM) images were taken using the Bruker NanoScope V in the ScanAsyst mode. Reflected light micrographs were recorded using an Olympus BX51M microscope equipped with a ColorView CCD camera and plan fluor objectives with 5x, 10x and 50x magnifications.

Structural Characterization

The X-ray diffraction experiment was performed under ambient conditions using a Bruker D8 Advanced diffractometer in Bragg-Brentano geometry

and operating with Cu a K_{α} radiation source ($\lambda = 1.54 \text{ \AA}$) and a Lynxeye detector.

Optical Characterization

Absorption measurements were taken using UV-vis-NIR spectrophotometer (Shimadzu UV-3600). The photoluminescence measurements were performed using the second harmonic (400 nm) of a Ti:sapphire laser (repetition rate, 76 MHz; Mira 900, Coherent) to excite the samples. The illumination power was adjusted using a variable neutral density filter. The excitation beam was spatially limited by an iris and focused with a 150-mm focal length lens. Emitted photons were collected with a lens and directed to a spectrograph. Steady-state spectra were collected using a Hamamatsu EM-CCD camera.

Confocal laser scanning microscopy (CLSM) measurements were performed using a Nikon Eclipse Ti microscope. Samples were excited using an Ar^+ laser with an excitation wavelength of 488 nm. The excitation beam was focused on the sample using a 100x (oil immersion Plan Apo) objective. Spatial mapping of the photoluminescence was obtained by raster scanning the sample and recording the PL signal using a 650 nm long pass detection channel.

3.3. RESULTS AND DISCUSSION

Figure 3.1: Schematic of the doctor-blade setup used for the deposition of the 2D PEA_2PbI_4 and reference 3D FAPbI_3 perovskite film.

2D PEA_2PbI_4 perovskite thin films were fabricated from a solution containing 2-phenylethylammonium iodide (PEAI) and PbI_2 in a solvent mixture of *N,N'*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) using both spin coating and doctor-blade coating techniques. Unlike the 3D perovskites, this 2D material exhibited good film formability even when deposited using one-step solution deposition techniques. Figure 3.1 shows the schematic of the deposition procedure for the doctor-blade coating technique. The detailed fabrication procedure of the 2D films using both spin-coating and doctor-blade coating methods are described in the experimental section.

Figure 3.2: Structural, optical and morphological characterization of spin coated and doctor-blade coated 2D PEA_2PbI_4 perovskite films on glass substrates. (a) X-ray diffraction patterns, (b) UV-vis absorbance spectra. AFM topographical images of spin coated (c) and doctor-blade coated films (d).

The structure, morphology and band-gap of the prepared thin films were examined using x-ray diffraction (XRD), atomic force microscopy (AFM) and UV-Vis spectroscopy, respectively. The two deposition techniques result

in thin films with similar XRD patterns and absorption profiles, but very different morphology. As shown in Figure 3.2(a), the XRD patterns of the two samples exhibit similar diffraction peaks with preferential orientation at 2θ values of 5.45° , 10.88° , 16.30° , 21.79° , 27.29° , 32.92° and 38.56° . However, the doctor-blade coated film exhibits more than three orders of magnitude stronger peak intensity compared to the spin coated film. This proves the higher crystallinity of the doctor-blade coated film.

The absorption spectra of these thin films closely resemble those previously reported with an excitonic peak at 515 nm.^[33] The doctor-blade coated film however, has a higher absorbance than the spin-coated film, implying that the film is thicker and/or has better surface coverage [Figure 3.2(b)].

The morphological properties of the films were characterized using atomic force microscopy (AFM). While the spin coated film shows high inhomogeneity and roughness with surface grains of nanometer-sizes, the doctor-blade coated film is flatter, smoother and has crystalline domains as large as $15\ \mu\text{m}$ as evident from Figure 3.2(c) and 3.2(d), respectively. The surface roughness of these films extracted from the AFM images is 22 and 50 nm in favor of the doctor-blade coated film.

The 2D perovskite films were dipped into a solution containing FAI dissolved in isopropyl alcohol (IPA) to convert them into 3D FAPbI_3 perovskite by ion (organic-cation) exchange reaction. This approach follows previous works, where various 2D perovskites were used as starting materials to grow multidimensional (2D/3D)^[34] or 3D^[27,28,32] hybrid perovskites. The schematic of the ion exchange reaction process is depicted in Figure 3.3(a). The photographs of the 2D perovskite films before and after conversion to 3D films without and with rinsing in IPA are shown in Figure 3.3(b-d). We observed that without the washing steps in IPA, the 3D perovskite film degrades immediately after drying [Figure 3.3(c)], while the washed samples remain stable for many days. This shows that the exchange reaction is kinetically driven and in the absence of the washing step, it will be thermodynamically driven backward to the starting material. We therefore attribute this unstable behaviour of the unwashed samples to the presence of long organic ligands on the surface of the film that readily promotes further reactions detrimental to the stability of the converted 3D perovskite film.

Figure 3.3: (a) Schematic illustration of 2D to 3D conversion by cation exchange reaction. (b) Photographs of spin-dried 2D perovskite film, (c) converted 3D perovskite film without washing in isopropyl alcohol (IPA) and (d) converted 3D perovskite film with washing in IPA.

To study the kinetics of the cation exchange in more detail, we performed an in-situ conversion experiment. The FAI/IPA ligand solution is injected into a cuvette containing the 2D perovskite film to initiate the 2D to 3D conversion while the photoluminescence (PL) of the sample is monitored simultaneously. Figure 3.4(a) shows the PL emission evolution of the conversion taken with 1-second time interval. Initially, only the narrow peak of the 2D perovskite at 530 nm is observed. The PL intensity of this 2D peak increases in the first second after adding the ligand solution, but then vanishes almost completely within another 10 seconds. At the same time, a much broader PL peak originating from the 3D FAPbI₃ emerges around 800 nm. The emission from the 3D perovskite shows a rapid decrease in PL intensity and a considerable redshift in the first seconds after its appearance. A detailed analysis of the dynamics of the 3D peak is shown in Figure 3.4(b) and 3.4(c). After the appearance of the feature at around 800 nm, a minimum

PL intensity is reached after 40 seconds, as shown in Figure 3.4(b). After this local minimum, the intensity steadily increases again while the peak continues exhibiting a small monotonic redshift [Figure 3.4(c)]. This redshift is most likely caused by the conversion of low-dimensional perovskite intermediates into the 3D perovskite phase. It is important to underline that an eventual PL signal from the 2D and other low-dimensional perovskite phases, after the beginning of the conversion towards the 3D perovskite, might not be directly detectable because of reabsorption and energy transfer. The slow recovery of PL in the final stage of the conversion process is considered to be the result of further growth of the 3D domains and minimization of defects through laser-induced healing.

Figure 3.4: 2D-3D conversion kinetics and results of the Gaussian fitting to the 3D emission peak at different times during the conversion process. (a) In-situ photoluminescence (PL) emission spectra showing the conversion kinetics of the evolution from 2D to 3D perovskite. (b) The PL intensity normalized to the first occurrence of the 3D emission (100%) and (c) center of gravity of the fitted peak wavelength.

After the full conversion from 2D into 3D, the films were characterized to investigate the quality of the films. The comparison of the converted 3D films based on the spin coated and doctor-blade coated 2D films showed that the latter exhibited better film properties, mimicking the quality of the 2D films. The structural and morphological characteristics of the converted film based on the spin coated 2D film are shown in Figure 3.5(a,b).

Figure 3.5: Structural and morphological characterization of the converted 3D FAPbI₃ perovskite film based on a spin coated 2D film. (a) X-ray diffraction pattern, and (b) top-view SEM micrograph.

As a reference for the converted films based on the doctor-blade coated 2D films, 3D FAPbI₃ thin films were doctor-blade coated on a glass substrate. The XRD patterns illustrating the structural properties of the converted and this reference 3D perovskite film are displayed in Figure 3.6. The converted film exhibits highly oriented crystal domains with characteristic peaks at 2θ values of 13.97°, 28.13° and 42.71°, corresponding to scattering from (111), (222) and (333) crystal planes. The reference film, on the other hand, exhibits additional diffraction peaks at 12.74°, 19.79°, 24.30°, 31.56°, 34.65°, 38.81° and 40.22°, which correspond to randomly arranged crystal planes. Although no signature peak of the photoinactive (δ -phase) perovskite is observed in either film, the characteristic peak from PbI₂ (12.74°), which is a result of the rapid degradation of the sample in air, is observed for the reference film. The diffraction peaks from the converted films are about two orders of magnitude stronger in intensity than the one of

the reference films. The peak intensity of the reference film is thus magnified by a factor of 100. The FWHM of the characteristic peak at 13.97° is 0.14° and 0.21° for the converted and the reference sample, respectively. This shows that the converted perovskite film has a better crystallinity, and lower level of disorder with respect to the reference sample. It is worth mentioning at this point, that no diffraction peaks from the 2D perovskite are observed in the diffraction pattern of the converted film.

Figure 3.6: X-ray diffraction profiles of the converted and reference film fabricated by doctor-blade coating.

As explained above, the morphological quality of thin films defines the success of a deposition technique. The SEM images portraying the film topography (secondary electrons) and the composition (backscattered electrons) of the 2D, converted 3D and the reference 3D perovskite films are shown in Figure 3.7. In Figure 3.7(a), the secondary electron image of the 2D perovskite depicts a continuously smooth and homogeneous film with excellent surface coverage and very large crystalline domains ($> 10 \mu\text{m}$), consistent with that seen in the AFM images. The uniform brightness of the backscattered electron images also reflects the highly uniform compositional distribution of the 2D film [Figure 3.7(b)]. These morphological features are directly translated to the converted 3D films except for the domain sizes,

Figure 3.7: SEM images showing the surface topography and compositional properties of the 2D PEA_2PbI_4 , the converted and the reference 3D FAPbI_3 perovskite films all fabricated with the doctor-blade coating technique. Secondary electron (**a**, **c** and **e**) and backscattered electron (**b**, **d** and **f**) images of the 2D, converted and reference 3D perovskite films, respectively.

which appear smaller ($> 3 \mu\text{m}$) and the presence of pinhole-like features at the domain boundaries as shown in Figure 3.7(c) and 3.7(d) for the secondary electron and backscattered electron images, respectively. The roughness of the converted 3D film, as extracted from the AFM topographical image, is approximately 40 nm. Interestingly, laser scanning

confocal microscopy measurements performed on the converted film show that the pitted domain boundaries have brighter photoluminescence (see Figure 3.8). In stark contrast, the topographical image of the 3D reference film in Figure 3.7(e) shows the formation of hexagonal-like crystalline domains, resulting in a non-uniform film. As revealed in the backscattered electron image of Figure 3.7(f), the surface coverage of the film is very poor.

Figure 3.8: Confocal laser scanning micrograph of the converted 3D FAPbI₃ perovskite film. Brighter colors indicate higher intensity of the PL. The image size is 100 x 100 μm^2 .

The absorbance spectra of the converted and reference 3D FAPbI₃ perovskite films are shown in Figure 3.9(a). The spectra are normalized at 840 nm to aid in the comparison of the spectral shape and estimation of the band-edge [see Figure 3.9(b)]. The films have an absorption band-edge around 830 nm, confirming the formation of 3D FAPbI₃ perovskite. However, the spectral profiles of the films are very different. The converted film has a characteristic absorption profile that depicts a continuous increase in light absorption from the near-infrared (NIR) to the visible region while

the reference film shows an almost constant light absorption in the same range. Moreover, as shown in Figure 3.9(a), the reference film has a very high background signal in the NIR compared to the converted film. These features are directly related to the film quality, specifically, the degree of surface coverage and homogeneity. While the observed high background absorption from the reference film is attributed to the high inhomogeneity of the film, which gives rise to large scattering of the incident light, the flattening of the spectrum in the visible is attributed to poor surface coverage. These observations are in agreement with previous studies by Tian *et al.*, who examined the correlation between absorption spectral shapes and surface coverage and inhomogeneity of MAPbI₃ thin films.^[35]

Figure 3.9: Optical characterization of converted and reference 3D perovskite films on glass substrates. **(a-b)** UV-vis absorbance spectra without normalization (a) and with normalization at 840 nm (b), **(c)** Steady-state PL spectra. Note that 3D_ref and 3D_conv as indicated in figures denote the reference one-step coated and converted FAPbI₃ perovskite respectively.

Figure 3.10: Characterization of the moisture stability of the reference and converted 3D FAPbI₃ perovskite films under ambient conditions. (a) Photographs showing the evolution of color of the reference (top) and converted (bottom) perovskite films over a 21-day period. UV-vis absorbance spectra of the reference (b) and the converted (c) films normalized at 890 nm.

Figure 3.9(c) shows the photoluminescence spectra of both the reference and the converted film upon excitation with a 400 nm laser. The converted film shows a PL intensity that is over 20 times higher than that of the reference film. This large difference in PL intensity has two main causes; firstly, as mentioned before, the converted film shows much higher surface coverage than the reference film. Therefore, more photons are absorbed in the converted film and the PL intensity scales accordingly. Secondly, as the quality of the converted film is better than that of the reference film, it is to be expected that the excited charge carriers suffer less from non-radiative recombination in this film. This notion is further confirmed by the large redshift of the PL spectrum of the reference film (845 nm) with respect to

that of the converted film (823 nm), such a redshift is typically associated with a high density of trap states.^[32]

At this point it is interesting to verify if the stability of the material is also affected by the preparation method. The stability under ambient conditions is evaluated by probing the changes in the absorbance of the films under a relative humidity (RH) of 40~50% and temperature of ~23°C. The stability test under ambient conditions is performed on several films and a clear correlation of the film degradation over time on the quality of the film is found. Photographs of the most stable converted and reference films stored in air over a period of 21 days are presented in Figure 3.10(a). Whereas the best of the reference films degraded rapidly within a day with consequent severe color bleaching, the best converted sample showed minimal degradation with negligible change in color even after 15 days. The corresponding absorbance spectra of the films are shown in Figure 3.10(b) and 3.10(c) for the reference and converted films, respectively.

The absorbance of the reference film dropped drastically on the second day and as shown, no absorption peak was observed after 15 days. On the contrary, the converted film maintained a high absorbance without spectral modification for 21 days as shown in Figure 3.10(c). We attribute the degradation to the penetration of moisture at the grain or domain boundaries.

Furthermore, the stability under illumination of both the converted 3D and reference films was assessed by exposing them to a focused laser beam of 400 nm ($2.5 \mu\text{J cm}^{-2}$) wavelength, under ambient condition. Figure 3.11 displays color maps of the PL spectra as a function of exposure time for (a) the 3D reference sample and (b) the converted film. PL spectra at selected time intervals are plotted alongside in (c) and (d). It is evident from these plots that the films behave distinctly differently under illumination. In the case of the reference 3D film, the low PL initially increases due to the laser-induced healing of trap states, which is accompanied by a slight blue shift of the emission. After this initial healing stage, however, degradation begins, and the intensity steadily drops until the signal reaches about 20% of its maximum intensity. During this degradation phase, a broad emission feature gradually arises at high energy, as highlighted in the inset of Figure 3.11(c). We assign this feature to degradation products of FAPbI_3 , the most likely

Figure 3.11: Photostability of the reference and converted 3D FAPbI₃ perovskite films. 2D pseudo-color plot of the PL spectra of the reference (a) and converted (b) films as a function of continuous laser excitation time. Evolution of the PL spectra of the reference film(c) and converted (d) films at selected times.

being PbI₂, resulting from evaporation of the volatile organic cation as observed in the case of MAPbI₃.^[36,37] At the laser excitation point, the decomposition of the perovskite is visible by eye as a yellow spot. A cross-polarized light micrograph showing the strong change in birefringence of this degraded spot is shown in Figure 3.12. In stark contrast to this, the converted film only shows a steady decrease in PL intensity and no degradation byproduct can be observed under the same excitation conditions. Moreover, it should be noted that even after prolonged laser illumination, the final PL intensity of the converted film is still considerably higher than the maximal value that the reference film ever reaches, which again highlights the superior quality of the converted films. Furthermore, the substantially higher PL intensity, narrower FWHM and the blue-shifted emission wavelength as shown in Figure 3.13 all indicate the superior quality of the converted film with respect to the reference film.

Figure 3.12: Bright-field microscopy images showing the decomposition of the reference film under laser excitation (a) without and (b) under cross-polarization.

Figure 3.13: PL parameters extracted from the data in Figure 3.10(a) and 3.10(b) demonstrating the superior film quality of the converted film. (a) Peak intensity, (b) FWHM, and (c) center wavelength of the PL tracked over time. The sharp rise in the FWHM stems from the broad emission feature at high energy.

We can therefore conclude that the here reported conversion mechanism from a highly crystalline 2D film gives rise to highly oriented 3D films with superior ambient and photo-stability.

3.4. CONCLUSION

In summary, doctor-blade coated 2D 2-phenylethylammonium lead iodide (PEA_2PbI_4) films are employed as a growth template to fabricate high-quality photoactive 3D FAPbI_3 thin films using a cation exchange reaction. The resultant perovskite film exhibits better film formability, excellent surface coverage and improved morphology with crystalline domain sizes as large as $\sim 10\ \mu\text{m}$. XRD patterns of the converted 3D perovskite film reveal very high crystallinity and highly preferential orientation that mimics the orientation of the 2D perovskite template. The improved perovskite film leads to enhanced photoluminescence intensity, about 20 times higher than the one of the reference one-step blade-coated FAPbI_3 perovskite film. Furthermore, stability studies under continuous laser illumination and under ambient conditions show that the converted film exhibits a significantly enhanced photo- and moisture stability compared to the reference film. The enhanced optoelectronic quality and high stability of the phase-pure FAPbI_3 perovskite thin films obtained by cation exchange reaction of a doctor-blade coated thin film is of extreme importance toward the engineering and stabilization of perovskite thin films for optoelectronic applications.

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CHAPTER 4

Effect of the Device Architecture on the Performance of $\text{FA}_{0.85}\text{MA}_{0.15}\text{PbBr}_{0.45}\text{I}_{2.55}$ Planar Perovskite Solar Cells

Abstract

Hybrid perovskite solar cells (PSCs) have attracted an unprecedented research attention due to their skyrocketing record power conversion efficiency (PCE), which now exceeds 23% in less than a decade from the initial PCE of 3.8%. Besides the excellent optoelectronic properties of the perovskite absorbers, the high efficiencies also depend on preparation methods and advanced device engineering. In this study, the role of the device architecture (planar n-i-p versus inverted p-i-n structure) and of the charge-selective interlayer on the photophysical properties of the perovskite absorber and device performance are explored. We employ $\text{FA}_{0.85}\text{MA}_{0.15}\text{PbBr}_{0.45}\text{I}_{2.55}$ (MA = methylammonium, FA = formamidinium) as the perovskite absorber and chloride-capped TiO_2 colloidal nanocrystals ($\text{TiO}_2\text{-Cl}$) and poly(3,4-ethylene dioxathiophene):poly(styrenesulfonate) (PEDOT:PSS) as close-to-the-substrate layers in the conventional and inverted structures, respectively. Strikingly different device performances are demonstrated by the two structures. The device in which the active layer is deposited on $\text{TiO}_2\text{-Cl}$ displays a champion PCE of 19.9%, while the one using PEDOT:PSS gives about 15.1% efficiency. The photophysical and electrical investigations indicate that the $\text{TiO}_2\text{-Cl}$ /perovskite interface has a lower number of traps, underlining the importance of interfaces for achieving highly performing perovskite solar cells.

This chapter is based on the publication:

S. Adjokatse, J. Kardula, H.-H Fang, S. Shao, G.H. ten Brink and M.A. Loi,
Advanced Materials Interfaces, **2019**, 6(6), 1801667.

4.1. INTRODUCTION

The rapid advances in perovskite photovoltaic (PV) research can generally be attributed to the quest to soon commercialize the technology by improving device efficiency and overcoming the major challenging issues that hinder these steps, such as the long-term device operational stability, the material toxicity and the functioning instability (hysteresis). Efforts towards improving efficiency and mitigating the above-mentioned crucial challenges have therefore led to various advances that can be attributed to three primary factors: deposition methods, chemical engineering, device architecture engineering.^[1] For instance, to achieve high-quality perovskite films with the right morphology, crystallinity and phase purity, deposition techniques such as one-step solution deposition,^[2,3] two-step solution deposition,^[4,5] vapor-assisted solution deposition,^[6] and thermal vapor deposition^[7,8] methods have been developed. To further improve the perovskite film morphology, and crystallinity, solvent engineering (e.g. use of mixed-solvents and solvent additives),^[9,10] anti-solvent treatment, solvent annealing and hot-casting,^[9,11,12] have also been developed. The chemical engineering of the hybrid perovskite has been used to modify the bandgap^[13,14] and increase the crystallographic and thermal stability of the active layer.^[15]

Lastly, different device architectures have been utilized. Depending on which electrode is on the glass substrate or which charge-selective material is encountered first by the light, two primary device architectures can be classified: conventional (n-i-p)^[2,16] and inverted^[17–19] (p-i-n) device architectures. Thus, whereas in the conventional device architecture the electron-extracting electrode encounters the light first, in the inverted device architecture, the hole-extracting electrode is the first. These device architectures can further be sub-categorized based on whether the perovskite absorber is infiltrated into a mesoporous material (mesoscopic device structure)^[16,20,21] or sandwiched between an electron- and hole-selective material (planar).^[6,7,18,22]

In general, the performances of PSCs are known to dependent on device architecture and although the excellent PCEs reported are not limited to any particular device configuration, most of the top-performing devices with PCEs above 20% are based on the conventional (both mesoscopic and planar) device architectures.^[15,23] On the other hand, few high-performing devices based on the inverted architecture have been reported with highest uncertified PCE been of 19.4%, using poly(triaryl amine) (PTAA) as the close-to-the-substrate layer.^[24]

Although Momblona et al. were the first to directly compare the performance of opposite device configurations, their study was focused on the demonstration of fully vacuum deposited perovskite solar cells and also, the impact of p- and n-type doped organic semiconductor transport layers on device performance.^[25] Thus, due to the excitement surrounding the rapidly increasing efficiencies, not much attention has been devoted to the fundamental study of the impact of the material on which the perovskite is deposited and the device architecture on the device performances and the corresponding photophysics.

The composition of the perovskite plays a key role in the efficiency and stability of devices. For instance, most of the PCEs above 17% which are certified, are based on the (FA/MA)Pb(I/Br) perovskite composition^[26,27] and the (Cs/FA/MA)Pb(I/Br) system, which were shown to be much more stable.^[15,27] It is also important to note that all these devices are fabricated based on the conventional device architecture. Hence, to examine the applicability and dependence of (FA/MA)Pb(I/Br) perovskite on the material on which the active layer is deposited and on an alternative device architecture, we fabricated inverted planar PSCs with the commonly used organic hole-selective material, PEDOT:PSS. Our champion device in this architecture reached a PCE of 15.1% with an average PCE of $12.2 \pm 1.1\%$. For comparison, we fabricated devices based on conventional planar device architecture with identical processing of the perovskite absorber. The perovskite was deposited on chloride-capped TiO₂ (TiO₂-Cl) nanocrystals (NC) film,^[23] a low temperature processed transport material which acts as electron-selective layer (ESL). In this architecture, champion PCE of 19.9% and an average PCE of $16.8 \pm 1.2\%$ is achieved. This striking difference in performance motivated us to further investigate the morphological, structural and photophysical properties of the perovskite films and devices, in order to gain insight into the impact of the substrate material and the device architecture on the device performances. Our results show that the TiO₂-Cl NC film serves as a better surface for the formation of a more compact and pinhole-free perovskite film than PEDOT:PSS. Additionally, we attribute the better performance of the conventional device to a lower number of traps at the interfaces with the extracting layers. Particularly the TiO₂-Cl / perovskite interface is shown to be superior to the PEDOT:PSS / perovskite interface. This underlines the importance of interfaces for achieving highly performing perovskite solar cells.

4.2. EXPERIMENTAL DETAILS

Materials

Materials for the synthesis, cleaning and preparation of colloidal solutions of TiO₂ nanocrystals include titanium (IV) chloride (TiCl₄) (99.9% Sigma-Aldrich), ethanol, benzyl alcohol, diethyl ether, anhydrous methanol and anhydrous chloroform that were acquired from Sigma-Aldrich. The PEDOT:PSS (Clevios VP Al 4083) water dispersion was acquired from Heraeus. The perovskite precursors: lead (II) iodide (PbI₂) (99.99%), lead (II) bromide (PbBr₂), methylamine hydrobromide (MABr) (>98%) and formamidine hydroiodide (FAI) (>98%) were purchased from TCI EUROPE N.V. *N,N'*-dimethylformamide (DMF) (99.8%), and dimethyl sulfoxide (DMSO) (99.9%, Alfa Aesar) and all other materials were acquired from Sigma-Aldrich. All materials were used as received without further purification.

The synthesis of the Cl-capped TiO₂ (TiO₂-Cl) nanocrystals and the perovskite precursor solution were prepared following previously reported work by Tan *et al.*^[23]

Film and Device Fabrication

Films and devices were fabricated on pre-patterned indium tin oxide (ITO) coated glass substrates, which were ultrasonically cleaned in detergent solution, deionized water, acetone and isopropanol, sequentially. After drying them in an oven at 140 °C for about 10 min, they were treated with ultraviolet ozone (UV-O₃) plasma for 20 min. The PEDOT:PSS and the TiO₂-Cl films were deposited onto the substrates by spin coating in ambient conditions at the speed of 3000 and 4000 rpm, respectively. The PEDOT:PSS films were dried at 140 °C for 10 min in an oven while the TiO₂-Cl films were dried at 150 °C for 30 min on a hotplate. The thicknesses of the obtained PEDOT:PSS and the TiO₂-Cl films are about 45 and 20 nm, respectively. The substrates were transferred into a nitrogen-filled glovebox immediately after cooling for further processing. The FA_{0.85}MA_{0.15}PbBr_{0.45}I_{2.55} perovskite solution was prepared following the recipe described in ^[23] and stirred overnight at room temperature. The molar ratio of (FAI + MABr) and (PbI₂ + PbBr₂) was 1:1, dissolved in a mixed solvent of DMF and DMSO at a volume ratio of 4:1 to form a precursor solution of 1.2 M. The FA_{0.85}MA_{0.15}PbBr_{0.45}I_{2.55}

perovskite films were deposited by a one-step spin coating method involving a two-step spin program with anti-solvent (chlorobenzene) treatment. The program included spinning at 1000 rpm for 10 s and 4000 rpm for 30 s with the anti-solvent dripped at about 2-10 s prior to the end of the spinning. The variation in the anti-solvent dripping time is to aid in the optimization of the perovskite morphology while maintaining the same film thickness. The films were immediately annealed at 100 °C for 10 min. For the inverted devices, [60]PCBM dissolved in chlorobenzene at a concentration of 20 mg/mL was spin coated on the perovskite layer at 1500 rpm while for the conventional devices, 70 mg of Spiro-OMeTAD, 20 μ L of tert-butylpyridine and 70 μ L of bis(trifluoromethane)sulfonimide lithium (Li-TFSI) salt (170 mg/mL in acetonitrile) dissolved in 1 mL of chlorobenzene was spin coated at 3000 rpm. To complete the devices, 100 nm of Al and 80 nm of Au contacts were deposited on the [60]PCBM and Spiro-OMeTAD layers, respectively, by thermal evaporation under high vacuum ($< 10^{-7}$ mbar).

Solar cell Characterization

The current density-voltage (*J-V*) characteristics of the solar cells were measured under simulated AM 1.5 solar illumination using an Osram HMI 1200W/DXS lamp in a nitrogen filled glovebox. The light intensity was adjusted to give 100 mW cm⁻² using a calibrated silicon reference cell (SRC-1000-RTD-QZ, VSLI Standards Inc.). The *J-V* curves were recorded using a Keithley 2400 source-meter. The active area of the solar cells was defined with a metal aperture mask of 0.1 cm². Light intensity dependence measurements were performed using a set of neutral density filters to attenuate the illumination intensity. The temperature of the solar cells was controlled by an adjustable N₂ gas flow through a liquid N₂ bath.

The external quantum efficiency (EQE) measurements were carried out under short-circuit conditions using monochromatic light from a 250 W quartz tungsten halogen lamp (Osram 64655 HLX). A set of band pass filters with full width at half maximum (FWHM) of 10 ± 2 nm were used to obtain the monochromatic light.

Impedance Spectroscopy measurements were performed using an SP-200 Bio-Logic potentiostat with a forward bias superimposed with a 25 mV AC perturbation over the frequency range from 1 MHz to 100 Hz.

Morphological Characterization

The scanning electron microscopy (SEM) images were obtained using the FEI Nova Nano SEM 650 with an accelerating voltage of 5kV while the Atomic force microscopy (AFM) images were taken using the Bruker NanoScope V in ScanAsyst mode.

Structural and Optical Characterizations

The X-ray diffraction experiment was performed under ambient conditions using a Bruker D8 Advanced diffractometer in Bragg-Brentano geometry and operating with Cu K α radiation source ($\lambda = 1.54 \text{ \AA}$) and Lynxeye detector.

The photoluminescence measurements were performed using the second harmonic (400 nm) of a Ti:sapphire laser (repetition rate 76 MHz; Mira 900, Coherent) to excite the samples. The illumination power density was decreased to $5 \mu\text{J cm}^{-2}$ by using a neutral density filter. The excitation beam was spatially limited by an iris and focused with a 150-mm focal length lens. Emitted photons were collected with a lens and directed to a spectrograph. For the time-resolved photoluminescence measurement, a pulse picker was used to reduce the excitation frequency. Steady-state spectra were collected using a Hamamatsu EM-CCD camera and time resolved traces were recorded using a Hamamatsu streak camera.

4.3. RESULTS AND DISCUSSION

In this study, we fabricated mixed-cation mixed-halide perovskite solar cells based on two different planar device architectures (inverted p-i-n and conventional n-i-p) and investigated the effect of the layer on which the active material is deposited, from here thereof called substrate layer, and of the device structure on their PV performances. As shown in Figure 4.1(a) and 5.1(b), our inverted p-i-n device has the structure ITO / PEDOT:PSS / FA_{0.85}MA_{0.15}PbBr_{0.45}I_{2.55} / PCBM / Al and the conventional n-i-p device has the structure ITO/TiO₂-Cl / FA_{0.85}MA_{0.15}PbBr_{0.45}I_{2.55} / Spiro-OMeTAD / Au. For these configurations, PEDOT:PSS and TiO₂-Cl NC films which serve as substrate layers in both structures are deposited on patterned ITO coated glass, and act as the hole-selective and electron-selective contacts in the respective device architectures. PCBM and Spiro-OMeTAD are the electron-selective and hole-selective layers deposited before cathode and anode metals,

respectively. The perovskite absorber and all the transport layers were deposited by spin-coating. The perovskite active layers were deposited for both device configurations using the anti-solvent technique with identical set of solvents and processing parameters to ensure fully optimized perovskite films on the different substrate layers.^[9]

Figure 4.1: Device architecture and electrical characteristics. **(a,b)** Schematic diagrams of planar perovskite solar cells in (a) inverted p-i-n configuration and (b) conventional n-i-p configuration. **(c)** J - V curves of PSCs in p-i-n and n-i-p device configuration. **(d)** External quantum efficiency spectra of the devices reported in (c).

The current density-voltage (J - V) characteristics of the two types of devices under 1 sun illumination differ significantly. The cells based on the regular device

architecture perform much better than those based on the inverted device architecture. The J - V curves are reported in Figure 4.1(c), with the corresponding parameters listed in Table 4.1. The best-performing regular device gives a PCE of 19.9% (short-circuit current density, J_{sc} of 25.3 mA cm⁻², open-circuit voltage, V_{oc} of 1.09 V, and fill factor, FF of 0.72). The best inverted device instead gives a PCE of 15.1% (J_{sc} of 19.2 mA cm⁻², V_{oc} of 0.96 V, FF of 0.82). To the best of our knowledge, this is the highest PCE recorded using PEDOT:PSS and PCBM as transport layers without any interface engineering and based on the inverted structure. Although the perovskite absorber in both types of devices is nominally identical, the PV metrics show an increase of both J_{sc} (from 19.2 to 25.3 mA cm⁻²) and V_{oc} (from 0.96 to 1.09 V) in favor of the conventional architecture. However, the FF increases from 0.72 to 0.82 going from the regular to the inverted structure. The external quantum efficiency (EQE) spectra shown in Figure 4.1(d) also illustrate a vast difference in the light harvesting capabilities of the perovskite when used in the two different device architectures. Whereas the inverted device exhibits a broad plateau around 80% over the spectral range between 400 and 740 nm, the conventional device shows a light harvesting ability of over 90% within the same spectral range. The calculated photocurrent densities are 18.8 and 23.0 mA cm⁻², respectively, which are slightly lower but in reasonably good agreement with the J_{sc} values obtained from the J - V curves.

Table 4.1: Solar cell performance parameters extracted from the reverse J - V curves in Figure 4.1(c)

Architecture	J_{sc} [mA cm ⁻²]	V_{oc} [V]	FF	PCE [%]
Inverted p-i-n (Champion cell)	19.2	0.96	0.82	15.1
Inverted p-i-n (Average)	18.0 ± 1.2	0.88 ± 0.04	0.77 ± 0.05	12.2 ± 1.1
Regular n-i-p (Champion cell)	25.3	1.09	0.72	19.9
Regular n-i-p (Average)	25.0 ± 0.3	1.05 ± 0.03	0.65 ± 0.04	16.8 ± 1.2

Figure 4.2: Statistical performance of the planar perovskite solar cells. Histogram of the PCE values of the devices with (a) PEDOT:SSS and (b) $\text{TiO}_2\text{-Cl}$ as the substrate layer. Box chart of the *PV* metrics showing the comparison of the (c) short-circuit current (d) open-circuit voltage (e) fill factor and (f) PCE of the devices based on the inverted p-i-n and conventional n-i-p architectures.

Figure 4.2(a,b) displays the statistical performances measured for more than 30 inverted and more than 60 conventional devices. Their average PV metrics are also given in Table 4.1 and Figure 4.2(f) displays the data in a box chart. The wider PCE distribution for the inverted devices with respect to the conventional ones is mainly influenced by the different J_{sc} distribution [Figure 4.2(c)] of the two device types. On the other hand, the other PV parameters show relatively similar variation for the two structures (see Figure 4.2(d,e), for the open-circuit voltage and fill factor, respectively). Interestingly, although the J_{sc} and V_{oc} show not only high reproducibility but also superior values, the major limiting factor to the performance of the conventional devices is the fill factor.

Figure 4.3: Optical, structural and morphological characterization of perovskite films on PEDOT:PSS and $\text{TiO}_2\text{-Cl}$. (a) Absorbance and photoluminescence spectra, (b) XRD patterns, and (c and d) top-view SEM images of $\text{FA}_{0.85}\text{MA}_{0.15}\text{PbBr}_{0.45}\text{I}_{2.55}$ thin films on PEDOT:PSS- and $\text{TiO}_2\text{-Cl}$ -coated ITO substrates. The insets show a higher magnification.

To gain insight into why the different device architecture types with identically processed perovskite films exhibit different device performances, we first examine the optical, structural and morphological properties of the films when deposited on the different substrate layers. In general, high quality films with controlled morphology, high surface coverage and minimum pinholes are required for high performing planar perovskite solar cells. Since these requirements are influenced by factors such as material composition, additives, deposition method and film treatment, they controlled in the device fabrication process in order to obtain identically processed perovskite films. Of course, the surface energy of the substrate layer will also have a large influence on the morphology of the active layer.

Figure 4.3(a) shows both the absorbance and normalized steady-state photoluminescence (PL) spectra of the perovskite films deposited on PEDOT:PSS and TiO₂-Cl. While the identical absorbance spectra are indicative of the same thickness, the identical PL spectra show that both films exhibit identical composition. Similarly, the x-ray diffraction (XRD) patterns of the perovskite films on both substrate layers exhibit identical diffraction peaks with no traces of secondary phases [see Figure 4.3(b)]. The peak intensities as well as the full width at half maximum (FWHM) are also identical, indicating an identical structure and disorder. Figure 4.3(c) and 4.3(d) show the top-view scanning electron microscopy (SEM) images of the perovskite thin films formed on PEDOT:PSS and on Cl-capped TiO₂ films, respectively. The insets are higher magnification micrographs of the same thin films. Although the films exhibit high surface coverage on both surfaces, with identical grain sizes, the overall morphological quality is different. Whereas the film on the Cl-capped TiO₂-coated layer exhibits higher compactness with minimal occurrence of pinholes, the films deposited on PEDOT:PSS show a much higher number of pinholes and pronounced open grain boundaries, which are known to be detrimental to device performance.^[28] For example, the pinholes are likely to cause direct contact between the anode and cathode interfacial materials and therefore lead to high leakage current and thus shunt losses in the device. The grain boundaries induce Schottky defects and cause significant trap assisted recombination.^[28–30] These conditions lead to higher charge recombination and directly affect both the V_{oc} and J_{sc} . Besides the macroscopic appearance of pinholes and the more open grains exhibited by the perovskites grown on PEDOT:PSS, the atomic force microscopy (AFM) micrographs show a root mean square (RMS) roughness of ~11 nm for the perovskite film grown on PEDOT:PSS and ~26 nm

for the sample grown on TiO₂-Cl. We believe that this difference in roughness could be induced by the different morphology of the underlying substrate layers.

Effective PL quenching of the perovskite emission by the charge transport materials and consequently, a shorter PL decay lifetime can be considered as an indicator for effective charge transfer. It can also give insight into the charge recombination dynamics at the perovskite/ESL(HSL) interfaces and in eventual trapping of the photoexcited charge carriers. Hence, we employ steady-state and time-resolved photoluminescence (TRPL) spectroscopy to investigate the charge transfer kinetics between the perovskite films and the transport layers. To avoid selective interrogation, the samples are photo-excited from both the glass (bottom layer) and the film sides (top layer). The data obtained for excitations from the glass side are similar to those obtained from the film side and are indicative of the degree of the charge recombination, charge trapping, or the effectiveness of charge extraction by the charge selective layers. The steady-state PL and TRPL response of the perovskite films coated on/below the *n*- and *p*-type transport materials are shown in Figure 4.4. Among the *n*-type materials, PCBM shows stronger PL quenching than the TiO₂-Cl NC film [Figure 4.4(a)], while among the *p*-type transport layers, both PEDOT:PSS and Spiro-OMeTAD exhibit similar PL quenching capabilities [Figure 4.4(b)]. This observation is consistent with the previous work by Snaith and coworkers who showed that the PL quenching of CH₃NH₃PbI_{3-x}Cl_x perovskite emission by *n*-type quenchers such as high-temperature sintered sol-gel TiO₂ and PCBM and the *p*-type quenchers follow the same trend^[22]. On the other hand, Tan *et al.* demonstrated an effective PL quenching by the colloidal nanocrystal-based films of TiO₂ and TiO₂-Cl to a similar degree which they attributed to excellent band alignment and fast charge extraction by these transport materials.^[23]

It is important to underline that a strong quenching does not automatically correlate to an effective extraction of charge carrier and therefore to good solar cells performance. Recently, we have shown the comparison of two different fullerene derivatives for which the PL quenching and the device performance did not correlate with each other. This was attributed to the fact that trapping of charge carriers also reduces the effective PL intensity.^[31]

The corresponding PL decays for the *n*- and *p*-type transport materials are shown in Figure 4.4(c,d), respectively. The decay profiles are fitted with bi-exponential functions, exhibiting fast (τ_1) and slow (τ_2) decay lifetimes. The

Figure 4.4: Photoluminescence response of $\text{FA}_{0.85}\text{MA}_{0.15}\text{PbBr}_{0.45}\text{I}_{2.55}$ pvsk films coated on/with n- and p-type quenchers. (a) Steady-state photoluminescence spectra of n-type quenchers and (b) p-type quenchers of perovskite films processed in a bi-layer configuration. (c) Corresponding time-resolved photoluminescence decay of perovskite thin films for n-type quenchers and (d) p-type quenchers. The excitation was performed from both the glass and the side of the deposited layers.

perovskite film on the ITO-coated glass has a fast decay lifetime (τ_1) of 54.7 ns and a slow decay lifetime (τ_2) of 170.4 ns. When the perovskite films are deposited on PEDOT:PSS, the PL decay becomes overall faster with a first component of $\tau_1 = 3.2$ ns and a second component of $\tau_2 = 53.5$ ns. For the interface with Spiro-OMeTAD, the measured lifetimes are $\tau_1 = 5.5$ ns, and $\tau_2 = 16.5$ ns. When considering the average decay lifetimes, the interface with Spiro-OMeTAD has a much shorter lifetime of $\tau_{\text{avg}} = 10.2$ ns than that of the PEDOT:PSS interface with $\tau_{\text{avg}} = 25.2$ ns. On the other hand, the rate of electron extraction by PCBM and $\text{TiO}_2\text{-Cl}$ is clearly distinguished. PCBM gives a shorter average lifetime of 32.9 ns, while the average PL lifetime of the perovskite film on $\text{TiO}_2\text{-Cl}$ NC film is 152.0 ns, which is comparable to that on ITO-coated glass, 156.7 ns. Therefore, the

significant PL quenching by the $\text{TiO}_2\text{-Cl}$ NC film does not correlate with the observed long decay lifetime, implying that either the extraction of the electrons occurs at a faster time-scale beyond the resolution of the measuring instrument or that the $\text{TiO}_2\text{-Cl}$ NC film is after all a poor electron extraction layer. Clearly, the excellent PV performances of the devices based on the $\text{TiO}_2\text{-Cl}$ NC films allow us to exclude the latter. It is important however, to emphasize again that a fast decay could also be due to trapping of the photoexcited charge carriers at the interface, as discussed above. ^[31]

Figure 4.5: Light intensity dependence characteristics of planar perovskite solar cells. (a) Light intensity dependent J-V characteristics for the PEDOT:PSS-based (p-i-n) device and (b) $\text{TiO}_2\text{-Cl}$ NC film-based (n-i-p) device. (c) Corresponding light intensity dependence of the short circuit current density. Markers indicate the experimental data points while solid lines are linear fitting from which α is extracted based on the equation $J_{sc} = cI^\alpha$, where I is illumination intensity. (d) Corresponding V_{oc} dependence on the illumination intensity.

To gain deeper understanding of the charge carrier recombination mechanisms in the solar cells, we investigated light intensity dependent J - V characteristics. The dependence of the current density (J) on applied voltage (V) can be expressed using the Shockley diode equation,

$$J = J_0 \left[\exp \left(\frac{qV}{nkT} \right) - 1 \right] - J_{sc} \quad (4.1)$$

where J_0 is the reverse saturation current density, q is the elementary charge, n is the ideality factor, k is Boltzmann's constant and T is the temperature. At open circuit conditions ($J = 0$), the above equation can be rearranged to show the dependence of V_{oc} on illumination intensity (I),

$$V_{oc} = \frac{nkT}{q} \ln \left(\frac{J_{sc}}{J_0} \right) = \frac{nkT}{q} \ln(I^\alpha) + c \quad (4.2)$$

where c is a constant that takes into account all the terms that are independent of light intensity and α is an empirical parameter which determines the linearity of the photocurrent with light intensity. α is unity for ideal devices. Similarly, the ideality factor (n) gives insight into the dominant recombination mechanisms in solar cells. Devices with dominant bimolecular recombination have an ideality factor close to unity while those with dominant trap-assisted recombination have values close to 2

The J - V characteristics of the two types of devices for illumination intensities ranging from 3.2 to 100 mW cm⁻² are shown in Figure 4.5(a) and 5.5(b) respectively. The variation of the J_{sc} as a function of the illumination intensity is plotted on a log-log scale [Figure 4.5(c)] and fitted with the power law $J_{sc} \propto I^\alpha$. The α values extracted are 0.94 and 1.00 for devices using PEDOT:PSS and TiO₂-Cl NC films, respectively. Figure 4.5(d) also shows the dependence of V_{oc} on the light intensity from which the ideality factor n is extracted. The ideality factor for the PEDOT:PSS-based and TiO₂-Cl NC film-based solar cells are calculated to be 1.55 and 1.49, respectively. This indicates that, both bimolecular and trap-assisted recombination are present in these devices. The dominant trap-assisted charge recombination effect in the p-i-n device compared to the n-i-p device is in agreement with the observed performance of the devices and previous studies, where it was shown that devices based on compact perovskite films exhibited less trap-assisted recombination and better J - V characteristics than non-compact perovskite films with open grain boundaries.^[28] Hence, the differences in the J - V characteristics and particularly, the low V_{oc} and low J_{sc} observed in the p-i-n device

can directly be attributed to higher rate of trap-assisted charge recombination as also demonstrated by Tvingstedt *et al.* and Shekar *et al.*^[29,32]

Figure 4.6: Impedance spectroscopy measurements under 1 Sun illumination at open circuit conditions. The inset shows the equivalent circuit used for the analysis. The circuit consists of a series resistance R_1 , a constant phase element (CPE) and a recombination resistance R_2 .

To elucidate the effect of the interfaces on the performance of the devices and determine the recombination rate of charge carriers at the interfaces, impedance spectroscopy was performed. The impedance spectra of the n-i-p and p-i-n devices shown in Figure 4.6, were recorded under one sun illumination at open circuit condition. The equivalent circuit consisting of series resistance R_1 , constant phase element (CPE) and recombination resistance R_2 , as shown in the inset of Figure 4.6 is used to fit the Nyquist plot. The fitting parameters are shown in Table 4.2. The characteristic lifetime τ of the charge carriers in the devices is obtained from the product of the recombination resistance and the chemical capacitance given by $C_2 = Q_2 (2\pi f_{\text{peak}})^{a-1}$ (i.e. $\tau = R_2 C_2$), where f_{peak} is the frequency at the maximum imaginary component of the Nyquist spectrum, a indicates the deviation from an

ideal capacitor and Q is the constant phase element value. The Nyquist plot of the p-i-n device shows a severely depressed semi-circles with a lower than unity (0.72), which is indicative of significant inhomogeneity probably due to the pinholes and open grain boundaries in the perovskite film, which are responsible for significant trap-assisted recombination in the device. On the other hand, the n-i-p device displays almost perfect semi-circle and behaves like a pure capacitor with a value close to unity (0.95). This is an indication of the homogeneity of the device, which is in good agreement with the compactness of the perovskite film observed in the SEM investigation [Figure 4.3(d)]. The charge carriers in the p-i-n device have a shorter lifetime of about 1.2 μ s due to charge carrier recombination at the interfaces, while those in the n-i-p device have a lifetime of about 1.6 μ s implying a lower number of traps at the interfaces.

Table 4.2: Impedance spectroscopy fitting parameters for the inverted p-i-n and regular n-i-p perovskite devices

Architecture	R_1 [Ω]	R_2 [Ω]	Q_2	a	f_{peak} [Hz]	τ [μ s]
Inverted p-i-n	31.3	26.9	2.42×10^{-6}	0.718	177832	1.28
Regular n-i-p	24.08	46.41	7.35×10^{-8}	0.945	125889	1.62

Therefore, by correlating the electrical performance of the devices to the spectroscopic study, we can deduce that the effective PL quenching by the transport layers and the decay lifetimes are not entirely indicative of effective charge transfer between the perovskite films and the charge selective materials. This implies that, the shorter decay lifetime and the corresponding poor performance of the inverted p-i-n devices can be attributed to the presence of a higher number of interface traps leading to charge carrier recombination. Interestingly, the better performance of the conventional n-i-p device confirms the effective trap passivation at the $\text{TiO}_2\text{-Cl}$ /perovskite interface as proposed earlier by Tan *et al.*^[23]

4.4. CONCLUSION

In summary, we studied the effect of the device architecture on the performance of $\text{FA}_{0.85}\text{MA}_{0.15}\text{PbBr}_{0.45}\text{I}_{2.55}$ planar perovskite solar cells. The inverted p-i-n and

conventional n-i-p device architectures were fabricated, using PEDOT:PSS and Cl-capped TiO_2 as close-to-substrate/transport layers respectively. The power conversion efficiency of the top-performing device based on the Cl-capped TiO_2 is 19.9%, which is much higher than the efficiency of about 15.1% obtained for the best device based on the p-i-n structure with PEDOT:PSS as substrate layer. To understand the extreme difference in device performance, we investigated the dependence of structural and morphological properties of the $\text{FA}_{0.85}\text{MA}_{0.15}\text{PbBr}_{0.45}\text{I}_{2.55}$ perovskite thin films on the nature of the under layers. We find that the perovskite films formed on the Cl-capped TiO_2 NC layer are more compact and homogeneous with no, or minimum pinholes in comparison with the perovskite films on the PEDOT:PSS. X-ray diffraction characteristics show that the perovskite films are structurally identical. The photoluminescence and impedance spectroscopy measurements show that a lower amount of traps are present at the TiO_2 -Cl/perovskite and perovskite/Spiro-OMeTAD interfaces than at the PEDOT:PSS/perovskite and perovskite/PCBM interfaces. Thus, the work presented here underlines the importance of device architecture and interfaces for achieving highly performing perovskite solar cells.

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CHAPTER 5

Effects of Strontium Insertion on the Morphological, Structural and Photophysical Properties of FASnI₃ Perovskite Thin Films

Abstract

Compositional engineering has been an effective technique applied extensively to enrich semiconductors and modulate their fundamental properties for electronic and optoelectronic applications. In this work, we report the influence of strontium (Sr) insertion into solution-processed formamidinium tin iodide (FASnI₃) perovskite thin films. We show that the addition of the Sr²⁺ dopant to the host perovskite drastically changes the morphology of the material but has no significant effect on the structural phase for concentrations lower than 10%. Using photoluminescence spectroscopy, we showed that for Sr contents below 15%, the film is heterogeneously doped, and strontium predominantly resides at the surface of the film. Above 15% of Sr, the bulk of the material is significantly doped. Our results show that Sr insertion into FASnI₃ perovskite can be a route for the attainment of new perovskites with interesting physical properties

This chapter is based on the publication:

S. Adjokatse, S. Kahmann, H. Duim and M.A. Loi, *APL Materials*, **2019, 7(3), 031116.**

5.1. INTRODUCTION

The most extensively studied halide perovskites are the lead (Pb) and tin (Sn) perovskites. Among them, the more stable and high-performing devices are based on the lead-containing perovskites. Unfortunately, they are toxic and water-soluble. Hence, their large-scale and long-term use are not environmentally sustainable, a fact that could in future pose limitations towards commercialization. Sn halide perovskites are supposedly less toxic and have a narrower band gap, which make them better potential candidates for high-performance solar cells. The main problem, however, is their instability, as they are prone to self-doping when Sn^{2+} transforms into Sn^{4+} . To circumvent this mechanism, compositional and doping engineering are plausible strategies to employ, having been shown to be viable means of controlling the crystal growth, structural stability and light conversion properties of most perovskite materials.^[1-5] Strontium (Sr) is one of the metal dopants found to exhibit multiple functions such as enhancing device performance and stability of the host perovskite. The ionic radius of Sr is virtually identical to the one of Sn (Sr^{2+} : 1.18 Å and Sn^{2+} : 1.18 Å) and only has +2 oxidation state, giving rise to the possibility of doping the crystal structure of Sn-based perovskites to stabilize and tune their optoelectronic properties. Furthermore, Sr is highly abundant and environmentally friendly. Although neat Sr halide perovskite is reported to have a very wide band gap (e.g. 3.6 eV for MASrI_3),^[6] the observation of a band gap bowing in Sn-Pb mixtures suggests that a similar effect might also be present in the Sn-Sr system.^[7]

Recently, Sr has been explored as a dopant in Pb perovskites and found to have a direct effect on the optoelectronic properties and performance of the devices as well as the material's structural stability. Perez-del-Rey *et al.*, have reported a significant increase in the device fill factor from 78% for the neat perovskite to 85% for 2% Sr^{2+} doping in methylammonium lead iodide (MAPbI_3) perovskite.^[4] Shai *et al.* also reported significant increase in the stability of $\text{MAPbI}_{3-x}\text{Cl}_x$, which they attributed to suppression of the unsaturated Pb in the presence of Sr dopant.^[8] Additionally, doping with Sr^{2+} has been shown to be effective in surface passivation with resultant films that had fewer defects.^[5,9] Most recently, metal doping has been extended to Sn perovskites. Dimesso *et al.*, have reported enhanced thermal stability of MASnI_3 ^[10] and FASnX_3 ($\text{X} = \text{I}, \text{Br}$)^[11] under nitrogen environment after doping with earth-alkaline ions (Ca^{2+} , Sr^{2+} , Mg^{2+}).

However, no work has been reported on the influence of strontium doping on formamidinium-based tin perovskite thin films. In fact, the above-mentioned work reported stability of the perovskite only in powder systems. Hence, here we explore the effects of strontium insertion on the morphological, structural and photophysical properties of formamidinium tin iodide perovskite thin films. We show drastic changes in the morphology of the perovskite with the addition of strontium. Crystallographic analysis showed, however, no structural changes with respect to the neat tin perovskite below a concentration of 15%. Finally, PL spectroscopy reveals the accumulation of strontium on the surface of the films also for concentrations below 15%.

5.2. EXPERIMENTAL DETAILS

Materials and solution preparation

The perovskite precursors: tin (II) iodide (SnI_2) (99.999%) and strontium iodide (SrI_2) (99.99%) were purchased from Sigma Aldrich which formamidine hydroiodide (FAI) was purchased from TCI EUROPE N.V. *N,N'*-dimethylformamide (DMF) (99.8%) was acquired from Sigma-Aldrich, gamma-butyrolactone (GBL) and dimethyl sulfoxide (DMSO) (99.9%) from Alfa Aesar.

The precursor solution of formamidinium tin iodide (FASnI_3) perovskite was obtained by dissolving equimolar amounts of formamidinium iodide (FAI) and tin iodide (SnI_2) precursors in a mixed solvent of DMF and DMSO at a volume ratio of 4:1 to form a solution of 0.5 M. To prevent the rapid oxidation of Sn^{2+} to Sn^{4+} in solution, the solution is doped with 10% of tin fluoride (SnF_2). The formamidinium strontium iodide (FASrI_3) precursor solution is obtained by dissolving equimolar amounts of FAI and strontium iodide (SrI_2) precursors in gamma-butyrolactone (GBL) to form a solution of 0.5 M. To obtain the alloyed $\text{FASn}_{1-x}\text{Sr}_x\text{I}_3$ solution, we mixed stoichiometric amounts of FASnI_3 and FASrI_3 to form solutions with varying Sr/Sn ratios, representing 0% to 50% molar concentration of Sr^{2+} in solution.

Perovskite film fabrication

The films were fabricated on glass substrates, which were ultrasonically cleaned in detergent solution, deionized water, acetone and isopropanol, sequentially. After

drying them in an oven at 140 °C for about 10 min, they were treated with ultraviolet ozone (UV-O₃) plasma for 20 min and then transferred into a nitrogen-filled glovebox immediately for the film deposition. The films were fabricated using a two-step spin program with anti-solvent treatment. The spin program was set to 1000 rpm for 10 s and 4000 rpm for 30 s. The anti-solvent (chlorobenzene) was dropped onto the film at about 5 s prior to the end of spinning. The films were immediately annealed at 100 °C for 10 min.

Morphological Characterization

The scanning electron microscopy (SEM) images were obtained using the FEI Nova Nano SEM 650 with an accelerating voltage of 2 - 10 kV for the secondary electron images and ~10 kV for the backscattered electron images. The Atomic force microscopy (AFM) images were taken using the Bruker NanoScope V in the ScanAsyst mode.

Structural Characterization

The X-ray diffraction was performed at ambient conditions. The x-ray data were collected using a Bruker D8 Advanced diffractometer in Bragg-Brentano geometry and operating with Cu K_α radiation source ($\lambda = 1.54 \text{ \AA}$) and Lynxeye detector.

Optical Characterization

Absorption measurements were taken using a UV-vis-NIR spectrophotometer (Shimadzu UV-3600). The photoluminescence measurements were performed using the second harmonic (400 nm) of a Ti:sapphire laser (repetition rate, 76 MHz; Mira 900, Coherent) to excite the samples. Unless stated otherwise, the illumination power was decreased to 300 μW cw-equivalent by using a neutral density filter, which amounts to a fluence of approximately 337 nJ cm⁻² on the sample. The excitation beam was spatially limited by an iris and focused with a 150-mm focal length lens. Emitted photons were collected with a lens in reflection geometry from the sample side. Steady-state spectra were collected using a Hamamatsu EM-CCD camera and time resolved spectra were measured using a streak camera in synchroscan mode. Samples were kept under nitrogen atmosphere during the measurement.

Confocal laser scanning microscopy was performed by coupling the aforementioned Ti:Sapphire laser into an inverted Nikon Eclipse Ti-E microscope system. A 40x plan Fluor objective was used for focusing of the excitation beam and collection of the PL signal. PL signals were recorded by photomultiplier tubes operating with detection ranges of (i) 540 nm to 640 nm and (ii) 650 nm long-pass.

5.3. RESULTS AND DISCUSSION

The alloyed $\text{FASn}_{1-x}\text{Sr}_x\text{I}_3$ ($0 \leq x \leq 0.5$) perovskite thin films investigated in this work are deposited from solution on glass substrates. Figure 5.1(a) presents photographs of the $\text{FASn}_{1-x}\text{Sr}_x\text{I}_3$ perovskite thin films showing the effect of the Sr doping on their colors. While the neat tin-based films are dark brown with a lackluster surface, films with 1 – 7.5 % Sr are dark brown with increased surface reflectivity. Interestingly, as the Sr concentration increases, a noticeable higher surface reflectivity is observed, which indicates an increased uniformity of the films. The film color gradually changes to reddish brown as the Sr concentration is increased further from 7.5% to 50%. The absorption spectra of the fabricated thin films are reported in Figure 5.1(b). The absorption band onset of the neat FASnI_3 perovskite is clearly observed at 900 nm, consistent with previous reports.^[2] However, upon addition of Sr to the neat FASnI_3 , we observe a clear blue-shift in the absorption spectra with increasing Sr concentration. Moreover, contrary to what appears to be a strong blue-shift in the absorption peak for the doped samples, the peak intensity reduces substantially compared to the neat perovskite film for the 1% Sr sample in comparison to the neat film.

To find the motivation of this band gap variation, the crystallinity and the structural properties of the films are examined with x-ray diffraction (XRD) measurements. The instability of the films in ambient conditions, which increases with the amount of Sr made these measurements extremely challenging allowing measurement of samples with concentrations of Sr between 0% and 10% only. As shown in the XRD patterns in Figure 5.1(c), the Bragg peaks for both the neat and the strontium-containing films are observed at 2θ values of 14.09° , 24.51° , 28.32° , 31.77° , 40.50° and 43.11° . Therefore, the addition of Sr has no significant effect on the structural phase of the material at these concentrations. Analysis of the peaks at 14.09° shows that the full-width at half-maximum broadens with increasing Sr content, which indicates decrease in the crystal grain sizes. The diffraction intensities of the peaks are also reduced as the Sr content is increased, which could

be due to either the low crystallinity of the films with higher Sr concentration or to the reduction of crystallinity due to degradation. The decrease of the diffraction peak intensities determined by degradation has been reported for Sr-doped CsPbI_2Br perovskites.^[5]

Figure 5.1: Photographs, optical and structural characterization of alloyed $\text{FASn}_{1-x}\text{Sr}_x\text{I}_3$ perovskite thin films. **(a)** Photographs showing FASnI_3 thin films with various amount of Sr doping. **(b)** UV-vis absorption spectra normalized at 950 nm, showing the blue-shift of the absorption upon Sr addition. **(d)** X-ray diffraction patterns of FASnI_3 thin films with various Sr contents.

The morphological control of thin films is one of the challenges of hybrid perovskite optoelectronics. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) micrographs of the different samples are shown in Figure 5.2 and Figure 5.3, respectively. Figure 5.2(a) shows the morphology of the neat FASnI_3 perovskite film, which is composed of closely packed crystals with sizes in the range of 0.5 – 1 μm and is characterized by many pores of several hundreds of nanometers width, as well as sharp grain boundaries. The morphology of this reference film is similar to the one previously reported by Shao *et al.*, who showed that such morphology is a contributing limiting factor to the low efficiency of Sn-based perovskite solar cells.^[12] The addition of Sr to the neat perovskite, however, transforms the morphology substantially. Extreme differences can be observed,

depending on the amount of the Sr^{2+} introduced in the films. The addition of 1 - 2.5 % of Sr to the neat perovskite, for instance, leads to fused, flatter and more homogeneous thin films, with grain sizes in the 50 – 200 nm range and fewer pinholes [Figure 5.2(a) and 5.2(c)]. This fits the perception of a more reflective film. The films with 5% and 7.5% Sr content also exhibit a unique morphology that varies slightly for the films with 10% and 15% Sr, as shown in Figure 5.2(d-g). These films are formed by much smaller grain sizes that are densely packed.

Figure 5.2: Thin film morphological characterization. (a-i) Top-view SEM images of the alloyed $\text{FASn}_{1-x}\text{Sr}_x\text{I}_3$ perovskite thin films showing the film's morphological characteristics for 0% to 50% Sr doping.

As clearly shown in the AFM images (Figure 5.3), the films with 10% Sr are highly uniform with completely smeared out grains, except for the appearance of crystallites on the surface. However, as the Sr content is further increased to and above 25%, crystallites appear and the homogeneous and fused domains begin to shrink, leading to the formation of non-continuous films [Figure 5.2(h) and 5.2(i)]. Thus, in general, increasing the Sr content first decreases the crystal grain sizes and

then drastically changes the film morphology. The measurement of the film roughness from the AFM images in Figure 5.3 shows a decrease in the root-mean-square (rms) roughness from ~ 50 to ~ 30 nm going from 0% to 10% Sr. An interesting observation is the formation of large crystallites on the surface of the films for Sr concentrations above 7.5%. As will be validated in the following, our speculation is that these crystallites are composed mainly of Sr-dominated perovskites.

Figure 5.3: Atomic force microscopy images of alloyed $\text{FASn}_{1-x}\text{Sr}_x\text{I}_3$ ($0 \leq x \leq 0.5$) perovskite thin films showing the film's morphological characteristics for 0% to 10% Sr content.

Figure 5.4(a) shows a photoluminescence intensity map of the neat FASnI_3 film obtained using confocal laser scanning microscopy as detected by a photomultiplier with a 650 nm long pass filter in front (red channel). Likewise, Figure 5.4(b) and 5.4(c) show the spatial distribution of the PL for the 15% and 50% Sr films. Congruent with the SEM micrographs, the neat film shows a relatively uniform PL distribution interrupted by a high density of micrometer-sized pinholes. Upon increasing the Sr content to 15%, the PL distribution becomes less homogeneous

and bright features appear throughout the film. The size and distribution of these bright features closely match the features observed in the SEM images of the same film, indicating that the increased PL originates from these surface structures. Increasing the Sr content even further to 50% leads to the formation of larger clusters as well as singular bright spots of various sizes and intensities. For both the neat and 15% Sr films, no PL is detected in the wavelength range from 540 nm to 640 nm [Figure 5.4(d) and 5.4(e)] (green channel). In the case of the 50% Sr film, however, significant PL intensity is recorded in this high-energy channel [Figure 5.4(f)]. Comparison of the red and green channels reveals that for the 50% Sr film, we can identify two different types of features in the PL maps; some of the large features that appear brightened in the red channel appear to be dimmer in the green, while some of the smaller spots are relatively bright in both channels. This difference in the local emission spectra corroborates the notion that the film's surface exhibits structures that are compositionally different from the surrounding or underlying perovskite material.

Figure 5.4: Confocal laser scanning micrographs of the PL from (a) pristine, (b) 15% and (c) 50% strontium-containing FASnI₃ films as detected by a 650 nm long pass detection channel. (d, e, f) PL maps of the same films recorded with a detection channel operating in the wavelength range of 540 nm to 640 nm.

In Figure 5.5, we report the photoluminescence spectra of the thin films upon increasing the strontium content. As displayed in the semi-logarithmic plot in Figure 5.5(a), the maximum PL intensity decreases by three orders of magnitude when going from 0% to 50% Sr content. Simultaneously, the emission maximum shifts towards higher energy and thus follows the trend of the band gaps of the two neat materials (FASnI₃ at 1.37 eV and a calculated E_{gap} of 3.6 eV for MASrI₃).^[2,6] Importantly, this contrasts with the behavior of mixed Sn and Pb perovskites, where the band gap is narrower for the mixtures than for neat FASnI₃.^[7] Besides this peak shift, the normalized spectra in Figure 5.5(b) also show a broadening of the emission band. This broadening is mostly due to the appearance of a shoulder in the emission spectra at around 1.38 eV – the energy of the FASnI₃ emission peak – whilst the main emission shifts to higher energy for increased Sr-content. As we shall discuss further below, we attribute this feature to the presence of two different phases in the film.

Figure 5.5: Photoluminescence (PL) characteristics of Sr-doped FASnI₃ perovskite thin films. **(a)** Absolute and **(b)** normalized steady-state PL emission spectra of FASnI₃ perovskite thin films with 0% to 50% Sr content. **(c)** Corresponding time-resolved PL taken at emission maximum.

Table 5.1: Summary of the decay lifetimes of the 7.5% Sr-doped perovskite film with excitation power of 300 μ W

Sr content (%)	A₁	τ_1 (ps)	A₂	τ_2 (ps)	τ_{av} (ps)
0	1	739			739
1	0.06	168	0.94	671.25	642
2.5	1	600			600
5	0.42	200	0.58	508.00	389
7.5	1	128			128
10	1	27			27
15	1	14			14
25	1	12			12
50	1	12			12

The transient PL in Figure 5.5(c) (taken at the emission maximum) shows a significant PL lifetime reduction already for the smallest additions of Sr to FASnI₃. The extracted lifetime amounts to approximately 700 ps for neat FASnI₃ and decreases to the instrumental resolution-limited 12 ps for Sr contents exceeding 10% (see Table 5.1). This behavior is in line with the drastic reduction in PL intensity and underlines the poor quality of these Sr-Sn mixtures.

In all cases, the PL shifts towards higher energy upon increasing the excitation power [Figure 5.6(a)]. This effect was previously addressed for neat FASnI₃ and attributed to a combination of state filling and emission due to hot charge carriers.^[12] Exposure to laser intensities exceeding 20 mW furthermore leads to the macroscopic ablation of surface material, as indicated by the black spectrum in Figure 5.5(a). The PL from the “bulk” of the thin film is significantly red-shifted (peaking at 1.38 eV for 15% Sr) and much narrower than when compared to the original surface-related PL. A close look also shows that the above-mentioned shoulder around 1.38 eV in the PL spectra is consequently due to this “bulk”-related emission. We thus conclude that our samples possess distinctly different compositions in the “bulk” and at the surface. The blue-shifted PL furthermore suggests that Sr is predominantly located at the surface, whilst the emission from the “bulk” is virtually identical to the one of neat FASnI₃ or of films with Sr contents below 10%. Crucially, increasing the Sr content beyond 10% also leads to

a blue-shift of the bulk-related PL, which shows that Sr is at these concentrations also incorporated into the “bulk” of the film [Figure 5.6(b)]. As additional evidence, the streak camera images presented in Figure 5.7 also exemplify this effect.

Figure 5.6: Excitation power-dependent PL characteristics of Sr-doped FASnI₃ thin films. (a) Normalized power-dependent PL spectra of the FASnI₃ thin film with excitation power increased from 100 μ W to 20 mW for the 15% Sr-doped sample (112 nJ cm^{-2} - 22.5 mJ cm^{-2}). (b) Normalized PL spectra of FASnI₃ perovskite thin films with 0% to 50% Sr content obtained after surface ablation of the film. (c) Power-dependent time-resolved PL decay of FASnI₃ thin film pumped with different laser intensities for the 7.5% Sr-doped sample.

Besides the spectral shift, the bulk-related PL also shows a much longer lifetime than the emission from the surface. Exemplarily, we show the corresponding data for the 7.5% Sr sample in Figure 5.6(c). Whilst the emission decays relatively fast on the surface ($\tau = 128 \text{ ps}$) and becomes even faster for higher excitation intensity,

the “bulk” PL shows a much longer lifetime that is close to the one obtained from neat FASnI_3 (especially for small Sr concentration).

Figure 5.7: Streak camera images of the 15% Sr containing sample (a) before and (b) after surface ablation due to high laser exposure. The plots clearly indicate the ultrafast emission centered around 800 nm in the original film, which shifts towards 850 nm and becomes much longer-lived upon high-intensity exposure. The stark contrast indicates a different composition of the film surface and bulk.

5.4. CONCLUSION

In summary, we have fabricated $\text{FASn}_{1-x}\text{Sr}_x\text{I}_3$ perovskite thin films with varying concentrations of Sr^{2+} in the range of 0% to 50%. The addition of Sr substantially changes the morphology of the perovskite films and blue-shifts the absorption spectra with increasing Sr content. XRD analysis of 1-10% Sr-doped perovskite films showed no significant changes to the crystal structure at these concentrations. PL analysis of the doped samples revealed the presence of two distinct phases of the material for Sr contents below 10%: the Sr-deficient bulk and Sr-rich surface phases. However, for Sr contents above 15%, we observed Sr incorporation in the bulk of the material. We therefore conclude that Sr incorporation in these films occurs heterogeneously and predominantly at the surface while samples of high Sr concentration clearly contain Sr also in the bulk of the sample. This work gives an insight into the properties of alloyed $\text{FASn}_{1-x}\text{Sr}_x\text{I}_3$ perovskites showing both, interesting properties, but also the large potential of Sr-doping in tin perovskites.

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Summary

The quest for novel semiconductor materials with facile processing and versatile properties as light absorbers in solar cells has led to the discovery of hybrid metal halide perovskites and a whole new generation of materials for solar cells, which gave rise to remarkable power conversion efficiency. This impressive performance in solar cells has also spawned the exploration of diverse applications from light emitting diodes and lasers to photodetectors. Perovskites have been shown to possess superior optoelectronic properties such as high optical absorption coefficient, long charge carrier lifetimes, high carrier mobilities, long diffusion lengths, low trap densities and broadly tuneable bandgaps from the visible to the near-infrared spectral range. Despite these outstanding properties, and the vast areas of application, the commercialization of perovskite technology will not be successful until the major issues concerning the composition and stability of the active material are solved. Namely, the best performing perovskites contain Pb and are characterized by ionic bonds that make them soluble in water and therefore unstable in ambient condition. Additionally, there is still room for improvement of the power conversion efficiency towards the theoretical limit. To achieve these goals, a deeper understanding of the physical properties of this class of materials and devices and the search for non-toxic perovskites are essential.

This thesis focuses on the understanding of the photophysics and optoelectronic properties of these materials and their application in solar cells.

A key factor to the improvement of the efficiency of the perovskite solar cells lies in the development of high-quality perovskite active layers with reduced defect density. Therefore, to understand the defect physics of perovskites, (in Chapter 2) we synthesized MAPbBr₃ single crystals from solution and investigated their optical properties in vacuum and in the presence of environment gases using single-photon and two-photon excitation. We show that the photoluminescence (PL) properties which are extremely sensitive to the defect states of the material can be drastically modulated by the physisorption of O₂ and H₂O molecules, thereby controlling the surface recombination velocity of the crystal. Surface recombination velocities as low as 4 cm s⁻¹ are measured when the single crystals are exposed to ambient conditions. As the passivation of the trap states is due to physisorption, the process is fully reversible when the sample is again put in

vacuum. Interestingly, also the charge transport properties measured on the surface of the crystal are sensitive to the surface trap passivation.

In Chapter 3, we explore a new scalable technique to fabricate high-quality photoactive 3D FAPbI₃ thin films. First, 2D PEA₂PbI₄ films are doctor-blade coated and subsequently converted to the 3D FAPbI₃ thin films using a cation exchange reaction. The converted 3D perovskite films exhibit excellent surface coverage and improved morphology with crystalline domain sizes as large as ~10 μ m. They are also very crystalline with highly preferential crystal orientations that mimic the orientation of the 2D perovskite template. The improved perovskite films result in enhanced PL intensities that are about 20 times higher compared to the one of the reference one-step blade-coated FAPbI₃ perovskite films. Additionally, we show that the converted films exhibit a significantly enhanced photo- and moisture stability under continuous laser illumination and under ambient conditions compared to the reference films.

In Chapter 4, we investigate the role of device architecture on the performance of FA_{0.85}MA_{0.15}PbBr_{0.45}I_{2.55} planar perovskite solar cells. Devices based on the p-i-n and n-i-p device architectures were fabricated, using PEDOT:PSS and Cl-capped TiO₂ as close-to-substrate/transport layers, respectively. The power conversion efficiency of the top-performing devices based on the Cl-capped TiO₂ is 19.9%, which is much higher than the 15% efficiency obtained for the best device based on the p-i-n structure with PEDOT:PSS as substrate layer. To understand the extreme difference in device performance, we investigated the dependence of structural and morphological properties of the FA_{0.85}MA_{0.15}PbBr_{0.45}I_{2.55} perovskite thin films on the nature of the under layers. We find that the perovskite films formed on the Cl-capped TiO₂ NC layer are more compact and homogeneous with no, or minimum pinholes in comparison with the perovskite films on the PEDOT:PSS. Although x-ray diffraction characteristics show that the perovskite films are structurally identical, PL and impedance spectroscopy measurements show that a lower amount of traps are present at the TiO₂-Cl / perovskite and perovskite / Spiro-OMeTAD interfaces than at the PEDOT:PSS / perovskite and perovskite / PCBM interfaces.

Finally, in Chapter 5, we explore non-toxic perovskites based on Sn/Sr mixtures. We have fabricated FASn_{1-x}Sr_xI₃ perovskite thin films with varying concentrations of Sr²⁺ in the range of 0% to 50%. The addition of Sr substantially changes the morphology of the perovskite films and blue-shifts the absorption spectra with increasing Sr content. XRD analysis of 1-10% Sr-doped perovskite

films showed no significant changes to the crystal structure at these concentrations. The PL analysis of the mixed samples revealed the presence of two distinct phases of the material for Sr contents below 10%: the Sr-deficient bulk and Sr-rich surface phases. However, for Sr contents above 15%, we observed Sr incorporation in the bulk of the material.

Samenvatting

De zoektocht naar nieuwe halfgeleidermaterialen die eenvoudig verwerkbaar zijn en veelzijdige eigenschappen hebben als lichtabsorberende laag in zonnecellen heeft geleid tot de ontdekking van hybride metaalhalideperovskieten, alsmede een geheel nieuwe generatie van zonnecelmaterialen, resulterend in een uitzonderlijk vermogensomzettingsrendement. Deze indrukwekkende prestatie in zonnecellen heeft daarnaast de exploratie van diverse andere applicaties van lichtgevende diodes en lasers tot fotodetectoren teweeggebracht. Perovskieten beschikken over superieure opto-elektronische eigenschappen zoals een hoge optische absorptiecoëfficiënt, lange levensduur van ladingsdragers, hoge ladingsdragermobiliteiten, grote diffusielengtes, lage ladingsvallendichtheid en een bandkloof die afstembaar is van het zichtbare tot nabij-infrarode deel van het spectrum. Ondanks deze uitmuntende eigenschappen en alle mogelijke applicaties, zal de commercialisatie van perovskiettechnologie niet succesvol zijn totdat de voornaamste problemen omtrent de compositie en stabiliteit van het actieve materiaal zijn opgelost. De best presterende perovskieten bevatten namelijk Pb en worden gekarakteriseerd door ionische bindingen die deze materialen gemakkelijk oplosbaar maken in water, wat leidt tot instabiliteit onder omgevingscondities.

Deze thesis richt zich op het begrip van de fotofysische en opto-elektronische eigenschappen van deze materialen en hun toepassing in zonnecellen.

Een belangrijke factor voor de verbetering van de efficiëntie van perovskiete zonnecellen ligt in de ontwikkeling van hoogwaardige actieve lagen van perovskiet met een gereduceerde defectdichtheid. Met als doel het begrijpen van de fysica van defecten in perovskieten (in Hoofdstuk 2), synthetiseren we monokristallen van MAPbBr_3 vanuit oplossing en onderzoeken we hun optische eigenschappen in zowel vacuüm als in de aanwezigheid van omgevingsgassen met behulp van één-foton- en twee-fotonexcitatie. We laten zien dat de fotoluminescentie (FL) eigenschappen, die extreem gevoelig zijn voor defecten in het materiaal, sterk gemoduleerd kunnen worden door middel van de fysisorptie van O_2 en H_2O moleculen, en dat daarmee dan ook de oppervlakterecombinatiesnelheid beheerst kan worden. Wanneer de monokristallen blootgesteld worden aan omgevingscondities worden oppervlakterecombinatiesnelheden zo laag als 4 cm s^{-1} gemeten. Aangezien de passivatie van ladingsvallen geschiedt via fysisorptie, is het proces volledig omkeerbaar wanneer het monster weer in vacuüm wordt gebracht.

Het is interessant te noemen dat ook het transport van ladingsdragers aan het kristaloppervlak gevoelig is voor deze passivatie van ladingsvallen.

In Hoofdstuk 3 onderzoeken we een nieuwe schaalbare techniek om hoogwaardige fotoactieve dunne lagen van 3D FAPbI₃ te produceren. Eerst worden lagen van 2D PEA₂PbI₄ met behulp van een rakel aangebracht en vervolgens omgezet in de 3D FAPbI₃ lagen met behulp van een kationuitwisselingsreactie. De geconverteerde 3D perovskietlagen beschikken over een uitstekende oppervlaktedekking en verbeterde morfologie met kristallijne domeinen zo groot als ~10 µm. Daarnaast zijn ze in hoge mate kristallijn met een zeer sterke preferentiële kristaloriëntatie die dat van de 2D-perovskietsjabloon nabootst. De verbeterde perovskietlagen leiden tot FL-intensiteiten tot wel 20 keer hoger dan die van de FAPbI₃-referentielagen die via een enkele rakelstap zijn gemaakt. Bovendien laten we zien dat de geconverteerde lagen een significante verbetering in stabiliteit tegen licht en vochtigheid tentoonspreiden onder continue laser-illuminatie en blootstelling aan omgevingscondities ten opzichte van de referentielagen.

In Hoofdstuk 4 bestuderen we de rol die de apparaatarchitectuur heeft op de prestatie van FA_{0.85}MA_{0.15}PbBr_{0.45}I_{2.55} planaire perovskiete zonnecellen. Zonnecellen gebaseerd op zowel een p-i-n- en n-i-p-architectuur zijn gefabriceerd met respectievelijk PEDOT:PSS en met chloor afgetopte TiO₂ als de transportlagen aan de substraatzijde. Het vermogensomzettingsrendement van de best presterende apparaten gebaseerd op de met chloor afgetopte TiO₂ is 19.9%, wat veel hoger is dan de 15% die behaald wordt met het beste apparaat gebaseerd op de p-i-n-structuur met PEDOT:PSS als substraatlaag. Om het extreem grote verschil in prestaties te begrijpen, onderzochten we hoe de structurele en morfologische eigenschappen van de FA_{0.85}MA_{0.15}PbBr_{0.45}I_{2.55} perovskietlaag afhangen van de aard van de onderliggende lagen. We ontdekten dat de perovskietlagen die zijn gevormd op de chloor-afgetopte TiO₂-nanokristallaag compacter en homogener zijn met vrijwel geen of slechts een minimale hoeveelheid aan gaten vergeleken met de perovskietlaag op PEDOT:PSS. Hoewel Röntgendiffractiekarakterisatie (XRD) aantoont dat de perovskietlagen structureel identiek zijn, laten FL- en impedantiespectroscopie zien dat een kleinere hoeveelheid ladingsvallen aanwezig zijn aan de TiO₂-Cl/perovskiet en perovskiet/Spiro-OMeTAD raakvlakken dan aan de PEDOT:PSS/perovskiet en perovskiet/PCBM raakvlakken.

Ten slotte verkennen we in Hoofdstuk 5 niet-toxische perovskieten gebaseerd op mengsels van Sn/Sr. We hebben dunne lagen van de perovskiet FASnSrI_3 gefabriceerd met wisselende concentraties van Sr^{2+} variërend van 0 tot 50 %. De toevoeging van Sr brengt een substantiële verandering in de morfologie van de perovskietlaag teweeg en leidt tot een blauwverschuiving van het absorptiespectrum met een toenemend Sr-gehalte. XRD-analyse van perovskietlagen met een doteringsgehalte van 1-10% Sr lieten geen significante verschillen in de kristalstructuur zien voor deze concentraties. De FL-analyse van de gemengde monsters onthulde de aanwezigheid van twee verschillende materiaalfasen voor Sr-gehalten lager dan 10%: de Sr-arme bulk- en Sr-rijke oppervlakfasen. Voor Sr-gehalten hoger dan 15% nemen we echter ook incorporatie van Sr in de bulk van het materiaal waar.

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- 2014 – 2019 Ph.D. candidate in Physics
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- 2008 – 2009 M.Sc. in Theoretical Physics

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GRANTS & AWARDS

- 2019 Best poster prize award, NIPHO 2019 Conference, Jerusalem, Israel
- 2014 NWO Graduate (Ph.D.) Grant, Zernike Institute for Advanced Materials, University of Groningen, Netherlands
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PUBLICATIONS

1. Herman Duim Hong-Hua Fang, **Sampson Adjokatse**, Gert ten Brink, Miguel A. L. Marques, Bart Kooi, G. R. Blake, Silvana Botti, and Maria Antonietta Loi: Mechanism of Surface Passivation of Methylammonium Lead Tribromide Single Crystals by Benzylamine, *Applied Physics Review* 6, 031401 (2019)

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Acknowledgments

I would like to acknowledge the various people whose support, guidance and encouragement, I have depended upon over the past five years for the successful completion of this journey.

My first and foremost appreciation goes to my promotor, Prof. dr. Maria A. Loi. Maria, you have been very supportive right from the word go. You first accepted me into the Photophysics and Opto-Electronics (PO-E) research group as a master student to pioneer the field of organic-inorganic hybrid perovskites in the research group. At the time, perovskite solar cell was an emerging field in the photovoltaic community with great opportunities and major challenges. With your unwavering support and insightful direction, I successfully completed my master research project. During this period, you guided me with the writing of my Topmaster research proposal which won the Netherlands Organisation for Scientific Research (NWO) Graduate Research Grant, the fund which financed the work presented in this PhD thesis. You generously shared knowledge and also motivated me to work hard even in the face of tormenting challenges, and this has inspired the discovery of novel ideas and the results of this thesis. For this and many other reasons, I am deeply grateful.

Special thanks go to my co-promotors. Prof. dr. T.T.M. (Tom) Palstra, until you became the rector magnificus of University of Twente, you were my co-promotor, both during my master research project and as a PhD student, lending your support in various ways. Prof. dr. L.J.A. (Jan Anton) Koster, thank you for accepting to replace Tom as my co-promotor even at a very short notice. I appreciate the enthusiasm you always convey and your constructive feedback during research group meetings. These feedbacks have been beneficial to the shaping of research ideas and the improvement of scientific results.

My PhD would have been just a dream, if not for the funding I received from NWO through the Zernike Institute for Advanced Materials (ZIAM) and the Graduate School of Science. I would therefore like to acknowledge the financial support from NWO (Graduate Programme 2013, No. 022.005.006) and all those who contributed to the securing of this funding.

I am grateful to all the members of the assessment committee, comprising of Prof. dr. Christoph J. Brabec, Prof. dr. Bart J. Kooi and Prof. dr. Mohammed D.K. Nazeeruddin for taking the time to carefully review my thesis.

The technical and administrative staff of ZIAM have been very resourceful and I am grateful to all of them. The indispensable technical support of Arjen Kamp and Teodor Zaharia cannot be overlooked. You guys were truly amazing, not only for providing the technical support that was required for my success, but also lending personal support whenever needed. Gert ten Brink, you are my man. We didn't only enjoy working behind the SEM/EDX setup, but we also had a lot of fun talking about many diverse interesting topics. "My Nigerian prince", is what you affectionately call me even though you know I am not from Nigeria, but this was as a result of the many funny jokes you like to share which I truly appreciate. Reinder Gooijarts, Jan Harkema, Jacob Baas and Rick van der Reijnd, you have all been supportive in teaching me how to use the different equipment in the your respective labs or helping to solve various technical problems just like Arjen, Teo and Gert. A big thank you to you all. Renate, Jeannette and Annelies, what can a PhD student do without your swift administrative services. They were always very handy and timely.

The next group of people I would like to acknowledge are colleagues and group members of the PO-E. Dr. Hong-Hua Fang, you are my distinguished friend and teammate. "Dr. Fang", as I like to call you, the stories about our work and friendship cannot be written in a few words. I am highly indebted to you. Your ardour for science, objective approach to problems, calmness and resilience has been a great motivation to me. You supported me tremendously during my masters and PhD research and this is reflective in the several publications we have together. Your generosity and selflessness will always be valued.

Daniel, it all started with you as my daily supervisor during my master research. Your regular criticism and alerts have been helpful in shaping my research work and so I am very grateful. Herman, Simon and Bart, what else can I say besides expressing my appreciation for the wonderful collaborations and the laughs together. Herman, you became a great working partner and I am grateful for all your assistances including the translation of the thesis summary. Musty and Doumon, you guys have been a great bedrock for me and I truly appreciate you guys. Mark Speirs, you are a true brother. Thank you for your immense support both at and outside work.

Herman and Musty, thank you once again for accepting to be my paranymphs. I wish you both the very best in also completing your PhDs successfully.

In no particular order, thanks to Jane, Shuyan, Irene, Natasha, Dima, Wytse, Martha, Azi, Vincent, Jian, Marten, Artem, Jorge, Lai-Hung, Marianna, Widi, Satria, Vlad, Niels, Solmaz, Davide, Tejas, Insan, Kush, Eelco, Christian, Max, Karolina, Qingqian, Evgenius, Miina, Matthijs, Raissa, Mehrdad, Bauke, etc. A special thanks to all the students I was privileged to either supervise or co-supervise: Sytze, Saksham, Jane, Jan-Willem and Sameer.

To all the local and international collaborators: Graeme Blake, Bart J. Kooi, Jie Yang, Machteld Kamminga, Jacky Even, Feng Wang, Ni Zhao, Loredana Protesescu, Maksym V. Kovalenko, Haotong Wei, Jinsong Huang, etc., I say thank you so much for contributing enormously to this work.

My heartfelt appreciation also goes to the following individuals and organizations or groups for their immense support on this academic journey. Brosi (Nelson) and family, Maurits Stevens and family, Jariathu and family, Jessica and Hinrichs family, Neeraj ji, Martine, Meredith, Chris & Ann, I am forever grateful to you guys. The support of the Vineyard Groningen International Church, Vineyard Student Ministry (VSM), former and current board members of VSM, former and current ‘teanocoffee’ home group members, the GH connect group and my dance teachers (Mary, Feline, Juan Carlos) and friends will always be held dear. To those whose names are not acknowledged, know that your support is equally appreciated.

To my dearest family, Seyram (wife) and Xose (son), my mom and siblings, my gratitude to you is immeasurable. You have been a constant source of encouragement and inspiration to me. Your patience and understanding and prayers have yielded much.

Ultimately, I am very grateful to God Almighty who granted me strength to begin and complete this race. To Him be glory now and forevermore!