PHYSICS, CHEMISTRY AND OPTIMIZATION OF
PEROVSKITE LIGHT EMITTING DIODES

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Abstract

The desire for high color quality, low cost and stable lighting and display technology has driven intense research and development of better light emitting materials and devices. Organic-inorganic hybrid perovskites have demonstrated the potential to develop into a new generation of light emitting diodes (LEDs) that have unique advantages such as high color purity, wide emission wavelength tunability, solution processability, and easy fabrication at low cost. In this work, we focus on understanding the physics, chemistry and processing of perovskite materials, and how best to exploit that understanding to optimize device performance of perovskite LEDs.

We begin by investigating the defect physics and crystallization mechanisms of perovskites and demonstrating a facile method for preparing perovskite nanocrystalline films in situ, which involves the use of large organoammonium halides as additives to confine crystal growth, achieving ultra-smooth perovskite films with small grain sizes. Based on extensive theoretical calculations and supported directly by experimental evidence, we identify important design considerations for the choice of the additives, and find that molecular structure and dipole moment are important for both efficient defect passivation and improving material flexibility, overcoming the common tradeoffs between optoelectronic and mechanical properties. Using all these various techniques, it is shown how record efficiencies have been achieved for highly robust and flexible perovskite LEDs. In addition, we show that, due to the high refractive index of the perovskite layer, waveguiding loss is significant in perovskite LEDs. Using a thinner perovskite layer can effectively suppress waveguiding and improve light outcoupling.

The second major theme of this work involves understanding the stability and degradation mechanisms of perovskite devices. The roles of material properties, device structures and operational conditions are approached through extensive in-situ and ex-situ characterization techniques. Our findings revealed that Joule heating
plays an important role in device degradation, which is closely related to ionic motion within perovskites. Adopting a thinner perovskite layer could significantly improve operational stability by reducing Joule heating. Finally, we determine that perovskites are considerably redox active, and that redox chemistry dictates material and device degradation, which brings important insight regarding electrode and buffer layer choices in perovskite devices.
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Chapter 1

Introduction

The desire for high color quality, low cost and stable lighting and display technology has driven intense research in and development of better light emitting materials and devices. Among all materials under investigation, metal halide perovskites are emerging as a promising option with the potential to develop into a new generation of light emitting technology. This introductory chapter is to provide the reader a brief overview of the properties of metal halide perovskite semiconductors, their unique advantages in lighting and display applications, and concepts that are important for the understanding of the subsequent chapters.

1.1 Metal Halide Perovskite Semiconductors

Metal halide perovskites are a class of materials with an ABX$_3$ stoichiometry and crystal structure shown in Figure 1.1, where A is a monovalent cation (e.g., Cs$^+$ or CH$_3$NH$_3^+$), B a divalent metal cation (e.g., Pb$^{2+}$ or Sn$^{2+}$), and X a halide (Cl$^-$, Br$^-$, or I$^-$). Metal halide perovskites have drawn significant interest in lighting and display applications because of many superior optoelectronic properties and manufacturing advantages they have shown, such as precise and facile tunable luminescence wavelength over the entire visible spectrum, high tolerance to defects, high photolu-
minescence quantum yield and low-temperature solution processing [1]. Since the first demonstration of metal halide perovskite LEDs in 2014 with an efficiency on the order of 1% [2], the development of metal halide perovskite LEDs have been progressed dramatically with efficiencies exceeding 20% in 2018 [3]. However, the development and optimization of perovskite LEDs are still largely empirical. The motivation of this thesis is to identify important design principles for perovskite LEDs, contributing to the rapid developing research area.

1.1.1 Color Tunability

Given their direct bandgap, perovskites emit nearly monochromatic light either under optical excitation (photoluminescence) or when electrically excited (electroluminescence), with the color of the emitted light determined by the materials’ bandgap energies.
The bandgap energy of perovskites can be tuned within a very wide range of wavelengths, from violet to near infrared. This is made possible by changing perovskite composition as shown in Figure 1.2. For example, by controlling the stoichiometry of chloride, bromide, and iodide (X sites) in lead-based perovskites, bandgaps can be tuned across blue, green and red regions. This can be further extended to the infrared by replacing lead with tin (B site). Furthermore, replacing the relatively small A site cations with bulkier organic cations, the perovskite crystal structure can be altered into two-dimensional Ruddlesden–Popper phases, which provide more opportunities for color tuning, even into the deep blue or violet spectral regions.

Color purity is an important indicator for display quality. Regardless of preparation techniques and grain sizes, luminescence spectra of perovskites are generally narrow (typical spectral widths of 0.07-0.09 eV, or 12 nm for blue light emission, 20 nm for green, and 40 nm for red/near infrared), which make perovskites highly suitable for high-end display applications. Perovskite LEDs represent a large advantage over quantum dot LEDs because quantum dots require a narrow particle size distribution to achieve narrow spectral width. The requirement of a narrow particle size distribution of quantum dots inevitably increases the fabrication complexity and cost, whereas narrow spectral widths can be manufactured easily for perovskites without dedicated processing techniques to control their grain size distribution.

1.1.2 Solution Processing

One important potential advantage of perovskite LEDs over other inorganic or organic LEDs is their low cost. Perovskites can be synthesized and processed from solution at relatively low temperatures. This means perovskites are suitable for large-area deposition on a wide range of substrates such as glass or flexible plastic substrates. Perovskite preparation techniques, in general, can be divided into two categories, which leads to two different product formats: colloidal perovskite nanocrystals or
Figure 1.2: Wavelength-tunable light emission from various perovskite compositions.

perovskite thin films. See Figure 1.3 for a summary of several common methods for perovskite colloidal nanocrystals synthesis and thin film deposition.

Direct synthesis of colloidal perovskite nanocrystals typically occurs via ligand-assisted reprecipitation or hot injection [6]. For ligand-assisted reprecipitation, perovskite precursors (e.g., lead halide and organic halide salts) are dissolved in strong polar solvents and then subsequently added to nonpolar solvents in the presence of surfactants, often in large excess. The different solubility in polar and nonpolar solvents triggers the recrystallization of perovskite nanocrystals, and the ligands prevent them from aggregation to bulky forms that would inhibit their ability to be suspended in a solvent. In the hot injection method, organic or cesium cations and metal cations are dissolved in nonpolar solvents and heated to a desirable temperature (typically in the range of 140 - 200 °C). Then, halide precursors are injected to trigger the nucleation and growth of perovskite nanocrystals. The process of ligand-assisted reprecipitation is simpler, often performed at lower temperatures in air, whereas the hot-injection method requires air-free conditions and fine control of the reaction tem-
Figure 1.3: Examples of diverse methods applied to perovskite processing. (a) Representative colloidal perovskite nanocrystal synthesis methods. (b) Representative perovskite thin film deposition methods. Adapted with permissions from Ref. [4,5].

temperatures because the size of the colloidal crystals is highly dependent on the processing temperature. However, one major advantage of the hot-injection approach is an absence of polar solvents, which prevents any possible dissolution or decomposition of the formed perovskite nanocrystals. The hot-injection method is currently the most popular strategy, which provides effective control over the size of the nanocrystals and their size distribution.

As for perovskite thin film deposition, common solution-processed thin film deposition methods are compatible with perovskite precursors, such as chemical bath, spin coating, dip coating, doctor blade coating, metering rod, slot-casting, spray coating, screen printing, inkjet printing and aerosol jet printing [7]. Nonsolvent processing
methods, such as thermal evaporation, are also available for perovskite thin film deposition \[8\]. As will be discussed in the subsequent chapters, ultrathin and pinhole-free perovskite films are desirable for high performance perovskite LEDs.

### 1.1.3 Defect Tolerance

Metal halide perovskites are known for their defect tolerance. Numerous theoretical studies have shown that structural defects including iodide and methylammonium vacancies have energy levels that fall within the conduction and valence bands, respectively (Figure 1.4) \[9\]. These defect states within the conduction and valence bands do not result in non-radiative recombination, thus the electronic properties of perovskites are not significantly affected by these intrinsic defects. Experimentally, a wide I/Pb tolerance (as low as 2.5) for CH\(_3\)NH\(_3\)PbI\(_3\) (MAPbI\(_3\)) has been shown to maintain stable valence band, Fermi and core levels (Figure 1.5) \[10\], indicating that perovskites are extremely tolerant to self-compensating MA and I vacancies. The unique defect tolerance properties make perovskites compelling for a range of optoelectronic applications with low-temperature solution processing, as thin films deposited from solution processing usually contain a considerable amount of structural defects.

It should be noted that, despite this defect tolerance, there is a high density of defects at surfaces and grain boundaries of polycrystalline grains that are not electrically benign \[11\]. To further improve device performance, passivation of defects at surfaces and grain boundaries is critical.

### 1.1.4 Material Stability

Organic-inorganic hybrid perovskites have shown significant promise for optoelectronics, but unusual behaviors such as current-voltage hysteresis and low-frequency giant dielectric response have been commonly observed for perovskite based electronic de-
Figure 1.4: The transition energy levels of (a) intrinsic acceptors and (b) intrinsic donors in MAPbI$_3$. Reprinted with permission from Ref. [9].

Ionic migration has been suggested to be an important factor contributing to these effects [12]. Organic-inorganic hybrid perovskites have long been known to be mixed electronic-ionic conductors. Relatively low activation energies for the migration of halide-ion vacancies have been reported by many theorists [13], and halide migration has been observed experimentally in various device structures [12,14].

Ionic migration in perovskites will inevitably cause stability concerns, especially given that chemical reactions might occur between perovskites and other layers within a device. For example, irreversible redox reactions have been observed between migrating I$^-$ ions and spiro-OMeTAD$^+$ (a commonly used organic molecule in perovskite solar cells) [15], and various metal-contact-induced degradation has been seen due to the reactivity of metal and halides [16,17].

These characteristics of perovskites deserve particular attention when working on perovskite based materials and devices. In Chapter 5 we will show the unique device behavior of perovskite LEDs induced by ionic motion, and in Chapter 6 we will present our findings on the chemical stability of perovskite devices in detail.
Figure 1.5: Electronic defect tolerance in MAPbI$_3$. Valence band shift relative to the Fermi level is plotted against the I/Pb ratio. Tolerance to self-regulating defect pairs (MA and I vacancies) results in a large allowable I/Pb region (i). As defect densities overcome the tolerance level, a mixed phase emerges (ii) and progresses toward PbI$_2$ formation (iii). Reprinted with permission from Ref. [10].

1.2 Perovskite Light Emitting Diodes

1.2.1 Device Structure

A typical bottom-emitting perovskite LED structure is shown in Figure 1.6a. The perovskite layer along with other functional layers such as electron transport layer (ETL) and hole transparent layer (HTL) are sandwiched between an anode and a cathode. At least one of the electrodes needs to be transparent (e.g., indium tin oxide, ITO) for light emission. While applying a voltage, electrons from the cathode are injected through ETL into the perovskite layer, and holes from the anode are
Figure 1.6: (a) A schematic device structure of perovskite LEDs. (b) An ideal schematic energy band diagram of perovskite LEDs.

Injected through HTL into the perovskite layer, where they recombine radiatively, emitting photons.

Figure 1.6 shows an ideal energy diagram of a perovskite LED structure. The hole transport layer and the electron transport layer should have the proper highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies: these are chosen such that there are no energy barriers for electron injection from the cathode and hole injection from the anode. On the other hand, a large energy barrier is formed for electrons at the HTL/perovskite interface so that the HTL can act as an electron blocking layer (EBL) to prevent electrons from entering the anode. Similarly, the ETL can be used as a hole blocking layer (HBL) to prevent holes from entering the cathode. As a result, electrons and holes are confined within the perovskite layer, significantly increasing the recombination rate of electrons and holes.
Both organic and inorganic materials could be used as HTL or ETL. Common HTL materials used for perovskite LEDs are PEDOT:PSS, PVK, poly-TPD, TFB, NiO$_x$, etc, while common ETL materials used for perovskite LEDs include TPBi, Bphen, POPy2, PEIE, ZnO, etc, where PEDOT:PSS is poly(3,4-ethylenedioxythiophene) polystyrene sulfonate, PVK is poly(N-vinylcarbazole), poly-TPD is poly[N,N’-bis(4-butylphenyl)-N,N’-bisphenylbenzidine], TFB is poly(9,9-dioctylfluorene-alt-N-(4-sec-butylphenyl)-diphenylamine), TPBi is 2,2’,2”-(1,3,5-benzenetriyl)-tris(1-phenyl-1-H-benzimidazole), Bphen is bathophenanthroline, POPy2 is phenyl-dipyrenylphosphine oxide, PEIE is polyethylenimine ethoxylated (Figure 1.7). Aluminum (Al), silver (Ag), gold (Au) and copper (Cu) are common metal electrodes. Indium tin oxide (ITO), fluorine doped tin oxide (FTO), carbon nanotubes, graphene, nanowire meshes and ultra thin metal films are common transparent conducting electrodes.

While spray-coating and inject printing are more suitable for mass production, spin coating is the most common method to prepare polymeric thin films in a laboratory setting. Polymers are typically dissolved in organic solvents such as chlorobenzene, chloroform, or toluene, and dispensed onto a substrate. Then, the substrate is rotated rapidly to uniformly spread the solution and evaporate the solvent. Following spinning, a thermal annealing step is common to remove residual solvent.

Small organic molecules may also be solution processed in a similar way. Alternatively, vacuum thermal evaporation is very common for small organic molecule deposition, with additional advantages such as precise control of film thickness and deposition rate. The vacuum thermal evaporation process involves the subliming of the source materials at elevated temperature under high vacuum, which re-condense on the target substrate. Perovskite and polymeric thin films used in this thesis are all prepared by spin coating, while small organic molecule layers and metal electrodes are thermally evaporated.
Figure 1.7: Molecular structure of common organic HTL and ETL materials.
1.2.2 Efficiency Evaluation

There are several ways to evaluate efficiency of perovskite LEDs. Namely, external quantum efficiency (EQE), power efficiency (PE), and current efficiency (CE). The EQE is the ratio of the number of photons emitted by the LED into the viewing direction to the number of injected electrons. The PE is the ratio of retrieved optical power to consumed electrical power. The CE is the ratio of forward light output to electric current flow. In this thesis, EQE is used to evaluate perovskite LED efficiency.

The EQE can further be expressed as

\[ EQE = \eta_{\text{inj}} \cdot IQE \cdot \eta_{\text{out}} \]

where injection efficiency (\(\eta_{\text{inj}}\)) is defined as the ratio of carriers injected into the active region to total carriers passing through the device. Internal quantum efficiency (IQE) is determined by the ratio of radiative recombination to all radiative and nonradiative electron-hole recombinations (e.g., R-G center recombination, Auger recombination, etc.) in the active region. Extraction efficiency (\(\eta_{\text{out}}\)) is the proportion of photons generated that escape from the device into the viewing direction.

We aim to achieve an IQE near 100% for perovskite LEDs through proper material/processing innovation, such as interface/defect passivation and perovskite composition optimization, while more than 75% of produced photons would still be optically trapped in a bottom-emitting perovskite LED. Major losses limiting \(\eta_{\text{out}}\) include substrate-trapped loss, waveguiding loss, surface plasmon polariton (SPP) loss, and self-absorption loss. As will be detailed in Chapter 4 due to high refractive index of the perovskite layer (approximately 2.3 near the emission wavelength), waveguiding loss is significant in perovskite LEDs. Better light outcoupling strategies will be needed to improve \(\eta_{\text{out}}\).
1.2.3 Efficiency Characterization

Regarding efficiency characterization, here we focus on the EQE characterization and discuss three common methods in detail [18]:

The first and simplest means for measuring the EQE employs a large, calibrated photodetector with the LED being placed very close to the detector (Figure 1.8a). It is important that there is no intervening optics. A photodetector with area considerably larger than that of the LED being tested is required to detect every photon emitted into the forward direction. To obtain an accurate characterization of the EQE, it is also necessary to mask photons emitted from the substrate edges from the photodetector. One can achieve this by simply coating the edges with black paint or wax, or ensuring that the photodetector is considerably smaller than the substrate of the LED.

Another common method to measure the EQE involves the use of an integrating sphere containing a calibrated detector (Figure 1.8b). Notably, placing the LED inside the sphere will collect all photons emitted, including those from the edges of the substrate following in-plane waveguiding, which should not be counted according to the definition of the EQE. To make a more reasonable measurement of the EQE, the edge-emitted light must be prevented from reaching the photodetector by masking the LED with black paint or wax that absorbs the in-plane waveguided and scattered light.

The third method to characterize the EQE is to use a goniometer setup, which consists of a calibrated photodetector, a spectrophotometer and a computer-controlled rotational stage (Figure 1.9). Photons emitted at a particular angle are detected by the photodetector, and the EQE is calculated based on data collected at various angles with the rotational stage. In this kind of a setup, a relatively small photodetector placed relatively far from the LED is required to accurately measure the light emission in a particular angle.
Figure 1.8: Schematic diagrams of LED measurement setups. (a) With a large photodetector. (b) with an integrating sphere.

Figure 1.9: A photo of a goniometer setup for LED characterization.

Notably, a careful measurement on the angular dependent emission pattern could provide more information on whether the measured device efficiencies represent an improvement in materials properties or the result of an optical geometry that favors forward directed emission. However, for the first two methods discussed above, a separate goniometer setup is required to obtain the emission pattern. In this thesis, we adopt the third method to characterize the EQE.
1.2.4 Device Development

Perovskite LEDs have achieved rapid and remarkable progress over the last several years. Figure 1.10 compares the highest EQE and brightness of organic LEDs (OLEDs), quantum dot LEDs (QLEDs) and perovskite LEDs fabricated so far. Although the highest EQEs of perovskite LEDs are still lower than that of OLEDs and QLEDs, the maximum brightness of perovskite LEDs are similar to state-of-the-art OLEDs. Notably, the highest EQE achieved for perovskite LEDs varies considerably in terms of the emitted color. Table 1.1 summarizes representative perovskite LEDs of different colors. Green and red perovskite LEDs currently lead in performance, while blue and infrared perovskite LEDs require further attention.

1.3 Thesis Organization

This thesis provides an examination of the physics, chemistry and processing of perovskite light emitting diodes, and also an explanation of how best to exploit that understanding to optimize device performance.
Table 1.1: State-of-the-art metrics for perovskite LEDs. (PEA = phenethylammonium, BA = butylammonium, MA = methylammonium, and FA = formamidinium.)

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<th>Color</th>
<th>Peak emission wavelength (nm)</th>
<th>Perovskite composition</th>
<th>Maximum EQE (%)</th>
</tr>
</thead>
<tbody>
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<td>Violet</td>
<td>410</td>
<td>PEA₂PbBr₄</td>
<td>0.04</td>
</tr>
<tr>
<td>Blue</td>
<td>487</td>
<td>BA₂Csₙ₋₁Pbₙ(ClBr)ₙ₊₁</td>
<td>6.2</td>
</tr>
<tr>
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<td>CsPbBr₃</td>
<td>20.3</td>
</tr>
<tr>
<td>Red</td>
<td>653</td>
<td>CsPb(BrI)₃</td>
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<tr>
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<td>803</td>
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<tr>
<td>Near infrared</td>
<td>917</td>
<td>MAPb₀.₆Sn₀.₄I₃</td>
<td>5.0</td>
</tr>
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</table>

In Chapter 2, ultra-small perovskite grain size is revealed as an important design principle for perovskite LEDs. We investigate the crystallization mechanisms and defect physics of perovskites and demonstrate a facile method for preparing perovskite nanocrystalline films in-situ, which involves the use of relatively large organoammonium halides as additives to confine crystal growth, achieving ultra-smooth perovskite films with small grain sizes of ≈10 nm. Highly efficient red and green perovskite LEDs are demonstrated based on this method.

In Chapter 3, we further investigate the influence of the organoammonium halide additive choice on the properties of perovskite thin films. Based on extensive theoretical calculations and supported directly by experimental evidence, we identify important design considerations for the choice of the additives to improve perovskite flexibility and defect passivation. Finally, it is shown how record efficiencies have been achieved for highly robust and flexible perovskite LEDs.

In Chapter 4, the ultra-thin perovskite layer is revealed as another important design principle for perovskite LEDs. Due to the high refractive index of the perovskite layer, waveguiding loss is significant in perovskite LEDs. Using a thinner perovskite layer can effectively suppress waveguiding and improve light outcoupling. Furthermore, we show that Joule heating plays an important role in device degradation,
and reducing Joule heating by adopting a thinner perovskite layer could significantly improve operational stability.

Chapter 5 details our understanding about the origin of operational instability of perovskite LEDs. It is found that electrical stress could either increase or decrease device efficiency, which is closely related to ionic motion in perovskites. It is suggested that developing strategies to mitigate ion migration is critical to ensure stable device operation.

Chapter 6 shows our study about the chemical stability of perovskites and reveal an important degradation path of perovskite LEDs. We determine that perovskites are considerably redox active, and that redox chemistry dictates material and device degradation, which brings important insight regarding electrode and buffer layer choices in perovskite devices. Finally, we present our outlook in Chapter 7.
Chapter 2

*In-Situ* Preparation of Perovskite Nanocrystalline Thin Films for Efficient Light Emission

2.1 Introduction

Three-dimensional (3D) hybrid organic-inorganic metal halide perovskite semiconductors (e.g., CH$_3$NH$_3$PbI$_3$ or MAPbI$_3$) possess low exciton binding energies of only a few millielectronvolts [24]; therefore, electrons and holes in perovskites mainly present as free carriers rather than as tightly bound electron-hole pairs (excitons), which significantly reduces electrons and holes recombining radiatively. Therefore, a small perovskite grain size is needed to spatially confine electrons and holes to promote radiative recombination.

Traditional solution synthesis methods for perovskite nanocrystals have three main drawbacks for device applications. First, the synthesis process is complicated, typically requiring several cycles of purification by washing and centrifugation [25]. Additionally, long and insulating ligands (such as oleylamine and oleic acid) are required...
for the synthesis of colloidal nanocrystals in solution, but they strongly bond to the nanocrystal surface and reduce device performance [26]. Finally, it is difficult to achieve uniform, dense films of colloidal nanocrystals. This is because nanocrystal suspensions aggregate at low concentration (approximately 0.5 mg/ml) [27] and, during film formation, substantial aggregation, or even transformation into bulk phases, compromises film uniformity and prevents the formation of pinhole free films [28]. Some alternative “in-situ” synthesis methods have been proposed, where perovskite nanocrystals can be formed within a polymer matrix during film preparation [29]. However, LEDs based on perovskite-polymer matrices suffer from high turn-on voltage and low power efficiency as a result of large resistivity and injection barriers imparted by the polymer. Consequently, there is a need for facile, alternative synthetic strategies for perovskite nanocrystals that can overcome these shortcomings.

Here, we demonstrate an in-situ strategy for the synthesis of metal halide perovskite nanocrystal thin films. Rather than casting films from pre-prepared nanocrystal suspensions, we promote in-situ growth of perovskite nanocrystals during the film formation process by incorporating organoammonium (larger than methylammonium so that it cannot fit into the metal halide perovskite crystal structure) halides as additives into the starting precursor solution. This confines the crystal growth of 3D perovskites and passivate the surface of perovskite nanocrystals, increasing time-resolved photoluminescence (TRPL) decay lifetime and quantum yield (QY) significantly. Using this strategy, highly efficient methylammonium lead iodide (MAPbI$_3$) and methylammonium lead bromide (MAPbBr$_3$) LEDs are demonstrated with peak external quantum efficiencies (EQEs) of 7.9% and 7.0%, respectively. These values represent a 40-fold and 23-fold improvement over control devices fabricated without the additives.

It should be noted that, the motivation for the perovskite nanocrystalline thin film preparation method developed here is different from that of conventional quantum dot
preparation methods. Quantum dots are nanocrystals with sizes smaller than their Bohr radii, which have strong size-dependent quantization effects. The luminescence wavelength of quantum dots is tuned either by changing their crystal size or by doping. In contrast, the luminescence wavelength of perovskites are tuned by their chemical composition, avoiding the limitations of available dopants and the dedicated crystal size controlling techniques for quantum dots. The grain size of the perovskite films developed in this chapter is larger than their Bohr radii, and thus the bandgap is insensitive to their grain sizes.

2.2 Results and Discussion

2.2.1 Thin Film Characterization

A one-step solvent exchange method is used to prepare MAPbI$_3$ perovskite films. Perovskite precursors were pre-mixed in stoichiometric ratios ("stoichiometric") in dimethylformamide (DMF), and a solvent exchange step is performed during spin coating by dropping toluene onto the spinning sample, resulting in uniform perovskite films as observed by scanning electron microscope (SEM) (Figure 2.1a). The toluene extracts the DMF solvent and stops morphological evolution during crystallization. Although full coverage is achieved, the perovskite film is rough, with grains ranging from 30 nm to 170 nm, and notably with a large volume of unpassivated grain boundaries. The root mean square (RMS) roughness is measured to be 5.7 nm using an atomic force microscope (AFM) (Figure 2.1b).

Organoammonium halide additives inhibit the growth of 3D perovskites, resulting in layered Ruddlesden-Popper phases if the precursors satisfy the stoichiometry of that phase \[30\]. Here, we use a stoichiometric 3D MAPbI$_3$ perovskite precursor solution with 20 mol% 4-fluorobenzylammonium iodide (FPMAI) as an additive. Using the same film preparation method, the resulting perovskite films are ultrasmooth (Figure
2.1d) with only 1.2 nm RMS roughness (Figure 2.1e). Furthermore, the grains become so small that they can no longer be properly resolved by AFM with a tip radius of 20 nm. The motivation for the use of FPMAI in the current study is that the presence of fluorine provides us with a distinct chemical signature of the additive.

X-ray diffraction (XRD) measurements show the same tetragonal perovskite crystal structure for samples with and without FPMAI additives (Figure 2.1f), indicating that the FPMAI additives are not incorporated into the grains in a Ruddlesden-Popper phases, but rather allow the nanocrystals to retain 3D MAPbI$_3$ perovskite structure. The full width at half maximum (FWHM) of the (110) peak at 14° is larger for samples with FPMAI additives, in agreement with the smaller crystal size seen in the AFM results. X-ray photoelectron spectroscopy (XPS) analysis was used to verify the presence of FPMAI additives in the film. Figure 2.1f shows the F 1s spectrum of samples with and without additives. A prominent F 1s peak is observed for samples with FPMAI additives, while no F 1s peak is observed for samples without FPMAI additives, proving that the FPMAI additives are indeed incorporated within the film.

To further understand the morphology and composition of additive-induced ultrasmooth perovskite films, cross-sectional transmission electron microscopy (TEM) measurements of MAPbI$_3$ perovskite films with and without FPMAI were performed, as shown in Figure 2.2. The view in Figure 2.2a shows that, without the processing additive, the stoichiometric solution produces a compact polycrystalline film, featuring perovskite grains exhibiting various orientations. Figure 2.2c shows a high-resolution TEM (HRTEM) image for a perovskite film without additives and with lattice fringes spaced by 3.2 Å. This fringe spacing corresponds to the (004) plane spacing for MAPbI$_3$ crystals [31]. In contrast, MAPbI$_3$ perovskite films processed with FPMAI possess a “nanocrystal-in-matrix” morphology, as shown in Figure 2.2b. The lattice fringes of one representative nanocrystal are shown in Figure 2.2d, where the inter-plane spacing of 2.2 Å is indexed to the (224) plane of MAPbI$_3$ [32]. Fig-
Figure 2.1: (a) SEM image, and (b) AFM image of MAPbI$_3$ films without FPMAI additives. (c) XRD patterns of MAPbI$_3$ films with and without FPMAI additives. (d) SEM image, and (e) AFM image of MAPbI$_3$ films with FPMAI additives. (f) F 1s XPS spectra of MAPbI$_3$ films with and without FPMAI additives.

Figure 2.2e shows the size distribution of MAPbI$_3$ perovskite nanocrystals. An average crystal size of 5.4 nm is achieved, with a standard deviation of 0.8 nm when fitted with a normal distribution. The crystal size distribution is narrower than that reported using other in-situ fabrication techniques [29], although still broader than that of nanocrystals synthesized in solution, where narrow size distributions are achieved through centrifugation [25].

To further investigate the morphology and distribution of MAPbI$_3$ perovskites within films, scanning transmission electron microscopy (STEM) and energy-dispersive X-ray spectroscopy (EDS) measurements were carried out for elemental mapping, with results shown in Figure 2.3. That dense perovskite film formed without additives is further confirmed by the uniform distribution of Pb (Figure 2.3a and d). In contrast, the distribution of Pb for MAPbI$_3$ perovskites formed using FPMAI additives is consistent with the nanocrystal distribution observed in the STEM image (Figure 2.3b and e), proving that MAPbI$_3$ perovskites are confined...
into nanocrystals embedded in the matrix. The corresponding electron diffraction patterns of the MAPbI$_3$ nanocrystal and the matrix are shown in Figure 2.3c and f, respectively, showing that the MAPbI$_3$ nanocrystals are crystalline, while the matrix is amorphous. Other elemental (F, N, I, C) mapping results are shown in Figure 2.4. The distribution of N and I is also consistent with the “nanocrystal-in-matrix” morphology, while the distribution of C is not, and the signal of C is very strong in the matrix area. We thus believe the matrix is primarily composed of excess additives, rather than crystalline or amorphous MAPbI$_3$. Due to the excess FPMAI used in the precursor and our assumption that the additive attaches over the entire 3D perovskite nanocrystal surface, the distribution map of F is not well resolved by EDS.

Based on our observations regarding the different morphologies of perovskite films formed with and without additives, we propose the following mechanism for the
Figure 2.3: (a) Cross-sectional STEM image, and (d) corresponding elemental EDS map showing the distribution of Pb for MAPbI$_3$ films without FPMAI additives. (b) Cross-sectional STEM image, and (e) corresponding elemental EDS map showing the distribution of Pb for MAPbI$_3$ films with FPMAI additives. Electron diffraction patterns of MAPbI$_3$ (c) nanocrystal and (f) matrix.

Figure 2.4: STEM image (a), and corresponding elemental EDS maps showing the distribution of (a) F, (b) N, (c) I, and (d) C for MAPbI$_3$ films with FPMAI additives. (e) STEM image, and corresponding elemental EDS maps showing the distribution of (f) N, (g) I, and (h) C for MAPbI$_3$ films without FPMAI additives.
Figure 2.5: TEM morphology characterization for perovskite films with 20 mol% additional MAI. Grain size is approximately 100 nm, showing that additional MAI cannot confine perovskite crystal growth.

additive-confined perovskite crystallization process. Without additives, perovskite crystals grow from different nucleation sites and aggregate, forming compact polycrystalline perovskite films (confirmed by the TEM image in Figure 2.2a) that possess a large volume of unpassivated grain boundaries. However, when organoammonium halide additives are introduced in the processing, the outward growth of perovskite crystals from the initial nucleation sites is terminated. This results in sub-10 nm perovskite nanocrystals with additives capping the nanocrystal surface, forming a “nanocrystal-in-matrix” morphology (Figure 2.2b).

It should be noted that perovskite crystal growth can only be confined through the usage of the relatively larger additives—adding 20 mol% more methylammonium iodide (MAI) into the precursor solution still leads to large grains and rough films because MAI is small enough to fit in the perovskite crystals and thus unable to suppress the perovskite crystal growth (Figure 2.5).

Based on our understanding of the mechanism of the additive-confined perovskite crystallization process, maintaining a stoichiometric ratio of the 3D MAPbI₃ pre-
cursors with a suitable amount (20 mol% in this work) of organoammonium halide additives is key to the success of this in-situ nanocrystal preparation strategy. We confirmed by XRD and TEM that, at this percentage of loading, the additives do not incorporate into the 3D tetragonal MAPbI$_3$ perovskite structure (as no change is observed in the XRD patterns), but only serve to confine the perovskite crystal growth. These observations indicate that the 3D tetragonal perovskite nucleates and grows prior to the lower dimensional Ruddlesden-Popper phase. However, at higher loadings of FPMAI additives (e.g., 40 mol% or 60 mol%), the structure of the resulting films shifts to that of the lower dimensional Ruddlesden-Popper phase (Figure 2.6). Additionally, adopting a solvent exchange technique during film processing is necessary because it stops the subsequent morphological evolution during crystallization. Figure 2.7a shows the XRD pattern for the film processed with 20 mol% FPMAI additives but without using the solvent exchange technique. Without the solvent exchange, films still remain the 3D tetragonal MAPbI$_3$ perovskite structure, but the narrower FWHM of the (110) peak at 14° indicates a larger crystal size. This is because the gel is given more time to age and crystallites are given more time to grow $^{33}$, resulting in a film without full coverage (Figure 2.7b). It should be noted that, when precursor solutions with organoammonium halides are prepared according to the stoichiometry of the layered Ruddlesden-Popper phase, the resulting perovskite films are compact polycrystalline films with the Ruddlesden-Popper phase structure, as opposed to the “nanocrystal-in-matrix” morphology, as confirmed using TEM in recent reports $^{34}$. In addition, when excess MAI is used in MAPbI$_3$ precursor solutions instead of the FPMAI additive, the resulting perovskite films are still compact and polycrystalline with large grains, with MAI at crystallite surfaces or, owing to the high vapor pressure of methylamine, ultimately exiting the film in the form of methylamine and HI. The fact that our technique of using relatively large organoammonium halide addi-
Figure 2.6: XRD patterns of MAPbI$_3$ films with 20 mol%, 40 mol%, and 60 mol% FPMAI additives and without FPMAI additives. Additional peaks are marked with *.

The addition of FPMAI additives (that cannot fit in the 3D perovskite lattice) results in “nanocrystal-in-matrix” morphology, which distinguishes our strategy from other recent work.

To investigate the effects of our strategy on the optical properties of the perovskite films, we characterized the steady-state PL spectra, PLQY, and TRPL of MAPbI$_3$ films with and without the FPMAI additives. Figure 2.8a and b show the steady state PL spectra and TRPL data, respectively. With FPMAI additives, the steady-state PL emission peak is blue-shifted from 764 nm to 749 nm. This is not a quantum confinement effect, since this would only manifest for nanocrystal diameters approaching the Bohr radius, approximately 2.1 nm. Instead, this may be understood as an effect of increased disorder. As shown in Figure 2.8a, the sub-10 nm nanocrystals contain approximately 15 lattice plane spacings. While this size is not small enough to in-
duce quantum confinement and thus create a dependence of bandgap on size, the long-range, infinite lattice periodicity of a bulk material is nevertheless disturbed in the nanoscale system. Also, the dielectric constant of the local environment for these nanocrystals (which is the organic matrix) is substantially lower than the perovskite, thus further confining the wave-function to the crystallite. Additionally, the reduced absorption coefficient and thus the reabsorption may also induce the PL shift. At an excitation intensity of 2 mW/cm², QY is increased from 0.1% to 4.4%, while the TRPL decay lifetime is increased from 3 to 9 ns for films processed with FPMAI additives, indicating that the FPMAI additives can passivate trap states and reduce non-radiative recombination. One likely channel for non-radiative recombination is quenching on under-coordinated Pb sites \[35\]. It has been reported that excess MAI in MAPbI₃ can form a layer at grain boundaries, which can help suppress non-radiative recombination \[36\]. Given the similar nature of excess MAI and FPMAI, we suspect that FPMAI passivates under-coordinated Pb atoms in a similar manner.

Figure 2.7: (a) XRD patterns of MAPbI₃ films with and without applying a solvent exchange, both with 20 mol% FPMAI additives. (b) SEM image of a MAPbI₃ film with 20 mol% FPMAI additives, but without applying a solvent exchange.
2.2.2 Device Performance

To examine the effect of the film composition on device functionality, MAPbI\textsubscript{3} LEDs were fabricated with a device structure of ITO (150 nm) / poly-TPD (25 nm) / MAPbI\textsubscript{3} perovskite (50 nm) / TPBi (40 nm) / LiF (1.2 nm) / Al (100 nm) (ITO: indium tin oxide; poly-TPD: poly[N,N’-bis(4-butylphenyl)-N,N’-bis(phenyl)benzidine]; TPBi: 2,2’,2”-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole)), where poly-TPD serves as a hole-transporting and electron-blocking layer and TPBi as an electron-transporting and hole-blocking layer. The corresponding schematic energy band diagram of the device is shown in Figure 2.9. Figure 2.10a shows the electroluminescence (EL) spectra of devices with and without FPMAI additives, with an image of a working LED (with FPMAI additives) shown as an inset. Similar to the PL spectra, the EL emission peak is also blue-shifted from 764 to 749 nm for devices with FPMAI additives. Figure 2.10b shows the current density-radiance-voltage (\( J-R-V \)) curves for devices with and without FPMAI additives. A maximum radiance as high as 72 W/(sr·m\(^2\)) is achieved, which is 12 times higher than that of a device without additives. The EQE vs. current density curves are shown in Figure 2.10c. Without the FPMAI additives, a peak EQE of 0.2% was observed.
With the additives, a peak EQE of 7.9% was achieved, a 40-fold improvement. This device performance enhancement is consistent with the improvements in PLQY and PL lifetime observed due to FPMAI surface passivation effects. However, it should be noted that the bimolecular recombination pathway responsible for radiative recombination that controls the value of both EQE and PLQY is dependent on carrier density. The peak EQE is achieved at a condition with a higher carrier density than the condition when we perform the PLQY measurement, which explains the higher value of peak EQE than the measured PLQY.

To demonstrate the versatility of our technique, we employed similar in-situ preparation strategies with another kind of organoammonium halide (phenethylammonium bromide, PEABr) as an additive to form MAPbBr$_3$ nanocrystalline films. Green MAPbBr$_3$ LEDs were fabricated with a similar device structure as MAPbI$_3$ LEDs except for substituting poly(N-vinylcarbazole) (PVK) for poly-TPD as the hole-transporting and electron-blocking layer. Electroluminescence spectra, current density-luminance-voltage ($J$-$R$-$V$) and EQE curves are shown in Figure 2.10d-f. The peak luminance is increased from 220 to 11400 cd/m$^2$, and EQE is increased from 0.3% to 7.0% by introducing the additives into the perovskite layer.

2.3 Conclusion

In summary, we have described and demonstrated a facile, in-situ perovskite nanocrystal preparation method where relatively large organoammonium halides are used as additives to confine the crystal growth of perovskites, achieving perovskite nanocrystals with sub-10 nm crystal size. Furthermore, these additives have passivation effects on perovskite surfaces, improving the PLQY and TRPL decay lifetime from 0.1% to 4.4% and 3 to 9 ns. With this strategy, high performance MAPbI$_3$ and MAPbBr$_3$ LEDs are demonstrated, with a peak EQE of 7.9% and 7.0%, respectively,
2.4 Experimental

*Synthesis of organic cation salts.* MAI, FPMAI, MABr and PEABr crystals were synthesized by mixing methylamine, 4-fluorobenzylamine, and phenethylamine (Sigma Aldrich) with HI or HBr (Sigma Aldrich) in a 1:1 molar ratio, respectively. The reaction was performed in an ice bath while stirring for 3 h. The solvent of the resulting solution was evaporated using a rotary evaporator. The MAI, FPMAI, MABr and PEABr was recrystallized from an isopropyl alcohol: toluene mixture. Finally, the large crystals were filtered and dried under low heat. Recrystallization, filtration, and drying were performed inside a N\(_2\) filled glovebox.

*Perovskite film deposition and device fabrication.* PbI\(_2\) (PbBr\(_2\)) and MAI (MABr) were dissolved in DMF (Sigma Aldrich, 99.8% anhydrous) to obtain 0.4 M MAPbI\(_3\) (MAPbBr\(_3\)) solution. Additives (FPMAI or PEABr) were mixed with the perovskite
Figure 2.10: (a) EL spectra, (b) $J$-$R$-$V$ curves, and (c) EQE curves of MAPbI$_3$ red LEDs with and without FPMAI additives. Inset in (a) shows a working LED based on MAPbI$_3$ films with additives. (d) EL spectra, (e) $J$-$R$-$V$ curves, and (f) EQE curves of MAPbBr$_3$ LEDs with and without PEABr additives. Inset in (d) shows a working LED based on MAPbBr$_3$ films with additives.
precursor (MAPbI$_3$ or MAPbBr$_3$) in a 0.2:1 molar ratio. Poly-TPD (6 mg/ml in chlorobenzene) or PVK (6 mg/ml in chlorobenzene) was spin coated on glass substrates with pre-patterned indium-tin-oxide (ITO) at 1500 rpm for 70 s followed by thermal annealing at 150 or 120°C for 20 min. Poly-TPD was then treated with O$_2$ plasma for 1 s to improve wetting. Perovskite films (with or without additives) were deposited on poly-TPD or PVK by spin coating at 6000 rpm. A solvent exchange step is performed after 3.5 s by dropping toluene on the spinning samples. Then, samples were annealed at 70°C for 5 min. TPBi, LiF and Al layers were thermally evaporated with thicknesses of 40 nm, 1.2 nm and 100 nm, respectively. Device area is 0.1 cm$^2$.

Material and device characterization. Film surface morphologies were surveyed by an FEI Verios 460 XHR SEM. Crystal structures of the films were studied by using a Bruker D8 Discover X-ray diffractometer with incident wavelength of 0.154 nm. Surface topography of the films were imaged with a Bruker Nanoman AFM. Chemical contents of the films were characterized by using a Thermo Scientific Kalpha XPS System. Samples were directly transferred to the XPS chamber without air exposure in order to avoid surface contamination and oxidation. Cross-section TEM lamella samples of the devices were prepared by an FEI Helios DualBeam microscope. HRTEM images, electron nanodiffraction and EDS measurements were carried out in an FEI Talos (S)TEM at 200 kV. Steady-state and TRPL measurements were carried out using an FLS980 spectrometer (Edinburgh Instruments). Samples were excited at 470 nm from a Xe arc lamp for the steady-state PL measurements. For the TRPL measurements, MAPbI$_3$ samples with (without) additives were excited at 634.8 nm by a pulsed laser diode with a 500 ns pulse period and detection wavelength of 749 nm (764 nm). PLQY was measured using a Petite integrating sphere coupled to the PTI QuantaMaster 400 Steady State Fluorometer system with an excitation wavelength of 450 nm for MAPbI$_3$ films. The following settings were kept the same for all films:
bandpass values of 5 nm for both the excitation and emission slits, step increments of 1 nm and integration times of 0.5 s per data point. The excitation intensity was 2 mW/cm$^2$. Characteristics of perovskite LEDs were measured in a N$_2$ glovebox using a custom motorized goniometer consisting of a Keithley 2400 sourcemeter unit, a picoammeter (4140B, Agilent), a calibrated Si photodiode (FDS-100-CAL, Thorlabs), and a calibrated fiber optic spectrophotometer (UVN-SR, StellarNet Inc.).
Chapter 3

Role of Organoammonium Halide Additives on the Flexibility and Efficiency of Perovskite Light Emitting Diodes

3.1 Introduction

Perovskites have defect tolerance properties and are insensitive to point defects inside the perovskite crystals [9]. However, there is a high density of defects at surfaces of polycrystalline grains that are not electrically benign [11]. In Chapter 2 we have shown that small grain size is required for efficient radiative recombination of electrons and holes in perovskite thin films. However, as grain size decreases, surface defects become increasingly important and limit device performance. To further improve device performance, passivation of defects at surfaces and grain boundaries is critical.

Mechanical robustness is another important aspect that needs to be considered for perovskite thin films, especially for applications in flexible electronics. Due to the
inherent highly brittle, salt-like perovskite crystal structure, perovskite films suffer from extreme mechanical fragility with low resistance to fracture \cite{37}. Furthermore, a tradeoff has been observed where improving electrical performance occurs at the expense of mechanical stability. For example, researchers have developed mixed-cation perovskites solar cells containing cesium (Cs) and formamidinium (FA), which have proven to be effective strategies to enhance power conversion efficiency \cite{38}. However, mixed-cation perovskites are more susceptible to fracture than pure methylammonium (MA) based perovskites due to differences in grain size \cite{39}. Keeping mechanical properties in mind and developing methods that can enhance both optoelectronic properties and mechanical toughness are important to realize highly efficient, robust and flexible perovskite devices.

Developing high performance flexible LEDs is an important research topic with growing practical applications, such as in wearable electronics, lighting, and curved or foldable displays. However, the performance of flexible perovskite LEDs currently lags behind those on rigid substrates. More effective approaches are therefore needed to simultaneously enable highly efficient, mechanically robust, and flexible perovskite LEDs.

In Chapter 2 we have shown that the addition of 20 mol% organoammonium halides can confine the crystal growth of perovskites, leading to ultra-smooth perovskite films with small crystal sizes. The additives serve as a matrix that covers and passivates the perovskite nanodomain surface. Inspired by the idea that these additives may be helpful to both passivate surface traps (e.g., under-coordinated Pb) and improve flexibility, in this chapter, we investigate the effects of five different additives— butylammonium iodide (BAI), dodecylammonium iodide (DDAI), benzylammonium iodide (PMAI), phenethylammonium iodide (PEAI), and 4-fluorobenzylammonium iodide (FPMAI)—with different molecular size, alkyl chain length and dipole moments, on the optoelectronic and mechanical properties of
perovskite films, along with their potential for flexible device applications. We find
that for families of additives with alkyl chains, a tradeoff exists between mechanical
properties and optical properties when tuning alkyl chain length. To overcome the
tradeoff, increasing the polarity of the additives by introducing electron-withdrawing
groups (in our case, fluorination) is a promising approach, yielding flexible perovskite
LEDs with a record high EQE of 13% and no efficiency degradation after 10,000
bending cycles at a radius of 2 mm. Insight of the improvements at the atomic
level is obtained, enabling the ability to provide design principles for future highly
efficient, robust and flexible perovskite electronic device development.

3.2 Results and Discussion

3.2.1 Enhancing Mechanical Stability and Optical Properties

Using the same perovskite thin film preparation method described in Chapter 2 with
20 mol% of BAI, DDAI, PMAI, PEAI or FPMAI additives, ultra-smooth perovskite
films are achieved with similar average grain sizes in the range of 10.5 – 12.4 nm,
as measured by transmission electron microscopy (TEM) (Figure 3.1). The addi-
tives coat the surfaces of the perovskite nanocrystals and form a matrix that hosts
perovskite nanocrystals. Despite different grain sizes for samples with and without
additives, all perovskite films maintain the same tetragonal perovskite crystal struc-
ture (Figure 3.2), confirming that the additives do not incorporate into the unit cell.

To study the effects of the additives on the mechanical and optical properties of
the perovskite films, we report the cohesion energy ($G_c$), a measurement of mate-
rial resistance to crack propagation \[37\], and the photoluminescence quantum yield
(PLQY). As shown in Figure 3.3 all perovskite films with additives show increased
$G_c$ and PLQY compared to the control samples, suggesting that additives attach
to and passivate the perovskite nanocrystal surface, enhancing both mechanical and
optoelectronic properties. In fact, the cohesion energies of most perovskite devices are below 0.5 J/m$^2$, making these samples over 2 times more mechanically robust than other perovskite devices tested [37]. The higher fracture energy indicates that perovskite films with additives are less likely to crack compared to control films on flexible substrates subjected to mechanical stress.

A detailed analysis reveals two trends about the influence of these additives on $G_c$ and PLQY. First, additives with a longer alkyl chain increase $G_c$ compared to additives with a shorter alkyl chain (1.6 J/m$^2$ for DDAI compared to 0.87 J/m$^2$ for BAI, 1.3 J/m$^2$ for PEAI compared to 0.75 J/m$^2$ for PMAI). However, the PLQY decreases for samples with longer alkyl chains (0.5% for DDAI compared to 1.6% for BAI, 1.8% for PEAI compared to 2.5% for PMAI), meaning that, for families of ad-
Figure 3.2: XRD patterns of perovskite films without or with various additives. All films show the same tetragonal perovskite crystal structure.

Additives with alkyl chains, a tradeoff exists between mechanical properties and optical properties when tuning alkyl chain length. Second, fluorination improves both $G_c$ and PLQY compared to additives without fluorination ($G_c$ of 1.1 J/m$^2$ and PLQY of 3.1% for FPMAI, compared to $G_c$ of 0.75 J/m$^2$ and PLQY of 2.5% for PMAI). In this case, fluorination overcomes the tradeoff between mechanical and optical properties. Notably, the impact of additive choice is more significant than the impact of film morphology on the values of $G_c$ and PLQY. While all films with additives have similar morphology, the maximum difference of $G_c$ and PLQY is significant (1.6 J/m$^2$ and 0.75 J/m$^2$ for $G_c$, and 3.1% and 0.5% for PLQY). In contrast, the film morphology without additives is very distinct compared to the films with additives, while the minimum difference of $G_c$ and PLQY is relatively small (0.67 J/m$^2$ and 0.75 J/m$^2$ for $G_c$, 0.14% and 0.5% for PLQY). Consequently, a detailed study is
Figure 3.3: Fracture energy and PLQY of perovskite films without or with various additives.

It should also be noted that PLQY is strongly dependent on carrier density owing to bimolecular radiative recombination in these films with low intrinsic carrier concentration \[34\]. A relatively low excitation power density (thus low carrier density) is used here, which is the reason for the relatively low PLQY compared to previous studies \[34\].

The mechanisms for the improved optical and mechanical properties induced by these additives are different, in terms of the effects of fluorination and alkyl chain length. These are discussed in detail below.
3.2.2 Mechanisms of the Improved Optical Properties by Fluorination and Reducing Alkyl Chain Length

Time-resolved photoluminescence (TRPL) decay measurements are conducted to study the origin of the improved PLQY (Figure 3.4). A bi-exponential decay with fast and slow components are observed for all of the films, which are fitted with a bi-exponential decay model; \( R(t) = B_1 e^{-t/\tau_1} + B_2 e^{-t/\tau_2} \), where \( \tau_1, \tau_2 \) are time constants, \( B_1, B_2 \) are coefficients (Table 3.1). The inclusion of additives increases both the fast and slow decay lifetimes, and the trend among different additives is the same as that for PLQY. The increased decay lifetime and PLQY indicates that the additives suppress trap-assisted non-radiative recombination.

Table 3.1: Fitting parameters for the TRPL measurements of perovskite films without or with various additives.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \tau_1 ) (ns)</th>
<th>Std. Dev.</th>
<th>( B_1 ) (ns)</th>
<th>Std. Dev.</th>
<th>( \tau_2 ) (ns)</th>
<th>Std. Dev.</th>
<th>( B_2 ) (ns)</th>
<th>Std. Dev.</th>
<th>( x^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>w/o</td>
<td>0.7</td>
<td>0.03</td>
<td>180.31</td>
<td>0.33</td>
<td>5.0</td>
<td>0.25</td>
<td>28.98</td>
<td>0.1</td>
<td>1.11</td>
</tr>
<tr>
<td>BAI</td>
<td>1.3</td>
<td>0.02</td>
<td>765.76</td>
<td>0.47</td>
<td>6.6</td>
<td>0.12</td>
<td>121.11</td>
<td>0.21</td>
<td>0.89</td>
</tr>
<tr>
<td>DDAI</td>
<td>1.0</td>
<td>0.02</td>
<td>941.71</td>
<td>0.57</td>
<td>5.6</td>
<td>0.1</td>
<td>120.33</td>
<td>0.21</td>
<td>0.78</td>
</tr>
<tr>
<td>PMAI</td>
<td>2.2</td>
<td>0.03</td>
<td>748.64</td>
<td>0.38</td>
<td>11.0</td>
<td>0.15</td>
<td>169.82</td>
<td>0.21</td>
<td>1.26</td>
</tr>
<tr>
<td>PEAI</td>
<td>1.4</td>
<td>0.02</td>
<td>802.49</td>
<td>0.46</td>
<td>6.8</td>
<td>0.13</td>
<td>104.44</td>
<td>0.2</td>
<td>0.87</td>
</tr>
<tr>
<td>FPMAI</td>
<td>3.3</td>
<td>0.05</td>
<td>716.55</td>
<td>0.34</td>
<td>14.3</td>
<td>0.22</td>
<td>203.59</td>
<td>0.27</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Under-coordinated Pb on the perovskite surface creates the major trap states that cause the non-radiative recombination in perovskite LEDs. Therefore, the passivation mechanisms of the various additives can be understood by investigating the way they passivate the under-coordinated Pb defects.

Proton transfer between the ammonium group and iodide is the major degradation path that generate iodide vacancies and under-coordinated Pb, which can be described by equation (3.1):
Figure 3.4: TRPL characterization of perovskite films without or with various additives: (a) without additives, (b) with BAI additives, (c) with DDAI additives, (d) with PMAI additives, (e) with PEAI additives, (f) with FPMAI additives.
\[
\text{RNH}_3^+ + I^- \leftrightarrow \text{RNH}_2 + HI
\]  \hspace{1cm} (3.1)

where R is an organic group such as a butyl group.

The improved passivation effects by fluorination of the phenyl substituter can be explained properly by the different acidity for the FPMAI and PMAI additives. Due to the strong electron withdrawing ability of fluorine, FPMAI is more acidic than PMAI. Once proton transfer-induced degradation occurs at the surface of perovskite nanocrystals as described by equation (3.1), the more acidic FPMAI additives can convert \(\text{RNH}_2\) back to \(\text{RNH}_3^+\) more readily than PMAI, preventing the formation of the iodide vacancies and under-coordinated Pb.

On the other hand, in terms of explaining the alkyl chain length dependent passivation effects, the orientation of these molecular additives (BAI and DDAI) with respective to the perovskite surface could play a major role. For additives with a long alkyl chain like DDAI, molecules tend to form a head-to-tail arrangement. Therefore, not all the ammonium group is oriented near the perovskite surface. An iodide vacancy is formed easily without the presence of the ammonium group near the perovskite surface. Additionally, the space is insufficient for the DDAI molecule to rotate freely along the C-C bond. Once the molecule is oriented with the ammonium group facing away from the perovskite surface, the ammonium group no longer can readily attach to the perovskite surface by molecular rotation. In contrast, for smaller additives like BAI, the ammonium group is more likely to attach to the perovskite surface. Therefore, additives with a shorter alkyl chain are more likely to achieve a better surface coverage, minimizing surface iodide vacancies, passivating traps, and allowing for improved optical properties.
3.2.3 Mechanisms of the Improved Mechanical Properties by Fluorination and Increasing Alkyl Chain Length

Fluorine has the highest electronegativity among all elements in the periodic table, and replacing H with F undoubtedly alters the charge distribution in the molecule. As shown in Figure 3.5a, quantum chemical calculations demonstrate that the fluorinated end of FPMAI is made more negatively charged while the NH$_3$-end becomes more positively charged with respect to unsubstituted PMAI, resulting in an increase in the molecular dipole moment. To quantify the changes, we partition the electron density distribution with the Bader partial charge scheme [40] and find the H of PMAI has a net charge of 0.02 e, whereas F in FPMAI has a net charge of -0.81 e (Figure 3.5b).

The redistributed electron density in the FPMAI molecule enhances the bonding energy between FPMAI molecules and the perovskite surface, and results in enhanced mechanical stability. As noted in Figure 3.5c, the calculated bonding energy between the first monolayer of FPMAI (PMAI) and the perovskite surface is -4.33 eV (-4.28 eV), and that between the first and second monolayers of FPMAI (PMAI) is -3.52 eV (-3.40 eV). The more negative values after fluorination correlate with stronger adhesion. Further evidence for the enhanced interactions between FPMAI molecules is the presence of F-H hydrogen bonds with a length of 2.1 Å (Figure 3.5c). The counterpart H to H distance between PMAI molecules of 3.8 Å is much larger. Given the similar molecular structure and size between FPMAI and PMAI, van der Waals interactions between these molecules are similar, and therefore the increased bonding energy after fluorination likely accounts for the stronger mechanical properties. Our assumption of molecular–molecular interactions in this model is predicated on images (cf. Figure 3.1) that show that the additive capping layer on the surface of perovskite crystals is in the range of 2.5 - 6 nm, considerably larger than the size of the additive molecules (0.75 nm for FPMAI).
Figure 3.5: Calculations of the effects of fluorination on mechanical properties. (a) Electron density distribution difference between FPMA and PMA cations. Positive values (electron density accumulation) are plotted in yellow, negative values (electron density depletion) are plotted in green. (b) Calculated Bader charge with (without) F substitution. (c) Model of the interface between perovskite and the FPMA (PMA) organic additives. The numbers labeled at the interfaces are the bonding energies between FPMAI (PMAI) additives and FPMAI (PMAI) with perovskite. More negative values correspond to stronger adhesion. Carbon (C), hydrogen (H), iodine (I), nitrogen (N), fluorine (F), and lead (Pb) are represented by brown, white, purple, blue, cyan and dark-grey, respectively.

The mechanisms for the enhanced mechanical properties by longer alkyl chains, however, are distinct from the effects of fluorination. Unlike the increased bonding energy between additives induced by fluorination, it has been reported that bonding energy is insensitive to the alkyl chain length [41]. Instead, increased molecular interactions (e.g., van der Waals forces) for additives with longer alkyl chains play the major role for the enhanced mechanical stability.

Based on the properties detailed above, we have shown that although increasing the alkyl chain length of additives can enhance mechanical stability, it also has the unwanted effect of degrading optical functionality. To overcome the tradeoff between enhancing mechanical and optical properties, introducing electron-withdrawing groups (in our case, fluorination) is a promising approach, which can be used as an
important design principle for future highly efficient, robust and flexible perovskite optoelectronic device development.

3.2.4 Flexible Perovskite LEDs

Flexible perovskite LEDs were fabricated with a device structure of flexible silver nanowire (AgNW) electrodes, PEDOT:PSS (60 nm), poly-TPD (25 nm), perovskite (65 nm), TPBi (40 nm), LiF (1.2 nm) and Al electrodes, where PEDOT:PSS is poly(3,4-ethylenedioxythiophene): polystyrene sulfonate, poly-TPD is \[\text{poly[N,N'-bis(4-butylphenyl)-N,N'-bisphenylbenzidine]}\], and TPBi is \[2,2',2''-(1,3,5-benzenetriyl)-tris(1-phenyl-1-H-benzimidazole)\]. Cross-sectional SEM images of the flexible perovskite LEDs are shown in Figure 3.6. The AgNWs are coated with titania sol-gel prior to thermal crosslinking in colorless polyimide, leading to a robust, ultra-smooth surface with a root mean square roughness of only 0.7 nm (Figure 3.7). This provides a suitable platform for ultra-smooth, pin-hole free perovskite thin film deposition. Furthermore, flexible AgNW substrates prepared by this method have shown excellent mechanical flexibility, with no obvious conductivity degradation after bending for 20000 cycles at a radius of 1 mm [42], and have demonstrated promise as flexible electrodes for device applications [43].

An optimized balance between transmission above 85% (averaged over the wavelength range from 500 nm to 800 nm) and sheet resistance of 25 \(\Omega/\text{sq}\) is used here for device fabrication by tuning the concentration of AgNW inks and spin coating cycles (Figure 3.8a). Figure 3.8b shows an operating flexible perovskite LED exhibiting bright red/near infrared light emission. Figure 3.8c shows the measured EQE of the LEDs, with the highest EQE of 13% achieved for devices with FPMAI additives. Consistent with the PLQY results, devices utilizing additives with shorter alkyl chains show higher EQE than those with longer alkyl chains, and the highest EQE values are achieved using the fluorinated FPMAI additives. Notably, the enhanced EQE
Figure 3.6: Cross-sectional SEM images of flexible perovskite LEDs: (a) at low magnification, (b) at high magnification.

Figure 3.7: Morphology characterization of flexible Ag nanowire substrates. (a) An SEM image. (b) An AFM image. Because Ag nanowires are embedded in the polymer substrate, an ultra-smooth surface is achieved with an RMS roughness of 0.7 nm, measured from the AFM image.
and PLQY for these films with various additives are not due to quantum confinement effects, which only manifest for nanocrystal diameters approaching the Bohr radius, $\approx 2.1$ nm \[44\]. Instead, the enhancement is dominated by the passivation effects of these additives that increase the relative fraction of bimolecular radiative recombination. The current density - voltage ($J-V$) curves, radiance - voltage curves, EL spectra and angle-dependent EL intensity profiles are shown in Figure 3.9. The EQE for flexible perovskite LEDs based on AgNW electrodes is higher than that fabricated on rigid glass/indium tin oxide (ITO) (Figure 3.10) due to the lower work function of AgNWs compared to ITO and the enhanced light outcoupling by AgNW scattering. It should be noted that we exclude the possibility that the different device performance is a result of molecular weight variations among the additives. Considering the larger molecular weight of DDAI, we reduced the DDAI additive concentration from 20 mol% to 15 mol%, 10 mol%, and 5 mol%. If the lower EQE for the samples with DDAI additives were due to an additive overload, we would expect a higher EQE after reducing the amount of DDAI. On the contrary, lowering the DDAI concentration reduces the EQE due to inferior surface trap passivation (Figure 3.11), proving that the low EQE for the samples with DDAI compared with the samples using other additives is not due to an overloading dose of DDAI in terms of material weight.

These flexible perovskite LEDs show excellent mechanical robustness and flexibility. Figure 3.8d shows a working high-efficiency FPMAI added perovskite LED with many creases that resulted from folding five times per device area, evidence for their robustness. A bending test shows no EQE degradation after bending for 10,000 cycles at a radius of 2 mm, and the EQE maintained approximately 80% after bending for 10,000 cycles at a radius of 1 mm (Figure 3.8e). Furthermore, no significant EQE degradation is observed when bending at extremely small radii of 1 mm, 0.6 mm and 0.25 mm for 10 cycles for devices with various additives (Figure 3.8f). In contrast, devices without additives degrade much faster than devices with additives. A detailed
comparison shows that devices with longer alkyl chain additives or fluorinated additives are more robust than those with shorter alkyl chain additives or nonfluorinated additives, which are consistent with the fracture energy results of these perovskite films. In addition, thanks to the strong adhesion of the perovskite materials to the adjacent layers, our device structure is robust against delamination at extremely small bending radii. These mechanical properties including flexibility combined with high resistance to fracture and delamination make our perovskite LEDs an ideal structure and platform for applications in flexible electronics.

3.3 Conclusion

In summary, we have described and demonstrated a facile method to improve both the optoelectronic and mechanical properties of perovskites by additive engineering, yielding highly efficient, robust and flexible perovskite LEDs with an EQE of 13% and no degradation after 10,000 bending cycles at a radius of 2 mm. We find that for families of additives with alkyl chains, a tradeoff exists between mechanical properties and optical properties when tuning alkyl chain length. To overcome the tradeoff, increasing the polarity of the additives by introducing electron-withdrawing groups (in our case, fluorination) is a promising approach. Insight of the improvements at the atomic level is obtained, through which we provide design principles for future highly efficient, robust and flexible perovskite optoelectronic device development.

3.4 Experimental

Silver Nanowire Substrate Preparation. A rigid glass substrate was used as a carrier substrate to deposit 30 nm diameter AgNWs by spin coating. The AgNWs used in this work were on average 30 nm in diameter and 100-200 µm in length, purchased from ACS Materials. This AgNW ink was dispersed in ethanol to yield a concentration of
Figure 3.8: Flexible perovskite LED characterization and bending tests. (a) Optical transmission spectrum of a flexible AgNW substrate. A photo of a flexible AgNW substrate is shown as an inset. (b) A photo of a working flexible perovskite LED with FPMAI additives. (c) EQE vs. current density curves of perovskite LEDs without or with various additives. (d) A photo of a working flexible LED with FPMAI additives after folding five times per device area. (e) Normalized EQE vs. bending cycles at bending radii of 1 and 2 mm for the flexible perovskite LEDs with FPMAI additives. (f) Normalized EQE vs. bending radius after 10 bending cycles for flexible perovskite LEDs without or with various additives.
Figure 3.9: Characterization of flexible perovskite LEDs without or with various additives. (a) Current density vs. voltage curves, (b) radiance vs. voltage curves, (c) electroluminescence spectra, and (d) angle-dependent EL intensity profiles of the flexible perovskite LEDs without or various additives.
Figure 3.10: Comparison of perovskite LEDs on flexible AgNW or rigid glass/ITO substrates. (a) EQE vs. current density curves, (b) current density vs. voltage curves, (c) electroluminescence spectra, (d) angle-dependent EL intensity profiles of perovskite LEDs with 20 mol% FPMAI additives on flexible AgNW or rigid glass/ITO substrates. The improved EQE for the samples with AgNW electrodes compared to the samples on glass/ITO is likely due to (1) less efficient hole injection from the lower work function AgNW electrodes that improves electron/hole charge balance, and (2) enhanced light scattering and outcoupling by the AgNWs. The former point is evidenced by the lower current density curves for the AgNW device compared to that with ITO. Additionally, that the angular emission profile of the AgNW electrode device is closer to Lambertian is evidence of light scattering by the AgNW electrode.
approximately 2.5 wt%. Titania sol-gel was synthesized \cite{42}, and a thin \(\approx 2\) nm layer was spin coated on the AgNW network to prevent them from breaking up during thermal imidization of colorless polyimide. 10 wt% colorless polyimide precursors were synthesized \cite{43}, and then blade coated on the carrier substrate which was then imidized (20 min at 160°C followed by 20 min at 360°C). Finally, the conductive polyimide substrate (\(\approx 15\) µm) was delaminated from the glass substrate.

**Flexible Perovskite LED Fabrication.** Poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) with 0.01% (volume ratio) polyethylene glycol tert-octylphenyl ether (Triton X-100, Sigma Aldrich) was spin coated on the prepared
AgNW embedded polyimide substrates and annealed at 130°C for 10 min. Triton X-100 acts as a surfactant to improve wetting on the polyimide substrates. Then, poly-TPD (6 mg/ml in chlorobenzene) was spin coated on the PEDOT:PSS layer at 1500 rpm for 70 s followed by thermal annealing at 150°C for 20 min. Poly-TPD was then treated with O₂ plasma for 4 s to improve wetting. The perovskite precursor solution was prepared by mixing PbI₂ and MAI in DMF (Sigma Aldrich, 99.8% anhydrous) in a 1:1 molar ratio to obtain 0.4 M MAPbI₃ solution. For solutions with BAI, DDAI, PMAI, PEAI, or FPMAI, 20 mol% additives were mixed with the stoichiometric MAPbI₃ perovskite precursors. Perovskite films with or without additives were deposited on poly-TPD by spin coating at 6000 rpm. A solvent exchange step was performed after 3.5 s by dropping toluene on the spinning samples. Then, samples were annealed at 70°C for 5 min. TPBi, LiF and Al layers were thermally evaporated with thicknesses of 40 nm, 1.2 nm and 100 nm, respectively. Device area was 0.1 cm².

Material and device characterization. The AFM measurements were performed with a Bruker Dimension ICON3 atomic force microscope. The TRPL measurements were carried out using an FLS980 spectrometer (Edinburgh Instruments). Samples were excited at 634.8 nm by a pulsed laser diode with a 500 ns pulse period. The PLQY was measured using a Petite integrating sphere coupled to the PTI QuantaMaster 400 Steady State Fluorometer system. An excitation wavelength of 450 nm was used. The following settings were kept the same for all films: bandpass values of 5 nm for both the excitation and emission slits, step increments of 1 nm and integration times of 0.5 s per data point. The excitation intensity was ≈ 0.3 mW/cm². The transmittance spectra were measured using an Agilent Cary 5000 UV-Vis-NIR spectrophotometer. Perovskite LEDs were characterized in a N₂ glovebox using a custom motorized goniometer consisting of a Keithley 2400 sourcemeter unit, a pi-
Fracture energy testing. The mechanical testing was performed using double cantilever beam (DCB) specimens fabricated by sandwiching the perovskite films of interest between glass beams with a thin, brittle epoxy (E-20NS, Hysol) cured overnight under pressure in a \( \text{N}_2 \) glovebox at 25\( ^\circ \text{C} \). Before bonding, a protective, cross-linked PTAA polymer layer \[45\] at a concentration of 15 mg/mL (Solaris Chem.) with 3 mg/mL of 1,3,5,7-tetrakis-(p-benzylazide)-adamantane was spin coated onto the perovskite films, and a metal barrier film (Ti/Al) was e-beam evaporated onto the PTAA to prevent epoxy diffusion. Specimens were cleaned with a razor blade after curing to remove epoxy from the edges of the beams. DCB specimens were tested under displacement control in a thin-film mechanical testing system (Delaminator DTS, Menlo Park, CA) from which a load, \( P \), versus displacement, \( \Delta \), curve was recorded. The fracture energy, \( G_c \) (J/m\(^2\)), was calculated in terms of the critical value of the applied strain energy release rate, \( G \). \( G_c \) can be formulated in terms of the critical load, \( P_c \), at which crack growth initiates, the crack length, \( a \), the plane-strain elastic modulus, \( E_t \), of the substrates and the specimen dimensions: width, \( B \) and half-thickness, \( h \). \( G_c \) was calculated from equation \[3.2\]:

\[
G_c = \frac{12P_c^2a^2}{B^3E'h^3} \left(1 + 0.64\frac{h}{a}\right)^2
\]  

An approximation of the crack length was empirically found from a measurement of the elastic compliance, \( d\Delta/dP \), using the compliance relationship in equation \[3.3\]:

\[
a = \left(\frac{d\Delta}{dP} \times \frac{BE'h^3}{8}\right)^{1/3} - 0.64 \times h
\]  

All \( G_c \) testing was carried out in standard laboratory conditions at \( \approx 25 ^\circ \text{C} \) and \( \approx 40 \% \) R.H. The specimen was pulled apart with a displacement rate of 1.0 \( \mu \text{m/s} \) until
reaching $P_c$ before slightly unloading to calculate $d\Delta/dP$. The specimens were then loaded again to $P_c$ and the process repeated until the crack propagated through the entire length of the perovskite film.

*Computational details.* The perovskite surface was represented by a 4-layer slab of the crystal. The interface was modelled by adding 2 monolayers of the additives (FPMAI or PMAI). The slab was stoichiometric and neutral in charge. The total energies and electronic structures were calculated with the first-principles code Quantum-espresso [47] and the GGA functional PBE [48] was used. A Wavefunction (charge density) cutoff value of 40 (320) Rydberg and $3 \times 3 \times 1$ k-grid were used in all calculations after testing larger values. Dipole-correction in the surface normal direction was employed for all calculations [49]. The bonding energy was defined as

$$E_{\text{bond}} = \frac{(E_{\text{aft.}} - E_{\text{bef.}} - nE_{\text{adsobates}})}{n}$$ (3.4)

In the first layer adsorption, for instance, $E_{\text{bef.}}$ is the total energy without FPMAI (PMAI) adsorption, $E_{\text{aft.}}$ is the total energy with one monolayer FPMAI (PMAI) adsorption, $E_{\text{adsobates}}$ is the total energy sum of the isolated additive molecules. In this model, $n=4$. 

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Chapter 4

Reduced Perovskite Film

Thickness for Improved Light Outcoupling and Operational Stability

4.1 Introduction

To date, many techniques have been developed to improve perovskite LED performance, such as grain size and composition tuning as well as interface passivation. However, general guidelines for perovskite LED optimization are still unclear. For example, the thickness of the perovskite emitting layer used in LEDs varies considerably. Yang et al. used 110 nm perovskite layers and demonstrated EQE of 14.36% for green LEDs [50], whereas in Chapter 3 we used 65 nm perovskite layers and demonstrated EQE of 13% for red/near infrared LEDs [51]. It is thus presently unclear whether the optimization of perovskite thickness is critical for efficient light emission. The varied techniques that have been reported to improve perovskite LED
performance may not reach full potential if the thickness of the emitting layer is not optimized.

In this chapter we show that the thickness of the perovskite emitting layer is critical for device performance, and an optimized thickness in the range of 35 - 40 nm allows for improved efficiency and stability. We also show this to be a general perovskite LED design principle that can be applied to various perovskite compositions. Maximal EQEs of 17.6% for Cs$_{0.2}$FA$_{0.8}$PbI$_{2.8}$Br$_{0.2}$, 14.3% for CH$_3$NH$_3$PbI$_3$ (MAPbI$_3$), 10.1% for formamidinium-lead-iodide (FAPbI$_3$), and 11.3% for FAPbBr$_3$ based LEDs are demonstrated with a thin perovskite layer (35 - 40 nm). Optical simulations confirm that waveguiding loss is significant in perovskite LEDs due to the high refractive index of the perovskite layer with respect to the transport layers. Reducing the thickness of the perovskite layer can effectively suppress waveguiding and improve light outcoupling. Furthermore, we show that elevated device temperature caused by Joule heating is an important factor contributing to device degradation. We observe improved operational stability for LEDs with a thin perovskite layer, in correlation with reduced Joule heating and lower junction temperature during operation.

Notably, it is a prerequisite that the thin perovskite layer (35 - 40 nm) is still pin-hole free and continuous. The method proposed in Chapter 2 allows us to prepare ultra-smooth (approximately 1 nm surface roughness), pin-hole free perovskite thin films with a wide tunability of film thickness from above 160 nm down to 35 nm, which is critical for the study in this chapter.

4.2 Results and Discussion

4.2.1 Improved Light Outcoupling

Multiple types of perovskite thin films including MAPbI$_3$, Cs$_{0.2}$FA$_{0.8}$PbI$_{2.8}$Br$_{0.2}$, FAPbI$_3$, and FAPbBr$_3$ were prepared using our established \textit{in-situ} perovskite
nanocrystalline film preparation technique with 20 mol% phenylmethylammonium (PMA, also called benzylammonium) halide additives. A common perovskite LED structure was used in this work (Figure 4.1a), consisting of ITO (150 nm), poly-TPD (25 nm), perovskite emitting layer (multiple thicknesses), TPBi (40 nm), LiF (1.2 nm) and Al (100 nm), where ITO is short for indium tin oxide, poly-TPD for poly[N,N'-bis(4-butylphenyl)-N,N'-bis(phenyl)-benzidine], and TPBi for 2,2’,2”-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole). Poly-TPD serves as a hole-transport layer (HTL), TPBi as an electron-transport layer (ETL), and perovskite as an emission layer (EML).

Figures 4.1b-e show EQE vs. current density curves for the various types of perovskites with different thicknesses. Improved EQEs are observed, regardless of perovskite composition, when reducing the thickness from greater than 80 nm to 35-40 nm. Notably, a high EQE of 17.6% is achieved with perovskite LEDs based on 40 nm Cs$_{0.2}$FA$_{0.8}$PbI$_{2.8}$Br$_{0.2}$ thin films. In comparison, LEDs based on 80 nm Cs$_{0.2}$FA$_{0.8}$PbI$_{2.8}$Br$_{0.2}$ thin films only show a maximum EQE of 11.3%. Perovskite films with mixed cations and halide anions have been intensively studied for solar cell applications, which generally show higher power conversion efficiencies than those based on pure MAPbI$_3$ perovskite films. The composition of Cs$_{0.2}$FA$_{0.8}$PbI$_{2.8}$Br$_{0.2}$ used in this work is adopted from established perovskite solar cell technologies, and shows improved efficiency (17.6%) in comparison to LEDs based on pure MAPbI$_3$ films (14.3%).

The primary origin of the improved EQE using a thinner perovskite emitting layer is due to improved light outcoupling, as confirmed by optical simulations (Figure 4.2). Due to the high refractive index of perovskite semiconductors (approximately 2.3 near the emission wavelength), waveguiding mode loss is a major loss channel for perovskite LEDs, and strongly dependent on the thickness of the perovskite layer. Consistent with our experimental observations, optimal outcoupling efficiency occurs
Figure 4.1: (a) Device structure of the perovskite LEDs. (b-e) EQE versus current density of perovskite LEDs based on (b) MAPbI$_3$, (c) Cs$_{0.2}$FA$_{0.8}$PbI$_{2.8}$Br$_{0.2}$, (d) FAPbI$_3$, and (f) FAPbBr$_3$ thin films with various thicknesses.

with perovskite thicknesses in the range of 35 - 40 nm, where waveguiding mode loss is minimized. Furthermore, substrate mode loss is also increased for 35 - 40 nm thick perovskite emitting layers, which provides potential for outcoupling enhancement when well established outcoupling strategies (e.g., microlens arrays) are employed [54]. It is important to note that both the thickness of the emission zone within the perovskite emitting layer and its corresponding position are still unclear in perovskite LEDs. The simulation results shown in Figure 4.2 are based on a classical oscillating dipole model [55] with the assumption of an ultrathin (characterized by a delta function) emission zone near the EML/HTL interface. However, similar light outcoupling trends with the same optimized perovskite thickness of 35 - 40 nm are found when assuming the emission zone is at the middle of the perovskite layer or near the EML/ETL interface.
Figure 4.2: Optical power distribution analysis versus perovskite emitting layer thickness for MAPbI$_3$ based perovskite LEDs with the assumption of an ultrathin emission zone near the EML/HTL interface.

4.2.2 Improved Operational Stability

The operational stability of each of the perovskite LEDs was also investigated. We discovered that the optimized perovskite thickness of 35 - 40 nm is beneficial not only for light outcoupling and thus EQE, but also for operational stability. Figure 4.3 shows normalized EQE versus time under a constant current density of 10 mA/cm$^2$ for various types of perovskite LEDs. In particular, the degradation rate is significantly reduced for all perovskite compositions when reducing the perovskite thickness from above 80 nm to 35 - 40 nm. As the degradation rate is highly dependent on current density, higher constant current densities (40 mA/cm$^2$, 100 mA/cm$^2$) were also applied to test device stability (Figure 4.4). The same trend is preserved, in that stability is improved for devices with thinner perovskite emitting layers. Notably, LEDs based on FAPbI$_3$ thin films degrade considerably faster than other perovskite LEDs.
Figure 4.3: Operational stability of perovskite LEDs at a constant current density of 10 mA/cm\(^2\) for LEDs based on (a) MAPbI\(_3\), (b) Cs\(_{0.2}\)FA\(_{0.8}\)PbI\(_{2.8}\)Br\(_{0.2}\), (c) FAPbI\(_3\), and (d) FAPbBr\(_3\) thin films with various thicknesses.

We suspect it is the intrinsic phase instability of FAPbI\(_3\) that makes this particular perovskite composition vulnerable to electrical-stress-induced degradation.

In terms of an underlying reason for the increased stability, we have correlated the improved operational stability with reduced Joule heating. The surface temperature of the glass substrate was monitored during operation using an infrared thermal camera (Figure 4.5). For LEDs based on 80 nm Cs\(_{0.2}\)FA\(_{0.8}\)PbI\(_{2.8}\)Br\(_{0.2}\), the surface temperature increases to \(\approx 30^\circ\text{C}\) after operation for 60 s, and continues to increase to approximately 32.5\(^\circ\text{C}\) after operation for 120 s. In contrast, the surface temperature of LEDs based on 40 nm Cs\(_{0.2}\)FA\(_{0.8}\)PbI\(_{2.8}\)Br\(_{0.2}\) only increases to 28\(^\circ\text{C}\) after operation.
Figure 4.4: Operational stability of perovskite LEDs at various constant current densities for LEDs based on (a) 40 nm Cs$_{0.2}$FA$_{0.8}$PbI$_{2.8}$Br$_{0.2}$, (b) 80 nm Cs$_{0.2}$FA$_{0.8}$PbI$_{2.8}$Br$_{0.2}$, (c) 35 nm MAPbI$_3$, and (d) 80 nm MAPbI$_3$ thin films.

for 60 s and reaches thermal equilibrium throughout the measurement period of 180 s. The junction temperature is, of course, higher than the surface temperature of the glass substrates. Figures 4.5c–d show the junction temperature extracted from the high energy EL tail (Figure 4.6) according to the generalized Planck equation [56–60]. The junction temperature of LEDs with 80 nm Cs$_{0.2}$FA$_{0.8}$PbI$_{2.8}$Br$_{0.2}$ or MAPbI$_3$ thin films increases rapidly to $\approx 41^\circ$C within the first 70 s of operation. In contrast, the junction temperature of LEDs with 40 nm Cs$_{0.2}$FA$_{0.8}$PbI$_{2.8}$Br$_{0.2}$ or 35 nm MAPbI$_3$ emitting layers reaches thermal equilibrium at 29 - 32$^\circ$C throughout the measurement period ($\approx 1245$ s and $\approx 6600$ s, respectively). Several factors could contribute
to the higher junction temperature of LEDs with a thicker perovskite layer. First, thermal conductivity of MAPbI$_3$ perovskites have been shown to be ultralow (0.3 W/m-K) [61]. Consequently, a thicker perovskite layer forms a stronger barrier for efficient thermal dissipation. Second, the initial EQE of LEDs with a thicker perovskite layer is lower, meaning that a larger portion of the input power is converted to heat. Third, the EQE degradation is faster for LEDs with a thicker perovskite layer, thus forming a positive feedback with heat generation/accumulation.

To further confirm that temperature plays a critical role in operational stability, perovskite LEDs were encapsulated with poly(methyl methacrylate) and transferred into a cryostat, and EQE monitored under a constant current density of 10 mA/cm$^2$ at various environmental temperatures from 10°C to 40°C (Figure 4.7). We found that the device degradation rate is highly sensitive to the background environmental temperature. Working at relatively lower temperatures significantly extends device lifetime. For example, perovskite LEDs working at an environmental temperature of 10°C degraded to 80% of their initial EQE value after $\approx$150 min, which is $\approx$40 times slower than at an environmental temperature of 40°C. This is consistent with our observations that LEDs with a thinner perovskite layer have a lower junction temperature and a longer lifetime compared to LEDs with a thicker perovskite layer.

Notably, although we have shown that elevated operational temperature accelerates device degradation, temperature is not the sole factor that causes degradation. In fact, junction temperatures during operation are not high enough to trigger thermal decomposition of perovskites (e.g., heating at 85°C for 24 h) and therefore device degradation [62]. To confirm this, we annealed LEDs at 50°C for 5 h (without applying any voltage) and no device degradation was observed. Instead, in Chapter 5 we will show that ionic processes under electrical stress play an important role in perovskite LED stability [63], a property that is extremely sensitive to temperature. Reducing Joule heating could significantly suppress these ion-related effects,
Figure 4.5: Temperature analysis of perovskite LEDs during operation. (a-b) Spatial surface temperature images of the glass substrate monitored at various time points (0 s, 60 s, and 120 s) for LEDs based on (a) 40 nm and (b) 80 nm Cs$_{0.2}$FA$_{0.8}$PbI$_{2.8}$Br$_{0.2}$ emitting layers. (c-d) Junction temperature extracted from high energy EL tails for LEDs based on (c) MAPbI$_3$ and (d) Cs$_{0.2}$FA$_{0.8}$PbI$_{2.8}$Br$_{0.2}$ emitting layers of various thicknesses.
Figure 4.6: High energy portion of the EL spectra recorded during operation of perovskite LEDs based on (a) 40 nm Cs$_{0.2}$FA$_{0.8}$PbI$_{2.8}$Br$_{0.2}$, (b) 80 nm Cs$_{0.2}$FA$_{0.8}$PbI$_{2.8}$Br$_{0.2}$, (c) 35 nm MAPbI$_3$, and (d) 80 nm MAPbI$_3$ thin films.
Figure 4.7: Operational stability of perovskite LEDs based on 35 nm MAPbI₃ thin films working at various temperatures operating at a constant current density of 10 mA/cm². Time points for refilling of the cryogenic liquid N₂ (LN₂) are marked as red asterisks; the LN₂ flow rate undergoes a sudden increase at these time points, which induces abrupt EQE changes. Furthermore, the EQE degradation rate becomes slower after refilling LN₂ due to better thermal dissipation as the LN₂ flow rate increases. which explains the correlation between temperature and device stability. Finally, although LEDs based on Cs₀.₂FA₀.₈PbI₂₈Br₀.₂ thin films reach higher EQE than that of MAPbI₃ thin films, they are less stable than LEDs based on MAPbI₃ thin films. A possible reason is the inclusion of bromide in the film, which is consistent with our observations and other previously reported results that bromide-based perovskite LEDs are less stable than iodide-based devices [64]. However, detailed mechanisms are still open to explore.
4.3 Conclusion

In summary, an important design principle for perovskite LEDs has been discovered regarding optimal perovskite thickness. Adopting a thinner perovskite layer in the range of 35 - 40 nm is beneficial for both device efficiency and stability, with EQE as high as 17.6% achieved based on mixed-cation perovskite emitting layers. Optical simulations show that the improved EQE is primarily due to better light outcoupling owing to reduced waveguiding. The improved stability is correlated with reduced Joule heating, which in turn suppresses thermally activated ionic processes. This work also points out the importance of thermal management for perovskite LED operation.

4.4 Experimental

Materials. PMAI or PMABr were synthesized by mixing phenethylamine (Sigma Aldrich) with HI or HBr (Sigma Aldrich) in a 1:1 molar ratio. The reaction was performed in an ice bath while stirring for 3 h. The solvent of the resulting solution was evaporated using a rotary evaporator. The PMAI and PMABr were recrystallized from an isopropyl alcohol: toluene mixture. Finally, the large crystals were filtered and dried under low heat. Recrystallization, filtration, and drying were performed inside a N₂ filled glovebox. MAI, FAI, and FABr (Greatcell Solar) and PbI₂, PbBr₂, and CsI (Alfa Aesar) were used as received.

Perovskite film deposition and device fabrication. PbI₂, PbBr₂, MAI, FAI, CsI, FABr were dissolved in dimethylformamide (Sigma Aldrich, 99.8% anhydrous) and mixed to obtain MAPbI₃, Cs₀.₂FA₀.₈PbI₂₄Br₀.₂, FAPbI₃, or FAPbBr₃ perovskite precursor solutions with varied concentrations from 0.2 M to 0.8 M to tune thickness. Additives (PMAI or PMABr) were mixed with the perovskite precursor in a 0.2:1 molar ratio. Poly-TPD (6 mg/ml in chlorobenzene) was spin coated on glass sub-
substrates with pre-patterned ITO at 1500 rpm for 70 s followed by thermal annealing at 150 °C for 20 min. Poly-TPD was then treated with O₂ plasma for 12 s to improve wetting. Perovskite films were deposited on poly-TPD by spin coating at 6000 rpm for MAPbI₃, Cs₀.₂FA₀.₈PbI₂₈Br₀.₂, FAPbI₃ and 4500 rpm for FAPbBr₃. A solvent exchange step was performed after 3.5 s by dropping toluene on the spinning samples. Then, samples were annealed at 70 °C for 5 min. TPBi, LiF and Al layers were thermally evaporated with thicknesses of 40 nm, 1.2 nm and 100 nm, respectively. Device area is 0.1 cm². Some perovskite LEDs were encapsulated by spin coating poly(methyl methacrylate) (50 mg/ml in chlorobenzene) with a spinning rate of 2000 rpm for sample transfer between a N₂ filled glovebox and a cryostat.

**Material and device characterization.** Characteristics of perovskite LEDs at room temperature were measured in a N₂ glovebox using a custom motorized goniometer consisting of a Keithley 2400 sourcemeter unit, a picoammeter (4140B, Agilent), a calibrated Si photodiode (FDS-100-CAL, Thorlabs), and a calibrated fiber optic spectrophotometer (UVN-SR, StellarNet Inc.). Temperature dependent electrical characterization was performed in a VNF-100 Cryostat System (Janis). Thermal images were recorded with a ThermaCAM SC640 thermal imaging camera (FLIR). Junction temperatures were extracted following previous protocols [57]. Thicknesses of perovskite thin films were measured by two different methods, which gave similar values: profilometer (KLA-Tencor P-15, scan speed: 10 μm/s, sampling rate: 200 Hz, tip force: 1 mg) and variable-angle ellipsometer (Gaertner LSE Stokes Ellipsometer, single wavelength at 632.8 nm).

**Optical simulations.** Optical simulations were based on a classical oscillating dipole model [55]. The power ratio radiated to each in-plane wavevector range (out-coupled, substrate, waveguiding, surface plasmonic, and absorption) was simulated by using the experimentally obtained optical constants (refractive index and absorption coefficient) of each layer to construct the model device. We assume that the
emission zone in the perovskite emitting layer is confined to an infinitely thin zone. We also assume 100% internal quantum efficiency, isotropic emission pattern, and no electrical loss.
Chapter 5

Influence of Electrical Stress on the Efficiency of Perovskite Light Emitting Diodes

5.1 Introduction

Trap states leading to non-radiative decay pathways are key factors that limit the performance of perovskite LEDs. The mechanisms of defect formation and their impact on perovskite device performance are not fully understood, and effective methods to reliably reduce these defects are still needed. It is suggested that the formation of metallic Pb may increase trap states, and that this metallic Pb formation can be suppressed by using excess organic cations [65]. It has been shown that illumination-induced halide redistribution may result in an order-of-magnitude reduction in trap-state density with the halides filling vacancies and reducing interstitial sites, thus increasing the photoluminescence quantum yield [14]. Trap states may also be influenced by the ambient environment, in particular, oxygen and water [66].
In this chapter, we show that electrical stress in the form of subsequent electrical scans can influence the performance of MAPbI$_3$ perovskite LEDs significantly, increasing the EQE from an initial 5.9% to 7.4%. Consistent with the enhanced device performance, both the steady-state PL intensity and the time-resolved PL decay lifetime increase after electrical stress, indicating a reduction in non-radiative recombination in the perovskite film. By investigating the temperature-dependent characteristics of the perovskite LEDs and the cross-sectional elemental depth profile, we propose that trap reduction and resulting device-performance enhancement is due to local ionic motion of ions, most likely iodide, in the perovskite film that passivate under-coordinated Pb defects. On the other hand, we found that over-stressed LEDs show irreversibly degraded device performance, possibly because ions initially on the perovskite lattice sites are displaced during extended electrical stress, and thus create defects.

5.2 Results and Discussion

Perovskite LEDs were fabricated with a device structure of ITO (150 nm) / poly-TPD (20 nm) / MAPbI$_3$ perovskite (300 nm) / TPBi (40 nm) / LiF (1.2 nm) / Al (100 nm) (ITO: indium tin oxide; poly-TPD: poly[N,N’-bis(4-butylphenyl)-N,N’-bis(phenyl)benzidine]; TPBi: 2,2’,2”-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole)). A two-step interdiffusion method is used to prepare the perovskite film [67], and an initial EQE of 5.9% is achieved.

Interestingly, we find that the EL and EQE increase with subsequent electrical scans (Figure 5.1a and b). As shown in Figure 5.1b, after 30 consecutive electrical scans, the EQE is increased from initial 5.9% to 7.4%, an enhancement of 26%. The EQE enhancement gradually saturates as electrical scans are repeated. During subsequent electrical scans, the $J$-$V$ curves also change appreciably, as shown in
Figure 5.1c. The origin of this change is not from burning out of local shorts as has been observed previously with thin film LEDs, as the leakage current is unaffected. In the range of 2.0 - 2.2 V, we observe a steep increase of the current caused by a diffusion-dominated current \[68\]. The slope of the \( J-V \) curves in this region increases as the device is scanned multiple times. In this region, the current can be described by the Shockley diode equation 5.1:

\[
J = J_0 \left( e^{qV/nkT} - 1 \right)
\] (5.1)

where \( J_0 \) denotes the saturation current density, \( k \) the Boltzmann constant, \( T \) the temperature, \( q \) the electron charge, and \( n \) the ideality factor. The ideality factor is a measure of the slope of the \( J-V \) curve and can be determined via equation (5.2):

\[
n = \left( \frac{kT}{q} \frac{\partial \ln J}{\partial V} \right)^{-1}
\] (5.2)

An increase in the slope, and thus reduction of \( n \), of the \( J-V \) curves in this region indicates a reduction in trap-assisted recombination \[69\], and under ideal conditions without non-radiative recombination, \( n \) equals unity. In Figure 5.1d, we observe that, with sequential voltage scans, \( n \) decreases dramatically, indicating a significant reduction in trap-assisted recombination. This is consistent with the increased EL intensity and EQE, all of which confirm that the reduction in trap density plays the dominant role in performance enhancement. It should be noted that the extracted \( n \) is greater than 2, likely a result of non-ideal series and shunt resistances \[70\].

The emissive properties of the perovskite film within the device structure before and after electrical stress are investigated to further understand the origin of the device performance enhancement. After the EQE improvement saturates, the steady-state PL intensity is increased by 4 times (Figure 5.1e). The time-resolved PL (TRPL) measurement shows that the average decay lifetime increases from 0.35\( \mu \)s
Figure 5.1: (a) Radiance vs. voltage of an as-produced perovskite LED for subsequent voltage scans; (b) EQE vs. current density of an as-produced perovskite LED for subsequent voltage scans; (c) Current density, and (d) ideality factor vs. voltage of an as-produced perovskite LED for subsequent voltage scans; (e) Steady-state PL of encapsulated perovskite LEDs before and after electrical stress; (f) Transient PL of encapsulated perovskite LEDs before and after electrical stress.

to 1.05 µs (Figure 5.1f), which supports the hypothesis that the device performance enhancement is due to the reduction of defects in the MAPbI$_3$ film that cause non-radiative recombination.

To further investigate the mechanisms of device-performance enhancement induced by the electrical stress, we performed temperature-dependent electrical char-

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acterization of the perovskite LEDs. Figure 5.2 summarizes the luminance and EQE of the devices measured at four different temperatures (180 K, 220 K, 260 K, and 300 K), all of which are higher than the orthorhombic-tetragonal phase transition temperature of MAPbI$_3$ at approximately 160 K \[71\]. At lower temperatures (180 K and 220 K), applying multiple electrical scans produce similar luminance curves (Figure 5.2a and b). In contrast, at higher temperatures (260 K and 300 K), increased luminance is observed upon subsequent voltage sweeps (Figure 5.2c and d). Figure 5.2e shows the normalized peak EQE versus voltage scan number at different temperatures. Clearly, the EQE is improved with electrical stress at 260 K and 300 K, whereas no performance enhancement is observed at 180 K and 220 K. It should be noted that the EQE enhancement induced by the electrical stress is 2.4 and 1.5 times at 300 K and 260 K, respectively, both of which are higher than the 26% enhancement for the high performance LED measured in N$_2$ at room temperature shown in Figure 5.1. This is because during the sample transfer process for the temperature dependent measurements, samples are exposed to air for 1 min, which slightly degrades the initial EQE \[72\]. Under this condition, multiple electrical scans have the capability to improve the performance more significantly than devices without exposure to air.

Previous research has investigated the temperature dependent hysteresis of perovskite solar cells and shown that minimal hysteresis is observed at 170 - 250 K because of the impeded drift and diffusion of ionic species while hysteresis becomes significant at 250 - 290 K \[73\]. Those observations are very similar to ours for the device-performance enhancement induced by subsequent electrical scans. It therefore appears that the electrical stress reduces trap-assisted non-radiative recombination via ionic motion and redistribution in the perovskite film. Ionic motion is widely invoked in perovskite photovoltaic cells, which can be induced by either electrical bias or illumination \[14,74,75\]. It has been reported that the trap-assisted recombination is caused by quenching sites at grain boundaries \[65\] and that illumination-induced
Figure 5.2: Luminance vs. voltage curves at (a) 180 K, (b) 220 K, (c) 260 K, and (d) 300 K. (e) The corresponding peak EQE vs. scan number at different temperatures.
halide redistribution may lead to an order-of-magnitude reduction in trap state density by filling iodide vacancies with mobile iodides and reducing interstitial sites, thus increasing the PL significantly [14]. Based on these observations, we propose that within the as-produced perovskite film, and especially at grain boundaries, iodide vacancies (under-coordinated lead sites) with associated interstitial iodide ions generate a large trap population that serve as non-radiative recombination sites. Upon applying a voltage bias, the increased electric field aids ionic motion, filling these iodide vacancies. As a result, after applying the electrical stress, EL efficiency, PL intensity, and PL lifetime all increase. However, electrical stress does not influence device performance at lower temperatures (180 K and 220 K) because both trap-induced non-radiative recombination and other non-radiative decay coupling to phonon modes are reduced at these temperatures, offsetting the effects of electrical stress. This is confirmed by temperature dependent steady-state PL measurements (Figure 5.3). At 180 K, the PL intensity is 15 times higher than at room temperature, while the electrical stress treatment only leads to a four-fold enhancement in PL intensity at room temperature.

It is still an open question as to how, exactly, ion motions passivate traps. We propose two possible mechanisms here. First, upon the crystallization of perovskites, structural defects are formed at perovskite grain boundaries and surfaces. The applied electrical stress assists the reorganization of these defective surfaces and grain boundaries via ion motion that reduces traps. Second, iodides that are not initially on the perovskite lattice sites migrate under the assistance of the applied electric field, which fill iodide vacancies and passivate under-coordinated Pb defects. Notably, given that iodine (I$_2$) is much more mobile than iodide, trace amount of iodine in the perovskite film may play a role as a catalyst for the iodide migration in a way that involves the reduction and oxidation between iodide and iodine.
Figure 5.3: Temperature dependent steady-state PL of the prepared perovskite films.

It should be noted that, during the time and voltage scale of the electrical stress discussed above, the electrical stress-induced ionic motion is short-range that reduces local traps. Figure 5.4 shows cross-sectional scanning transmission electron microscopy (STEM) images and corresponding energy-dispersive X-ray spectroscopy (EDS) elemental depth profiles of the devices before and after electrical stress. They show that the distribution of various elements (Pb, I, C, Al, In) is not significantly altered by the electrical stress, suggesting that ion motion is a local phenomenon. It also confirms that iodine is highly mobile, as it has diffused into both organic transport layers (TPBi and poly-TPD), even in the as-produced device before electrical stress. The diffusion of ions into the transport layers may also improve charge injection and the electron/hole balance in the device [76], which may be another factor for the improved device performance, and warrants further investigation.

We further investigated the effectiveness of the device performance enhancement induced by subsequent electrical scans over extended periods of time. When stored in
**Figure 5.4**: Cross-sectional STEM images of LEDs (a) before, and (b) after electrical stress. (c) Corresponding EDS elemental depth profile of I, Pb, C, Al and In before (solid line) and after (dash line) electrical stress.

\[ N_2, \text{ the elevated EQE decreases in a much slower manner compared to the timescale of the enhancement, as shown in Figure 5.5. Devices maintain } > 95\% \text{ of the enhanced EQE after 3 days, } \approx 90\% \text{ after 7 days, and } > 80\% \text{ after 18 days, which were measured only once without additional electrical scans to reduce the influence of the device performance enhancement effects induced by subsequent electrical scans as much as possible. The gradually decreased EQE is possibly due to defect regeneration by ion back diffusion, and the much slower rate of efficiency reduction is because “non-excess” ion back diffusion has to overcome the activation energy of ion migration in perovskites, unlike the excess mobile ion concentration [12]. If electrical stress is applied again, in the form of multiple current-voltage sweeps, the EQE can be enhanced again, as shown in red in Figure 5.5. Furthermore, the electrical stress can be applied at any time to enhance device performance, as shown in blue in Figure 5.5 with a similar device efficiency enhancement achieved when applying electrical stress 22 days after device fabrication. This comparison suggests that electrical stress is important not only for the short term but also for long-term device performance.\]
Figure 5.5: The effectiveness of the device performance enhancement induced by subsequent electrical scans. Red: Normalized EQE of devices with an initial electrical stress on the day of device fabrication, as well as 3, 7, and 18 days after the treatment. A second electrical stress is applied after 18 days, showing that performance enhancements are possible multiple times. Blue: Normalized EQE of devices on the day of and 22 days after device fabrication. The electrical stress is applied 22 days after device fabrication, and is beneficial for device performance.

We report data on electrical stress primarily in the form of subsequent electrical scans as it provides more detailed information in terms of device performance, extracted from changes to the $J-V$, $L-V$, and EQE characteristics. Electrical stress in the form of constant electrical bias provides additional insight as it can also influence device performance, as shown in Figure 5.6. The EQE increases and gradually saturates after approximately 10 min for a constant current of 3 mA/cm$^2$. As discussed above, in this region, local ion motion that reduces defects are the origin for the improved device efficiency. However, after approximately 15 min, EQE starts irreversibly decreasing. This is possibly because some of the non-excess ions initially comprising the perovskite lattice sites migrate and create more defects due to long-term electrical stressing in one direction. This suggests that the perovskite layer...
Figure 5.6: EQE vs. time under constant current bias. A relatively small constant current (3 mA/cm$^2$), where the corresponding EQE is not at its maximum point, is used here in order to avoid any significant impact from Joule heating.

must be formed such that defect density is low, and the possibility of ion migration is reduced to the fullest extent. Such approaches should allow for stable and efficient LEDs.

Notably, although a two-step interdiffusion method is used to prepare the perovskite film in this chapter [67], similar efficiency change driven by a constant current density is observed for LEDs studied in Chapter 4 (e.g., Figure 4.3). In fact, this is a general phenomenon that has been observed by other researchers and for other types of perovskites [77, 78]. However, when driven at a relatively high constant current density, device degradation sets in instantly, and thus we could not observe any performance improvement resulting from ion rearrangement (see Figure 4.4).
5.3 Conclusion

In summary, the influence of electrical stress on the performance of perovskite LEDs is studied in this chapter. Electrical stress is shown to initially improve device efficiency, owing to local ionic motions in the perovskite film that are able to fill local defects that cause non-radiative recombination. On the other hand, long-term electrical stressing will degrade device performance, possibly due to the migration of non-excess ions creating more defects. Therefore, this work points to a need to develop strategies to mitigate ion migration to ensure stable device operation.

5.4 Experimental

Fabrication. MAI was synthesized by mixing aqueous methylamine (Sigma Aldrich) and aqueous HI (Sigma Aldrich) at 0 °C with constant stirring. MAPbI$_3$ perovskite LEDs were fabricated using indium-tin-oxide (ITO) patterned glass substrates with a sheet resistance of 15 Ω/sq. Substrates were sequentially cleaned using soapy water, deionized water, acetone, and isopropyl alcohol in an ultrasonicator for 15 min each, and then treated with O$_2$ plasma for 5 min prior to film deposition. Poly-TPD in chlorobenzene (6 mg/ml) was spin coated on top of the ITO substrates at 1500 rpm followed by thermal annealing at 150 °C for 20 min. Samples were then treated with O$_2$ plasma for 1 s to improve wetting. PbI$_2$ dissolved in hot dimethylformamide (DMF) (500 mg/ml, 100 °C) was cooled to 70 °C for spin coating at 6000 rpm, followed by thermal annealing at 70 °C for 5 min. MAI in isopropyl alcohol (50 mg/ml) was then spin coated on top of PbI$_2$ films at the same spin speed, which was followed by sequential thermal annealing at 70 °C for 10 min, 100 °C for 70 min and 60 °C for 300 min. Then, samples were brought into a vacuum evaporation chamber (EvoVac, Angstrom Engineering) for thermal evaporation of TPBi (40 nm), LiF (1.2 nm) and Al (100 nm) layers on top of the perovskite film. The device area was 0.1 cm$^2$. 
Characterization. The fabricated devices were measured in a N\textsubscript{2}-atmosphere glovebox using a homemade motorized goniometer setup consisting of a Keithley 2400 sourcemeter unit, a calibrated Si photodiode (FDS-100-CAL, Thorlabs), a picoammeter (4140B, Agilent), and a calibrated fiber optic spectrophotometer (UVN-SR, StellarNet Inc.). Temperature dependent \textit{I-L-V} measurements were made under vacuum ($< 2 \times 10^{-5}$ Torr) by transferring the devices into a Lakeshore probe station (Lake Shore Cryotronics, Inc., Westerville, USA) connected with a Keithley 2400 sourcemeter unit, a calibrated Si photodiode (FDS-100-CAL, Thorlabs), and a picoammeter (4140B, Agilent). SEM measurements were made using an FEI Verios 460 XHR SEM. Cross-sectional TEM lamella samples of the devices were prepared by an FEI Helios DualBeam microscope. STEM images and EDS measurements were carried out in an FEI Talos (S)TEM at 200 kV. Steady-state and TRPL measurements were performed using an FLS980 spectrometer (Edinburgh Instruments). Samples were excited at 470 nm from a Xe arc lamp source for the steady-state PL measurements. Samples were excited at 635 nm by a pulsed laser diode with a 10 µs pulse period and detection wavelength of 770 nm for the TRPL measurements.
Chapter 6

Redox Chemistry Induced Degradation of Perovskite Light Emitting Diodes

6.1 Introduction

Although perovskite LEDs have improved rapidly in terms of efficiency, device stability remains a considerable concern that must be overcome before this technology can reach its potential; to enable improvements in such stability, a better understanding of chemical degradation pathways is imperative.

Metal halide perovskites are known to be sensitive to various environmental factors, including moisture, light, and oxygen. For example, it has been reported that moisture will induce perovskite decomposition into its precursor components via intermediate hydrated phases, a process that is accelerated by light and oxygen \[79, 81\]. It is significant that most stability studies have thus far been limited to the effects of external reagents on stand-alone perovskite films. Consequently, the importance of interactions between the perovskite and dissimilar material layers of the device itself
has largely been underestimated. Although several reports exist on the reaction of Al electrodes with perovskites \[17\,\text{[82]}\], detailed chemical degradation paths have not heretofore been well understood; most pathways proposed involve reactions in which HI is released by the decomposition of MAPbI\(_3\).

In this chapter, we report a comprehensive degradation study on perovskite optoelectronic devices using \textit{in-situ} and \textit{ex-situ} techniques, including \textit{in-situ} scanning electron microscopy (SEM) and x-ray diffraction (XRD) measured under controlled humidity and vacuum pressure, and \textit{ex-situ} x-ray photoelectron spectroscopy (XPS) and energy-dispersive x-ray spectroscopy (EDS). Our studies shed light on important chemistry that takes place and show that degradation and ultimate decomposition of devices can be understood only in view of the chemistry of the overall device stack. In particular, and in the case of Al electrodes, \textit{in-situ} XRD and XPS measurements reveal a redox reaction between Al and MAPbI\(_3\) in which Pb\(^{2+}\) is reduced to Pb\(^0\), converting MAPbI\(_3\) first to MA\(_4\)PbI\(_6\)·2H\(_2\)O and then to MAI. This redox reaction occurs spontaneously when Al is in direct contact with MAPbI\(_3\) despite the absence of external factors such as light, moisture, or oxygen. Even in efficient perovskite solar cells and LEDs where the Al electrode and the perovskite film are separated by transport layers, reaction with the electrode material still considerably accelerates device degradation. As shown by \textit{in-situ} SEM measurements, decomposition in the device stack occurs under conditions where an isolated MAPbI\(_3\) film is stable. We propose that moisture simply promotes diffusion, facilitating continued reaction between the metal and perovskite layers; this occurs well before moisture serves as a decomposition agent, itself, for the perovskite film. Furthermore, we show that the redox reaction induced degradation also applies to other type of perovskites (such as CsPbI\(_3\) and CsPbBr\(_3\)) and other metals (such as Ag, Cr, Yb), indicating a need to identify contacts to allow for stable perovskite devices.
6.2 Results and Discussion

6.2.1 Degradation Phenomenon

Perovskite LEDs were fabricated having the structure indium tin oxide (ITO)/hole transport layer (HTL)/MAPbI$_3$ perovskite/electron transport layer (ETL)/LiF/Al. Poly[N,N’-bis(4-butylphenyl)-N,N’-bis(phenyl)-benzidine] (poly-TPD) was used as an HTL, and 2,2’,2”-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBi) was used as an ETL.

Although perovskite LEDs based on the structure outlined above maintain their initial efficiency for months when stored under N$_2$, if exposed to ambient conditions at various humidity levels (ranging from $\approx$27% to $\approx$90% relative humidity, RH), the EQE is reduced by three orders of magnitude within 10 min (Figure 6.1a). Furthermore, the rate of degradation is highly dependent on RH: at $\approx$90% RH complete degradation is observed within 2 min, whereas no apparent degradation is observed in 2 hours in dry air. The $J$-$V$ curve at 27% RH (Figure 6.1b) shows that the leakage current is increased by 5 orders of magnitude in 6 min, indicating a dramatic degradation of the diode, which is related to the degradation of the active layers and/or their interfaces. In contrast, leakage current is maintained in dry air at the same order of magnitude for more than 9 days with reduced on-state current (Figure 6.1c), indicating that the device becomes more resistive, perhaps due to the introduction of an injection barrier at the metal/semiconductor interface. If a device is exposed to high humidity ($\approx$90% RH) for 4 h, which is well beyond the point of performance degradation, the entire device stack, including the Al electrode, becomes transparent. To illustrate, a device geometry with a larger Al pad was used. A freshly prepared device stack and one following degradation are shown in Figure 6.1d; note that after degradation the full device stack becomes transparent in the central area, but edges not covered by Al become yellow.
Figure 6.1: Degradation of MAPbI$_3$ perovskite LEDs. (a) Dependence of EQE of the perovskite LEDs vs. time under different environmental conditions; (b) $J - V$ curves of perovskite LEDs at different times exposed to 27% RH; (c) $J - V$ curves of perovskite LEDs at different times stored in dry air. (d) Photos of the LED stack before and after degradation (Samples were exposed to ambient conditions with $\approx$90% RH for 4 h.).
To rule out the possibility that one of the interlayers participates in the degradation reactions that yield transparency, control device stacks having only TPBi or LiF as interlayers were tested; both control devices degraded to the transparent state (Figure 6.2a and b). Furthermore, control devices with insulating interlayers of poly(ethylene oxide) (PEO) and poly(methyl methacrylate) (PMMA) were also constructed. These structures showed the same degradation as our original devices, and were rendered transparent (Figure 6.2c and d). Based on these observations, we believe that these interlayers serve only to physically separate the Al and perovskite. It should be noted that, although we proved that interlayers are not involved in the degradation reactions, certain interlayer properties such as hydrophobicity may influence device degradation rate. Since a range of structurally different interlayers gave similar results, in the following experiments we employ the full LED device structure to investigate degradation mechanisms in detail.

To rule out the role of oxygen and light on the degradation process, LED stacks were exposed to moisture under a N\textsubscript{2} atmosphere either in the dark or under light; in the latter case they also degrade and become transparent (Figure 6.3a), with an overall transmittance of \( \approx 70\% \). It should be noted that the edges of the perovskite not covered by the Al electrode also become transparent by conversion to hydrated perovskite and not by decomposition to PbI\textsubscript{2}. If this material is dried under N\textsubscript{2} for 30 min, the film edges reverted to brown (Figure 6.3b), showing that perovskite hydration is reversible as previously described \cite{81}. In marked contrast, however, the area initially covered by Al remains transparent even after drying, showing that degradation of the full device stack is irreversible if in the presence of the metal. There was no observed difference in degradation behavior between samples exposed to ambient light or kept in the dark (Figure 6.3c). After prolonged exposure to moisture (5 days), perovskites and hydrated perovskites decompose to PbI\textsubscript{2} and become yellow in color (Figure 6.3d). An SEM image of the central area of the degraded stack is
Figure 6.2: Photos of degraded device stacks with: (a) TPBi; (b) LiF; (c) PEO and (d) PMMA as interlayers.

shown in Figure 6.3e along with corresponding EDS maps of Pb, I, and Al (Figure 6.3f-h, respectively). The Pb is concentrated in several spots, suggesting that Pb is mobile under the degradation conditions, while Al and I are more broadly distributed.

6.2.2 Chemical Degradation Paths

In-situ XRD analysis of the LED stack that was performed in a moist, dark environment provides critical details about the chemical degradation process (Figure 6.4a). We find that it can be divided into three stages:
Stage (1): In the first 1.8 h, diffraction peaks for MAPbI$_3$ ($\approx 14^{\circ}$ and $\approx 28^{\circ}$) and Al ($38.47^{\circ}$) decrease rapidly, while those for metallic Pb$^0$ ($31.27^{\circ}$) and hydrated MA$_4$PbI$_6$·2H$_2$O ($\approx 11.6^{\circ}$) increase [81]. This transformation is driven by the redox reaction between Al and perovskite, which causes a loss of Pb$^{2+}$ from the MAPbI$_3$ structure and MA$_4$PbI$_6$·2H$_2$O crystals to nucleate.

Stage (2): As the redox reaction of Al with Pb$^{2+}$ continues, further loss of Pb$^{2+}$ from MA$_4$PbI$_6$·2H$_2$O leads to the formation of MAI ($9.8^{\circ}$, $19.6^{\circ}$ and $29.7^{\circ}$). It should be noted that at this stage, although there is little change in the Pb diffraction signal intensity, the thin film has decomposed to yield the transparent region shown in Figure 6.3a.

Stage (3): Once the metallic Al has fully reacted to give Al$^{3+}$, further exposure to moist air causes the Pb signal to shift from $31.27^{\circ}$ to $31.20^{\circ}$ and with reduced intensity (Figure 6.4), which we attribute to the reoxidation of Pb$^0$ and hydration.
to form PbO·xH₂O (31.20°). The peaks for MAI gradually disappear because of the prolonged exposure to air and the high vapor pressure of methylamine. However, proceeding to stage (3) is not required to render the degraded device stack transparent, as the generated metallic Pb⁰ atoms exist as sequestered aggregates rather than as films (cf. Figure 6.3f) that do not significantly block light.

To better elucidate the chemical reaction paths and the generation / reduction of key materials, XRD intensities were integrated for the most prominent peaks of MAPbI₃ (14°), Pb⁰ (31.27°), MAI (9.8°), MA₄PbI₆·2H₂O (11.6°) and Al (38.47°) and were plotted versus time (Figure 6.4b); these clearly show the intensity changes for these key materials through the three stages we describe. Based on this analysis, device degradation paths induced by the Al electrode can be summarized by reactions (6.1) - (6.3):

\[
2\text{Al} + 4\text{MAPbI}_3 + 2\text{H}_2\text{O} \rightarrow \text{MA}_4\text{PbI}_6 \cdot 2\text{H}_2\text{O} + 3\text{Pb} + 2\text{Al}^{3+} + 6\text{I}^- \tag{6.1}
\]

\[
2\text{Al} + 3\text{MA}_4\text{PbI}_6 \cdot 2\text{H}_2\text{O} \rightarrow 12\text{MAI} + 3\text{Pb} + 2\text{Al}^{3+} + 6\text{I}^- \tag{6.2}
\]

\[
\text{MAI} \xleftrightarrow{\text{MAI}} \rightarrow \text{MA} + \text{HI} \tag{6.3}
\]

where reactions (6.1) and (6.2) correspond to the redox reactions in Stages (1) and (2), respectively, and reaction (6.3) represents the equilibrium between methylammonium iodide and methylamine plus HI; and in this sequence, the presence of iodide does not significantly impact the redox reaction. It should be noted that Al³⁺ and I⁻ related products produced by reactions (6.1) and (6.2) are amorphous, and are thus undetectable by XRD. The disappearance of MAI and the reoxidation/hydration of Pb⁰ during Stage (3) as discussed above are not induced by the Al electrode, but rather result from exposure to air and time.

It is important to note that no PbI₂ peaks were detected during the entire in-situ XRD analysis procedure for the LED device stack, which shows that Al-induced
Figure 6.4: *In-situ* XRD analysis of the degradation of the LED stack with moist air in the dark: (a) *In-situ* XRD spectra versus time; (b) Integrated XRD peak intensities of key materials versus time; (c) XRD patterns in the Pb diffraction window at various time points.
degradation is independent of the decomposition of MAPbI₃ into MAI and PbI₂, as is expected for the decomposition of stand-alone MAPbI₃ films. *In-situ* SEM analysis on the LED stack done in a moist environmental chamber shows that Al will induce the degradation of perovskite devices even under conditions where the decomposition of stand-alone MAPbI₃ does not occur (Figure 6.5). At first, a clean, smooth surface is found for the Al-covered area (Figure 6.5a). Next, some spots are generated in the first 95 min (Figure 6.5b-e), which are due to the nucleation of metallic Pb⁰ following reaction with the Al electrode. Then, some needles are generated gradually over the following 85 min (Figure 6.5f-h), which are likely hydrated perovskite, as observed by others [80]. It should be noted that, in our time frame, perovskite areas that are not covered by Al do not degrade but remain smooth (Figure 6.5); this confirms that Al accelerates the degradation of perovskite layers that are exposed to moisture. It should also be noted that *in-situ* SEM analysis is conducted under low vacuum with moisture; these conditions are different from ambient. Thus the time stamps cannot be directly correlated with those from other analyses.

The XPS analysis confirms our contention that redox chemistry between Al and MAPbI₃ happens spontaneously, and does not require moisture, oxygen, or light (Figure 6.6). As further evidence, when thin layers of Al (5 or 50 nm) are deposited directly onto MAPbI₃, Pb 4f spectra (Figure 6.6a) show prominent metallic peaks for Pb⁰; no Pb⁰ peaks are observed for the starting MAPbI₃ film. Moreover, Al 2p spectra (Figure 6.6b) show no remaining Al⁰ for samples using a 5 nm Al film; the entire 5 nm Al film has reacted with the perovskite. A small metallic Al⁰ peak remains for samples using a 50 nm Al film.

We conclude that the function of moisture is to facilitate the diffusion of ions, rather than to act as a reagent in the decomposition of the perovskite device stack. In support of this argument, device stacks were exposed to moderate humidity (≈30% RH) in the dark, and the degradation process was tracked versus time (Figure 6.7).
Figure 6.5: (a)-(h) In-situ SEM analysis on the LED stack in an environmental chamber at various time points from 0 to 180 min; (i) SEM image near the boundary of the Al area after 180 min exposure showing that only the area covered with Al undergoes H$_2$O-mediated decomposition.
Figure 6.6: XPS spectra of (a) Pb 4f and (b) Al 2p with different thickness of Al films on MAPbI$_3$ perovskite.

d). We could clearly see the degradation proceeding, and part of the Al pad became transparent on day 5. Areas that were not covered by Al still had the characteristic brown of MAPbI$_3$ perovskite. On day 15, the edge areas started to become yellow, indicating the conversion of MAPbI$_3$ to PbI$_2$. However, the entire Al pad area did not become transparent, even after 15 days; apparently under moderate humidity conditions, diffusion is limited, so reaction of the Al layer is incomplete. A similar series of experiments were carried out under the same humidity conditions, but with exposure to ambient light, which did accelerate conversion of the perovskite film to PbI$_2$ (Figure 6.7e-h).

Because we assert a reaction involving the metal cation (in this case Pb$^{2+}$) and a neutral metal film, we would expect redox chemistry to occur across other metal/perovskite interfaces. To check, Au, Ag, Cr, or Yb films were deposited directly onto MAPbI$_3$ and the Pb 4f XPS spectra (Figure 6.8) of all except Au show metallic peaks for Pb$^0$, indicating that redox chemistry of lead perovskites and Ag, Yb, and Cr can happen spontaneously. Based upon standard electrochemical potentials, which are measured in water, one would expect redox reactions with Al, Cr, and Yb as expressed in reactions (6.1) - (6.3). However, for the case of Ag,
Figure 6.7: Photos of the LED stack stored under ambient conditions (≈30% RH) for several days: in the dark (a-d) and with light (e-h).
the redox reaction requires the presence of iodide because the oxidation potential of Ag in the presence of iodide is 1 V more favorable than it would be in water [83]. Although no metallic Pb\(^0\) peaks are observed for samples with Au, shoulders are observed at \(\approx 137.5\) and \(\approx 142.5\) eV. We attribute this to partial charge transfer at the perovskite/Au interface, similar to observations at metal/organic interfaces [84].

Considering our finding that redox reactions between Pb\(^{2+}\) and the neutral metal contact are the main culprit for device degradation, devices with other types of lead halide perovskite active layers, such as formamidinium cesium lead iodide (FA\(_x\)Cs\(_{1-x}\)PbI\(_3\)), may also degrade through redox chemistry. To test this, Al was deposited directly onto CsPbI\(_3\) and CsPbBr\(_3\), and the Pb 4f XPS spectra (Figure 6.8) show prominent metallic peaks for Pb\(^0\). Moreover, Al 2s XPS spectra show both metallic Al\(^0\) and Al\(^{3+}\) peaks (Figure 6.9). These results prove that redox reactions between Al and other types of perovskites also occur spontaneously. This is consistent with previous reports of degradation rates of FA\(_{0.9}\)Cs\(_{0.1}\)PbI\(_3\) solar cells using Ag electrodes where devices only maintain 20% of their initial efficiency after exposure to air for 60 min [85].

### 6.2.3 Discussion

Our demonstration of redox reactions between metal electrodes and perovskite films helps to explain observed device degradation phenomena. Guerrero et al. found that, in the absence of moisture, if a device is illuminated for 4 h at an illumination intensity of 1 sun, efficiency is dramatically reduced. Their SEM images show corrosion of the metal contact for Ca, Al, Ag and Au, and they propose replacing these metals with Cr\(_2\)O\(_3\)/Cr to improve device stability [82]. Kato et al. showed that AgI is formed when a Ag electrode is used for perovskite solar cells [16]; it is speculated that I\(^-\) contributes to the corrosion of the metal contacts. Although the role of I\(^-\) in the reaction between the Al contact and the perovskite Pb\(^{2+}\) was not investigated in this
Figure 6.8: Pb 4f XPS spectra of samples with Al, Yb, Cr, Ag, and Au metals directly on CsPbBr$_3$, CsPbI$_3$, and MAPbI$_3$ perovskite films. All perovskite/metal interfaces show evidence of redox chemistry via the presence of a Pb$^0$ peak except the MAPbI$_3$/Au sample which shows evidence of partial charge transfer.

Figure 6.9: XPS spectra of Al 2s for (a) Al on CsPbI$_3$, (b) Al on CsPbBr$_3$. 

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work, it may in fact increase the rate of reaction. We were able to show in models that MAI alone cannot induce the corrosion of the Al: we submerged an Al film in MAI aqueous solution; the Al film exhibited no sign of corrosion (Figure 6.10a). In contrast, submerging an Al film in PbI$_2$ solutions in either water or dimethylformamide (DMF) showed markedly increased corrosion (Figure 6.10b-c). It is also interesting in this context that replacing MAPbI$_3$ with PbI$_2$ in an LED stack showed similar degradation results, which provides further evidence that it is only Pb$^{2+}$, and not the perovskite, per se, in the redox reaction with Al (Figure 6.11).

### 6.3 Conclusion

In summary, we have examined the fundamental chemistry at the interface between the lead complex of metal halide perovskites and superdeposited metal electrodes in perovskite-based optoelectronic devices. Through in-situ SEM and XRD analyses...
under controlled humidity and vacuum pressure and ex-situ XPS and EDS measurements, we showed that the Al electrode material degrades perovskite LEDs via classical redox chemistry, which occurs spontaneously and without the need for oxygen or light. This redox reaction has been heretofore overlooked as the dominant pathway for device degradation. We also showed that a primary function of moisture is to facilitate ion diffusion to enable continuous reaction between the metal and the perovskite; moisture acting as a decomposition reagent for the perovskite film is secondary. We also found that redox chemistry happens between perovskites that do not contain protonic cations (CsPbI$_3$ and CsPbBr$_3$) and other metals (Ag, Cr, Yb), indicating that redox reactions, rather than proton (e.g., HI or HBr) chemistry, dominate interfacial degradation. Our study brings new insights into choices of electrode and buffer layers for perovskite solar cells to impart enhanced stability. Finally, we emphasize that, because instability may be triggered not only in any of the various layers of a device, but also at the interfaces between such layers, degradation studies...
must consider the device as a whole and the chemistry at the various interfaces, rather than relying solely on studies of an isolated perovskite film.

### 6.4 Experimental

MAI was synthesized by mixing aqueous methylamine (Sigma Aldrich) and aqueous HI (Sigma Aldrich) at 0°C with constant stirring. MAPbI$_3$ perovskite LEDs were fabricated using indium-tin-oxide (ITO) coated glass substrates with a sheet resistance of 15 Ω/sq. Substrates were cleaned sequentially with soapy water, deionized water, acetone, and isopropyl alcohol, and were then treated with O$_2$ plasma for 5 min prior to film deposition. 6 mg/ml of poly-TPD was dissolved in chlorobenzene and was spin coated on top of ITO substrates at 1500 rpm for 70 s followed by thermal annealing at 150°C for 20 min. Samples were then treated with O$_2$ plasma for 1 s to improve wetting. 500 mg/ml PbI$_2$ was dissolved in hot dimethylformamide (DMF) at 100°C and was then cooled to 70°C for spin coating at 6000 rpm. 50 mg/ml MAI dissolved in isopropyl alcohol (IPA) was then coated on top of PbI$_2$ films at the same spin speed, which was followed by thermal annealing first at 70°C for 10 min and then at 100°C for 70 min to ensure full conversion of PbI$_2$ and MAI to MAPbI$_3$. TPBi, LiF and Al layers were evaporated sequentially on top of the perovskite film, with thicknesses of 40 nm, 1.2 nm and 100 nm, respectively. The device area was 0.1 cm$^2$.

CsPbI$_3$ and CsPbBr$_3$ films were prepared using a one-step solvent-exchange method [33]. CsPbI$_3$ precursor solution was prepared by mixing CsI and PbI$_2$ in DMF with a concentration of 0.5 M and was spin coated at 5000 rpm. Toluene was dropped on the spinning substrate at 4 s. Then, the prepared CsPbI$_3$ films were annealed at 350°C for 1 min. CsPbBr$_3$ precursor solution was prepared by mixing CsBr and PbBr$_2$ in dimethyl sulfoxide (DMSO) with a concentration of 0.5 M and
was spin coated at 5000 rpm. Chloroform was dropped on the spinning substrate at 60 s. The prepared CsPbBr$_3$ films were then annealed at 100°C for 1 min.

Properties of perovskite LEDs were measured in a N$_2$-atmosphere glovebox using a custom motorized goniometer consisting of a Keithley 2400 sourcemeter unit, a calibrated Si photodiode (FDS-100-CAL, Thorlabs), a picoammeter (4140B, Agilent), and a calibrated fiber optic spectrophotometer (UVN-SR, StellarNet Inc.). XRD measurements were made using a Bruker D8 Discover X-ray diffractometer. Related XRD patterns were identified for Al (PDF: 03-065-2869), Pb (PDF: 03-065-2873), PbO$\cdot$xH$_2$O (PDF: 00-022-0665). SEM measurements were made using an FEI Quanta 200 FEG Environmental-SEM. In-situ SEM measurements were made in the environment mode with the chamber kept at −8°C and with 3 Torr water vapor pressure to generate approximately 100% relative humidity. EDS measurements were made using an Oxford energy and wave dispersed x-ray spectroscopy operated with the FEI Quanta 200 FEG ESEM. XPS measurements were made using a Thermo Scientific Kalpha XPS System. A vacuum transfer module was used to directly transfer samples from the N$_2$-filled glovebox to the XPS chamber to avoid surface contamination and oxidation.
Chapter 7

Outlook

The development of metal halide perovskite optoelectronics is still a relatively new research area, leaving numerous fundamental and technical questions open to be explored. This thesis has revealed some important design principles and insights on the optimization of perovskite LEDs. Although the implications and applications of perovskite LEDs are exciting, some challenges facing perovskite LEDs remain to be addressed before they can become a commercial reality. First, blue perovskite LEDs have lagged considerably behind the performance of red and green ones and thus a solution to these low quantum efficiencies must be found. Second, the best-performing perovskite compositions for LEDs contain lead and, as such, raise toxicity concerns. Therefore, the development of lead-free perovskites is important to increase the likelihood of commercial success. At this point, no electroluminescence has been achieved in lead-free perovskites except for tin-based infrared perovskite LEDs [86]. Nonetheless, replacing lead in perovskites represents a critical issue that deserves further research and development. Third, operational stability of perovskite LEDs remains a major challenge. Perovskites are considerably redox-active and moisture sensitive, resulting in rapid degradation under typical LED-driving conditions [72]. As is the case for commercialized organic LEDs, sufficient encapsulation will be needed
for perovskite LEDs to prevent extrinsic stability issues. In terms of intrinsic stability, operational lifetimes exceeding 46 hours have been demonstrated under relatively low current density \[21\], but perovskite LEDs degrade rapidly when a larger current is applied or after operation for an extended period. Better defect passivation, perovskite composition engineering and thermal management appear to be key to further improving device stability. Searching for new material systems that do not contain the reactive halide (especially iodide) species, while maintain desirable optoelectronic properties, is another direction that warrants attention.

Beyond LEDs, metal halide perovskites have drawn great attention and shown promising application for lasers. To date, many optically driven amplified spontaneous emission and lasing operation have been demonstrated from the near infrared (NIR) to the green in various configurations (e.g., distributed feedback, Fabry-Perot cavity, and photonic crystals) at low threshold \[87\]. More encouragingly, continuous-wave (CW) operation of lasing has been demonstrated \[56\], an important prerequisite toward practical laser applications. In addition, we have shown recently that perovskite LEDs can operate in pulsed mode under extremely high current density of up to \(600 \text{ A/cm}^2\) \[88\]. Therefore, perovskite semiconductors hold considerable promise for realizing an electrically driven laser device from a non-epitaxial and solution-processed semiconductor thin film, opening the door to a wide range of substrates formerly precluded by high processing temperatures. Once solution processed thin film laser diodes become a reality as a low-cost replacement for the existing epitaxial III–V compound semiconductor lasers, the laser landscape will inevitably change the way people conceive and use them in practice.
Appendix A

List of Publications and Conference Presentations

A.1 Journal Articles


### A.2 Conference Presentations


Bibliography


[29] Yanan Wang, Juan He, Hao Chen, Jiangshan Chen, Ruidong Zhu, Pin Ma, Andrew Towers, Yuan Lin, Andre J Gesquiere, Shin-Tson Wu, et al. Ultrastable,


[39] Nicholas Rolston, Adam D Printz, Jared M Tracy, Hasitha C Weerasinghe, Doojin Vak, Lew Jia Haur, Anish Priyadarshi, Nripan Mathews, Daniel J Slotcavage,


