Single-crystalline hybrid halide perovskites : heterostructure growth and electroluminescence characteristics

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**SINGLE-CRYSTALLINE HYBRID HALIDE PEROVSKITES:
HETEROSTRUCTURE GROWTH AND
ELECTROLUMINESCENCE CHARACTERISTICS**

HETTIARACHCHI HETTI ARACHCHILAGE CHATHURANGA

SCHOOL OF ELECTRICAL & ELECTRONIC ENGINEERING

2019

**SINGLE-CRYSTALLINE HYBRID HALIDE PEROVSKITES:
HETEROSTRUCTURE GROWTH AND
ELECTROLUMINESCENCE CHARACTERISTICS**

Hettiarachchi Hetti Arachchilage Chathuranga

School of Electrical & Electronic Engineering

A thesis submitted to the Nanyang Technological University
in partial fulfillment of the requirement for the degree of
Doctor of Philosophy

2019

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarized materials and has not been submitted for a higher degree to any other University or Institution.

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Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

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Asst. Prof. Cuong Dang

Authorship Attribution Statement

This thesis contains material from two papers published in the following peer-reviewed journals where I was the first author.

Chapter 4 is published as [1] Hettiarachchi, C., Birowosuto, M. D., Nguyen, T. H., Ahmad, R., Pita, K., Mathews, N., & Dang, C., “Solution grown double heterostructure on a large hybrid halide perovskite crystal”. *CrystEngComm*, 20(42), pp. 6653–6661, 2018. <https://doi.org/10.1039/C8CE01298A>

The contributions of the co-authors are as follows:

- Asst. Prof. Cuong Dang provided the project direction.
- I prepared the manuscript drafts. The manuscript was edited by Dr. Danang Birowosuto and Asst. Prof. Cuong Dang.
- I co-designed the study with Asst. Prof. Cuong Dang and Dr. Tien-Hoa Nguyen, performed all the laboratory work at the School of Electrical and Electronic and Engineering, ERI@N and FACTS. I and Dr. Danang Birowosuto analyzed the data first before every weekly meeting for discussion with all other authors in Asst. Prof. Dang’s group.
- All sample preparation was conducted by me, assisted by Dr. Tien-Hoa Nguyen.
- Riyas Ahmad assisted in the collection of powder X-ray diffraction (XRD) data.
- Samples for Electron Back Scatter Diffraction (EBSD) experiments were prepared by me and the data collection was done at Facility for Analysis Characterization Testing & Simulation, assisted by Dr. Jason Scott. The data was analyzed by me.
- Assoc. Prof. Nripan Mathews and Assoc. Prof. Pita revised the manuscript and provided critical reviews.
- I and Dr. Danang Birowosuto prepared the answers for referees’ comments, then thoroughly discussed with Asst. Prof. Dang.

Chapter 5 is published as [2] Hettiarachchi, C., Xie, A., Nguyen, T. H., Junhong, Y., Maddalena, F., Dinh, Q., Birowosuto, M. D., & Dang, C., “Current Oscillations and Intermittent Emission Near an Electrode Interface in a Hybrid Organic–Inorganic Perovskite Single Crystal”. ACS Appl. Mater. Interfaces, 11(45), pp. 42838-42845, 2019. <https://doi.org/10.1021/acsami.9b15791>

The contributions of the co-authors are as follows:

- Asst. Prof. Cuong Dang proposed the idea for the device structure.
- I and Dr. Danang Birowosuto drafted the manuscript. The manuscript was edited and revised by Dr. Francesco Maddalena and Asst. Prof. Cuong Dang.
- I fabricated the devices and collected all the data.
- Aozhen Xie and Dr. Danang Birowosuto assisted in data collection.
- Aozhen Xie, Yu Junhong, Dr. Danang Birowosuto, Dr Tien-Hoa Nguyen and Asst. Prof. Cuong Dang participated in analyzing the results.
- I performed the Monte-Carlo simulation and Dr. Francesco Maddalena assisted the Monte-Carlo simulation and modeling.
- Dr. Quyen Dinh revised the manuscript.

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Summary

Mobile ions play a crucial role in hybrid halide perovskites, especially as single crystals, from heterostructure growth to optoelectronic properties. Heterostructure growth in the solvothermal route was known to be severely affected by the halide ion interdiffusion process. Optimizing the solution concentration and growth temperature systematically is recognized as the key to limit ion interdiffusion. We demonstrate a controlled perovskite heterostructure for the first time, with detailed characterization. As there is widespread use of semiconductor heterostructure in modern optoelectronic devices, our new structures promise many potential applications. In addition to the diffusion process under neutral conditions, some ions also can drift within the crystal under an electric field, which is important to investigate for optoelectronic applications. However, the exact mechanism still remains elusive. Unlike electrons and holes, the ions cannot be injected or extracted from electrodes and therefore accumulate at the interface. Putting this phenomenon to use, a temporary junction can be formed. However, it is critical to isolate this effect from external factors such as grain boundary mechanisms and surface reactions with moisture and air. A fully encapsulated metal-semiconductor-metal single crystal device is introduced, which can be ‘configured’ with an electric field for electroluminescence. Our newly developed technique enables an encapsulated pristine device throughout the full process from fabrication to characterization. The device exhibits the native signatures of ionic drift within a perovskite single crystal, leading to a fascinating electroluminescence blinking behavior and a slow, quasi-periodic current oscillation, even at constant bias conditions. The thesis’ results show both drift and diffusion processes of ionic species within perovskite single crystals. Our ionic diffusion control approach enables single-crystal perovskite hetero structures, while our investigation of ionic drift provides

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Chapter 1 Introduction

1.1 Motivation

The invention of solid-state Light Emitting Diodes (LEDs) is one of the advanced achievements of human civilization during past few decades, enhancing the life quality of billions of people by providing safer and brighter artificial illumination. Alternative lighting which can complement to the sunlight has been a quest for many scientists for centuries, and they have been successful in many stages by providing plausible solutions according to the advancement of scientific knowledge of their time[1]. The transformation of single use burner flash lamps to long lasting incandescent bulbs, and then the fluorescent lighting and the solid-state lighting available today, represents the shift of the viewpoint of scientific knowledge on how to convert electrical energy to light in a safer and more efficient way. Energy efficiency, device lifetime, safety and the cost have been the driving factors of this evolution.

The International Energy Agency (IEA) expect nearly 80% of the residential lighting sales will be LEDs by year 2030 [2]. Average efficiency of commercial LEDs has almost reached 100 lumens per Watt (lm/W) by 2018, and could surpass all other commercial lighting technologies available today, proving its market potential. The key long-term technology innovation gaps declared by IEA to meet the long-term clean energy transition goals states the research and development focus areas for reduced costs, improve lifespan and material resistance. “Solution processed OLEDs for lighting (EU SOLEDLIGHT)” project and “exploring quantum materials - new ways to realize innovative optoelectronic components” project to study “electroluminescent quantum materials-based light-emitting diode (ELQ-LED)” are

some of the major initiatives to fill these gaps[3].

Today, few steps beyond, scientists also seek the perfection and control over the emitted light with engineered spectral features. This can enable the bottom-up approach of how to generate light with very high efficiencies, enabling novel possibilities of practical applications beyond current knowledge. Thus, the search for low cost, efficient and most importantly, versatile light emission, is still an ongoing frontier of research.

Fundamental understanding of semiconductor materials and the technologies associated with engineering their properties are at the heart of the entire solid-state lighting industry. Numerous materials have been studied over many years to find the best alternatives for highly efficient, cost-effective, robust and versatile light emitters. However, while tackling on intricate tradeoffs in each material system, it is important to deepen the understanding of the fundamental physics and explore peculiarities in the material systems in view of the greater domains of applications. For example, the understanding of organic light emitting devices has evolved dramatically in recent years, and quantum dot LEDs also reaching the commercialization phase[4]. Bio photonics, genetics, development of various types of sensors are some of the thriving applications, which have enormously benefited from the understanding of these material systems. Therefore, while studying these various novel materials in seek of better light emitting devices, keeping an open eye for novel physical phenomena could be rewarding in many unthought-of applications as well.

Nonetheless, the major demands in the field of light emitting devices and display technology are color purity, wavelength tunability and efficiency. Obtaining the emission of pure color constituents and combining those together to meet the various

requirements is the bottom-up approach of generating efficient light emission. Considering the versatility, devices that could emit any wavelength within the visible spectrum without dramatically changing the underlying material systems and emission mechanism is a desired feature of future light sources. Low dimensional (2D, 1D or 0D) solid state quantum structures have been the trend of research on addressing these demands in recent years. However, the recently discovered properties of a material group known as halide perovskites has caught the scientists' attention almost by surprise. Proving its identity initially in photovoltaics research, "hybrid halide perovskites" are believed to have a high potential to perform well in light emitting devices as well.

A widely known group of materials named "Perovskites" is identified by its unique identity of crystalline structure, with constituents of ABX_3 . Organic-inorganic hybrid halide perovskite materials constitute a versatile class of materials which has been known to scientists for decades: however, the optoelectronic properties of these material groups had not been studied very well until recently[5, 6]. Typically, in organic-inorganic hybrid lead tri-halide perovskites, the constituents are a single valent organic cation (for example $CH_3NH_3^+$), Lead (II) ion and three halide anions. The most popular perovskite material today is $CH_3NH_3PbI_3$ for its application in solar cells. With the newly-discovered knowledge about this material, it has been widely adopted in photovoltaic research, showing a rapid development in the efficiency of solar energy conversion, surpassing the commercial polycrystalline silicon solar cells and reaching the theoretical limits[7, 8]. Further, the possibility of adjusting the bandgap of the material just by changing the halide ion composition has led to studying the possibility of using this material in "any color" light absorbing tandem solar cells[9], photodetectors[10] or any color emission with LEDs[11]. The pure color

bright photoluminescence observed in the material is a major reassurance for pursuing perovskite light emitting devices (PeLEDs) and many researchers have been successful in demonstrating such devices with thin film architectures of 0D, and 2D perovskite materials. However, these devices still need many improvements to compete with commercial LEDs in terms of efficiency and stability[3, 12-15].

When considering the cutting-edge LED device architectures that are designed for efficiency and performance such as GaN/InGaN blue LEDs, an unavoidable fact is that they are based on a single crystalline structure with a precisely engineered stack of ultra-thin layers with specific alterations to the composition[16, 17]. However, obtaining such structure could only be done using extremely elegant technologies such as plasma enhanced chemical vapor deposition (PECVD), molecular beam epitaxy (MBE) or atomic layer deposition (ALD). The equipment/infrastructure costs for these technologies are in multi-millions of dollars, and maintenance is also costly. Growing even pure single crystals of traditional III-V semiconductor materials is also a challenging task to date, even after decades of research. With such a background, these expensive technologies and infrastructure limit the possibility of research and development with novel materials. However, with the hybrid halide perovskite materials, the possibility of growing single crystals using a solvothermal route has been demonstrated recently[18-20]. Unlike traditional III-V semiconductors, high quality hybrid perovskites can be grown to large single crystals within few hours with nothing but a precursor solution heated on a hotplate.

This seemingly absurd opportunity however comes with several glitches. The material is as versatile as it gets; however, the stability is a major issue. The humidity and photo-bleaching are known to affect the quality of the crystals and degrade their well-

desired properties over a short time period. The presence of highly toxic lead in the perovskite material also poses a major concern regarding commercializing these materials [21-23]. Hence, these concerns have encouraged the researchers to explore the physics and mechanisms of perovskites further, look for solutions to enhance the advantages and mitigate the disadvantages, or even search for lead-free perovskite materials with comparable performance. Such research is essential for innovations which would produce highly efficient PeLEDs, and perhaps many other novel devices in the future.

This research is an attempt to study an aspect of this wonder material, especially with regard to compatibility for hetero-structure formation and the role of mobile ions in perovskite crystals. If it is possible to grow single crystalline heterostructures with the solvothermal method and make devices from them, it would revolutionize the possibilities of research and development for perovskite devices in the future; providing a low cost, infrastructure independent platform for many academic research and industrial developments.

1.2 Objectives

The following points are the primary objectives of this project.

- Developing a liquid phase epitaxy technique to fabricate thin single crystalline layers of perovskites with different halide compositions on a perovskite substrate, i.e. the heterostructure.
- Establishing well-controlled growth conditions and determining growth rates to obtain high quality thin single crystalline layers
- Optical, structural, and electronic characterizations of heterojunctions and double heterojunctions of single crystalline perovskites
- Design, fabrication and characterization of a large single-crystalline perovskite

light-emitting device with pristine material quality.

Ensuring the interface quality between layers of two materials is the crucial factor which makes the single crystalline structures more efficient than the other polycrystalline thin film alternatives in opto-electronic devices. Hence, the development and characterizations of heterojunctions of single crystalline perovskites precede the development of single/multiple quantum well structures; which is the vision behind this research.

As discussed in the literature review in next chapter, perovskite single-crystal growth has been developed within last few years and there have been only few attempts to prepare single-crystal heterostructures. However, these have certain drawbacks such as uncontrolled and dominant diffusion mechanism over epitaxial growth. Hence, our study on single-crystal epitaxial heterostructure growth is novel to the best of our knowledge. Enabling successful perovskite epitaxial growth with such a simple technique is expected to open-up many more opportunities to expand the understanding of the material and the building of efficient perovskite devices, as well as to experiment with novel heterostructure devices. Our large single-crystalline perovskite light-emitting device reveals fundamental properties of materials and devices due to pristine material quality thanks to our developed fabrication technique and a simple metal-semiconductor-metal device.

1.3 Approach

Growing perovskite single crystals using supersaturation-based solvothermal crystallization method was invented a few years back and well established today. In this research, we propose to extend this technique to grow epitaxial thin films on

perovskite substrates. In the early stages of semiconductor research, many researchers attempted to use a technique known as liquid phase epitaxy (LPE) to grow epitaxial layers of inorganic semiconductors at high temperatures. These techniques have been overruled by the gas or vapor-based techniques, especially for ultra-thin film growth. However, the LPE technique is still being investigated for several specialized applications [24, 25]. Several variants, like sliding boat technique and the cylindrical rotating boat technique exist; however, the conditions with respect to perovskites are completely different. Perovskites require much lower temperatures; $<120^{\circ}\text{C}$ compared to typical inorganic materials, and the supersaturation shows a retrograde relationship with temperature [26, 27]. Under these conditions, LPE could be much easier for perovskites than the inorganic semiconductors; therefore, we try to adapt a simpler version of LPE to fabricate sample structures.

Fabricating the semiconductor heterojunction itself is sufficient to characterize the physical parameters such as layer thickness, layer and interface quality and many optical properties of the heterostructure. For electrical characterizations and functional devices, a proper device structure is necessary. Without proper hetero-valent doping, another research concern, which is not yet fully developed, is that perovskite is almost an intrinsic semiconductor with high resistivity in the dark. However, it shows good conductivity under illumination, which enables the material to be easily used efficiently as a photodetector. Hence, we intend to characterize such devices alongside designing and optimizing perovskite heterostructure growth techniques. Demonstration of single crystal light emitting device with integrated heterojunction is the ultimate goal to assess the achievement of stated objectives.

1.4 Major contribution of the thesis

While the hybrid halide perovskite materials has been with researchers because of its ease of synthesis and low-cost processability, instabilities and less-understood processes, such as halide ion diffusion ‘still make many researchers skeptical about the full potential of this material. Wide theoretical and experimental efforts are necessary to fully understand this material and to determine whether it can be a commercially viable opto-electronic material. We believe that understanding the fundamental mechanisms of the hybrid halide perovskites should begin with pure single-crystalline devices which are the most pristine form of the material; this avoids other complex side-effects such as the surface, grain boundary and the external environment. However, most of the effort focused on the hybrid halide perovskites around the world is focused on polycrystalline thin films, following the common and conventional thin film device fabrication techniques. With the experiments in this thesis, we propose several techniques that can potentially inspire more researchers to study single-crystalline devices.

The first major contribution of this thesis is the finding that it is possible to grow epitaxial-like single crystal heterostructures by properly controlling several parameters related to the growth conditions, without succumbing to the halide-ion diffusion process. This systematic study was conducted in liquid phase epitaxy technique; however, we believe it could be an example to other techniques in the future for growing practical thin single crystalline structures with perovskite materials.

The second, and most important contribution, is the novel simple device structure and fabrication technique introduced in this thesis. The hybrid halide perovskite single-crystal growth technique is relatively low temperature process therefore unlocks the

possibility of growing semiconductor crystals after establishing the metal electrodes in place, even in a 3D space. With this technique, the metal semiconductor junction remains pristine, undamaged and unexposed to the external environment. Therefore, it can provide a better metal semiconductor metal junction that can be used to study the material properties more confidently.

Thirdly, we observe an interesting pattern in current-time and electroluminescence at a fixed voltage from the newly-introduced device. Even though previous experiments with other types of devices have shown similar behavior, our observations show a significant regularity rather than entirely random fluctuations, which we believe to be due to isolating the metal-semiconductor-metal channel from external factors. We believe this is a good indication for the necessity and importance of further investigation into pristine condition single perovskite crystals where the ionic processes could be as significant as the electronic processes. Therefore, this research will be a significant contribution towards understanding the material better and enabling more possibilities of applications in the future, and beyond the conventional utilities of a typical semiconductor material.

1.5 Organization of the thesis

The next chapters are arranged as follows:

In the second chapter, various established methods of fabricating light-emitting devices are discussed, along with the recent development of the perovskite light-emitting devices. The technical issues and strengths of the devices and their development so far are also explained. Also, the importance of studying perovskite single-crystalline device and crystal growth techniques are briefly discussed along

with the identified limitations presented in recent state-of-the-art publications. Literature on the growth of perovskite-single crystals and heterostructures is elaborated on. Recently-developed perovskite hetero-structures are still at a primitive level due to several drawbacks, so the techniques used, and their shortcomings are discussed. Some research groups have attempted to fabricate perovskite heterostructures using different techniques and their findings are important to identify better strategies. Also, the opto-electronic properties of perovskites are discussed in detail.

Techniques and tools used in fabrication and characterization are described in the third chapter. It is important to identify the available techniques and resources which are available. Newly proposed technique for extending the solvothermal growth process to grow single crystal hetero-structures is also introduced. These techniques are categorized as synthesis and crystal growth, structural characterization, optical characterization and electrical characterization techniques.

Chapter 4 is dedicated to establishing the growth conditions, growth rate. Selection of suitable materials for heterostructure growth, photoluminescence characteristics and structural characteristics are explained. Characterization and growth parameters for hetero-structure growth are discussed in detail. Results and challenges encountered during fabrication, especially the halide ion-diffusion and characterization of sample heterostructures is presented.

Chapter 5 considers the alternative route of stoichiometric polarization of a single crystal to achieve a light emitting device, which can be considered as a dynamic heterostructure. Here, we focus on obtaining a well-encapsulated narrow metal-perovskite-metal channel in order to study the ionic drift characteristic of a simple

perovskite channel isolated from the surface and environmental factors. The characterization is specially based on current-time characteristics. Further, this chapter elaborates on single-crystal electroluminescence, which is one of the major objectives of the project.

In Chapter 6, a discussion and self-assessment based on the results achieved during the project is given to conclude the report. We compare the prospects of heterostructure-based approach and stoichiometric polarization-based approach for LEDs in the future. We propose some future work to extend the results of our study, which can shed light on inner mechanisms and effects of ion drift and diffusion processes in perovskites, as well as how and where perovskites can be effectively used apart from light emitting devices. Finally, list of publications is provided. References lists are annexed at the end of each chapter.

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Chapter 2 Literature survey

2.1 Technologies and materials for light emitting devices

The first solid-state light emission was observed in 1907 from a crystal of Silicon Carbide. However, it took many decades of trial and error, efforts on various device concepts and materials to understand and develop a commercially relevant solid-state light emitting device [1]. First to publish a working theory of the phenomenon was Oleg Vladimirovich Losev in 1927, with his paper “Luminous carborundum detector and detection effect and oscillations with crystals” [2]. During the course of more than a century of development, the characteristics necessary for good material candidates for light emitting devices have been identified quite well. Direct bandgap semiconductor crystals were the priority candidates for the active material. The electron and hole carriers are injected to a junction to enforce recombination within a narrow region (quantum wells, quantum dots), yielding bright concentrated emission. Devices were continuously improved to enhance three stages of the processes; carrier injection efficiency, recombination efficiency and light extraction efficiency.

2.1.1 Inorganic semiconductor LEDs

Inorganic semiconductor light emitting devices were in the forefront of solid-state lighting technologies, in terms of efficiency and stability. These are mainly based on single crystalline devices, with carefully fine-tuned multiple quantum wells and heterostructures to enhance the injection efficiency and recombination efficiency [2]. Mass fabrication of the devices today has brought down the price of LEDs significantly; however, massive infrastructure cost is necessary to setup a fabrication facility with delicate epitaxial layer growth machinery [3]. III-V semiconductor

materials like GaAs, InAs, AlAs, InSb, GaP and InGaN are some of the principal materials which are used in LED devices. Many materials are necessary to obtain the different colors, which is directly related to the bandgap of the semiconductor. However, the bandgaps of these materials are limited to certain bands and there are still some forbidden bands for current semiconductor light emitting devices such as the green/yellow region. It is necessary to find other approaches to produce a light emitting device with a different specific bandgap. Or even better, a single material family to cover the full visible band. Alloying materials is commonly employed technique; however, it still cannot cover the full visible wavelength. For the three primary colors of red, green and blue, current technology employs three different materials with distinctly different approaches.

Many bottlenecks in inorganic light emitting devices were related to growing high quality crystalline layers. Growing and processing high quality single crystals for some of these materials are still a challenge today. One important benchmark is the development of the blue LED which took a few decades of trial-and-error improvements to establish single crystalline layer growth techniques [4]. This work ultimately led to the 2014 Nobel prize offered to Shuji Nakamura, Hiroshi Amano and Isamu Akasaki, due to their difficult endeavor and enormous advantages to our lives. Still, there are multiple drawbacks with current LED technology today. For example, sapphire substrates are still necessary to grow III-Nitride LED structures. This not only poses multiple technical challenges related to heat dissipation and light extraction efficiency, but also adds significant cost into the device. The most prioritized problem with these material systems is known as “Green Gap”, where the efficiency of the green light emitting devices is not as efficient as the other colors [5]. The problem is due to various reasons, such as the complication in materials’ exciton recombination

process, and especially the difficulties in monocrystalline layer growth of InGaN with a high concentration of In.

2.1.2 Colloidal quantum dots for LEDs

Monocrystalline light emitting devices confine the carriers within a thin layer, which is typically considered as a quantum well [6]. The carriers are injected into this layer and confined within, until they eventually recombine and generate light. If the layer is thin enough, the structure is named a quantum well, which enhances the recombination efficiency due to physical confinement of carriers into a smaller volume. By extending the quantum confinement concept into three dimensions, better confinement is achieved from quantum dots, where the carriers are forced to be in a very small volume and their wave functions are largely overlapped [7].

Colloidal quantum dots have been shown to enhance the efficiency accordingly and commercialized as down-conversion materials for high quality liquid crystal display (LCD) TVs. Together with the strong quantum confinement effect, colloidal quantum dots can cover the entire visible spectrum by simply controlling their size. They are also demonstrated in some light emitting devices at multiple research labs around the globe[8]. However, major challenges in quantum dots LED are related to the carrier injection mechanism which largely relies on organic compound. Stability, reliability and efficiency typically do not coexist in a quantum dot LED. In addition, quantum dots can show blinking if the confinement is not perfect [9]. More effort is needed to bring the quantum dot LED technology from the research laboratory to a commercial product.

2.1.3 Organic LEDs

Organic light emitting devices (OLED) are widely used in mobile device display

screens today, as well as in some indoor lighting applications. They use organic molecules with much simpler architecture than other technologies: however, the manufacturing costs are significantly higher, especially for large size displays. Also, the device lifetime can be short as the organic molecules tend to degrade quickly. The devices must be well encapsulated to avoid humidity damage since the active molecules used in these organic light emitters are sensitive to water. Even though the devices could be highly efficient with novel technologies, the quick degradation is the major issue for long term usage. Blue color OLEDs are the fastest to degrade due to non-radiative recombination mechanisms upon excitation, which dissociate the chemical bonds in the molecules [8, 10]. Also the carrier mobility of the organic semiconductor molecules is significantly lower than the inorganic counterparts, which ultimately limit the power output of the devices. Because of that, even though the materials are suitable for LEDs, they are rarely used for laser devices.

2.1.4 Perovskite LEDs

In recent years, perovskite materials have been developed for various aspects for light emission [11]. Spin-casting perovskite thin films have shown efficient photoluminescence and some electroluminescence too, with good color purity as well as color tunability by adjusting halide composition. However, the stability and repeatability of these light emitting devices is still a problem due to the complexity in behavior of this material such as; material decomposition, oxygen and moisture sensitivity, thin film cracks etc. Perovskite materials also can be used in form of nanocrystals, in expectations of better emission enhancement by quantum confinement [12]. While the perovskite quantum dots can increase the radiative recombination efficiency significantly, the lifetime of the material is significantly reduced due to high surface to volume ratio. At the same time, many low-dimensional perovskite materials

have been proposed, which can act as quantum well structures in its natural crystalline forms. This is done by carefully selecting a longer organic molecule which cannot fit in the perovskite lead halide cage, therefore it will form a layered structure automatically when the crystal is grown [10, 13, 14]. However, processes for growing these 2D crystals are not well developed yet. The emissions from the 2D materials are usually wide spectra, making white light emission. For growth techniques, material stability, color tunability and pure color emission, the bulk hybrid halide perovskites are still significantly better than the 2D materials available so far [15]. Also, a major challenge in further development of these low dimensional systems is the lack of understanding of fundamental working mechanisms of the material [8]. Therefore, studying the purest and simplest form of material which is the bulk single crystal to understand its working mechanisms is beneficial in the long term for the entire perovskite research knowledge base.

Perovskite single crystals have high carrier mobilities where the electrons and holes are free to move longer distances without recombining [8, 16]. This is desirable for solar cells where the carriers are extracted from the light absorption layer; but for light-emitting devices, high carrier mobilities in the active region reduce the radiative recombination efficiency, which is an adverse effect. So, single crystalline material must artificially trap the injected electrons and holes into a narrow area where they can recombine efficiently. Polycrystalline perovskite light emitting devices and Perovskite quantum dot light emitting devices could be the most popular approach, however, the grain boundary or surface effects [17] in these types of devices limits the stability and quantum efficiency of the material due to non-radiative recombination [18]. There were the similar problems which were common in classic inorganic semiconductors. Therefore, it is expected that an extremely thin layer of single crystalline perovskite

material will perform well; similar to inorganic semiconductor LED devices based on quantum well structures. The major challenge in using the hybrid halide perovskite in light-emitting devices is the difficulty in producing a thin film of single crystalline perovskite materials and the difficulties in maintaining the stability of the material. Therefore, the attempts to grow single crystalline thin layers on perovskite substrate and also some perovskite single crystal light emitting devices is discussed next.

2.2 Perovskite crystal structure and properties

Now, let us look into the crystal structure of the perovskite materials and then consider their basic optoelectronic properties. “perovskite” is a group of materials which has been named after Lev Perovski. First perovskite mineral was discovered in Ural Mountains of Russia in 1839 and since then, huge number of perovskite compounds has been discovered in nature, and also some novel materials have been artificially synthesized. The classification of a “perovskite” is primarily recognized by their basic crystallographic structure. Three types of lattice sites ABX_3 can be filled-up with various combinations of occupants to generate vast variety of perovskite compounds. Most of the natural perovskites are with an oxygen anion. However, it is found that a perovskite material with halide anions can be artificially synthesized easily under laboratory conditions where it needs to be kept away from moisture. Furthermore, the cation could be an organic cation as well, which enables the formation of an “organic-inorganic hybrid halide perovskite” material. In fact, vastly different combinations of alternatives could be selected to construct an energetically stable perovskite structure, which is roughly assessed by the Goldschmidt tolerance factor. This formula is based on ionic radii, and detailed information can be readily found in the literature, for example in [19].

Figure 2-1 Crystallographic structure of $\text{CH}_3\text{NH}_3\text{PbX}_3$ ($\text{X} = \text{I}, \text{Br}$ or Cl)

Organic-inorganic hybrid lead halide perovskites have a cubic structured Pm-3m space group at room temperature, where the organic part is methylammonium (CH_3NH_3^+), and the halide part is could be iodide (I^-), bromide (Br^-) or chloride (Cl^-) or a mixture of these halide ions. The crystal structure can be viewed as a methylammonium ion confined in a cubic cage made with Pb^{2+} and X^- . These Pb^{2+} and X^- ions are organized to eight octahedrons cubically connected corner to corner, leaving a space in the center of the cubic cage. Changing the halide directly influence the properties of the material [7]. For example, the lattice spacing is directly influenced by the type of halide ion, which determines the bond lengths between Pb^{2+} and X^- , and mixing halide ions could lead to an averaged lattice constant according to the proportional halide composition.

Figure 2-2 The single crystal XRD cell dimensions for $\text{CH}_3\text{NH}_3\text{Pb}(\text{Br}_{1-x}\text{Cl}_x)_3$ ($x = 0, 0.15, 0.25$) as a function of chloride inclusion[12]. Reproduced with the permission from T. Zhang *et al.*, "A facile solvothermal growth of single crystal mixed halide perovskite $\text{CH}_3\text{NH}_3\text{Pb}(\text{Br}_{1-x}\text{Cl}_x)_3$," *Chem. Commun.*, vol. 51, pp. 7820-7823, 2015. ©The Royal Society of Chemistry.

The corner-to-corner connection between lead halide octahedrons has a major implication on the stability of the material. It could either stay in a straight line with the neighboring lead ions, or wiggle in/out due to the attractive or repulsive forces from the caged cation. Due to the thermal vibrations, numerous phonon modes can exist in the crystal and the actual space group of the material could fluctuate between few variations. Such variations could be prominently expressed with temperature dependent studies; however, they could also occur even within the localized regions (domains) due to various conditions. Figure 2-1 shows the lattice structure of

perovskites and the Figure 2-2 demonstrates how mixing the Br^- and Cl^- ions affects the cell dimension, i.e. by changing the lattice constants of the crystal. Iodide ions could provide even larger lattice constants, i.e. even larger cell dimensions; it will possibly skew further to form a tetragonal structure at room temperature instead of a cubic structure.

2.2.1 Dynamic disorders

Even though the crystal structure has been shown for perovskite with advanced technology such as x-ray and neutron diffraction patterns [12, 16], the crystal structure is not quite stable at the microscopic level. The organic ion could orient at different angles, as well as the octahedral lead halide cage also is prone to skew locally [20] to form twin domains with slightly different crystallographic space groups. The chemical segregation between such groups has also been observed [12]. At the temperatures far above the absolute zero, kinetic energy in the crystal lattice could be sufficient to thermally activate such slight crystallographic restructuring. The mechanisms or impact of such processes are still not completely studied, but it has been suggested that this type of twin domains are some signs of ‘ferro-elasticity’. These dynamic disorders are believed to be significant contributors to the material secrets of the excellent semiconductor performance and instabilities of perovskites.

The implications of the dynamic crystal disorders to the optoelectronic properties are highly significant, despite the fact that analytical tools to study such dynamics are still lacking. Some work has been suggested using the concept of strong anharmonicity, which is an approach to systematically study the dynamic disorders [21]. Figure 2-3 shows the concept of anharmonicity, where existence of the two stable potentials near the equilibrium point can lead to two different lattice structures which have local

minimum energy. This concept can be found in the discussion on band structure later in this chapter. The typical parameters for a semiconductor in consideration for light emitting device are explained.

Figure 2-3 Sources of dynamic disorder in halide perovskites. a, Various shapes of energy potentials, from harmonic to strongly anharmonic. The violet sphere represents an atom moving in the potential around its equilibrium position. Scattering events that lead a charge (electron or hole, black sphere) to change its wavevector from k_i to k_f owing to its interaction with the anharmonic motion of a halide atom (in the example shown, the violet sphere represents an iodine atom; the dashed line is a guide to the eye to locate the equilibrium position on the axis connecting the two lead atoms [22]. Adapted with permission from L. Martiradonna, "Riddles in perovskite research," *Nature Materials*, vol. 17, pp. 377-377, 2018. © 2018 Macmillan Publishers Limited.

Most interestingly, these dynamic behaviors could exist independent of any defects which could originate in the crystal due to fast growth rate. Also, since the crystal is grown absorbing low thermal energy, the bonds could be easily dissociated as well. Free ion population in a dynamic equilibrium which can contribute to charge carrying

alongside with the electrons and holes can be anticipated, which could be an underlying cause of the peculiar carrier dynamics.

2.2.2 Perovskite electronic band structure and band gap

Based on the perovskite crystal structure, the E-k diagram of the material can be calculated. The band structure directly determines the major opto-electronic properties of the material. However, the accurate mathematical representation and solving the band structure is a computationally challenging problem. It has certain shortfalls, even in the well-studied semiconductors like silicon, and fails to determine even the exact bandgap. Yet, several widely used techniques can be used under significant assumptions to obtain some insights into the material, especially the direct-indirect behavior of the bandgap and effective mass of electrons and holes. With the electronic band structure, further information such as the density of states and side bands can be identified. Figure 2-4 is one of the calculated E-k diagrams for MAPbCl₃, MAPbBr₃ and MAPbI₃. With the change of lattice constant, the semiconductor bandgap also changes correspondingly. This phenomenon is related to bond strengths and has been observed in many semiconductor materials including perovskites. Bandgap variation with lattice constant provides essential information for designing possible hetero-epitaxial structures [23]. It can be used to determine the essential material composition to obtain the desired bandgap and to determine the lattice mismatch at hetero-epitaxial growth [10]. The widening of the bandgap with change of the halide ion from I⁻ to Br⁻ and Cl⁻ can be recognized. The rate of the gradient change, d^2E/dk^2 , at the conduction band minimum and valance band maximum is inversely related to the effective mass of electrons and holes respectively, which are mostly similar. However, it could be even complex in the study of perovskites due to several reasons, such as dynamic disorders and spin orbit coupling, which can split the narrowest

bandgap along the k axis [24]. Therefore the mobility could have a significant variance between different fabrication routes and the quality of the crystalline material [25].

Figure 2-4 Band structure calculated for MAPbI₃ (a), MAPbBr₃ (b) and MAPbCl₃ (c) at the SOC-GW level [26]. Reprinted with permission from E. Mosconi *et al.*, “Electronic and optical properties of MAPbX₃ perovskites (X = I, Br, Cl): A unified DFT and GW theoretical analysis” *Physical Chemistry Chemical Physics*, vol. 18, pp. 27158-27164, 2016. © Royal Society of Chemistry.

Apart from the theoretical calculation, hybrid halide perovskite bandgap can be determined experimentally using absorption spectrum, and the bandgap is directly related to the halide composition. When the halide ions change from Cl⁻ to Br⁻ and I⁻, the ionic radii increase, the band gap of the perovskites move from 3.06 eV (405 nm) to 2.31 eV (537 nm) and 1.57 eV (790 nm), respectively [27]. Similar to many other semiconductor material systems, perovskites also comply to an empirical relationship between the lattice constant and the bandgap. Electronic and ionic conductivity

In a typical semiconductor, only electrons and holes are the charge carriers, contributing to the charge transfer or the electrical current. However, it is known that perovskite crystals can be considered as solid electrolyte material [28] as well, apart from being a semiconductor material. So, when considering the electrical properties of perovskites, the ionic carriers also need to be taken into account. Therefore, at least four types of charge carriers can be defined, namely electrons, holes, ions and ion

vacancies. Different types of ions may also be present. Conductivity of the material due to each type of carrier is proportional to the product of mobility and carrier concentration. While the organic semiconductors have low electron and hole mobilities compared to inorganic counterparts, perovskites are known to have significantly higher and more balanced electron and hole mobilities [29, 30]. When the mobility is higher, the carriers can travel faster under electric field. We need doped perovskites with higher carrier concentrations as a building block for semiconductor devices. For example, the n-type and p-type perovskite layers will be excellent for carrier extraction in photovoltaic applications [31, 32] or carrier injection in light emitting devices [22]. Doping perovskites has been demonstrated with preliminary results and still requires lots of efforts.

Because perovskites have more than two conventional carrier types, the interpretation of the free carrier concentrations and mobilities is more complicated. Typically, slow transients in current are considered to be from ionic carriers. To distinguish between the ionic and electronic transport components, impedance spectroscopy experiments have been conducted [25, 30, 33, 34]. Various models have been proposed, and some studies proposed the ionic conductance could be even higher than the electronic conductance in some experiments. So far, no convincing consensus has been reached to completely and consistently explain the behavior of wide variations of experimental results from different research groups. Many measurements of carrier mobilities are summarized in the work by Laura Herz [35], considering only the electrons, holes or a single value by assuming the same mobilities for both types of carriers. A field effect transistor can be used to measure the mobility [36]. However, most of these measurements are heavily subject to the fabrication conditions and many other parameters such as measurement environment, which could vary drastically among

samples and laboratories around the world.

2.2.3 Diffusion length and carrier lifetimes

Hybrid halide perovskites have been thriving in the solar cell applications due to two significant parameters; excited electrons and holes could (1) live much longer than in the organic semiconductor materials, and (2) diffuse longer distances allowing them to be extracted before recombination. The diffusion length can be correlated to the product of mobility and lifetime. Lifetime is usually the characteristic of the recombination mechanism available in the semiconductor material. Monomolecular, bimolecular and trimolecular recombination routes are usually considered, while the useful recombination in light emitting devices is only the radiative bimolecular recombination. In a perovskite material with large carrier diffusion lengths, the excitons are typically dissociated under an electric field, reducing the bimolecular radiative recombination. So without a suitable carrier confinement technique, it is believed they are less efficient luminescence material. Yet, the perovskites are known to have a good quantum yield. The reason behind the high efficiency has not been verified yet, however, it is considered due to active participation of ionic carriers as well [37]. The electronic recombination properties are modulated by ionic mobilities, therefore effectively making the device a ‘light-emitting electrochemical cell’ (LEC). Considering the perovskite electroluminescence device as an electrochemical cell could explain the emission localizations as well.

2.2.4 Exciton binding energy

For light emitting applications, electrons and holes should radiatively recombine efficiently as a photon is generated for each radiative recombination of electron hole pair. However, there are multiple non-radiative processes which are possible for each

electron hole pair to recombine. For the radiative recombination process to dominate among other possible processes, electrons and holes have to come into the vicinity. Once they attract each other they form an “exciton” which has a correlated behavior; they then annihilate the exciton to emit a photon. For hybrid perovskites which have relatively large diffusion lengths, the exciton binding energy is relatively low. At room temperature, the kinetic (thermal) energy could dissociate excitons easily. For MAPbBr₃, ~40 meV exciton binding energy has been reported, while for MAPbI₃, it is as low as ~13 meV [38]. For MAPbCl₃, the exciton binding energy of 41 meV has been reported [35]. In another report [39], MAPbCl₃ has 51 meV binding energy while that of MAPbBr₃ is 21 meV. Given the thermal energy at room temperature (i.e., kT at 298K) is 25.7 meV, the probability of dissociation of excitons are very high for MAPbI₃; in fact, the electrons and holes are dissociated to be free electrons and holes rather than forming excitons in MAPbI₃. This significantly reduces the radiative recombination rate, which makes the material more desirable for charge extraction such as in solar cells, rather than the applications in light emitting devices. However, in MAPbBr₃ it is more probable for excitons to form and sustain at room temperature, leading to radiative recombination.

2.2.5 Photoluminescence quantum yield

The photoluminescence quantum yield (PLQY) or photoluminescence quantum efficiency is the parameter to represent radiative recombination efficiency of the material. Typically, three competing processes of monomolecular, bimolecular and trimolecular (Auger) recombination mechanisms could exist in a typical semiconductor material like perovskites. However, only the bimolecular recombination is contributing to the radiative recombination. Hence, maximizing bimolecular recombination is major focus of developing efficient light emitting

devices. The PLQY of perovskite materials are known to be varied with the excitation pump fluence, and the reported values spread in a wide range [40]. This is an indication of competing recombination processes which relate to fabrication procedure as well as the fabrication conditions. For bulk perovskite single crystals of MAPbBr_3 , the PLQY has been reported to be around 6.4% when excited at 405 nm with 1 W cm^{-2} power [41]. When the size of the particle reduces to the microscale and further down to the nano scale, the quantum efficiency could increase significantly [42]. This can be understood as quantum confinement effects that force electrons and holes into a small physical volume and therefore increase their wave function overlap. However, the PLQY for MAPbCl_3 is significantly low, probably due to more prominent non-radiative recombination and defect sensitivity, which is usual in high bandgap materials [43].

2.3 Perovskite crystal growth and heterostructures

2.3.1 Techniques used for crystal growth

Synthesis and growth of all inorganic halide perovskite single crystals (i.e. CsPbCl_3) has been known as far as 1959 [44, 45]. All-inorganic materials can melt into a liquid phase at high temperatures while remaining chemically stable. Hence growing crystals from a liquid melt, known as the standard Bridgeman's method can be used to grow large single crystals out of a molten liquid. However, organic materials cannot sustain such high temperatures because they can degrade easily. The organic-inorganic hybrid halide materials were first synthesized in 1978 [43] using a traditional solution-supersaturation-based crystallization technique. The solution was prepared by drop-by-drop addition of aqueous solution of $\text{Pb}(\text{CH}_3\text{CO}_2)_2$ to an excess quantity of hot aqueous solution of $\text{CH}_3\text{NH}_3\text{X}$ ($\text{X}=\text{Cl}, \text{Br}, \text{I}$), and a crystal can be grown by cooling

down the solution and also due to slow solvent (water) evaporation. This process is very slow; and controlling the nucleation and crystallization process to grow large crystals is not efficient.

However, an interesting behavior of decreased solubility of perovskite in a certain solvent at higher temperatures has made the perovskite crystallization process easier, faster and more reliable. First observation of inverse solubility behavior of $\text{CH}_3\text{NH}_3\text{PbI}_3$ in γ -Butyrolactone is reported recently in 2015 [46]. Since then, many studies on growth of perovskite single crystals up to few cm sizes have appeared in the literature.

2.3.2 Hetero-valent doping hybrid halide perovskites

A dopant profile and the bandgap profile determine the fundamental electronic device characteristics of a heterostructure. Intrinsic double heterostructure arrays (ideally multiple quantum wells) can be integrated within the intrinsic region of a p-i-n diode structure to obtain highly efficient light emitters. Intrinsic perovskite materials with limited carrier concentration can be excited by optical energy or electrical injection to provide considerable carrier densities. But for conventional heterostructures, hetero-valent-doped materials are used for extrinsic p-type and n-type semiconductor with better electrical characteristics [46, 47]. However, for perovskite materials, suitable doping techniques have not been fully developed yet [39].

Doping perovskite materials with different group (hetero-valent doping), which introduces imbalanced immobile charges to the semiconductor, is an important step in semiconductor material development, and active research is ongoing. Li^+ and Bi^{3+} are some candidates [48]. Eventually, it is essential to integrate these extrinsic n-type, p-type semiconductors together with the hetero-structures for a light emitting device and

other optoelectronic applications.

Due to different defects resulting from growth conditions, perovskite materials are known to be self-doped in many reports, for example [49]. This behavior has been also observed in several theoretical calculations and experimental observations. Studies on various types of crystal defects have revealed that the $\text{CH}_3\text{NH}_3\text{PbBr}_3$ material can have intrinsic unipolar doping characteristics allowing it to show prevailing p-type behavior, while $\text{CH}_3\text{NH}_3\text{PbI}_3$ could be ambipolar p-type or n-type self-doping [50] depending on dominant type of defects. Studies on point defects of vacancies, interstitials, anti-site substitutions can be made dominant by engineering the precursor mixing ratio. However, considering their formation energy and the energy levels, only some of them can be effective as doping. For example, the Br-rich Pb-poor growth condition would lead to more Pb^{2+} vacancies, allowing to be dominantly p-type owing to degenerate location if its (V_{Pb}) energy level near to valance band maximum. Considering $\text{CH}_3\text{NH}_3\text{PbCl}_3$, some studies suggest it can have intrinsic n-type behavior [51] due to Cl^- vacancies acting as shallow donors.

However, we specifically focus on undoped materials with different bandgaps in this project, while keeping space to hopefully incorporate dopants to the growth solutions when the perovskite doping techniques are fully developed in future.

2.3.3 Halide ion diffusion/drift

Perovskite materials are known as ion transporters, apart from being good semiconductor materials. In fact, the ionic conduction under an electric field in fully inorganic perovskite material CsPbBr_3 was known in 1983; even before their semiconductor properties were fully recognized [51]. Even though the first studies were conducted with extrinsic types of ions, the halide ions also behave similarly [52,

53]. In hybrid halide perovskites, ions can even move within a single crystal without an external bias, just as a result of diffusion process [48]. It has been theoretically calculated that apart from the halide ions, some fraction of the organic cations (i.e. CH_3NH_3^+) also can diffuse within the crystal [54]. If the mechanism is strictly vacancy assisted, improving the quality of the crystal may reduce the diffusion process. However, the quality of the crystal at room temperature is limited by its low kinetic activation energies. Theoretical calculations as well as experimental data suggest that the mechanism may be an interstitial process [27, 32, 50, 55, 56], which can be difficult to eliminate given the poor stability of the lattice structure.

Figure 2-5 Images of a MAPbBr_3 after several seconds of dipping halfway in MAPbI_3 solution. Cleaving the crystal reveals the unchanged interior, and the cross section of the thin surface layer. Reprinted with permission from “Formation of perovskite heterostructures by ion exchange” Nathan T. Shewmon, Hyeonggeun Yu, Iordania Constantinou, et al. Applied Materials [16]. Copyright (2016) American Chemical Society

The best example of this diffusion phenomenon can be demonstrated easily with

placing a perovskite single crystal in an environment with a high concentration of a different halide ion. shows a $\text{CH}_3\text{NH}_3\text{PbBr}_3$ crystal which is dipped in $\text{CH}_3\text{NH}_3\text{PbI}_3$ crystal growth solution for few seconds, in an attempt to create a heterostructure between MAPbBr_3 and MAPbI_3 materials.

In an ideal situation, a layer of MAPbI_3 should grow on top of the MAPbBr_3 substrate over a long-time span, or otherwise, the crystal should remain intact if the growth process is not initiated. However, it is evident in the mentioned experiment that the color of the crystal's outer crust has been changed, indicating the iodide ions (which appear as black color) have rapidly replaced the bromide ions (which appear as orange-red color) within the crystal lattice. This inter-diffusion phenomenon is indeed discouraging any attempts to grow a good heterostructure. However, there has been no systematic study on how to control such halide ion diffusion process in a facile solvothermal hetero-layer growth attempt.

While the ionic diffusion could severely hinder the growth and existence of useful heterostructures using perovskite materials, ion drift due to applied electric field could complicate the electronic behavior of perovskite semiconductor devices. The ions could accumulate at the electrodes as the electric field is applied and alter the device structure itself [57]. The current-voltage sweep across a perovskite crystal is usually subjected to a significant hysteresis curve due to the ionic currents, which are slow moving. The ions accumulate at the corresponding electrode, known as stoichiometric polarization [58]. Under certain conditions, the ionic conductance could be even larger than the electronic conductance [56]. Ion conductance has been shown to significantly modulated by the external atmosphere, specifically the halide under partial pressures and oxygen. Therefore, isolating the pristine perovskite semiconductor and its

optoelectronic devices for studying its behavior is necessary to understand how the perovskites work without any interference from environment such as air or moisture exposure.

2.3.4 Band alignment of perovskite materials

In a heterostructure, two materials with different bandgaps are interfaced together to obtain a desired electron-hole flow. However, only considering the bandgap is not sufficient to determine the exact nature of the heterojunction due to different work function/ionization potentials of the materials. The electron affinity and bandgap together determine the behavior of the electron and hole carriers [22].

Figure 2-6 Calculated band alignment of three pseudo-cubic hybrid halide perovskites. Based on Butler *et al.*, [13, 59].

Based on these parameters, the alignment between two materials can be of several types. An ideal heterostructure for light-emitting devices is a type 1 alignment, where both electrons and holes are energetically preferred to stay together so that the quantum well structures can be made to confine these carriers physically [54]. It is encouraging that the available literature suggests the type 1 alignment among hybrid halide perovskites with any halide composition. Furthermore, mixed halide perovskites are also possible to make with linearly interpolated characteristics from their pure

materials.

2.3.5 Challenges in perovskite heterostructure growth

Material instabilities

The hybrid halide perovskite synthesis will be discussed later in this chapter; however it is simple process with a slightly exothermic reaction [60, 61], which could be even sensitive to natural temperature fluctuations. Therefore, just mixing the reactants in powder form is sufficient to prepare perovskite material. In contrast, preparing an inorganic semiconductor material like GaAs is much more complicated. Especially for a crystallization process, inorganic materials are usually melted to a liquid by heating to very high temperatures, usually in a pressurized chamber [62] and then crystallized slowly. On the other hand, crystallizing hybrid halide perovskites just requires a solution of perovskite reactants in a solvent suitable to achieve supersaturation. In fact, the organic component cannot sustain temperatures more than $\sim 150^{\circ}\text{C}$, because the organic bonds will be damaged due to heat. The ease of the perovskite synthesis process is, on one hand, admired as an advantage for device fabrication, but on the other hand poses a challenge in maintaining the stability of the crystals.

Surface instabilities

The high sensitivity with moisture and air of perovskite materials is more prominent at their surfaces [63]. Optical properties of the perovskite surfaces change with exposure to oxygen and moisture, despite of the halide composition being pure or mixed. Typically for solar cell applications, perovskite thin films are grown in a nitrogen filled glovebox where moisture and oxygen are kept at low ppm levels. However, in large single crystals, the surface area to volume ratio is low and the additional problems such as grain boundaries are also not available. Hence, handling the single

crystals grown within the solution kept in air will experience less effect from atmosphere.

One of the main reason for perovskites' sensitivity to moisture is their reaction with water which breaks down perovskite to lead halide [62]. The polycrystalline or powder materials are the most vulnerable to degradation due to their large surface area, and certainly the most stable form is single crystals. Even with single crystals, the surface characteristics are usually found to be significantly different from the unexposed pristine material inside [62]. In fact, it could be also sensitive to other chemical molecules, as it could drastically change optoelectronic characteristics such as photoluminescence, just by changing the external environmental air composition and pressure[64].

Phase segregation instabilities

The mixed halide materials where two halide ions are in a perovskite structure also pose a stability concern related to phases segregation which creates more stable forms such as lead halide (PbX_2) triggered by external sources such as light or heat [65, 66]. The mixed halide perovskites at high mixing ratio are known to be unstable due to reasons which are not completely known yet [67]. The material would decompose into pure phases under laser illumination due to high energy density of mixed halide crystal structure. Many studies on such segregation between halide phases have been done in thin films, mainly with iodine due to its major application as solar absorbers [68-71] for photo-voltage applications. This phase segregation has been found to originate from “soaking light”, instead of heating, and partially reversible when returned to the dark [72]. This peculiar phenomenon is termed Hoke’s effect [50]; however, studies are mostly limited to Br and I. Similar decomposition between Cl and Br also has been

observed in thin films under thermal annealing [73]; however, thermal annealing may cause decomposition of organic cation, which is another concern. The stability or phase separation of single crystals has been studied less, and particularly rare with Cl. A study of Br (cubic) and Cl (cubic) mixed halide perovskite materials would provide a clearer picture about the phenomenon, to rule-out any defect related origins or crystal structure mismatch between pure phases of Br (cubic) and I (tetragonal) mixed halide perovskites. However, this effect is seemingly available in single crystals as well, most probably originating from the elusive ion migration within single crystals. But it has been established that the halide segregation under illumination could only happen at higher halide mixing ratios, which will segregate to two phases [74]. Sensitivity of the mixed-perovskite surface to light has been characterized using photoelectron spectroscopy techniques, and has an important impact on electronic band structure of the material as well [75].

2.3.6 Perovskite-perovskite heterojunction

State-of-the-art inorganic single crystalline hetero-structures are usually grown using metal organic chemical vapor decomposition (MOCVD) / molecular beam epitaxy (MBE) or atomic layer deposition (ALD) technologies to obtain abrupt material interfaces. Traditional inorganic material systems are comparatively more stable than the hybrid halide perovskite materials and can sustain higher temperatures. Perovskite single crystals are grown at relatively low temperatures, and hence the epitaxy also should be done in similarly low temperatures, which deem many other techniques not suitable. In fact, the low temperature processing capability can be considered as an additional advantage for perovskites, due to low cost and no necessity for high-end equipment. Whether it is possible to establish such a low-cost technique is still an open question, which might impact semiconductor technologies greatly by opening more

research and development opportunities for a wider community.

Growing single crystalline perovskite hetero-structures has been attempted by several research groups within last few years. Since the emergence of inexpensive fast solvothermal growth technique and other vapor-based growth technologies, epitaxial growth of perovskites has been attempted. The first appealing technique is liquid phase epitaxy (LPE), which was used in early semiconductor device manufacturing but disappeared after the arrival of the high-end gas-based technologies mentioned earlier. However, ion migration/diffusion seems to dominate in most of the attempts. In fact, several studies use the diffusion process itself instead of epitaxial growth for hetero-structure formation [75, 76]. In this work, the $\text{CH}_3\text{NH}_3\text{PbBr}_3$ crystal has been partially converted to $\text{CH}_3\text{NH}_3\text{PbI}_3$ just by dipping the crystal in the respective growth solution ($\text{CH}_3\text{NH}_3\text{PbI}_3$) for very short time of 2 seconds to 5 seconds. See . This extreme diffusion behavior is not easy to control and shows the extent of the capability of concentration driven ion migration in such materials. Even keeping a $\text{CH}_3\text{NH}_3\text{PbBr}_3$ single crystal in physical contact with $\text{CH}_3\text{NH}_3\text{Cl}$ powder at a slightly elevated temperature would prepare a heterojunction by halide ion diffusion [77]. Similarly, ion diffusion has been used to grow nanowires with a gradient in halide composition; hence the bandgap gradient which funnel the carriers in one direction [78]. However, there are no reports on clear epitaxial growth being observed on single crystals according to best of our knowledge.

Illumination activated heterojunction formation is another approach. First, a mixed halide single crystal is grown, and then selectively exposing it to light separates the halides into different regions [79][51]. This phase separation process has been explained using spinodal decomposition model where the pure halide phase is

energetically preferable than the mixed halide phase, and the decomposition is activated under white light illumination. With the knowledge of increased ionic phenomenon at steep halide concentration gradients and mixed halide perovskites, it is better to keep minimum halide gradients in attempts for heterojunction formation.

2.3.7 Single crystalline thin film growth

Thin film growth can be considered as one of the hallmark technological forefronts of the semiconductor industry. Polycrystalline thin films can be made by spin casting for research scale or spray paint technologies at roll-to-roll scale [59]; however, fabricating single crystalline thin films is far more challenging. In thin film epitaxial growth, the layer and substrate must be lattice correlated to obtain highest quality and least defective substrate-layer interface. Modern technologies are based on MBE, CVD or ALD techniques, which need to be meticulously designed to suit the desired material system [80]. However, for a novel material system like hybrid halide perovskites, setting-up such a system at a research scale is a cumbersome and expensive task; preliminary studies are necessary to understand the risks and benefits before investing in such a system. So, most of the research with perovskite single crystalline thin films is so far limited to simpler techniques, to understand and address the fundamental problems such as ionic diffusion. Liquid Phase Epitaxy (LPE) [81] is a simple technique which can be used to grow single crystalline layers with minimum infrastructure costs, and can be used to solve preliminary concerns about the issues involved in single crystalline layer growth. This technique is compatible with the solvothermal crystal growth techniques which have been introduced recently for perovskite materials. Also, it can benefit from the retrograde solubility characteristics of perovskite materials to achieve better control over the growth conditions [81, 82].

However, there are no reports on such layer growth on perovskite substrates, using this technique, which we address as one of the major objective of this project.

2.4 Perovskite single crystal LEDs.

While the layer growth techniques are still at a primitive stage, a working single crystal light-emitting device seems to be a far-fetched goal to achieve. Despite the preliminary status of the heterostructure growth, single thin layer of single crystal perovskite material is sufficient to show electroluminescence, usually at high bias conditions. Few perovskite single crystal devices have been demonstrated to emanate electroluminescence with a thin single crystalline perovskite layers during past few years. These devices have a very simple structure but are not specifically designed or optimized for light emission: however, they show bright electroluminescence. One such electroluminescence device has recently been demonstrated using a perovskite microcrystal [82] grown on an ITO substrate, and coated with gold on top surface. Figure 2-7 shows a micro-platelet and the electroluminescence from the device, as well as its emission intensity over more than 50 hours period at cryogenic temperatures. The device has an ITO/CH₃NH₃PbBr₃/Au structure, which is asymmetric, and therefore better suited for efficient carrier injection than a symmetric device structure. In this study, external voltage bias is used at room temperature to precondition the crystal with mobile ions. The mobile ions were expected to be fixed and immobilized, when the device was cooled down to cryogenic temperatures with the external bias applied.

The result of such bias preconditioning and subsequent “frozen junction” was essentially forming a heterostructure suitable for a light emitting device, despite the simple structure. However, the microcrystal was exposed to the external environment

and also coated with a 5 nm thick layer of gold using sputtering technique. Yet, the emission was predominantly localized at the point of probe tip. Hence, the emission could be a characteristic of the surface states and external environment related defects rather than the intrinsic characteristic of the perovskite single crystalline domain.

Figure 2-7 Relative light emission intensity vs time of an LED operated at a constant 1 mA current at -193°C . The LED had a starting luminance of $\sim 5000\text{ cd m}^{-2}$. Inset shows a microscopic image of the LED at $t=12\text{h}$ [83]. Reprinted with permission from M. Chen *et al.*, "Manipulating Ion Migration for Highly Stable Light-Emitting Diodes with Single-Crystalline Organometal Halide Perovskite Microplatelets," *ACS Nano*, vol. 11, pp. 6312-6318, 2017. Copyright © 2017, American Chemical Society

Another research group has been successful in obtaining a ‘very thin layer’ of perovskite single crystal between two ITO coated glasses. The ITO/ $\text{CH}_3\text{NH}_3\text{PbBr}_3$ /ITO device described in [84] has shown arbitrary blinking behavior as seen in Figure 2-8. The paper does not specify the current readings, and the emission blinking behavior is not explained.

Figure 2-8 (a) Optical micrograph of single-crystal MAPbBr₃ indicating “on” and “off” blinking emission at bias voltage of 4V. (b) Time profile showing EL blinking measured at $\lambda = 549.4$ nm [85]. Reprinted with permission from V.-c. Nguyen *et al.*, "Single-crystal perovskite CH₃NH₃PbBr₃ prepared by cast capping method for light-emitting diodes," *Japanese Journal of Applied Physics*, vol. 57, p. 04FL10, 2018 © 2018 The Japan Society of Applied Physics.

Further, it can be observed in Figure 2-8a that the emission is localized at the edge of the thin arbitrary-shaped perovskite crystal layer, and not in the center area. Hence, the emission could be from the surface states which are exposed to external environment with air and moisture, rather than from the bulk perovskite material. The importance of a fully encapsulated environment can be further recognized with this device.

In another device which uses carbon nanotubes to enhance the electron injection to the perovskite single crystal, similar blinking behavior has been observed [85]. The device is termed “Light Emitting Electrochemical Cell” attributing to the contribution of the mobile ions within the crystal to influence the current and electroluminescence of the perovskite crystal. Figure 2-9 shows the localized emission spots in an image, whereas the current and luminescence measurements over a 20 second interval is also shown in black and blue graphs respectively. Yet, the cause of arbitrary blinking behavior and

fluctuating currents are concerning findings. The behaviors need to be well understood and the problems should be eliminated before fabricating advanced layer structures with further optimizations. So, devising methods to study the pristine crystals is the major focus of the next chapters of this thesis.

Figure 2-9 Luminance–current in time for an applied bias voltage of 20 V at room temperature. Inset: Optical image of >40 flashes of light of light during 20 s at room temperature[86]. Reprinted with permission from P. Andričević *et al.*, "Light-Emitting Electrochemical Cells of Single Crystal Hybrid Halide Perovskite with Vertically Aligned Carbon Nanotubes Contacts," *ACS Photonics*, vol. 6, no. 4, pp. 967-975, 2019. © 2019 American Chemical Society.

In this chapter, we have discussed the advantages and drawbacks of the general halide perovskites as an optoelectronic material, the importance and the difficulties in studying single crystalline perovskites, and the material properties which are pertinent to the applications. In the next chapter, the techniques and methods used to synthesize and characterize the material will be discussed.

2.5 References

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Chapter 3 Methods and characterization techniques

3.1 Perovskite synthesis and single crystal growth

3.1.1 Perovskite synthesis

The hybrid halide perovskite materials can be easily synthesized using following reaction:

This reaction can occur when precursors in solid powder form are mixed together at equimolar ratio at room temperature. The reaction can be easily identified especially in $CH_3NH_3PbBr_3$, by the change of color from white to orange-red during mixing two precursors. The perovskite material is easy to form, and similarly it is easy to disintegrate as well. It can react easily with moisture to form lead halide again, so it is necessary to keep the perovskite material isolated from moisture, especially when it is in powder form. In most applications, the material can be applied as a polycrystalline thin film by spin coating on a suitable substrate, and many processes have been developed for this task. For perovskite single crystals, techniques to grow a single bulk crystal is also available. However, it was not always easy to grow a single crystal of the material at high quality, which currently limits the development of device applications with perovskite single crystals. In this work, we are using single crystal growth process with well-controlled technique to achieve this goal.

3.1.2 Solvothermal perovskite single crystal growth

Solubility of the perovskite materials plays a crucial role in crystal growth using a solvothermal crystal growth. Hybrid halide perovskites are soft materials and can be grown into crystals by a supersaturated solution. For crystallization, the perovskite material needs to be dissolved in a suitable solvent. For $\text{CH}_3\text{NH}_3\text{PbCl}_3$, dimethyl sulfoxide and N,N-Dimethyl formamide mixture, DMSO:DMF 1:1 in volume is used as the solvent [1]. For $\text{CH}_3\text{NH}_3\text{PbBr}_3$ N,N-Dimethyl formamide (DMF) is used. The perovskites show an abnormal retrograde solubility behavior with these solvents, which allows crystal growth by increasing the temperature of a supersaturated solution.

Figure 3-1 Inverse solubility behaviour of $\text{CH}_3\text{NH}_3\text{PbI}_3$ in γ -Butyrolactone. Less solubility at higher temperature implies that the heating up a supersaturated solution can produce nucleation and crystal growth. Taken from [2] 'Facile route to

freestanding $\text{CH}_3\text{NH}_3\text{PbI}_3$ crystals using inverse solubility' by Jeannette M. Kadro et.,al. Scientific Reports (2015) CC BY 4.0

After discovering the retrograde solubility of perovskites in certain solvents [2], a new single crystal growth process was introduced. Due to the inverse temperature/retrograde solubility properties of the perovskite in selected solvents, a supersaturated solution is prepared at low temperature and then heated up to obtain the crystals. However, if the crystal is not extracted at the higher temperature, it will dissolve again in the same solvent when the temperature is lowered again.

There are many advantages of the retrograde solubility crystallization method. Mainly, large crystals can be obtained within hours. Better controllability over nucleation and crystal growth rate can be achieved by carefully adjusting the temperatures and concentrations. Most importantly, the necessary infrastructure and capital costs are negligible compared to any other techniques. In retrograde solubility crystallization method, a laboratory hotplate with a good temperature controller is the most significant infrastructure necessary. An MR Hei-Tec magnetic stirrer is used to grow all the crystals in this work. The temperature can be controlled at a one-degree resolution, however with a significant proportional–integral–derivative (PID) controller settling down time interval. An oil bath was used optionally, where the temperature is distributed evenly and measured more accurately. However, the PID controller needs the input from external temperature probe, and it could take a significantly long time to stabilize the temperature with an oil bath due to its large thermal mass. The precise temperature control is crucial in single crystal growth, especially at the critical temperature where the nucleation happens. At this critical moment, external vibrations or existence of excess undissolved precursor particulates

in the growth solution can severely increase the number of nuclei formed within the solution. Ideally, one or two nuclei are preferred if they land on the bottom of the vial in correct orientation, but it is rarely achieved. More than 5 to 10 nuclei could be a major drawback to growing a large single crystal since the supersaturated material suspended within the growth solution is now shared between multiple crystals, which will limit the maximum size of each crystal to exponentially smaller dimensions.

Figure 3-2 Setup for perovskite single crystal growth using inverse temperature crystallization process

For favourable nucleation the following steps should be taken; filter the growth solution with 0.2 μm PTFE filter, increase the temperature in gradual steps without solely relying on the PID controller and isolate the hotplate from any external

vibrations such as fans. The oil bath may cause significant PID overshoots, so the vial should be placed directly on the hotplate as well. However, in this case, external heat dissipation could be different and the hotplate reading on temperature which the nucleation happens could be slightly different from the reading with the oil bath. Once the nucleation happens, it can be seen within minutes due to large growth rate at small crystal size.

3.1.3 Mixed halide perovskite single crystal growth

Growth of crystals with mixed halide composition is as useful as the single halide perovskite crystal growth. The halide composition of the crystal is important in determining the bandgap of the material and plays a crucial role in applications.

We have grown a series of mixed halide perovskite single crystals to study their properties and to understand the impact of using different halide compositions on crystal growth conditions. However, changing the halide composition has multiple implications to the crystal growth process as well.

When the halide composition is changed, the solubility of the perovskites in selected solvent is different. Hence, the composition in the crystal is not similar to the composition in the growth solution. Therefore, we determine the exact halide composition of the crystals independently from the solution halide composition using XRD data. Solvent engineering is necessary to find a suitable solvent for the crystallization process where the inverse solubility behavior is preserved. The optimal temperatures for the growth also have been determined for selected compositions, which are to be used in the heterostructure.

Figure 3-3 Mixed Br-Cl crystal growth at higher than critical temperature. Multiple nucleations has happened, and given the same temperature, the number of nucleations apparently depend on halide composition as well.

However, when selecting the materials for perovskite heterostructure, a common solvent (i.e. DMF) has been used despite the small difference between solubility, which is convenient to handle the growth process with less variables. As shown in Figure 3-3 by different sizes and number of crystals grown at constant temperature, the crystal growth rate and nucleation conditions are significantly different for different compositions.

Determining lattice constants and crystallographic structure are an indispensable approach in determining the mixed halide single crystals, which is explained later in this chapter. Once the lattice constants of the crystal are calculated from the XRD spectra, the relationship between the solution and crystal compositions has been established; which is crucial information for determining the favorable parameters for layer growth process.

3.1.4 Enhanced perovskite single crystalline layer growth technique

Growth of a layer on perovskite substrate was done by introducing perovskite substrate into a growth solution with a composition suitable for layer growth. Optimization of concentration, temperature and growth time for the best layer quality and thickness is done using a sequence of experiments to observe the growth rate at different conditions. With the help of controlled composition and other parameters conditions suitable for growing a thinnest layer in a longest time period with minimum diffusion profile was established. This is the most essential improvement of the technique which allows the dominant epitaxial-like growth dominant with least impact from halide ion diffusion. The particulars of the technique derived from liquid phase epitaxy method and verification of improved results are elaborated in next chapter.

3.2 Structural characterization techniques

3.2.1 X-ray diffraction (XRD)

Powder x-ray diffraction spectra are crucial in determining the lattice constant of the powdered crystalline material. It can be used in an empirical formula known as Vegard's law [3, 4] to determine the composition of mixed halide perovskite single crystals. The Vegard's law states that the lattice constant of an alloyed crystal and the concentration of the constituent elements are linearly related. Using this relationship, the concentration of constituent elements can be calculated when the lattice constants are known. The lattice constants of the crystals are easily determined by the powder XRD technique and therefore useful in determining the elemental composition of the mixed halide single crystals.

X-Ray diffraction is a very powerful technique, and widely used in material science. It

can be used to determine crystallographic structures of materials; this is the most fundamental property of the material and is essential for analysis. Crystalline materials are essentially three-dimensional diffraction gratings and have regular spacing (d) between planes of atoms which are in the same order as the wavelengths of X-Rays (λ). Hence, the incident X-rays will reflect from the different planes of the crystalline material, causing them to interfere constructively and destructively at different angles (θ) according to the Bragg's law.

$$n\lambda = 2d \sin \theta$$

where n is refractive index of material. Hence, by scanning a range of angles to identify the constructive interference from the crystalline material, the X-ray peaks will appear at certain angles. Using these angles, the lattice plane spacing d can be calculated. The peaks appear at the lowest angles represents the lattice parameters, whereas the first peak is essentially the lattice constant if the material has any cubic structure. The single-crystal XRD technique can determine the complete crystallographic structure by scanning the diffraction peaks in an entire 2D space; however, it is more time consuming and not essential to repeat for all the samples.

Figure 3-4 Bruker D8 Discover HR-XRD machine

Figure 3-5 Bromide chloride mixed halide crystals $\text{CH}_3\text{NH}_3\text{Pb}(\text{Br}_{3-x}\text{Cl}_x)$, and powder samples prepared for XRD characterization

Instead of single crystal XRD, a powdered ensemble of crystals which are at random orientations can be used with a 1-dimensional scan, where many peaks can be observed at higher angles as well, which correspond to the low gap spaces within the

crystal at different angles. Using a powdered sample is more informative than using the single crystal surface for the single dimension XRD study at low resolution. The single crystal surface will provide only few peaks, which only contain the information about few lattice planes which are parallel to each other, whereas a powdered sample can provide many peaks which contain information about all the orientations of the material, which is useful to determine the crystallographic structure of the substance.

Further to the powder XRD analysis, High resolution XRD analysis can be conducted on single diffraction peak to study the degree of crystallinity and other scenarios such as thin films grown on top of a single crystalline substrate.

To characterize the single crystal samples prepared as explained in section 4.3, following specifications were used.

Samples for PXRD analysis were prepared by crushing crystals to an evenly sized fine powder and dispersing on double sided tape, supported by a glass substrate. A Bruker D8 Discover HRXRD set-up was used with a 0.6 mm absorber slit. For each sample, an unlocked coupled 2θ scan was performed in the 2θ range from 10° to 60° with a 0.005° angle resolution, at 0.05 s per step, after optimizing the z axis.

3.2.2 Scanning electron microscopy (SEM) imaging

Physical observations of the crystals at microscopic scales can reveal much information about the quality of the growth process. It is useful in identifying the surface morphological features of the crystal related to the growth mode, and also useful in identifying the quality of an interface on a cleaved cross-section of a crystal.

By observing a crystal cross-section under the SEM, layer thickness can be identified if there are some defects along the interface line. However, in an ideal sample with a

layer, the interface may not be detected just by observing a cross-section image, and other techniques are also necessary.

In contrast to a traditional optical microscope, the SEM can provide much higher resolution. Also, the SEM can provide several useful analytical features such as energy dispersive x-ray (EDX/EDS) study or electron back scatter diffraction (EBSD) study.

Figure 3-6 Field emission scanning electron microscope with EDS and EBSD

Perovskite single crystals are semiconductors and intrinsic material is mostly insulating under dark conditions. Due to this low conductivity, SEM imaging at high resolution is challenging due to accumulation of electrons from the microscope beam which induces static charge in the sample surface and deflects the beam thereafter. Such charging effects are common in many insulating materials, so the surface is typically coated with a thin gold/platinum or carbon layer and properly grounded before the imaging. However, such layers can also cause complications since they may

tend to peel-off and alter the morphology of the surface.

Further, the beam may damage the sample itself, especially at high acceleration voltages and currents. Such ‘burning’ may deform the sample surface, sometimes releasing gaseous compounds from the sample. For example, such burning could severe the defects, especially between the substrate-layer interface. So, spending the minimal time for imaging is recommended, especially at high resolutions. However, such damage is unavoidable for the long exposure experiments such as EDS.

Figure 3-7 Some low magnification SEM images to assess the morphology of crystal surfaces. Left: perspective view to assess the quality of a cleaved cross section surface and external surface. Half of the surface is coated with excess of a platinum layer. Right: A quality of a cleaved cross section of a crystal with a layer, where the discontinuities in cleaving fault lines can be seen.

3.2.3 Energy dispersive x-ray (EDX/EDS) spectroscopy

Energy dispersive x-ray spectroscopy (EDS) is used to determine the elemental composition of a sample. It can be used to obtain a spatially resolved elemental

mapping for a selected area. This technique has been used in the subsequent chapters to identify the heterostructure by analyzing differences in the elemental composition of different layers.

The EDS technique essentially detects the x-rays emitted by atoms in a sample when they are hit by the accelerated electron beam of the SEM. However, the elements with atomic number (Z) below 11 cannot be detected using the typical EDS study since the x-rays released by light elements is quantitatively less and mostly reabsorbed before reaching the detector. However, for our applications, we are focusing on quantitatively analyzing bromine and chlorine, which are well within the capacity of the technique. Further, the quantitative EDS analysis can be conducted to determine the ratio between expected elements within the sample and then calibrated against a known sample. This technique can provide essential information about the ratio of the bromine and chlorine within a mixed halide single crystal sample, which we extensively use in next chapter to assess the contrast between a layer and a substrate with different compositions, by elemental mapping within an area covering both layer and substrate.

When the electron beam hits a certain position in the sample, it cannot be guaranteed that an emitted x-ray will be detected each time. Therefore, longer the time to collect data could provide more information (higher signal to noise ratio (SNR)) which will provide statistically significant values for the composition. Since many materials could have x-ray emissions with similar energies, the expected materials are manually selected to narrow down the peak identifications. Therefore, it is helpful in quantitative analysis, where the percentage of each element within the sample is calculated based on the counts of each peak. To obtain significant x-ray counts from the sample, sometimes it is necessary to use higher current than usual, while higher

accelerating voltage is also useful. As a rule of thumb, the accelerating voltage needs to be at least twice the largest energy peak expected from the sample. These settings could usually damage the scanned area significantly in perovskite single crystals, especially due to the damage to the organic methylammonium cation. However, the samples used for EDS study are considered expendable for the purposes of determining the necessary parameters.

For the heterostructure samples prepared as explained in section 4.3, following specifications were used.

Cross sections of the freshly prepared samples were cleaved with a sharp edge from the back side of the sample, without damaging the layer. The cleaved surface was used as is, without polishing or applying a conductive coating. SEM micrographs were taken under a 6 kV accelerating voltage in the secondary-electron mode. EDS quantitative analysis was performed to show the contrast of composition between the two regions. The EDS elemental map of a selected region was collected until it achieved a sufficient contrast (~30 minutes), especially visible in the chlorine elemental map (Cl $K_{\alpha 1}$). The concentration profile with the depth from the surface was obtained by integrating the elemental map parallel to the surface. This profile is fitted with Grube's solution for Fick's diffusion equation for individual materials: chlorine and bromine.

3.2.4 Electron back scatter diffraction (EBSD) analysis

Agreement between crystallographic orientations of layer and substrate can have important implications in layer growth. Usually, analytical methods such as thin-film HR-XRD analysis are used to analyze the single crystalline heterostructures for electronic applications. However, in the case where the layer thickness is at

micrometer scale, the EBSD technique can be used.

The EBSD technique is prominently used in studying grain structures in polycrystalline materials such as in metals. In this technique, the scanning electron microscope is repurposed to focus an electron beam on a single point of a sample surface. When the electrons get diffracted from a crystalline sample and emanates to the surrounding space. This diffraction only happens at certain angles, forming specific patterns pertaining to the crystallographic structure and orientation of the sample and are known as Kikuchi patterns. Kikuchi patterns can be detected with an electron sensitive CCD device which is placed closer to the sample. As the diffracted electrons scatter as they travel further from the sample, blurring the diffraction pattern, it is best to detect them at the closest possible distances. Maintaining a direct line of sight between the detector and surface, while not blocking the incident electron beam, is essential too. To ensure the best conditions, the sample is usually placed tilted at an angle of 70° degrees to the electron beam. However, due to this steep angle, the sample must be significantly flat to obtain a satisfactory diffraction pattern which can be analyzed to determine the crystallographic orientation of a given position of the surface. The image is also corrected for the angular perspective. By scanning a surface area of interest, the variation of the crystallographic orientation can be studied.

In the application of ensuring the preserved crystallographic orientation while growing layers on perovskite substrate, first we obtain a sharply cleaved cross section of a sample. However, if the lattice constant differences between two layers are significantly different, it may not be possible to obtain a perfect interface due to lattice mismatch. Hence, the samples for the EBSD study were meticulously prepared by obtaining the best compositions, growth conditions and techniques. Multiple cleaved

cross sections were taken from the samples and observed under the optical microscope for mirror-like surface finish. Only the best samples were selected for the EBSD study.

Figure 3-8 Optical microscope image of a cleaved cross section surface of a sample with a layer, prepared for EBSD study.

Determining crystallographic orientation with the Kikuchi patterns is done in several steps. First, the known crystallographic structure is provided to automated software so that it can simulate a pattern which is oriented at any angle. Other parameters, such as the distance from sample to the detector and angle to the beam, are also fed into the software so that it can determine the parameters such as expected width of a line in the observed pattern. Then, a standard line detection algorithm using Hough transformation is conducted. Based on the identified lines and expected crystal structure, even the barely visible lines can be predicted and can be further verified visually.

Figure 3-9 Capturing Kikuchi Patterns using HKL Flamenco software through EBSD detector

Figure 3-10 Detecting lines in Kikuchi Patterns using Hough Transformation

Based on the relative positions of the lines, the crystallographic orientation is determined with respect to the sample surface plane and represented using three angles

For the specific characterization of the samples prepared in Chapter 4, the EBSD characterization procedure is as follows:

A sample with a buried layer was cleaved to obtain a smooth cross section, and coated with a ~ 10 nm thick carbon layer. The sample was placed in a JSM-7600F field emission scanning electron microscope (FESEM) at a 70° angle tilt, with a working distance of ~ 17 nm. An acceleration voltage of 30 kV was used to obtain the EBSD pattern. An area covering all three areas (i.e. substrate, layer and the capping layer) was selected to perform an automated indexing scan, and the pole figure was generated using the collected data. To verify the electron beam damage is insignificant during the period of the scan, SEM images were taken before and after the scanning procedure. The Pole figure was plotted using the orientation information taken from the indexed points using the Matlab toolbox for analysing crystallographic textures (MTEX),[5] after manually selecting and color coding the data from different regions.

3.3 Optical characterization techniques

3.3.1 Photoluminescence spectroscopy

Photoluminescence spectroscopy is the most widely used characterization technique applied in studying fluorescence semiconductor materials. A fluorescence sample is excited with a short wavelength light source, and the emission from the sample at longer wavelengths is detected through a monochromator. It is an inexpensive, repeatable and relatively easy technique which can be used in material optimization

processes. The emission peak from a fluorescence material can be captured in the photoluminescence spectrum, which is also closely related to the bandgap of the material.

Figure 3-12 Photoluminescence process.

The photoluminescence experiment can be setup in various configurations. A xenon lamp with a monochromator can be used as the illumination source to setup a configurable excitation wavelength. For high quantum yield samples such as $\text{CH}_3\text{NH}_3\text{PBr}_3$, a HORIBA Fluorolog 3 ® Fluorescence spectrometer was used initially. However, $\text{CH}_3\text{NH}_3\text{PbCl}_3$ emission has very low quantum yield, and a high-power excitation source was necessary. Further, using the Horiba Fluorolog system, the excitation source was not a focused beam. Therefore, significant normalization across the sample area is expected. An ACCENT Nanometric RPM200 system was also available for the experiments, which is a setup with a 325nm laser excitation source. However, this system is designed for thin wafer samples with a complete laser safety enclosure and a loading-unloading mechanism and loading single crystals with larger thicknesses was not feasible. Despite the limitations, this system can be used

additionally to create spatial maps of photoluminescence characteristics from a large area samples such as wafers. Nevertheless, this system was useful when working with $\text{CH}_3\text{NH}_3\text{PbCl}_3$, since the emission wavelength is 405 nm where the necessity of high-power ultraviolet excitation source is unavoidable. But for the other samples with low quantum efficiencies such as in chloride-bromide mixed halide single crystals with high chloride content, a high-power short wavelength laser light source can be used in a free space-setup. The most widely available laser source is at 405 nm wavelength, and it is generally suitable for many samples which have visible spectrum emission. This setup has been used widely for most of the experiments in this thesis such as temperature dependent photoluminescence spectra, where the free space setup is essential.

The exact procedure to characterize the samples in Chapter 4 is described below:

A 405 nm CW laser beam was focused on to the crystal surface at a 45° angle, and the emission was coupled to a fibre through a lens which was placed in a perpendicular plane to the crystal surface. The collected emission was directed through the fibre to a spectrometer (Andor Shamrock with iDus CCD). It is worth noting that the PL spectrum showed a red-shifted emission and a sharp cut-off at the blue side of the emission if the PL signal was not collected from the exact excitation point. The further it is from the excitation point, the redder the peak position is because of re-absorption effects. Hence, the measurements have to be conducted carefully with a fine-tuning of the PL collection point to the excitation spot to avoid this re-absorption effect and achieve the highest PL intensity. For all the spectra, the intensity was normalized to the [0,1] arbitrary unit (a.u.) scale and the Laplacian correction applied, after wavelength (nm) to energy (eV) conversion for the x-axis.

3.3.2 Uv-vis absorption spectroscopy

Absorption spectroscopy is the key technique to determine the bandgap of a semiconductor material. Usually it is measured in a transmission mode, where the light transmitted through the sample is recorded so that the absorbed portion of light can be calculated. A Shimadzu UV-2450 ® UV-Vis Spectrometer was used to collect the absorption spectra for this work.

However, hybrid halide perovskite materials are strong absorbers on energies above the bandgap. It can absorb most of the light at above bandgap energies with just few hundred nanometers thickness, whereas the crystals are usually thicker than few millimeters. Therefore, the transmission through the crystal at above bandgap energies (i.e. shorter wavelengths) are typically below the sensitivity levels of the detector. So the absorption is captured at maximum saturated level. Even though measurements above the bandgap are not possible, it is useful to identify the bandgap and below bandgap spectrum accurately, since the perovskite crystals are mostly transparent for the energies below the bandgap.

When the composition of the crystal is changed, it can be observed that the color of the crystals also gradually changes. This change is quantitatively measured in the UV Vis absorption spectra.

3.3.3 Time resolved photoluminescence spectroscopy (TRPL)

The optoelectronic quality of the bulk crystals is crucial for applications. For light emission applications, the energy introduced to the semiconductor material is expected to convert to the radiative emission efficiently. However, it is not the only process for energy dissipation in a material. There are several non-radiative processes which could have significant contribution toward the inefficiencies of the material. To recognize

the individual contributions from each process can be challenging with, steady state measurement such as absorption spectrum or photoluminescence spectrum. However, the time resolved photoluminescence technique can provide a significant insight to the material optoelectronic mechanisms.

Time resolved photoluminescence decay can be measured using time correlated single photon counting method. A high frequency pulsed laser is used as the excitation source, whereas the photoluminescence photons emitted from the sample are collected at the detector with exact timestamp of arrival, with respect to the timestamp of the excitation laser pulse signal. Then the photons are categorized into different bins based on the delay of arrival at the detector. Most of the photoluminescence photons are emitted right after the excitation pulse hit the sample, whereas some photons will be emitted few picoseconds or nanoseconds after the excitation pulse. After collecting data over multiple excitation pulses, the photoluminescence decay pattern emerges after accumulation of sufficient data.

The photoluminescence decay essentially represents the excited state population, and how long the electrons can stay in excited state before returning to the ground state. Using the TRPL decay curve, the exponential decay time constant can be calculated.

For a pure homogeneous single crystal, a single decay constant is expected, due to single uniform excited state spatially and temporal consistency of the material. However, despite being a single crystal, hybrid halide perovskites do not usually have a single decay behavior but rather a stretched exponential decay behaviour.

The emission decay could have two or three different time constants on some occasions, usually categorized as a stretched exponential decay. The origin of this behavior is complicated in perovskites and has been the subject many studies. For

example, multiple emitting photons have slightly different characteristics which are associated with materials at slightly different conditions such as the perovskite surface and the unexposed bulk material inside [6].

3.3.4 Temperature dependent photoluminescence spectroscopy

Photoluminescence spectroscopy at room temperature is essentially useful for optimization purposes. However, studying the changes in photoluminescence with temperature can provide a wealth of information about the physics of semiconductor materials. When the temperature of a semiconductor material is reduced down to cryogenic temperatures, its photoluminescence characteristics could pose some significant changes with (1) intensity, (2) emission linewidth, (3) peak position and (4) additional peaks. Each of them could reveal certain aspects of physical properties of the material.

Generally, the photoluminescence intensity increases with decreasing temperature as less kinetic energy is available to dissociate the excitons, so that radiative recombination can be increased. Full width half maximum of the photoluminescence peak is reduced gradually toward lower temperatures, due to less lattice vibrations and less ionic mobility. Also, the crystallographic phase transitions in hybrid halide perovskites at low temperatures manifest sharp transitions in the photoluminescence spectrum, as a sudden peak change of the peak position or a direction of peak shift. Usually, the natural peak shift of a material is due to the bandgap changes in the material. Most of the materials show a narrower bandgap (i.e. longer wavelengths peak) at increasing temperatures, however the hybrid halide perovskites tend to show a wider bandgap, shorter wavelengths peak at increasing temperatures[7, 8].

3.4 Electrical characterization

3.4.1 Current – voltage characteristics

Hybrid halide perovskite single crystals are good semiconductors. Their intrinsic conductivity in dark conditions is significantly low, and a narrow channel is required to measure current-voltage (IV) characteristics of the material with a generally available voltage supply or a source measure unit. However, obtaining a single crystalline device with a narrow channel is challenging due to the single crystal growth mechanism and the nature of the perovskite crystals itself. Unlike common inorganic semiconductor single crystals, hybrid halide perovskite single crystals are fragile and sensitive to many external environmental factors such as moisture in the air. In fact, major focus of this thesis is to introduce a device which can be independent from such external factors, so that electrical characterization can be performed on a pristine perovskite channel.

Even with a single crystalline perovskite device, the current–voltage characteristics could be difficult to document, since the behavior could be erratically arbitrary at times. Hybrid halide perovskites have a significant ionic conductivity, even in single crystals. If an I-V sweep is repeated under the same conditions, the characteristics may differ from one measurement to another due to the memory effects manifested by slow moving ionic species. Further, the set-reset resistive switching behavior could result in sudden peaks in the IV sweep, which complicates the measurement. Transients and shift of polarity in IV sweep also have significant effects on measurements.

Figure 3-13 Variation of IV Sweep in dark conditions with different scan speeds at room temperature

Most of the complications are thought to be originated from the defects of the crystal and its electrode interfaces. However, these effects persist even with the pristine device, confirming the effects are intrinsic. To further minimize these effects, immobilizing the ions by lowering the temperature is considered. Also, to characterize with minimum variations due to memory effects, the IV scans are conducted in a single polarity.

Cooling down the sample while applying a bias voltage is expected to form frozen junction conditions by reducing the ionic mobility, which could provide favorable conditions for electroluminescence. To maintain low temperature conditions, the sample is placed in a cryo-chamber under vacuum conditions to ensure less heat dissipation from environment. A closed loop liquid helium cryo-system is used to continuously remove the heat from the cold finger of the system. The temperature of

the sample holder is maintained using a heating element attached to a PID controller.

Collecting the IV data at low temperatures was primarily done using a Kiethley 2400 source measure unit controlled via a LabVIEW utility. This method was used to record the data for IV sweeps. However, it was noticed that the samples could show extremely slow evolution of current with time at constant voltage, which needed to be probed in depth. For this task, similar setup could be used with a different LabVIEW Utility. While maintaining a constant voltage bias, the current through the sample is recorded at every 5 seconds.

Additional measurements could be done using a function generator, a preamp device for current measurement and an oscilloscope to study the impedance behavior of the sample. With this setup, low frequency modulation behavior can be measured, and impedance spectrum of the sample can be derived.

The specific current-voltage characteristics of the samples presented in Chapter 5 were measured using the following procedure:

The gold wires, encapsulated by the perovskite crystal, were carefully soldered to a pair of sturdier wires, and silicone sealant was used to mechanically strengthen the connection. Subsequently, the sample was mounted in the cryo-chamber using silver paste at the back of the silicon wafer to ensure good thermal contact. Current-voltage (IV) curves were measured with Keithley 2400 source measurement unit. In a separate experiment to record the temperature dependence of current oscillations, the current through the sample is captured in Femto DLPCA 200 and observed in oscilloscopes rolling mode screen. The sample temperature was changed while fixing a constant bias of 6 V, and the current has been captured at temperature interval of 10 K and saved to the computer.

3.4.2 Electroluminescence characteristics

Electroluminescence is reported from the perovskite devices even at room temperature, with specially designed hole and electron injection mechanisms. However, the symmetric device does not possess an optimized carrier injection structure for electroluminescence. But, electroluminescence from a symmetric perovskite device is possible under a frozen junction conditions, where the device is cooled down with an applied bias. The device is usually installed in a cryochamber with external connections to the electrical contacts, and the emission must be collected externally from the quartz window of the cryostat.

For the collection of electroluminescence spectra, the emission is imaged into a fiber coupled photoluminescence spectrometer Ocean Optics HR4000. First, a free space setup is configured to capture the photoluminescence from the sample which is inside the cryochamber, using the 405nm laser as the excitation source. The free space setup consists of two convex lenses to focus the emission at the tip of the large diameter multi-mode fiber. A 450 nm long pass filter is also placed near the fiber to remove the reflected/scattered laser excitation light, when the photoluminescence is measured. The fiber is mounted on a three-axis micromanipulator, so that the captured emission peak can be optimized until the maximum emission peak intensity is achieved at the focal point of the lenses. Since the emission is captured in free space setup, the entire room is kept dark when the experiment is conducted. Once the optimum photoluminescence peak is achieved, the laser excitation is switched off and the electrical supply is used to obtain the electroluminescence.

Figure 3-14 Setup for electroluminescence spectroscopy

For electroluminescence and all the other experiments under the cryogenic conditions, it is essential to mount a systematically prepared sample in the cryostat cold finger, ensuring the maximum thermal conductivity and the proper electrical contacts. To ensure the thermal conductivity between the wire-embedded single crystal and the cold finger, a silicon wafer is used to mount the crystal. The silicon wafer substrate is then pasted on the sample holder with Silver paste to enhance the thermal conductivity and clamped tight as necessary.

The electrical contacts to the thin gold wire electrodes are soldered to two circuit wires before installing the sample in the chamber so that they can be handed easily to establish the electrical connection. The pre-installed sockets in the chamber are used as electrical connections from inside of the cryochamber to the external source measure unit.

Figure 3-15 Sample mounted in a cryochamber, and its electroluminescence image

To ensure the sample is ready for cooling down and for electroluminescence measurements, a simple photoconductivity test can be performed just after the sample is installed. The IV curve is measured under a bright white light, as well as under dark conditions, whereas the difference between two curves is attributed to the photo-generated carriers within the single crystal. The photocurrent is higher than the dark current only in one order of magnitude or less, due to the narrow channel buried deep inside the crystal, where only limited number of photoexcited carriers can reach. However, this is not a concern for the experiment as far as the contrast between dark and illuminated photocurrent can be decisively identified, so that it is possible to affirm all the electrical connections are good and the measured characteristics are indeed from the perovskite channel as expected.

The electroluminescence images also obtained by mounting a long working distance microscope with a camera, so that a magnified view of the crystal and even the electrodes, is achieved. A Thorlabs CMOS DCC1645C camera with an Olympus SZ1145 microscope was used in this setup. However, when the vacuum pump and cryostat introduce certain vibrations to the system, some blurring to the image occurs. However, the imaging experiment and the spectrum measurement with the cryostat

cannot be operated simultaneously at the current setup; one of the disadvantages due to need for realignment for each measurement.

The exact procedure for recording electroluminescence from the samples presented in Chapter 5 is given below:

The MSM device was installed in a cryo-vacuum chamber, then pumped to a vacuum below 1 mTorr. While a bias of 6 V was continuously applied, the device was cooled down to 160 K. The device was operated only at the preconditioned polarity, to minimize the resetting of ion accumulation. The emission was coupled to a multimode fiber through two convex lenses and captured using an Ocean Optics USB HR4000 UV-Vis spectroscope. For electroluminescence (EL) imaging, Thorlabs CMOS DCC1645C camera with SZ11 microscope was used. For the light-current versus voltage (LIV) behavior, the light response was obtained by a photomultiplier tube (PMT) biased at -1100 V. The EL signal from the PMT and the current signal captured through Femto DLPCA 200 current voltage trans-impedance amplifier was traced using a HP54615B oscilloscope.

3.4.3 Light – current – voltage (LIV) characteristics

To obtain a good electroluminescence spectrum, the measurement should be done with at least 500 ms integration time to gain significant SNR due to relatively dim signal and the present of noise floor (spectrometer signal at the dark conditions). This setup is not suitable for transient behaviour detection, such light – current – voltage trace. For the LIV measurements, highly sensitive and responsive light detector is necessary. For this task, the ideal detector is the photomultiplier tube (PMT) which has super-high gain. Maximizing the collection efficiency and reducing the stray light is critical to obtain a good performance with the PMT. The Olympus SZ1145 is used to focus the

emission to the PMT and complete isolation from the external stray light is ensured by thorough encapsulation with dark tape.

The PMT is supplied with high voltage supply up to -1200V which determines the PMT gain. The signal is captured with an oscilloscope. The intensity of the emission is converted to a voltage, and the emission from the sample can be recorded in the oscilloscope rolling mode during an I-V sweep. The I-V sweep is conducted with a Kiethley 2400 SMU controlled using a LabVIEW utility, and the PMT output is synchronized with the I-V sweep manually with timestamps to obtain the LIV data.

Alternative to the constant and sweep DC supply experiments, few experiments have been conducted to assess the performance of modulation under a pulsed voltage source. A function generator was used to apply a signal modulated at a specific frequency. However, these experiments were successful only at significantly low frequencies. The current through the sample is captured using a current to voltage trans-impedance pre-amplifier in this case. Both the current signal and PMT output were captured using the oscilloscope.

3.5 References

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Chapter 4 Solution grown double heterostructure on a large hybrid halide perovskite crystal

4.1 Abstract

Heterostructure plays a crucial role in current optoelectronic applications. Realizing the heterostructure in a recently exciting semiconductor material: hybrid halide perovskite crystals, has been a long-sought goal in the field. Here, we demonstrate modulation-doped layer growth on large hybrid halide perovskite crystals. We show that the well-known problem of halide ion interdiffusion can be controlled by (1) using low halide composition gradient and (2) adjusting solution concentrations just above the critical supersaturation, in the solvothermal liquid-phase growth process. In comparison to a few seconds dipping time previously reported for the ion-exchange processes, our layer growth time could be conveniently extended up to 80 minutes to grow a uniform and controllable layer, with a very thin inter-diffusion region. The growth of the $\text{CH}_3\text{NH}_3\text{PbBr}_3$ layer on top of the $\text{CH}_3\text{NH}_3\text{Pb}(\text{Br}_{0.85}\text{Cl}_{0.15})_3$ bulk substrate is studied for different growth times to obtain up to a 30 μm layer thickness. The ion diffusion profile and layer thickness are verified, respectively, by cross-sectional characterization using scanning electron microscopy, energy dispersive spectroscopy. Electron backscattering diffraction suggests a similar crystallographic orientation for both substrate and grown layers. Our diffusion model illustrates the halide ion concentration at the interface, correlating with the EDS mapping results. Optical imaging and photoluminescence characterization confirm the quality and bandgap of the grown layers. Especially, the growth process is further extended for two consecutive layers to create a double heterostructure for the first time with a large

perovskite crystal. Our low-cost process could pave the way for many optoelectronic applications such as color tunable light emitting diodes or photodetectors developed with perovskite crystals.

4.2 Introduction

Abrupt heterostructures or even multiple quantum-well structures are widely used in various opto-electronic devices such as light emitting diodes (LEDs), photo-diodes and lasers [1-5]. But, realizing abrupt interfaces in perovskites is difficult due to halide-ion inter-diffusion, with little understanding of the underlying physical mechanism [6]. Yet, a graded bandgap material with a quasielectric field or carrier funnels could also be useful, and has been realized with perovskites [7-11]. Techniques to grow perovskite heterostructures are essential for future perovskite based devices, but currently limited due to halide ion diffusion[12, 13] Fabricating hybrid halide perovskite crystals has been relatively easier compared to other semiconductor materials because of recently discovered low cost solvothermal crystal growth processes [14-17]. In this method, the solubility of perovskite in a selected solvent reduces with increasing temperature, allowing the supersaturated perovskite to precipitate as a crystal. This technology has been used to rapidly grow high quality crystals, but the possibility of growing compositionally varying layers has not been sufficiently explored. Growing a layer of different bandgap (i.e. different halide composition) material on a perovskite substrate could be possible in various methods such as ion exchange in solution or a chemical vapor deposition system[18-22]. The prospect of a low-cost solution fabrication process is desirable, whilst preserving the crystallinity throughout structures is also important to reach the maximum device performance.

In this work, we assess the liquid phase growth technique [18, 19] as a low-cost alternative to grow layers on perovskite substrates. In previously reported attempts to place perovskite crystals in contact with a growth solution of a different halide composition, halide ion inter-diffusion has been identified as the dominant mechanism, hindering the expected continuous growth process [9, 20, 21]. This approach could make a heterostructure, but the quality is low and could not be controlled since it is primarily assisted by crystal defects [23, 24]. A typical diffusion model could attest to the idea that the diffusion process is driven by a large halide composition gradient between the substrate and layer growth solution. Yet, the extent of the contribution of the co-existing continued growth process in the heterojunction formation whilst diffusion occurs is still unclear. In this context, it is essential to gain control over the diffusion process, making the growth process dominant and establishing a controlled growth rate. Based on the diffusion model and considering the crystalline nature of the material, minimizing interface defects and maintaining reduced halide composition gradient can be identified as a straightforward approach to support both requirements. The halide composition gradient should be selected according to the desired bandgap difference between the two materials (ΔE_g). Higher ΔE_g is usually desired, but it is associated with a higher lattice mismatch which results in higher interfacial defect densities [25]. To cater these concerns in our proof of concept heterostructure, we carefully chose the halide compositions for the substrate and layer, so that the halide composition gradient at the interface was kept at a balanced level to ensure both acceptable lattice mismatch and enough ΔE_g for an effective heterostructure at room temperature. We show that a dominant continued growth process could be attained while suppressing the diffusion process and in fact yielded a better quality $\text{CH}_3\text{NH}_3\text{PbBr}_3$ layer on top of the $\text{CH}_3\text{NH}_3\text{Pb}(\text{Br}_{0.85}\text{Cl}_{0.15})_3$

substrate.

4.3 Sample preparation method

For substrate growth, PbBr_2 , $\text{CH}_3\text{NH}_3\text{Br}$ and $\text{CH}_3\text{NH}_3\text{Cl}$ (Sigma Aldrich) were mixed in $1 : 1 - y : y$ molar ratio to obtain overall Br : Cl as $3 - y : y$ and dissolved completely in N,N dimethylformamide (DMF) with rigorous stirring at room temperature to prepare a 1.0 M solution of $\text{CH}_3\text{NH}_3\text{PbBr}_{3-y}\text{Cl}_y$ ($y = 0.25$) [14]. Note that the solution composition is different from the resulting crystal composition due to an imbalance in the solubility of the halides, and we used a pre-established recipe to obtain the desired crystal composition. Once the precipitates were completely dissolved, the solution was filtered through a 0.2 μm PTFE filter and distributed in to several vials; a few millilitres each. Then, the solution was heated up to 75 °C in an oil bath and left undisturbed for several hours for crystals to grow. Several suitable crystals were selected as substrates for layer growth. For other halide compositions, formulae are summarized in Table 4-1.

For layer growth, PbBr_2 and $\text{CH}_3\text{NH}_3\text{Br}$ (Sigma Aldrich) were mixed in a 1 : 1 molar ratio and dissolved in N,N dimethylformamide (DMF) to prepare a 1.0 M stock solution of $\text{CH}_3\text{NH}_3\text{PbBr}_3$, which was diluted to 0.65 M concentration (or 0.5 M, 0.6 M, 0.7 M) as necessary. 5 ml of the solution at a selected concentration was heated up to 75 °C in an oil bath. Several sufficiently large crystals (as substrates) were taken directly from the first (substrate growth) solution, rinsed with heated γ -butyrolactone (GBA), and transferred to the layer growth solution. After certain time intervals, crystals were extracted one by one, rinsed in heated GBA, and dried on a hot plate top at the same temperature.

4.4 Results and discussion

4.4.1 Material selection

Figure 4-1 Perovskite crystals and proposed layer growth process. (a) Photograph of $\sim 3 \times 3 \times 2\text{--}5 \times 5 \times 3\text{mm}^3$ sized Cl–Br mixed halide perovskite crystals ($\text{CH}_3\text{NH}_3\text{Pb}(\text{Br}_{1-x}\text{Cl}_x)_3$) grown using the solvothermal method. (b) Photoluminescence (PL) spectra and (c) powder x-ray diffraction (PXRD) pattern. (d) Proposed perovskite heterostructure, and (e) the liquid phase growth process is given on the right side.

The bandgap of perovskites is determined by the halide composition, which is related to the lattice constant of the crystalline structure [4, 26]. The bandgap can be engineered throughout the entire visible spectrum only by adjusting the precursor

halide composition. Figure 4-1a shows a few millimeter-sized perovskite crystals with different halide compositions grown by the solvothermal method, as explained in the Methods section, and Table 4-1. The band gap of these crystals can be derived from the photoluminescence (PL) spectra Figure 4-1b,c or absorbance spectra (Figure 4-2).

Figure 4-2 Normalized absorbance spectra of crystals grown from the solutions with different halide compositions, gathered using transmission mode uv-vis spectroscopy. Thickness of the crystal is in few millimetres; hence the transmission quickly becomes undetectable for photons with energy just higher than band gap (shorter wavelength).

Table 4-1 The relationship between the composition of growth solution and crystal. Solution composition were adopted from Zhang et. al,[14]. Note that the crystal composition change from the solution composition due to differences in solubility.

Crystal Composition	Reaction	Cl/(Cl+Br)% in solution	Solvent	~Temperature (with 1mol dm ⁻³ solution)
CH ₃ NH ₃ PbBr ₃	PbBr ₂ + CH ₃ NH ₃ Br	0%	DMF	80°C
CH ₃ NH ₃ Pb(Br _{0.85} Cl _{0.15}) ₃	PbBr ₂ + 0.75 CH ₃ NH ₃ Br + 0.25 CH ₃ NH ₃ Cl	8.3%	DMF	75°C
CH ₃ NH ₃ Pb(Br _{0.75} Cl _{0.25}) ₃	PbBr ₂ + 0.50 CH ₃ NH ₃ Br + 0.50 CH ₃ NH ₃ Cl	16.7%	DMF	65°C
CH ₃ NH ₃ PbCl ₃	PbCl ₂ + CH ₃ NH ₃ Cl	100%	DMF:DMSO 1:1 by vol	50°C

Figure 4-3 High resolution x-ray diffraction data for powdered mixed halide perovskite crystals.

We determine the elemental composition using the Vegard's law, based on the lattice constants calculated from the second order (200) peak positions of PXRD spectrum. Vegard's law is an empirical rule, which assumes a linear relation between the composition ratio of a binary alloy and ratio between the difference of lattice constants. If x is the Cl composition (i.e. CH₃NH₃Pb(Br_{1-x}Cl_x)₃), and we have experimental value for the lattice constant a_x , x can be estimated using the formula $x = (a_{Br} - a_x) / (a_{Br} - a_{Cl})$, given in Table 4-2.

Table 4-2 The estimation of single crystal compositions based on lattice constants.

Solution Composition	2 nd Order angle 2 θ (Degree)	Lattice Constant ($\text{\AA}$)	Estimated Cl/(Cl+Br) ratio	Expected Cl/(Cl+Br) ratio	Crystal Composition
$\text{CH}_3\text{NH}_3\text{PbBr}_3$	30.11(3)	5.93(1)	0%	0%	$\text{CH}_3\text{NH}_3\text{PbBr}_3$
$\text{CH}_3\text{NH}_3\text{PbBr}_{2.75}\text{Cl}_{0.25}$	30.25(4)	5.90(2)	13(3)%	15%	$\text{CH}_3\text{NH}_3\text{Pb}(\text{Br}_{0.85}\text{Cl}_{0.15})_3$
$\text{CH}_3\text{NH}_3\text{PbBr}_{2.50}\text{Cl}_{0.50}$	30.41(4)	5.87(2)	25(3)%	25%	$\text{CH}_3\text{NH}_3\text{Pb}(\text{Br}_{0.75}\text{Cl}_{0.25})_3$
$\text{CH}_3\text{NH}_3\text{PbCl}_3$	31.43(4)	5.69(2)	100%	100%	$\text{CH}_3\text{NH}_3\text{PbCl}_3$

Lattice constants for $\text{CH}_3\text{NH}_3\text{PbBr}_3$, $\text{CH}_3\text{NH}_3\text{Pb}(\text{Br}_{0.85}\text{Cl}_{0.15})_3$, $\text{CH}_3\text{NH}_3\text{Pb}(\text{Br}_{0.75}\text{Cl}_{0.25})_3$ and $\text{CH}_3\text{NH}_3\text{PbCl}_3$ were calculated based on the PXRD data in Figure 4-3 and were; 5.93(1), 5.90(2), 5.87(2) and 5.69(2) $\text{\AA}$, respectively. The data agreed with previously reported values by other groups [4, 14]. The composition of the mixed halide perovskite crystals can be empirically estimated according to Vegard's law (see Table 4-2). However, it is noteworthy that the composition of the mixed halide perovskite crystals could deviate from the composition in the growth solution due to differences in solubility. In our heterostructure growth experiments, we selected two compositions $\text{CH}_3\text{NH}_3\text{Pb}(\text{Br}_{0.85}\text{Cl}_{0.15})_3$ and $\text{CH}_3\text{NH}_3\text{PbBr}_3$ for the substrate and layer, respectively. They have cubic lattice structures with the same crystallographic phase and space group $\text{Pm}\bar{3}\text{m}$ [14] at room temperature and atmospheric pressure. Furthermore, a small lattice mismatch $\sim 2.5\%$, with a significant $\Delta E_g \sim 88 \text{ meV}$ ($\Delta\lambda \approx 20$) bandgap difference at room temperature is desirable to ensure the misfit dislocation density is kept to a minimum. In addition, the bandgap difference ΔE_g is more than three times the thermal energy at room temperature (kT) which is acceptable for heterostructure features in opto-electronic applications[8].

4.4.2 Heterostructure growth process

Here, we propose to extend the existing large crystal growth method for the purpose of layer growth. A perovskite crystal substrate (seed) placed in a supersaturated solution will continue to grow, precipitating the excess solute as a layer [14]. Even when the solution composition is changed, this process could continue unless the resulting lattice structure is severely incompatible with the substrate. However at the same time, halide-ions will inter-diffuse along the composition gradient, which is a known behavior for perovskites. Nevertheless, the growth process could dominate given the optimum composition gradient to limit the inter-diffusion process. The complete layer growth procedure is depicted in Fig. 1e and explained in the Methods section. The layer growth process is designed and fine-tuned carefully to alleviate the drawbacks of similar procedures used previously [20, 21]. Since the ion diffusion is driven by composition gradient, less diffusion is expected in the selected material combination [27]. Also, to gain control over the rate of the dominant growth process, parameters such as growth temperature, concentration and growth time have been probed from knowledge of liquid phase epitaxy in other material systems found in the literature [18]. To obtain a uniformly thick layer covering the entire substrate surface, control of both the growth mode and growth rate is crucial. Layer-by layer or step mode/Frank–van der Merwe (FM) growth is possible in liquid phase growth conditions by maintaining the lowest supersaturation in growth solution [18, 27]. In turn, the layer thickness can be controlled and determined by carefully controlling the process parameters. Note, both the concentration and growth temperature contribute to determining the growth mode and growth rate. Here, we used the solution concentration to control the supersaturation condition while fixing the growth temperature. For the temperature selection at 75 °C, we performed preliminary tests to

see if we could grow all the $\text{CH}_3\text{NH}_3\text{PbX}_3$ ($\text{X} = \text{Br}, \text{Cl}, \text{ and mix}$) crystals with different temperatures from 55 to 85 °C. In the case of the $\text{CH}_3\text{NH}_3\text{PbBr}_3$ layer growth on top of the $\text{CH}_3\text{NH}_3(\text{PbBr}_{0.85}\text{Cl}_{0.15})_3$ substrate, the layer can grow evenly at 75 °C without undesired nucleation as this secondary process may occur at higher temperatures.

Figure 4-4 PL spectra with different layer growth times, at various concentrations. (a) 0.5 M, (b) 0.6 M and (c) 0.7 M (d) 0.65 M at 75 °C. The peak position shifts from the high energy of substrate emission to the pure $\text{CH}_3\text{NH}_3\text{PbBr}_3$ emission (lower energy) when the growth time increases. (e) Sketch of the retrograde solubility curve of perovskites for crystallization upon heating, with the working temperature and concentration. We used (d) 0.65 M as the reference for our further growth process, as it is the optimal concentration.

A qualitative idea about the growth rate at different concentrations can be obtained by observing the photoluminescence (PL) spectra at different growth time intervals

(Figure 4-4a–c)[27]. At each concentration considered in Figure 4-4a–c, 0.5 M, 0.6 M and 0.7 M, the PL spectrum shows a shift from substrate emission spectrum to layer material emission spectrum, with increasing growth time. This change in rate of the PL peak shift can be understood using the solubility behavior of the crystallization process as presented in Figure 4-4e, which is sketched for illustrative purposes [4]. When the concentration is above the solubility curve (i.e. highly supersaturated), the growth rate is higher. Hence, the peak shift is more prominent when the concentration is high, implying a thicker layer or higher growth rate. Contrary to this condition, at low concentration as represented by the 0.5 M concentration, the layer growth may not be optimized significantly. This is especially so when the concentration critically reaches the solubility curve. The growth process can be disturbed by two other processes; namely dissolving and inter-diffusion/recrystallization [28].

Another explanation for the un-optimized layer growth process at low concentration can be due to temperature fluctuations caused by the hotplate PID control or environmental conditions. The temperature fluctuation problem has a severe effect for low concentrations around the solubility curve (Figure 4-4e). In any case, the low-concentration layer-growth process is not recommended for growing the layer. One of the indicators for the un-optimized layer growth process can be seen in the PL shift anomaly for a 3 min-growth sample of 0.5 M. The PL spectrum of this sample is apparently shifted to the lowest energy contrary to those of the 5 and 7 min growth samples. However, the trend for 1, 5, and 7 min growth samples still follows that for the higher concentrations. The data was used to identify a controlled, slow rate of growth over a longer time span. We have selected 0.65 M at 75 °C as a reasonable concentration to prepare our samples (Figure 4-4d), given the extended growth time span and easily observable change in PL spectra with growth time.

The PL spectrum from the samples with a layer growth time of 20 minutes almost resembles that of $\text{CH}_3\text{NH}_3\text{PbBr}_3$. The layer thickness is presumably large enough so that emission from the $\text{CH}_3\text{NH}_3\text{Pb}(\text{Br}_{0.85}\text{Cl}_{0.15})_3$ substrate is almost negligible. The PL spectrum of the sample consists of the emission components from the substrate, layered material and also from interface defects or inter-diffused regions. The PL was measured with front excitation and collection. The excitation beam is attenuated significantly when reaching the substrate, because of the large absorption coefficient (at excitation wavelength) of the thick $\text{CH}_3\text{NH}_3\text{PbBr}_3$ layer [29, 30]. The emission from the substrate and interface is also re-absorbed by the low band gap layer before being captured by our PL measurement system. With 20 minutes of growing time, the $\text{CH}_3\text{NH}_3\text{PbBr}_3$ layer is thick enough to eliminate all the PL contribution from the substrate and interface. The growth can be continued further, and direct measurement of layer thickness is described later. After the growing procedure, the surface quality can be verified by an optical imaging technique (Figure 4-5).

Figure 4-5 Surface of the crystals. At (a) 0 min (b) 5 min (c) 10 min (d) 20 min

growth time in 0.65M $\text{CH}_3\text{NH}_3\text{PbBr}_3$ solution at 75°C

Since we use as-grown crystal as a substrate without any polishing or lapping, it is important to keep the surface clean. Solvent residues, secondary nucleations or other polycrystalline precipitates, which might remain after extracting the substrate from the growth solution, could have adverse effects on the layer quality. To ensure the surface quality, the substrate is immediately rinsed after extraction, as per the details given in the Methods section. The image of the crystal surface is shown in the Figure 4-6, which shows a good surface quality after rinsing.

Figure 4-6 Effect of rinsing. Crystal surface unrinsed (a) and rinsed (b). Rinsing is important to avoid secondary seed formation and mixing growth solution after extraction.

4.4.3 Layer thickness characterization

The growth rate could be within a few tens of nanometers per second, considering the fast PL peak transition and the absorbance depth which are in the same order [31]. Hence, we expanded the growth time to obtain a better estimation of the growth rate by the cross-section imaging technique.

Figure 4-7 Cross-section image of a substrate-layer sample with EDS elemental mapping data. (a) SEM image of cross section with a layer of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ on a crystal of mixed halide $\text{CH}_3\text{NH}_3\text{Pb}(\text{Br}_{0.85}\text{Cl}_{0.15})_3$. Layer and substrate areas are indicated, respectively. The left side is the surface side edge of the cross section. A few features from imperfect cleaving of the cross section are also visible in the SEM image. Elemental maps for (b) chlorine and (c) bromine within the selected region (pink rectangle). The gradient in the chlorine map can be clearly identified. (d) Presents the concentration in the element map integrated along the surface (dots) and diffusion equation fitting (lines). Black and red colors correspond to chlorine and

bromine, respectively. Samples for different growth times are given in Figure 4-12

We should note here that the solution for layer growth is sufficient to grow a large crystal of a few mm size as a substrate. Therefore, given an excess volume of the solution, the growth rate should be constant over the growth of a few tens of micrometers on the substrate surface. Samples with a thicker layer have been prepared using up to an 80-minute growth time, and observed using cross-sectional images as presented in Figure 4-7a. The interface between the substrate and layer can be recognized in cross-section SEM images.

Figure 4-8 Thickness of the $\text{CH}_3\text{NH}_3\text{PbBr}_3$ layer with growth time.

In many regions, the substrate and layer are indistinguishable in the SEM image due to a seamless growth process. Figure 4-8 presents the layer thickness as a linear function of the growing time, where we can deduce a growth rate of $\sim 500 \text{ nm min}^{-1}$ or 8.3 nm

s^{-1} which is within the expected range.

Figure 4-9 Stitched optical image of a sample cross section with 20 min layer growth.

Figure 4-10 Comparison between EDS spectra from selected layer and seed regions of cross section from 20 min sample. Difference between Br and Cl. Corresponding SEM image is inset. Processing option: All elements analyzed. All results in atomic percentage

This uniform layer is also verified by cross-sectional optical images within the few millimeters range (see Figure 4-9). Along with the SEM images, an energy dispersive x-ray spectroscopy (EDS) elemental x-ray map of Cl and Br across the interface was collected (Figure 4-7b,c). Despite the low concentration gradient, the material interface is clearly identified by the contrast in the EDS elemental map for chlorine

(Figure 4-7b). Unlike the chlorine element contrast in these 2 regions (~15% vs. 0%), the bromine elemental map contrast is not significant (Figure 4-7c) since the bromine concentration is relatively high in both regions (~85% vs. 100%). EDS quantitative analysis was performed to show the contrast of composition between the two regions, given in Table 4-3

Table 4-3 Comparison of elemental composition of layer and seed regions of 20 min grown sample taken from the EDS elemental mapping quantitative analysis.

Spectrum	In stats.	C	N	Cl	Br	Pb
Layer	Yes	32.83	17.57	1.07	36.94	11.60
Substrate	Yes	29.51	21.48	4.15	33.57	11.29

Despite the low composition gradient of the material and the noise of the signal, the elemental line-profile shows a clear separation between the two layers. These data can be used to fit a mathematical solution for the diffusion process. For simplicity, we assume a sharp interface between the substrate and freshly grown layer initially; then the diffusion process occurs. Further, we assume the Cl and Br ions behave independently. Nevertheless, we acknowledge that the actual process is more complicated due to bi-directional inter-diffusion and diffusion during growth. The integrated EDS data line profile can now be fitted with Grube's solution for Fick's second law (Equation 4-1 and Equation 4-2) in order to find out the interface's position [32].

Figure 4-11 Cross-section optical imaging and the relationship among crystallographic orientations of the layers. Optical image of a cross section of a single layer sample with episcopic illumination (a) and diascope illumination (b). Optical image of an embedded layer of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ within the substrate and a capping layer of $\text{CH}_3\text{NH}_3\text{Pb}(\text{Br}_{0.85}\text{Cl}_{0.15})_3$ with episcopic (c) and diascope (d) illumination. (e) SEM image of a section of a similar embedded layer with EBSD indexed regions from substrate, layer and capping. The orientations determined by indexing EBSD patterns are plotted in the pole figures in (f), where all the data points overlap. The pole figure is from the upper hemisphere with an equal area projection for the perovskite ($m\bar{3}m$) phase. (g) The Euler angle representation of the orientation data, with respect to the SEM image reference, and (h) a representative EBSD pattern.

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad \text{Equation 4-1}$$

Initial Conditions

$$C(x, 0) = C_1 \quad x < 0$$

$$C(x, 0) = C_2 \quad x > 0$$

Boundary Conditions

$$C(-\infty, t) = C_1$$

$$C(\infty, t) = C_2$$

If the interface between two layers is at $x = 0$, the solution:

$$C(x, t) = C_s + C_i * \operatorname{erf} \left(\frac{x}{l_d} \right) \quad \text{Equation 4-2}$$

C is the concentration (Br or Cl) along the x direction across the interface, and the parameter a is the position of the interface and l_d is the diffusion length. $C_s = (C_1 + C_2)/2$ is the concentration (counts) at the surface and $C_i = (C_2 - C_s)$ is the concentration at the interface. $\operatorname{erf}(y) = \frac{2}{\pi} \int_0^y e^{-y^2} dy$, is the error function. The fitting results for the 80-minute sample are shown in Figure 4-7d where the Cl and Br concentration changes smoothly across the interface. For different growth times, please see Figure 4-12. The position of the median composition is the interface of the heterostructure which is consistent with the physical position identified in the corresponding SEM image (Figure 4-12). The results confirm the actual growth process of the low bandgap material $\text{CH}_3\text{NH}_3\text{PbBr}_3$ on top of the $\text{CH}_3\text{NH}_3\text{Pb}(\text{Br}_{0.85}\text{Cl}_{0.15})_3$ substrate as opposed to the ion exchange process recently reported [20]. The diffusion process is clearly limited to a few micrometers near the interface region, resulting in the expected heterostructure. We note that to make a heterostructure with a sharper interface, we would need an even better control of the growth and diffusion process.

A major advantage of limiting the halide ion diffusion region, allows the technique to grow multi layers as well. To demonstrate this possibility, we prepared a sample with an extra capping layer from the same material as the substrate, to create a double heterostructure.

Figure 4-12 SEM image and elemental mapping of the cross section of heterostructure with different growth time intervals from 5 min to 80 min (extended Figure 4-7). Layer growth solution concentration is 0.65 M and temperature maintained at 75 °C.

As an alternative to SEM, the cross section can be examined by an optical tool as well. Figure 4-11a is an optical microscope image of a cross-section of a sample with a smoother cleaved surface, and the differences in growth can be clearly observed under diascopic illumination conditions (Figure 4-11b) due to the transmission of white light through two materials with different bandgaps. Figure 4-11c and d are taken from a cleaved surface of a sample with a capping layer, and the difference in color is evident.

We then investigated the lattice relationship among multiple layers by using the electron back-scatter diffraction (EBSD) technique. This technique can analyze the diffraction pattern of electrons backscattered from a crystalline sample surface placed under a SEM electron beam, (known as Kikuchi pattern) to establish its crystallographic phase and orientation information. By scanning through various positions of the surface, it can be used to specify any grain boundaries, twinned crystals or any orientation distortions across a crystalline surface [33-35]. The complete procedure is explained in the Methods section. Figure 4-11e shows the SEM image of a double heterostructure sample cross section with an embedded layer of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ on the (100) plane of the substrate and a capping layer of $\text{CH}_3\text{NH}_3\text{Pb}(\text{Br}_{0.85}\text{Cl}_{0.15})_3$, which we selected to perform an EBSD analysis. The EBSD pattern could be clearly observed from the sample (Figure 4-13) at any random position, confirming the roughness of the cleaved surface is sufficiently low, which is crucial to the study. While collecting the EBSD pattern from each position at the surface by scanning the sample cross section surface in a grid, the software procedure was able to automatically index the pattern at a significant number of points. These indexed points are in all three regions: substrate, embedded layer and capping layer.

Figure 4-13 Indexed EBSD pattern. Pattern center is marked with the blue cross. The direct lattice indices (lattice vectors) of the zone axes are given at the high symmetry points

Indexing the EBSD pattern provides the orientation and the crystallographic phase, where the phase is the same throughout the sample in our case. The resulting indexing data are best represented in an inverse pole figure, which maps the orientation indexed at each position of the surface. The poles are color coded based on the position, whether they are from the substrate, layer or capping layer. All the indexed points overlapped clearly at the Euler angles $172(1)^\circ$, $359(3)^\circ$, $246(3)^\circ$ (i.e. within 3° deviation) in the pole figure representation given in Figure 4-11f. The orientation of the three crystallographic plane surface normal vector projections agreed well with the physical layer and surface orientation observed via the SEM image. Hence, the EBSD

study provides definitive evidence of similar crystal orientation among the three layers.

4.4.4 Carrier dynamics and optoelectronic quality

Figure 4-14 Photoluminescence decay. (a,b) from crystal substrates and (c,d) layers at short wavelengths (peak wavelengths - 7.5 nm) and long wavelengths (peak wavelengths + 7.5 nm). Peak wavelengths are described in Table S4. The solid lines are the double exponential fits. The fits for CH₃NH₃PbBr₃ crystals are shown in (c) and (d) as comparison with the grown layers.

To further examine the interface and grown material quality, we characterized the time resolved photoluminescence at different growth thicknesses as presented in Figure 4-14 and Table 4-4[16, 17, 25] It has been observed that the contribution of interface defects in PL signals is significant especially for thin-layer samples.

Table 4-4 Lifetime determined from the decay curves by fitting two exponential decay functions. The contribution has been calculated as the area under decay curve, for each component.

	Peak Wavelength (nm)	Lifetime at Short Wavelength (i.e. Peak -7.5 nm) (ns)		Lifetime at Long Wavelength (i.e. Peak +7.5 nm) (ns)	
		Fast	Slow	Fast	Slow
MAPbCl ₃	405	0.7±0.1 (15%)	9.8±0.7 (85%)	0.7±0.1 (14%)	10.4±0.2 (86%)
MAPb(Br _{0.85} Cl _{0.15}) ₃	519	1.1±0.1 (7%)	39.4±3.1 (93%)	1.0±0.1 (6%)	44.0±2.9 (94%)
MAPb(Br _{0.85} Cl _{0.15}) ₃ / 10 min MAPbBr ₃	524	2.0±0.1 (26%)	11.3±0.4 (74%)	0.9±0.1 (23%)	15.1±0.3 (77%)
MAPb(Br _{0.85} Cl _{0.15}) ₃ / 20 min MAPbBr ₃	539	1.9±0.1 (18%)	16.4±0.5 (82%)	1.4±0.1 (9%)	23.0±0.6 (91%)
MAPbBr ₃	539	1.5±0.1 (2%)	33.5±0.6 (98%)	1.4±0.2 (1%)	34.7±0.7 (99%)

These defects are not involved in the PL for thick-layer samples because of the limited excitation depth. These localized recombination centers can be due to the surface defects of the substrate before layer growth or carrier flows caused by graded bandgap carrier funnels as a result of halide interdiffusion regions [36-40].

Studying carrier dynamics of the thin layer is helpful in understanding its optoelectronic quality [25]. As an example, time resolved photoluminescence is one of the methods to identify various recombination processes, such as intrinsic radiative recombination or various recombination mechanisms at defect states associated with the bulk or surface of the layer [16, 17]. It is well known for perovskites to have different lifetime properties from bulk and surface regions [36-39]. In some cases, the energy bandgap difference between different origins can be low, and the PL spectra can overlap each other by their broadband characteristics. However, the origins still

can be characterized through TRPL as they may have different lifetimes.

Here we took two TRPL decay measurements filtered at two well separated wavelengths, namely short and long wavelengths with 10 nm resolution (see Methods section). We define the short and the long wavelengths as the peak wavelength minus and plus 7.5 nm, respectively. Before we measure heterostructures, we first measure the TRPL of the pure crystals of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ and $\text{CH}_3\text{NH}_3\text{Pb}(\text{Br}_{0.85}\text{Cl}_{0.15})_3$ as references to the layer samples as shown in Figure 4-14a-b. $\text{CH}_3\text{NH}_3\text{PbCl}_3$ TRPL data is also helpful to understand that the $\text{CH}_3\text{NH}_3\text{Pb}(\text{Br}_{0.85}\text{Cl}_{0.15})_3$ has an intermediate characteristic between its pure halide counterparts. For high quality crystals, there is no difference between the short and the long wavelength emission. Hence, the emission could be from pure high quality crystal material, with homogeneously broad line profile.

Among TRPL decay curves for three crystals studied in Figure 4-14a-b, the fastest decay curve is $\text{CH}_3\text{NH}_3\text{PbCl}_3$, while the curve of $\text{CH}_3\text{NH}_3\text{Pb}(\text{Br}_{0.85}\text{Cl}_{0.15})_3$ falls between $\text{CH}_3\text{NH}_3\text{PbCl}_3$ and $\text{CH}_3\text{NH}_3\text{PbBr}_3$. It is already known for a series of halide compounds, chloride-bromide-iodide, with the same structure, that the photoluminescence lifetime tends to be faster towards chloride [40]. Thus, the emission lifetimes of pure crystals are a good representation of the intrinsic emission in perovskite, since the crystals have limited extrinsic defects such as grain boundaries or interface defects. Then, the same characterization has been performed in layer samples for different growth times (Figure 4-14c-d). At shorter growth times, the decay characteristics deviate considerably from the substrate characteristics. With increased growth time, it approaches a resemblance to the pure $\text{CH}_3\text{NH}_3\text{PbBr}_3$ emission characteristics.

To understand this behavior, consideration of the contribution from bulk and surface/interface emissions is helpful. When the layer is thin, recombination mechanisms associated with defects at the surface and interface have a considerably high contribution to its rapid TRPL decay rate, with respect to the emission from bulk substrate or layer material [25]. This is evident from the drastic deviation of substrate emission decay behavior (Figure 4-14a-b) from the thin layer emission decay behavior (Figure 4-14c-d). At higher thicknesses, the sample gradually approaches the layer material behavior which only consists of surface and bulk of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ within the effective excitation and emission depth. However, it does not completely resemble the layer material decay characteristic due to the contribution from propagating defects such as screw or edge dislocations originating at the layer growth interface.

Further in Figure 4-14c-d, it is evident in thick layer sample that the decay process is slower at longer wavelengths than at shorter wavelengths. By fitting the decay curves with a double exponential decay function (Table 4-4), lifetime difference between short wavelength and long wavelength is clearly distinguishable, especially in the slow decay component. This observation suggests that more localized low energy states exists in the layer. The lifetime of the slow decay component gradually increases with the layer thickness at both short and long wavelengths. Also, contribution from the fast component reduces with increasing layer thickness where it reaches just 1%-2% at the pure $\text{CH}_3\text{NH}_3\text{PbBr}_3$. Hence, we think the fast decay component is associated with interface defects, and probably non-radiative recombination. Graded band gap and mixed halide phases introduced by ion diffusion process are probably responsible for lifetime difference from short wavelength to long wavelength, due to carrier funneling toward low energy regions.

4.5 Conclusions

We have shown that an adapted liquid phase growth technique can be used to grow layers of hybrid organic–inorganic perovskite materials for heterostructures. Unlike early attempts, overgrowing has become dominant over the halide-ion diffusion process by reducing the concentration gradient, and maintaining low super-saturation concentrations at minimum growth temperatures. By this approach, perovskite layers from several to a few tens of micrometers could be grown by controlling only the growth time. The material interface and layer quality have been assessed using SEM, EDS and EBSD methods. The results show multiple examples for layer growth with a limited diffusion region of $\sim 5\mu\text{m}$. We optimized the growth conditions for large perovskite heterostructures, with a well-controlled growth rate, minimized lattice mismatch and limited halide ion inter-diffusion. Further, for the first time, we report an embedded layer for double heterostructures by utilizing the newly established growth condition, without adverse effects from the ion-diffusion process. Further optimization needs to be investigated to reduce interface defects, create a sharper interface transition and fabricate thinner layers. Enhancing the accuracy and stability of the growth conditions is necessary to achieve a thinner layer, and currently limited by the error margins introduced by the parameters such as reactant concentration in the growth solution, growth time and exact temperature. Smaller error margins make it possible to operate as close as possible to the critical supersaturation point, without dissolving the substrate. Developing strategies to maintain minimum surface roughness of the substrate is also crucial for further optimizations. Also, quantitative characterizations of long-term evolution or stability of diffusion profile need to be verified by a technique such as radioactive trace elements. Our approach for epitaxial-like growth could be a significant step towards integrating perovskite substrate-based

heterostructures in various optoelectronic devices in the future.

4.6 References

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Chapter 5 Current oscillations and intermittent emission in perovskite single crystal light emitting devices

5.1 Abstract

A low temperature light emitting device with pure single crystalline $\text{CH}_3\text{NH}_3\text{PbBr}_3$ perovskite is demonstrated. Simple fabrication method was used to obtain a $10\pm 2\ \mu\text{m}$ channel between two gold wire electrodes, which showed bright intermittent electroluminescence after cooling down with a constant biasing voltage. The active region of the perovskite single crystal was pristine, well isolated from surroundings through the fabrication to characterization process. Our presented device provided an ideal condition to study bulk ionic-electronic transport properties of hybrid halide perovskites. At constant 6 V bias, the current through the device shows temperature dependent oscillation with Arrhenius behavior, suggesting a thermally activated process. The light emission from the device experiences an intermittent emission rate of once every 26 ± 6 minutes. Here we propose that the current oscillations and intermittent emission are probably caused by ion mediated negative differential resistance and conductive filament formation respectively.

5.2 Introduction

Perovskites are known to be ion conductors[1, 2], and the ions can be mobilized by various factors[3] such as electric field[2], illumination[4], and chemical gradients[5]. However, other factors such as cation polarization, ferroelectric/ferroelastic distortion[6], traps or effects of air and moisture[7, 8] can contribute to the instability

of perovskite devices as well. Hence, a deeper understanding of material behaviours is needed to achieve high performance and stable devices.

Recently, several studies have indicated that charge transport in polycrystalline hybrid lead halide perovskites is concurrently happening with ion migration, grain boundary effects, polarization disorder of the organic cations, and thermal vibrations of the inorganic lead halide octahedra[9]. In particular, it has become clear that ionic migration is the dominant factor at higher temperatures of above 160-180 K[10, 11]. Nevertheless, the effect of charge transport in grain boundary in polycrystalline perovskites is still significant and interfere our interpretation. The study of single crystals[12, 13] instead of polycrystalline thin films is necessary to simplify and isolate the effect of ionic migration. However, the crystals should be sufficiently thin to fabricate a device which is suitable for carrier injection in optoelectronic characterizations such as charge transport and electroluminescence[14]. Recently, light emission from single domain microcrystals with ITO/CH₃NH₃PbBr₃/Au structure[15], and thin encapsulated single crystals with ITO/CH₃NH₃PbBr₃/ITO structure[16] have been demonstrated up to room temperature. Recent result for light-emitting electrochemical cells of the Ag/CH₃NH₃PbBr₃/CNT structure also shows much faster intermittent emission rate of about 0.5 s[17]. However, they only observed one type of fluctuations and did not relate with a possible very slow intermittent emission in order of minutes or hours. In addition, there are still questions about the electroluminescence mechanism and the origins of second-long intermittent emission. Moreover, the effects related to surface-defects of the crystals, environmental effect (air, moisture) during the characterization or fabrication of the devices[18, 19] are not negligible in these devices.

In this work, we demonstrate an approach to achieve a perovskite single crystal device by entirely encapsulating the Au/CH₃NH₃PbBr₃/Au (metal/semiconductor/metal or MSM) architecture from the surrounding, where the electrodes and active perovskite single crystals stay pristine throughout the process from fabrication to characterization. Our approach with overgrown perovskite as a thick encapsulating layer is relatively simple and eliminates many factors affecting the device. This provides a better platform to study the intrinsic bulk properties of the material. We observe a quasi-periodic on/off electroluminescence with a cycle of 26±6 minutes at 160 K and 6 V constant bias, corresponding to fluctuation of electrical current between high (hundreds of μ A) and low level (tens of μ A), respectively. More interestingly, the electrical current oscillates in the time scale of seconds during the off period (low current) with temperature dependent frequency. Such regular and orderly quasi-periodic oscillation with period of seconds slows down when temperature decreases. We surmise that the quasi-periodic fluctuations in electroluminescence and current oscillation are behaviours of bulk single crystal perovskite, which is dominant in our proposed devices but shadowed by grain boundary or surface defect states in commonly reported perovskite devices[20].

5.3 Device fabrication and methods

Preparation of gold electrodes: A silicon wafer (1 cm x 1 cm) with 2 μ m thermal SiO₂ layer was used as a holder to grow the perovskite crystals with embedded electrodes. Two drops of acetic curable silicone sealant (Corning) were placed with 6±1 mm gap on top of the wafer to support the gold electrodes. Then, before the silicone is cured, two clean pieces of pure gold wire (diameter of 12.5±0.125 μ m, 4±2 cm long) were held parallelly several microns apart in place. The gap between two wires were

adjusted under the microscope. The sample was set aside for few hours for silicone to cure and firmly fix the position of two gold wires. The average length of the gap between the gold wires (electrodes) was confirmed by microscope as $10 \pm 2 \mu\text{m}$.

Crystal growth and device fabrication: The light-emitting device was fabricated by enveloping the prefixed wire electrodes with a methylammonium lead bromide ($\text{CH}_3\text{NH}_3\text{PbBr}_3$) crystal. methylammonium bromide and lead (II) bromide were mixed in 1:1 molar ratio, and dissolved in N,N-Dimethylformamide with vigorous stirring to obtain a 1 mol/L solution. Once the solutes were completely dissolved, the precursor solution was filtered by a $0.2 \mu\text{m}$ pore size PTFE syringe filter and was subsequently transferred into several 25 mL vials. One vial was kept on a hotplate at 363 K to grow seed crystals. While the seed crystals are forming, a silicon wafer with prefixed gold wires was transferred to the second vial containing the growth solution. When the seed crystals appear in first solution, one of the freshly grown seed crystal with about 1 mm^3 volume and cubic facets was transferred in to the second vial. The seed need to be placed close to the narrow channel between two gold wires using tweezers. The vial was then placed on a hotplate at 353 K to continue growing a large crystal from the seed. It is also important to avoid vibration or solution shaking as these would disturb the crystal growth. The process was allowed to continue until the $\text{CH}_3\text{NH}_3\text{PbBr}_3$ crystal completely enveloped the two gold wires [21]. Once the crystal is sufficiently large (more than 5 mm), the sample was removed from the growth solution and any residual solution is drained carefully with a tip of a wipe paper.

5.4 Results and discussion

5.4.1 Current-time characteristics of MSM structure and the effect of pre-conditioning

The MSM structure of the Au/CH₃NH₃PbBr₃/Au where the gold wire electrodes were enveloped by a large perovskite single crystal is shown schematically in Figure 5-1a. The narrowest distance between two electrodes was very small ($10\pm2\ \mu\text{m}$), while a large CH₃NH₃PbBr₃ perovskite crystal (5 mm) was grown around and completely covered the active electrode regions (more details in methods). Within a small region of $10\pm2\ \mu\text{m}$ gap between electrodes, the perovskite semiconductor could be considered as a single crystalline structure. The well-encapsulated MSM device with a high quality single crystalline perovskite allowed us to characterize the device without much interference from crystal grain boundaries and surface states related to environmental effects, which are all well known to play crucial roles in perovskite devices. We expected a pure characterization of charge transfer and electroluminescence in bulk single crystalline perovskite materials.

Figure 5-1 MSM device structure with perovskite single crystal and its electrical behaviours. (a) Sketch of the device, which is comprised of two gold wires embedded within a large hybrid halide perovskite single crystal. (b) Electrical current

development behaviour at different voltages, without any pre-conditioning while cooling down. (c) Electrical current behaviour in long time at 6V constant bias, after preconditioning at same voltage while cooling down. Inset is a sample from the low current region (indicated in blue).

The electrical properties of the MSM structure were first investigated (Figure 5-1b) with device's operation at a constant voltage and low temperatures, which has been cooled down to 160 K without applying any bias. The current gradually rose over 1-3 orders of magnitude, depending on the applied voltage, over the course of 30 minutes to 1 hour before stabilizing, as seen in Figure 5-1b. Brief current spikes ($> 100 \mu\text{A}$), lasting less than a minute, only occurred when the voltages were higher than 9 V. We also observed light emission from the single crystal devices, featuring a "blinking effect" correlated with sharp current spikes through the device. No light emission was detected without the current spikes. Flashing external illumination white light on the device, the photocurrent response was occurred as expected, however, with a brief current spike before stabilization. The electroluminescence can be observed associating with this brief current spike as well. After stopping the external illumination, the current decayed back to the normal level. Before the voltage was applied for each measurement, the device had been kept without any bias for 5 minutes under a sun simulator lamp to minimize hysteresis effects between measurements.

However, when a bias voltage was applied before and during the cooling down process, the device behaviour was very different. This implies that the material properties and device behaviours were susceptible to pre-conditioning of the device. Even though air-exposed single microcrystal device reports electroluminescence at room temperature[15], any electroluminescence could not be observed by the naked

eye from our samples at room temperature. Since the emission channel is encapsulated deep inside the crystal and lack of radiative surface features due to pristine channel, as well as non-radiative, absorbing point defects in the single crystal channel, electroluminescence could have been difficult to achieve at room temperature. At the temperature of 160 K, current spikes ($250 \pm 50 \mu\text{A}$) were observed even at the bias of 6 V (pre-conditioning). These current spikes sustained for about 4 ± 1 minutes, then returned to the lower current state ($\sim$ tens of μA) with quasi-periodical repetition of 26 ± 6 minutes interval as shown in Figure 5-1c. The different behaviours of a device with and without pre-conditioning might relate to ion migration, which is well-known in perovskite semiconductor[15]. The applied bias voltage created electrical field and caused ions to migrate. However, the ion migration was faster at room temperature than that at cryogenic temperature. The ion migration would be settled down and the MSM device behaved as a p-n junction device when reaching 160K temperature during pre-conditioning[15]. Without pre-conditioning, the ion migration happened at cryogenic temperatures would be very slow and require higher bias. As similar as the device without pre-conditioning, electroluminescence (EL) signal was observed during the high current periods, while no EL was observed in the lower current state. The difference is only the smaller bias voltage for EL in the pre-conditioned sample.

Reducing the temperature was useful to reduce the mobile ions. However, the MAPbBr_3 undergoes a phase transition[22] around 150 K from Tetragonal ($I4/mcm$) to Orthorhombic ($Pna2_1$) via a transitional phase of Tetragonal ($P4/mmm$). The phase transition of the perovskite crystal was reflected at its photoluminescence (PL) spectrum whose peak position was at the longest wavelength (547 nm) at 150-160 K (Figure 5-2). Hence, we limited the minimum temperature of the device to 160 K to study the electroluminescence properties of the device and material. Since the pre-

conditioning was useful to establish the high current and EL without waiting time, we focused our experiments below for devices with pre-conditioning. We now look at the device behaviours at two different regimes for the electric current through the device at a constant bias Voltage: high current spikes ($\sim$ hundreds of μA) and low current regions ($\sim$ tens of μA).

Figure 5-2 Temperature dependent photoluminescence (PL) spectra of $\text{CH}_3\text{NH}_3\text{PbBr}_3$.

5.4.2 Current oscillations of MSM device at low current regions

Figure 5-3 Current oscillation behaviors of the device while cooling down. (a) The variation of current with time at different temperatures. (b) The dependence of current oscillation frequency on temperature: Arrhenius plot.

Considering the lower current regime, it is interesting that the electrical current through the device showed an oscillation behaviour with different periodicity depending on the temperature. a and Figure 5-4 show these oscillatory behaviours investigated at different temperatures from 160 K to room temperature. The oscillation of the current was relatively slow at low temperatures, down to less than 0.100 ± 0.050 Hz at $T = 180$ K or even 0.010 ± 0.005 Hz observed at $T = 160$ K, see Figure 1c inset. However, the frequency of oscillation increased at higher temperatures. The trend continued up to room temperature, where the oscillations became relatively fast (above ~ 10 Hz). Together with higher contribution of random fluctuation at increasing temperatures, we can hardly notice the current oscillation at room temperature in oscilloscope trace. Plotting the logarithm of the oscillation frequency (f) versus the reciprocal of temperature T , as seen in b, shows a typical Arrhenius behaviour, $f(T) = A \cdot e^{-\frac{E_a}{RT}}$, where A is a constant pre-factor and R is the gas constant. Fitting the model, we deduced the activation energy E_a to be 23.4 kJ mol^{-1} (or 242.5 meV). The Arrhenius relationship between oscillation frequency and temperature suggests a thermally activated process. From this value, we extrapolate $f(160 \text{ K}) = 0.005 \pm 0.001$

Hz, which is still consistent with the frequency obtained from Figure 5-1c inset. Usually, Arrhenius behavior is characteristic in ionic migration mechanisms, where the rate of charge transfer (i.e. current) increase with temperature. However, our observation is the frequency increase of periodic current fluctuation with temperature. While various observations and models have been reported in literature on ionic migration in perovskites[10, 23-25], no one, to our knowledge, has yet reported the quasi-periodic oscillatory behavior in the current characteristics shown in this work. Presumably, the encapsulation of the bulk perovskite channel in our samples eliminated surface and grain boundary effects at the core device. Usually, the defects allow ions to move much faster than the ion movement within the pristine single crystalline bulk perovskite. In polycrystalline materials and air-exposed perovskite surfaces electrons, holes and ionic carriers transporting via various defects dominate the electrical conductance, suppressing the pristine bulk behavior in typical experiments.

Figure 5-4 Current oscillation behavior of the MSM device at a constant bias of 12V, at different temperatures.

Though our observed current oscillation is related to a thermally activated process, its mechanism is not well understood. Many natural oscillations which happen at constant external stimuli can be identified in several occasions, such as in electrochemical cells[26, 27], Gunn diodes[28], neuron axon conductance[29] and Plasma oscillations[30] to name a few. Many such processes have a common aspect, which is a negative differential resistance (NDR) characteristic. The origin of NDR characteristic could vary, ranging from an interface process to a spatiotemporal process. Usually, two types of carriers with different mobilities such as heavy vs. light electrons or electron vs. ion conductance could lead to spatiotemporal NDR.

Interfacial NDR processes are related to a tunneling current, such as in tunneling diodes. Both charge carriers in perovskite[31] (electronic and ionic) could be the source of the oscillatory behavior, either it is a spatiotemporal process due to different mobilities; or modified electron-hole injection at metal semiconductor interfaces due to ion accumulation near the electrodes.

5.4.3 EL properties of MSM device at high current regions

Figure 5-5 Device electroluminescence characteristics. (a) Image of an actual device under white light illumination. (b) The image of device's electroluminescence. (c) Electroluminescence spectra at different currents. The inset shows the corresponding coordinate in CIE diagram. (d) IV characteristics in log-log scale shows the different conduction regimes. LIV characteristics of the device is given in inset.

Looking at the higher current regime, we could observe bright green electroluminescence of MAPbBr₃ perovskite single crystal. Figure 5-5a and Figure

5-5b shows the optical images of an actual MSM device under white light illumination, and its electroluminescence associated with current spikes, respectively. The emission from the $\text{CH}_3\text{NH}_3\text{PbBr}_3$ originated in the narrow channel between two gold wires while the reflection in multiple surfaces of the perovskite crystal created virtually multiple bright spots around the crystal in the picture. The electroluminescence spectra of the single crystal perovskite MSM device, shown in Figure 5-5c, featured a sharp (FWHM 12 ± 1 nm) single peak at 563 nm with a steep rising edge around 560 nm. The chromaticity diagram in the inset of Figure 3c puts the emission in yellow-green range. The photoluminescence peak of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ was at 537 nm at room temperature and shifted to 546 nm at 160 K (Figure 5-2). The difference between the EL and the PL spectra was attributed to self-absorption by the material. While PL was emitted from the surface of materials because the excitation laser could not penetrate deep inside the crystal, the EL was from the space between the two electrodes, which were deep inside the perovskite crystal. The captured EL spectrum was the result of EL passing through and being absorbed by a thick layer of material. Our experimental PL at room temperature with laser excitation from one side and PL collection from the other side of a crystal showed the similar spectral profile as that of EL (Figure 5-6).

The significant red-shift of EL spectrum compared to PL spectrum was consistent with very strong self-absorption due to small Stokes shift in this bulk Perovskite material[32]. The asymmetry in the EL peaks, which can be fitted with an exponentially modified Gaussian profile (Figure 5-7), is another evidence for self-absorption at shorter wavelengths by the thick perovskite crystal.

Figure 5-6 Photoluminescence spectrum measured through the CH₃NH₃PbBr₃ crystal. The exponentially modified gaussian profile and the peak shift is caused by self-absorption.

Figure 5-7 Exponentially modified gaussian profile fitting for the electroluminescence spectra caused by self-absorption in CH₃NH₃PbBr₃ crystal.

With the pre-conditioned device, the “current spikes” were occurring regularly with typically 4 ± 1 minutes of ‘on’ time, which allowed us to characterize the electronic and optical properties of the device. The light-current-voltage (LIV) curves are presented in Figure 5-5d. The LIV behavior was similar to a typical light emitting diode with p-n junction and agreed well with other recent literature reports about single crystal perovskite under pre-conditioning[15, 16]. The device EL intensity correlated linearly with the current flowing through the device, while IV curve showed a turn on voltage of about 6 V. The LIV results were measured with voltage sweeping from 0 V to 28 V at speed of 3.75 V/s. The condition for voltage sweeping was important because the devices presented a history-dependent behavior, varying with the speed of Voltage sweep. As presented in Figure 5-1c, the current was 250 ± 50 μA at the current spikes when we applied a constant bias of 6 V. However, when we immediately swept the voltage the current only turned on and reached 200 μA at above 20 V. Hysteretic and history-dependent behavior is well known in hybrid perovskites, and attributed to ion segregation within the perovskite crystal[33].

Figure 5-8 Local evolution of the emission within the perovskite crystal channel. (a) Close-up optical image of the channel under a bright external illumination. The gold wires with diameter $12.5\ \mu\text{m}$ inside the crystal are slightly visible. Scale bar is $20\ \mu\text{m}$. (b-d) Emission localized at different positions within the channel. The appearance and dimming of emission at the red circled position due to growth of a filament and eventual burnout from short-circuit. (e) Emission is more prominent in a different

place due to eventual formation of another filament. (f) Depiction of the encapsulated perovskite channel and (g-j) corresponding stages of illustrated filament formation/destruction phenomenon within the channel. (not to scale). The star and the cross signs respectively indicate the filament positions where the emission appear, and eventually disappear due to filament short-circuit.

Besides the quasi-periodic current spikes concurrently happened with EL, our microscope images (Figure 5-8a-e) showed that EL was only happened at the perovskite region near the anode side. To explain these observations, we empirically propose a simple model based on filament formation[34, 35] driven by ionic motion, which is a known effect in lead halide perovskites [36, 37]. The simulation procedure is discussed in Section 5.5, an illustration is presented in Figure 5-8f-j. In our model, gold (Au) atoms are oxidized at the anode, which is known for gold in perovskite, leading to gold ion migration[38]. The formed Au^+ cations drift through the perovskite crystal to reach the cathode, hopping through interstitials or vacancy sites, following the electric field applied by external electrodes. Once the gold cations reach the cathode, a further redox reaction will occur to reduce the gold cations back to Au^0 atoms, which will be deposited on the cathode. The deposition of the gold atoms will modify the profile of the electric field, creating higher electric field at the tip of deposition position, hence leading more gold cations towards the tip and forming a filament of gold atoms as seen in Figure 5-8g. As the filament grows (Figure 5-8h), the local electric field increases and reaches a “threshold”, the current sharply increases, similar to filament-based memory devices, causing the current surges in Figure 5-1b-c. The current density is high enough to have significant density of electrons and holes in the perovskite for radiative recombination, resulting in electroluminescence. The number of growth filaments, thickness and structure of the filaments could depend on

various factors such as the voltage and temperature, ion diffusion constants and distance between the electrodes [17, 34]. The electroluminescence will increase as the filament grows further, as seen in Figure 5-8c and Figure 5-8h. This type of filament formation has been previously observed in perovskite devices, in particular in perovskite resistive memories[39, 40]. However, the increases in current through a small perovskite gap when the filament approaches anode will also lead to significant Joule heating, resulting into a sharp increase of the local temperature or even electrical breakdown as in Figure 5-8d and Figure 5-8i. This will lead to either the disintegration of the filament or damage to the local crystal structure of the perovskite. Thus, we can observe a sharp decrease in the current, and loss of electroluminescence. Eventually, another filament will form at a different position, repeating the process, as in Figure 5-8e and Figure 5-8j. Thus, at the same position, the material should not light-up again after the filament is broken. It is worth to note that the distance between our electrodes varies along the wire, and certainly the filament formation and EL happen around the smallest gap region where the electric field is the strongest. When the material at the narrowest position is damaged, another filament will grow at a nearest possible region[17, 34].

5.5 Monte-Carlo simulation procedure

The mechanism of filament formation through ion migration by random hops under applied electric field was modelled with a simplified Monte-Carlo simulation[34]. We used NetLogo[41] agent-based simulation to exemplify the idea. First, initial electric potentials were assigned to the electrodes, and the electric field at each lattice site can be calculated by agent based finite element method. Then, the probabilistic hopping of the ions was simulated with a calculated probability for each neighbour, based on the

electric field at the lattice site. These two procedures have been iterated regularly to observe the formation of filaments. The ions are assumed to be activated by lattice vibrational energy (i.e. temperature) and has a certain probability of hopping to another vacant lattice site or swap to a neighbouring lattice cite via an interstitial transition. In our model, two occupants of adjacent lattice sites could swap with a finite probability. However, under an electric field, the charge carrying ion which is released from electrode prefer to follow the electric field, providing preferential probabilities following the electric potential gradient. After a succeeding sequence of hops, the charge will eventually reach the counter-electrode and release its charge, its charge, modifying the surface profile of the electrode. This process is known as electroforming. Because of many such depositions, the distance between two electrodes, i.e. channel width, is altered. The profile of the electrode surface and therefore the electric field is also modified.

The filament formation is modelled in a 2-dimensional, 4-neighbour lattice concerning its simplicity. While keeping the externally applied voltage as a constant, the electric potential distribution inside the perovskite channel is iteratively updated until it reaches a steady state. For a 1-dimensional case, this can be a straight-forward analytical solution, however with odd shapes of the electrodes in 2D or 3D space, the potential need to be solved numerically[34]. In a simplified finite element discrete 2D representation, the spatial distribution of Electric Potential is calculated using the following formula,

$$\psi_i^{x,y} = \psi_{i-1}^{x,y} + D * \left(\sum_{\substack{p=-1,1 \\ q=-1,1}} \psi_{i-1}^{x+p,y+q} - 4 * \psi_{i-1}^{x,y} \right) \quad (S1)$$

The electric potential is iteratively updated until it is stable. The traversal of the gold

ion in the perovskite crystal is a multi-stage activated process, which we greatly simplify extensively. Based on the potential at each lattice site, the probabilities for each candidate transition to the nearest neighbour sites is modelled corresponding to the electric field and temperature, at each lattice cite with a charged ion using following formula[34, 42].

$$P_{1 \rightarrow 2} = A_0 e^{\frac{E_a - (ze\Delta\varphi/2)}{k_B T}} \quad (S2)$$

Where the E_a is activation energy barrier for the transition and $\Delta\varphi$ is the potential difference between two lattice cites. E_a and A_0 depend on the material on site 1, 2 and their neighbourhood which has been explained comprehensively by Manzel and group[34]. Different activation energies for oxidation and reduction of the gold, migration of gold on gold surface and the transition of gold ions within the perovskite matrix are the most significant processes.

Then a random number between 0 and 1 has been generated and evaluated against the transition probability to randomly activate the favoured operation. Iterating this Monte-Carlo procedure can model the phenomenon of filament formation. To re-emphasize, the potential gradient need to be re-optimized as the filament grow, due to modification of the morphology of the channel. The modified electric field direct the subsequent ions to the growing filament following the electric field.

Using this simplified model, the effect of parameters such as temperature, external bias, and channel width on the behaviour of current spikes can be predicted.

5.5.1 Effect of temperature.

Temperature and the probability of ion motion within perovskite also follows the Arrhenius relationship.

$$\ln(P_{1 \rightarrow 2}) = \ln(A_0) + -\frac{E_a - (ze\Delta\phi/2)}{k_B} \frac{1}{T}$$

5.5.2 Effect of external bias conditions.

The local electrical potential gradient and the probability of ion motion within perovskite also follows the Arrhenius relationship, reorganized as follows.

$$\ln(P_{1 \rightarrow 2}) = \ln(A_0) - \frac{E_a}{k_B T} + \frac{(ze/2)}{k_B T} \Delta\phi$$

Based on the presumed individual transition activation energies and pre-exponential parameters, the system could show different filament growth modes at different voltages and temperatures.

In an example scenario, as demonstrated by Manzel and group[34], lower voltages let the filament grow uniformly, and it could be thick and stable. It would bridge the gap very slowly and may not give a current spike, rather increase the current slowly over time. In an intermediate voltage regime, a dendritic structure with a narrow filament diameter could be formed. With higher voltages, the filament could be further dendritic and even narrower. The growth could be faster, and on the other hand, narrow filament could easily be quickly destroyed due to Joule heating. Hence, at high voltages above a threshold, the narrow filaments could form faster and more frequently. However, due to same reason the interval between two current spikes cannot be directly related.

At higher temperatures, the frequency of the transitions is higher, leading to speed-up

the filament growth process. So, more frequent and noisier current spikes can be expected as the temperature increases.

5.6 Conclusion

We demonstrated a simple and robust single crystal perovskite device, which showed electroluminescence at low temperatures and sufficiently high currents. The proposed device concept where the electrode-perovskite structure stayed pristine throughout the process from fabrication to characterization allowed us to observe more regular current oscillation in single crystal perovskites. We observed a novel oscillatory behavior, which relates to thermally activated process because of its Arrhenius dependency on the temperature. In addition, the MSM device showed a regular quasi-periodic sharp rise in current, corresponding to intermittent electroluminescence, which can be explained by filament formation within the device. These observations could shed new light on the inner behaviors of single crystalline perovskite devices, highlighting how important ionic motion is on the conduction in perovskite devices, which is important to use perovskites in novel applications in future. Further, the device fabrication technique introduced herein is just an initial step, whereas different metals as well as asymmetric MSM channel can be assessed to understand the working mechanisms of the device better. Different structures such as embedded planar electrodes also can be assessed in encapsulated conditions.

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Chapter 6 Conclusions and future work

6.1 Conclusions

Hybrid halide perovskites are a group of semiconductor materials with a unique combination of properties coming from the nature of both inorganic and organic material. While being an interesting semiconductor material class with lots of potentials in optoelectronic applications, certain drawbacks are hindering its performance and, of course, commercialization. The mobile ions are the most elusive characteristic of the perovskites; they severely augment the opto-electronic functions of the material. Mobile ions also affect the fabrication and stability of useful electronic devices such as solar cells or light emitting devices. This thesis is an attempt to address some of the remaining concerns in understanding and capturing the working mechanisms of the ionic movements in perovskites. We explore the mobile ions in two different perspectives. First perspective is the halide ion diffusion in a facile solvothermal layer growth process. Second is the ion drift in a single crystal under an electric field.

The effect of growth solution concentration, composition and temperature limitations of epitaxial-like growth is explored to minimize the halide ion diffusion during heterostructure growth. We introduce a modified ‘liquid phase epitaxy’ process, for epitaxial-like layer growth while limiting the halide ion interdiffusion between crystal substrate and the growth solution. Our study presented in chapter 4 reveals the growth rate can be certainly controlled while limiting the halide ion interdiffusion to a minimum. However, further improvements are necessary to reach the thickness regime that is required for quantum confinement (quasi-2D structure) at this level, especially

starting from substrates with less surface roughness. Also, this study provides preliminary results on layer growth conditions necessary for alternative layer growth techniques in gaseous or vapor phases, which may be used in future to obtain thinner layers. However, understanding the nature of halide ion drift under an electric field should be prioritized, because this can alter the device structure over time, making it difficult to sustain even a stable operating behavior for characterization, a distance from commercialization.

We have chosen to assess only the possibility of growing an iso-valent heterostructure and its properties, since the other research groups have been working on hetero-valent doping. After several years, no significant improvement to be seen in the doping techniques. However, other opportunities such as electrochemical cell operating mode and 2D perovskite materials which can inherently be a quantum well superlattice provide novel unforeseen opportunities, therefore we can be hopeful that the efforts for perovskite development would make an impact. So, successfully commercializing perovskite single crystalline materials in a general purpose electrically pumped light emitting diodes remain a daring, yet an exciting endeavor.

Large hysteresis and memory effects in current-voltage sweep are typical characteristics even in a single crystalline device, which is attributed to transient ionic currents within the perovskite. It is evident that the perovskite single crystal contains mobile ionic species, which can drift under an electric field, even for the purest materials without any grain boundary effects or surface defects. Therefore, electroluminescence is achieved by a ‘frozen junction’ technique where the metal-semiconductor-metal channel is cooled down under a bias. Yet, the current and electroluminescence shows an emission localization and a slow blinking behavior which seems to originate from the single crystalline material itself. Understanding the

random blinking is a major concern with previously reported single crystalline electroluminescence devices as well, however the intermittent emission characteristic of our novel encapsulated single crystal electroluminescence devices is shown to be not completely random, the first of its kind. We believe our fully encapsulated device limits the degrees of freedom to the essential parameters, eliminating secondary factors such as external air/moisture exposure and defective crystal surfaces, allowing this observation.

With the new experimental device fabrication technique and characterization, we can conclude that the previously observed random behaviors from ‘frozen junction’ electroluminescence devices are most likely governed by the irregularities of surfaces and interfaces. However, with the results from our studies where most of the secondary variables like defective interfaces and air contamination have been eliminated, we suggest that the intermittent emission may be an intrinsic characteristic of the gold-perovskite-gold device itself. The secondary parameters such as air and moisture are essentially increasing the randomness of this intrinsic process, which are dominant in other types of devices described in literature.

The research presented in this thesis contributes more comprehensive understand of organic-inorganic hybrid halide perovskites at their most pristine structure, i.e. single crystals. Our ‘liquid phase epitaxy’ process with precise parameters allows us to grow, for the first time, high quality heterostructure structures, which could be the first step to have building blocks for various optoelectronic applications with perovskites in future. The single crystal growth technique combined with our new ideas of making a pristine perovskite device allows us to investigate a light emitting device without worrying any secondary effects from environment. The devices are well protected

throughout the process from fabrication to characterization. The quasi-periodic current and light fluctuation in our frozen junction are significantly different from previously reported devices. Our results highlight the nature of perovskite materials and suggest the dominant roles of defects, surface states and moisture in unprotected devices reported in literature.

6.2 Future work

After gaining knowledge on the intrinsic current oscillations in the pristine gold-perovskite-gold device, we believe it opens up several fundamental questions, which could drive our research forward with this fascinating system of materials. Having established the crucial role of drifting ions even in the single crystalline material, the application prospects of the material in optoelectronic devices need to be considered to include the new variables. So far, eliminating grain boundaries and defective surfaces is unlikely to eliminate the ionic processes significantly. So a possible strategy is to look for a suitable doping technique or ion tolerant carrier injection to stabilize the crystal, where we can use hybrid halide perovskite materials in real world applications. However, on the other hand, this novel behavior may find different types of applications elsewhere, such as in resistive memory devices for neuromorphic computing. The slow current oscillations are probably a useful building block for future neuromorphic devices even in a three dimensional space.

Some experiments, which can be immediately valuable to complement our results in this project, would be done to utilize the encapsulated device fabrication technique. The gold wires used in our work as electrodes are currently small in effective cross

section area, which is limiting the measurement of capacitive contributions of the device significantly. Embedded electrodes with large area parallel plates in a single crystal could supplement our findings with further characterizations such as impedance spectroscopy.

One more aspect which can be immediately useful is the detailed characterization of a series of devices with different channel widths. Such experiment could provide crucial insights to model, understand and explain the oscillating behavior of the intrinsic perovskite materials in more elaborate details.

Among many other possible parameters for exploration, we think about utilizing our pristine device structure to investigate other electrode materials, and different halide compositions. Instead of gold, and instead of $\text{CH}_3\text{NH}_3\text{PbBr}_3$. Gold is known for less compatible with perovskites, platinum or silver could be the candidates. Other halide perovskite or even mixed-halide perovskites are important candidates to investigate for applications. Changing the electrode and perovskite materials could be useful to explain the Arrhenius behavior of the current-temperature measurements, especially to determine the source of activation energy, which is probably associated with the electrode/perovskite composition or both of them.

Given the stability of the single crystal material, the device structure should be applicable with any other halide composition which supports low temperature crystallization process. However, the mixed halide materials may be subjected to spinodal decomposition which separates halide concentrations spatially, causing the bandgap fluctuations to occur within the single crystals. Such fluctuations could lead to quantum wells or traps which leads to carrier localizations supporting either radiative or nonradiative recombination mechanism. As a result, the emission bandgap

may not directly correspond to the initial alloying composition of the crystal, and the emission profile may also evolve according to the spatial fluctuations. In fact, a mixed halide (Bromide and Chloride) sample also found to be having similar trend in our preliminary studies.

For the device to show its intrinsic behavior with electroluminescence at room temperature, several techniques such as reducing channel width and minimize the crystal volume to reduce reabsorption could be introduced. Also, extraction efficiency from the crystal surface can be enhanced by introducing some surface features. Also, to improve radiative electron hole recombination for room temperature electroluminescence from the sample, fabricating a heterojunction within the pristine perovskite channel to form a static p-n junction could be a promising prospect.

Our idea for embedded electrodes in perovskite single crystals suggests a promising device fabrication technique in future. The crystal is grown around a pre-arranged electrode configuration in a 3-dimensional space. Such structures could be designed and characterized with numerous configurations in future, with the unprecedented privilege of access to the pristine metal semiconductor interfaces without worrying about the secondary environmental factors.

Chapter 7 List of publications

Thesis Contributions

Hettiarachchi, C., Birowosuto, M. D., Nguyen, T. H., Pita, K., & Dang, C. (2017). “Hetero-structure of hybrid perovskite single crystals”. In Opto-Electronics and Communications Conference (OECC) and Photonics Global Conference (PGC). Singapore, IEEE, 2017, (pp. 1–3) <https://doi.org/10.1109/OECC.2017.8115016>

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Hettiarachchi, C., Birowosuto, M. D., Nguyen, T. H., Ahmad, R., Pita, K., Mathews, N., & Dang, C., “Solution grown double heterostructure on a large hybrid halide perovskite crystal”. CrystEngComm, 20(42), pp. 6653–6661, 2018. <https://doi.org/10.1039/C8CE01298A>

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Other Contributions

Jiang, Y., Yu, H., Fu, X., **Hettiarachchi, C.**, Xu, H., Li, Y., Nguyen, T. H., Dong, L., Dang, C., & Zhang, Q., “A Nano-Filter-Integrated CMOS Image Sensor for Fluorescent Biomedical Imaging”. In IEEE Biomedical Circuits and Systems Conference (BioCAS), IEEE, 2018, Vol. 1, pp. 1–4.

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