## STUDY OF THE IMPACT OF MICROSTRUCTURES AND INTERFACE ENERGETICS IN PEROVSKITE AND ORGANIC SOLAR CELLS

By

**Chuanpeng Jiang** 

## A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

Chemistry - Doctor of Philosophy

2018

#### ABSTRACT

## STUDY OF THE IMPACT OF MICROSTRUCTURES AND INTERFACE ENERGETICS IN PEROVSKITE AND ORGANIC SOLAR CELLS

#### By

### **Chuanpeng Jiang**

To deal with the increasing demand on energy and the concerns about fossil fuels, solar energy has become one of the most promising alternative energy. Photovoltaic technology has been developed to harnesses the solar energy. Different types of solar cells depending on the materials and structures of the devices have been developed, such as crystalline Si cells, dye sensitized solar cells, perovskite solar cells and organic photovoltaics. Solar cells with high efficiency, low cost, and excellent stability are desirable for the market.

The first part of this study focuses on the organic-inorganic hybrid perovskite photovoltaics. Solar cells consisting of polycrystalline perovskite thin films have demonstrated a rapid increase of power conversion efficiency (PCE) in the past few years. To further boost the device performance, it is crucial to understand how the microstructures, such as the film texture, grains and grain boundaries, impact the electrical properties of the perovskite thin film. The ramp-annealing treatment is adapted to tailor the texture of perovskite films, where a strong correlation between the device performance and the thin film texture is revealed by X-ray diffraction (XRD) and *J-V* characteristics. Electrochemical impedance spectroscopy (EIS) further suggests that the enhanced texture structure not only suppresses recombination at the contact but also improves the carrier diffusion length, which ultimately contributes to better device performance.

The other important feature of the polycrystalline thin film is grains and grain boundaries. To investigate the influence of these microstructures on device performance, photo-conducting atomic force microscopy (pc-AFM) and Kelvin probe force microscopy (KPFM) measurements, which provide the nano-scale resolution, are performed on perovskite thin films with columnar structures. Three discrete photocurrent levels are identified among perovskite grains, likely corresponding to the crystal orientation of each grain identified by electron backscattering diffraction (EBSD). Local *J*-*V* curves measured on these grains further suggest an anti-correlation behavior between short-circuit current ( $J_{sc}$ ) and open-circuit voltage ( $V_{oc}$ ). These results suggest the orientation-dependent carrier mobility in perovskite thin films. In addition, the photoresponse of perovskite films displays a pronounced heterogeneity across grain boundaries, with low-angle boundaries exhibiting even better performance than the adjacent grain interiors. KPFM further reveals the downward band bending at grain boundaries which draws electrons and repels holes. Thus, the low-angle grain boundaries facilitate the electron transport and suppress recombination.

The second part of this study focuses on the interface engineering of organic photovoltaics (OPVs). Organic photovoltaics have attracted a significant amount of attention as they offer potential benefits of low cost and mechanical flexibility. It is known that in OPV devices the energy level alignment at the interfaces between metal electrodes and the photoactive layer is critical in determining the charge collection efficiency. Here, zinc oxide (ZnO) buffer layer is introduced between the bulk heterojunction (BHJ) organic layer and the cathode material. By varying the processing condition of ZnO layer, the energy level alignment at the contact is tuned and thus the device performance. The interfacial energetics is further investigated by KPFM. Schottky barriers with varied widths are identified at ITO/ZnO interfaces. With electrons tunneling through the narrow Schottky barrier, the charge collection efficiency at the cathode is improved.

#### ACKNOWLEDGEMENTS

The work detailed in this dissertation was partially supported by Michigan State University Strategic Partnership Grant.

In the past 6 years, I have received the help from many people, not only with this work but also in my personal life. Without them, I won't be able to accomplish what I have achieved. I would like to take this chance to acknowledge them for their support.

First, I would like to thank Professor Pengpeng Zhang. It has been an honor to work with her. She provides me the opportunity to explore the world of the nanoscale. I really appreciate that she spent a large amount of time in training me on the operation of instruments and instructing me on how to form logical thinking and giving presentations. I really enjoyed every discussion we had which inspired me in my scientific career.

I had the opportunity to work with many group mates who help me a lot with my research. I would like to thank Dr. Sean Wagner. He is always willing to help me. I still remembered those late nights we worked together. It is a great experience working with him. Dr. Jiebing Sun taught me how to make semiconductor devices and helped me with the first publication. I really appreciate that.

I have to mention that it is a pleasure to work with Prof. Xianglin Ke, Dr. Tao Zou, and Dr. Mengze Zhu. They offered me different perspectives on my research and provided constructive suggestions. I really enjoyed the time when I sat next to them. We had so many interesting conversations. Please remember to return the tools you borrowed from our lab. Thank you.

iv

I would also like to thank Prof. Thomas Hamann and Dr. Yuling Xie. They offered great help with the impedance measurement and input on the manuscript. Prof. Hamann exposed me to the EIS measurement which has been quite useful throughout my studies. We also had many fruitful conversations about the impedance measurement as well as the design of experiment. Dr. Xie taught me how to use the instrument and helped me reserve the instrument, which I really appreciate.

In my second publication, we have reported the EBSD results on perovskite thin films for the first time. I have to mention the help from Quan Zhou. He spent lots of effort in the experiment and helped with the data processing. Though we had failed several times at the beginning, he never gave up and was always willing to help. I really appreciate that.

It is an honor to collaborate with Dr. Richard Lunt and his group members. Dr. Lunt is so passionate, creative and inspiring. He also offered great help in making the devices, especially when I was struggling with making perovskite solar cells. I would like to thank his group members: Dr. Dianyi Liu, Chenchen Yang and Dr. Peggy Young as well. Thank you for helping me with using the instruments in the lab and developing new instrument setup. Dr. Liu and Chenchen are also good friends to me and I would like to thank you for your help in my personal life.

It would be a regret to me if I do not acknowledge Dr. Reza Loloee and Dr. Baokang Bi. Dr. Loloee is the first one I would think of when the instrument in the basement went wrong. He is more like a magician who can fix everything. I also enjoyed the time I spent in the clean room with Dr. Bi. He taught me how to use many experimental instruments and skills which are of great help in my scientific career. In the last year of my Ph.D. study, I had been doing an internship at BASF-Battery Materials Ovonic. I would like to thank Dr. Kwo Young for providing me this opportunity. He is the smartest person I have ever met but he is also humble and willing to help others. Thank you for all the help at BASF. Also, I would like to acknowledge the coolest lady in the world, Rose Bertolini. I really cannot ask more from a colleague. I had so much fun working with her. Thank you for teaching me the real American culture and taking me in the break-the-week lunch group. I wish you the best! I would also like to thank William Mays, Sherry Hu, Vera Chang, Shuli Yan, Meng Xu, David Huang, Dr. Benjamin Reichman and Peifeng Li. Thank you for all the help you gave. I really appreciate that.

I would also like to thank my awesome friends: Dr. Yuan Gao, Dr. Xiaoran Zhang, Yanlian Xin, Shangguan Yang, Lin Song, Yang Zhou, Zhuoqin Yu, Zhao Peng, Dr. Yuling Xie, Ruiqiong Guo, Yujue Wang, Zhihui Liu, Lulu Shen and Nan Du. You made my life here wonderful. I cherish all the time we had spent together. It is sad to see some of you leave here but I am also very happy for you guys. I wish everyone the best.

I would like to acknowledge my friends from LCCChurch: Pastor Jiarong Peng, Xingran Wang, Yijun Zhao and Lihua Yang. When I first came to the US, they helped me settle down and took me to church. Especially, Uncle Zhao and Aunt Yang offered me so much help and I felt like they treated me as their own son. And in my most difficult time, they always took care of me and prayed for me. Thank you!

Last, I would like to thank my parents. Though they do not understand English, I would like to write down how much I love them. Thank you, mom, for praying for me every day in the early morning when other people are still in their dreams. Thank you, Dad, for working so hard to support me. I am sorry that I cannot always be around you guys. I really appreciate your understanding. I know that no matter how many thank you I say, it would not be enough. But please allow me wishing you best.

Thank you, everyone.

# TABLE OF CONTENTS

LIST OF TABLES	X
LIST OF FIGURES	xi
Chapter 1 Introduction	1
1.1 Motivation	
1.2 Outline of this work	6
Chapter 2 Solar cell physics	
2.1 Introduction to semiconductors	
2.1.1 Basics of semiconductors	
2.1.2 Intrinsic and extrinsic semiconductors	
2.1.3 Equilibrium distribution of carriers	
2.1.4 Junctions	
2.2 Planar structured solar cells	
2.2.1 Light absorption and exciton dissociation	
2.2.2 Charge transport	
2.2.3 Charge Collection	
2.2.4 Recombination, carrier lifetime and diffusion length	
2.3 <i>J-V</i> characteristics of photovoltaic devices	
2.3.1 Short-circuit current $(J_{sc})$	
2.3.2 Open-circuit voltage ( $V_{oc}$ )	
2.3.3 Fill factor, shunt resistance and series resistance	
Chapter 3 Perovskite solar cells and organic photovoltaics	
3.1 Organic-inorganic hybrid perovskite solar cells	
3.1.1 Basics of perovskite materials	
3.1.2 Structure of solid-state perovskite solar cells	
3.1.3 Fabrication of polycrystalline perovskite thin films	
3.1.4 Light absorption and carrier generation in perovskite solar cells	
3.1.5 Carrier transport and collection in perovskite solar cells	
3.1.6 Non-radiative recombination in perovskite solar cells	
3.1.7 Remaining challenges in perovskite solar cells	
3.2 Organic photovoltaics and the application of ZnO as a buffer layer	
Chapter 4 Device fabrication and experimental methods	59
4.1 Device fabrication	59
4.1.1 Fabrication of perovskite solar cells	59
4.1.2 Fabrication of organic photovoltaics	
4.2 Experimental conditions of characterizing tools	
4.2.1 <i>J-V</i> and EQE measurements	
4.2.2 SEM and EBSD measurements	

4.2.3 X-ray diffraction measurement	65
4.2.4 AFM measurement	
4.2.5 EIS measurement	
4.2.6 UV-vis spectroscopy	67
4.3 Working principles of experimental methods	
4.3.1 Atomic force microscopy	
4.3.2 Electrochemical impedance spectroscopy	
4.3.3 Electron backscattering diffraction measurement	
Chapter 5 Elucidating the impact of thin film texture on charge transport and	
collection in perovskite solar cells	
5.1 Ramp annealing treatment and crystalline structure of perovskite thin films	
5.2 Correlation between device performance and the thin film texture	
5.3 Impact of thin film texture on charge collection and transport	100
5.4 Conclusion	109
Chapter 6 Crystalline orientation dependent photoresponse and heterogeneous	
behaviors of grain boundaries in perovskite solar cells	110
6.1 Photocurrent mapping of perovskite thin films with columnar structures	110
6.2 Identification of grain orientations in perovskite thin films by EBSD	117
6.3 Photoresponse of low-angle and high angle grain boundaries	123
6.4 Electronic structure of grain boundaries investigated by KPFM	126
6.5 Conclusion	129
Chapter 7 High-performance inverted solar cells with a controlled ZnO buffer layer	r 131
7.1 Impact of ZnO preparation temperature on device performance of organic	
photovoltaics	131
7.2 Origin of the temperature dependence	134
7.3 Tuning of the ZnO work function and interface energetics at the cathode	138
7.4 Conclusion	141
Chapter 8 Conclusions and future work	142
8.1 Summary of results	142
8.2 Future work	145
APPENDIX	147
BIBLIOGRAPHY	153

# LIST OF TABLES

Table 4.1: Precursor concentration and film thickness	62
Table 5.1: Characteristic parameters of perovskite solar cells processed under different cond	lictions. 96
Table 5.2: Characteristic parameters of perovskite solar cells with different thickness	105
Table 6.1: Parameters of fitted point J-V curves.	115
Table 6.2: Miller indices derived from Euler angles	122
Table 7.1: Summary of the average solar cell performance parameters	133
Table 7.2: Work functions of ITO, ITO/ZnO, and ITO/ZnO/PCBM measured by KPFM	138

# LIST OF FIGURES

Figure 2.1: Band formation of semiconductors
Figure 2.2: Schematic of semiconductor doping 11
Figure 2.3: Temperature dependence of carrier concentrations in n-type semiconductors 14
Figure 2.4: Formation of Schottky barriers
Figure 2.5: Rectifying characteristics of the metal/semiconductor junction
Figure 2.6: Formation of Ohmic contacts at the metal/semiconductor junction
Figure 2.7: Schematics of the formation of junctions at the semiconducting organics and metal interface
Figure 2.8: Illustration of the band alignment at (a) p-n and (b) p-i-n junctions
Figure 2.9: Planar structured solar cells
Figure 2.10: Schematic of charge transport driven by the built-in electric-field
Figure 2.11: Schematic of charge collection at the interface
Figure 2.12: Schematics of the loss mechanisms
Figure 2.13: Illustration of <i>J-V</i> curves and the characteristic parameters of photovoltaic devices under dark and illumination conditions
Figure 2.14: Equivalent circuit of photovoltaic devices including series and shunt resistances 34
Figure 3.1: Crystal structure and band diagram of organic-inorganic hybrid perovskites
Figure 3.2: Illustration of the device architectures of perovskite solar cells
Figure 3.3: Illustration of preparing perovskite thin films by one-step method
Figure 3.4: Illustration of preparing perovskite thin films by two-step methods
Figure 3.5: Absorption coefficient of ITO/PEDOT:PSS/MAPbI <sub>3</sub> sample
Figure 3.6: Schematic of the ion migration in the perovskite material

Figure 3.7: Schematics of photocarrier separation, collection and recombination in OPVs 54
Figure 3.8: Schematics of work function tuning via the formation of interface dipole
Figure 4.1: Images of the spin-coater and the hotplate ensembled in the glovebox
Figure 4.2: Images of the thermal evaporator used for deposition of MoO <sub>3</sub> , C60, BCP and Ag layers
Figure 4.3: Illustration of the basic setup of AFM and tip-sample force $(F_{ts})$
Figure 4.4: Images of AFM (MFP-3D) and the cantilever holder
Figure 4.5: Examples of Lennard-Jones potential curve and the tip/sample force curve
Figure 4.6: Schematics of the contact and tapping modes, and an example of the tip-sample force curve
Figure 4.7: Illustration of the resonance frequency shift when the tip-sample interaction falls into attractive and repulsive regimes
Figure 4.8: Schematic of pc-AFM setup75
Figure 4.9: Schematics of KPFM setup and the operation mode
Figure 4.10: Illustration of the working principle of KPFM
Figure 4.11: Cosine-based phasor diagram for a purely capacitive circuit
Figure 4.12: Examples of Nyquist (a) and Bode (b), (c) plots of a RC parallel circuit
Figure 4.13: Schematics of the inelastic and elastic scattering of electrons
Figure 4.14: Schematic layout of EBSD system
Figure 4.15: Illustration of the backscattered electrons diffraction and the formation of Kikuchi bands on the phosphor detector
Figure 4.16: Illustration of Hough transform
Figure 5.1: SEM images of perovskite films processed under different conditions
Figure 5.2: XRD patterns and J-V characteristics of perovskite devices with different annealing treatments
Figure 5.3: Schematics of annealing profiles and nucleation/crystallization processes

Figure 5.4: Plot of <i>J-V</i> curves scanned in forward and reverse directions
Figure 5.5: Histograms of device characteristics of perovskite solar cells
Figure 5.6: Plots of EQE and absorbance spectra of perovskite devices
Figure 5.7: Plots of EIS results measured under illumination at varied bias
Figure 5.8: Plots of capacitances, resistances and recombination time constants at the open-circuit condition versus the light intensity
Figure 5.9: Plots of $V_{oc}$ and $J_{sc}$ versus the light intensity
Figure 5.10: Plots of resistances and capacitances at the short-circuit condition versus the light intensity
Figure 5.11: Plot of $J_{sc}$ and PCE dependence on the perovskite layer thickness
Figure 5.12: Plots of capacitances, resistances and recombination time constants of devices with thick perovskite films at the short-circuit condition versus the light intensity
Figure 5.13: Plots of capacitances and resistances of devices with thick perovskite films at the open-circuit condition versus the light intensity
Figure 6.1: SEM images of perovskite thin films and J-V characteristics of perovskite devices111
Figure 6.2: Photocurrent map and line profile of perovskite thin films
Figure 6.3: Illustration of the correlation between the grain area and the photocurrent of different types of grains
Figure 6.4: Plots of averaged photocurrents and point J-V curves of grains
Figure 6.5: Cross-sectional SEM image of the perovskite film with ~1 um thickness 118
Figure 6.6: Images of EBSD patterns on the same grain. EBSD patterns taken at three different locations within one grain, as marked on the top-view SEM image
Figure 6.7: Images of EBSD patterns and indexing taken on different grains
Figure 6.8: XRD pattern of perovskite thin film with columnar structures
Figure 6.9: Images of similar EBSD patters taken on different grains 122
Figure 6.10: Plots of averaged photocurrents and point J-V curves of grain boundaries

Figure 6.11: Schematic of the tip-sample contact and the electric field distribution at grain boundaries and grain interiors
Figure 6.12: Images of KPFM results and schematic of band bending at GBs 128
Figure 7.1: Band diagram and <i>J-V</i> curves of inverted OPVs with ZnO processed at different conditions
Figure 7.2: <i>J-V</i> characteristics for devices with varied ZnO film thickness. 0 layer, 1 layer, 2 layers
and 3 layers of ZnO buffer prepared at 300 and 450 °C, respectively
Figure 7.3: Transmittance and XRD spectra of ITO/ZnO films annealed at different temperatures
Figure 7.4: AFM images of ZnO films processed under different conditions
Figure 7.5: Schematic of the interface energy level alignment at different interfaces 139
Figure A.1: Solvent engineering of spin-coating method preparing halide perovskite thin film149
Figure A.2: SEM images of perovskite films prepared from precursors with different solvents150

#### Chapter 1

### Introduction

#### 1.1 Motivation

In the past few decades, many efforts have been spent on developing new techniques to utilize different energy sources to replace fossil fuels due to the limited supply and the severe environmental consequences. Though the formation of fossil fuels is a natural process, it takes millions of years to form and the depletion rate is much faster than the formation rate.<sup>1-2</sup> In addition, the carbon dioxide emission by human activities has broken the natural balance of carbon cycle which has existed for thousands of years, leading to the serious greenhouse effect.<sup>3-4</sup> In the US, for example, over 80% of the total energy consumption is provided by fossil fuels in 2016.<sup>5-7</sup>

The search for renewable energy sources has been going on for years. Considering the above facts, solar energy as a clean and renewable source draws an increasing amount of attention. First, solar energy is abundant. The energy striking the earth within one hour  $(4.3 \times 10^{20} \text{ J})$  is close to the world energy consumption in 2016  $(5.6 \times 10^{20} \text{ J})$ .<sup>8-9</sup> Second, it is a clean energy source which satisfies the need of a daunting amount of carbon-neutral energy. Last, the 6.5-billion-year lifetime of the sun makes solar energy quite sustainable. In order to utilize solar energy, solar cells are employed to convert solar power into electricity.

Since the photovoltaic effect was first observed in 1839 by Alexandre-Edmond Becquerel, solar cells have developed into the third generation. The first generation (wafer-based) solar cells are made of single/polycrystalline silicon.<sup>10-13</sup> And the second-generation cells are called thin film solar cells employing materials such as amorphous silicon<sup>12, 14-15</sup> and copper indium gallium selenide (CIGS)<sup>16-18</sup>. The emerging third generation consists of many different types of systems

such as organic photovoltaics,<sup>19-21</sup> dye-sensitized solar cells,<sup>22-25</sup> and perovskite solar cells<sup>26-28</sup>. So far, a large number of efforts have been spent on the research of third generation cells since they promise to accomplish the goal of low-cost and high-efficiency solar cells. In this work, the study focuses on investigating the impact of microstructures and interface energetics on the device performance and is carried out on perovskite and organic solar cells.

Organic-inorganic hybrid perovskite solar cells have drawn a tremendous amount of attention due to its low cost, facile fabrication and high efficiency.<sup>27-30</sup> Perovskite films are prepared simply by spin-coating the precursor solution onto the substrates, followed by a low-temperature annealing treatment.<sup>28, 31</sup> The high light absorption coefficient has been established in this class of material, where ~ 90 % of light (wavelength: 350-750nm) can be absorbed in a 400 nm thick film.<sup>32-33</sup> Additionally, the low exciton binding energy on the order of tens of millielectronvolt (meV) indicates that free charge carriers are predominantly generated under illumination.<sup>34-36</sup> Beyond the light harvesting capability, carrier transport and charge collection also collectively contribute to the efficiency of photovoltaic devices.<sup>37-40</sup>

Due to the polycrystalline nature of perovskite thin films, it is critical to investigate the impacts of microstructures, such as grain size, crystallinity and texture structure, on the electrical properties of thin films.<sup>30, 41-42</sup> More interestingly, studies have suggested that the texture of the perovskite thin film may play a more significant role in determining the device efficiency than the size of perovskite grains.<sup>32, 43</sup> Thus far, time-resolved photoluminescence(tr-PL) is the most commonly adopted technique for investigating the influence of crystal orientation and texture structure on charge carrier dynamics in perovskite solar cells. Although variations of the carrier lifetime are observed in perovskite thin films with different textures<sup>39, 41, 44-46</sup>, it is challenging to disentangle the texture effects on charge transport and collection processes since the trap states in

the bulk and at the surface would both influence the carrier lifetime determined from the tr-PL measurements<sup>47</sup>. By employing the ramp annealing treatment, it's possible to control the crystallinity and texture structure of perovskite thin films and thus investigate its correlation with device performance. In addition, through the use of EIS measurements on perovskite devices, the charge transport and collection processes can be differentiated based on their responses to the light intensity, the applied bias and the frequency. Taken together, the correlation between the crystallinity/texture structure and carrier dynamics in perovskite solar cells can be investigated.

The other important feature of polycrystalline thin films is grains and grain boundaries (GBs), which could demonstrate different photo-responses depending on the crystal orientation of grains and the type of GBs, such as high- and low-angle GBs. Thus far, many techniques with spatial resolutions have been employed to investigate their roles in perovskite thin films. The grain-to-grain variation has been revealed in the measurements including the electron beam-induced current and the confocal fluorescence microscopy, suggesting a heterogeneous contribution of crystalline grains to the photocurrent.<sup>48-50</sup> The effect of GBs on the device performance is still quite controversial. On one hand, a lower photoluminescence (PL) intensity and a shorter local PL lifetime have been identified at GBs as compared with grain interiors, indicating that GBs act as non-radiative recombination centers.<sup>51</sup> On the other hand, the density functional theory (DFT) calculation has predicted that GBs should be benign in halide perovskites due to the dominant shallow defect states, which distinguishes halide perovskites from other existing solar cell absorbers.<sup>52-53</sup>

Despite much progress, there are several outstanding questions that remain to be addressed. For instance, as mentioned above, studies have suggested that the texture of perovskite thin films may play a more significant role than the size of perovskite grains in determining the device efficiency.<sup>43, 54</sup> This indicates that the grain orientation as well as the grain boundary type, i.e., low-angle boundaries formed between grains of the identical crystal orientation vs. large-angle boundaries between grains of different orientations, could lead to drastically different photoresponses. From a fundamental perspective, beyond modulating the carrier diffusion length and transport efficiency, the grain orientation may also impact the charge transfer and collection efficiency at contacts.<sup>39, 55</sup> Scanning probe studies of perovskite thin films have reported substantial spatial variations in the local photo-response, including  $J_{sc}$  and  $V_{oc}$ .<sup>48-49, 51, 56</sup> One has attributed the significant intra-grain heterogeneity to the facet-dependent density of surface trap states.<sup>56</sup> While the interconnected aggregates of several adjacent grains, not just within individual grains, exhibiting similar current levels have also been identified, indicating that there is a network of beneficial and detrimental current pathways.<sup>49</sup> Nevertheless, because of the complications arising from the stacking of grains with buried grain boundaries and interfaces, it is challenging to identify, for instance, the high conductivity pathways that promote the transport across interconnected grain aggregates. Thus, it is necessary to carry out local J-V measurements with AFM on perovskite grains of columnar structures and distinct crystal orientations, and GBs of the well-classified type to evaluate their contributions to the overall power conversion efficiency.

In addition to perovskite solar cells, OPVs have also stood out as an alternative clean energy solution, offering potential benefits of low cost and mechanical flexibility<sup>57-58</sup>. It is known that in OPV devices the energy level alignment at the interfaces between metal electrodes and photoactive layers is important in determining  $J_{sc}$ ,  $V_{oc}$ , and fill factor (FF).<sup>59-66</sup> At weakly interacting interfaces such as the spin-coated polymers on non-reactive substrates, the vacuum level alignment is often assumed in the OPV design.<sup>67</sup> However, Fermi level pinning to the integer charge-transfer states of organic

semiconductors has been observed in a number of systems including poly-3-hexylthiophene (P3HT) and [6,6]-phenyl C61 butyric acid methyl ester (PCBM).<sup>61, 68</sup>

Interfacial buffer layers, therefore, play a critical role in adjusting the contact properties between active layers and electrodes. For instance, in the presence of non-ohmic contacts in BHJ devices, injection barriers may give rise to a reduction of the internal electric field and a decrease in  $V_{\rm oc}$ ,<sup>69-70</sup> while interfacial buffer layers can be readily utilized to optimize these contacts<sup>71-73</sup>. Additionally, interfacial buffer layers may contribute to the enhancement of charge collection and the reduction of the interfacial contact resistance and charge recombination, leading to a smaller series resistance ( $R_{\rm series}$ ), a larger shunt resistance ( $R_{\rm shunt}$ ), and hence the improved performance<sup>59, 62-63, 74-75</sup>.

Among the n-type buffers used in the inverted structures,<sup>59, 76-80</sup> ZnO offers the advantages of high conductivity, excellent optical transparency and environmental stability<sup>73, 81-82</sup>. Various preparation methods have been used to fabricate high-quality ZnO films in planar and nanowire configurations for solar cell applications<sup>83-90</sup>. Among them, the sol-gel method is considered to be cost-effective and compatible with the solution processing of organic solar cells. The sol-gel method also allows for ZnO-based nanostructuring,<sup>91-92</sup> elemental doping,<sup>75, 93</sup> and surface modification,<sup>63, 94</sup> to improve the ZnO functionality. Here we focus on inverted OPVs with the ZnO cathode buffer layer fabricated by the sol-gel method from zinc acetate decomposition. Several parameters can be tuned in the sol-gel process to improve the morphology, as well as its optical and electrical properties of ZnO thin films. However, there have been conflicting reports of this optimization in the literature<sup>74, 95</sup>. Optimal annealing temperatures reported in the literature range widely from 150 to 450 °C<sup>60, 74, 89, 91, 95-102</sup>, although it is recognized that low-temperature annealing is more compatible with the processing of plastic organic solar cells. Therefore, a thorough investigation of the physical characteristics of ZnO buffer layers annealed at different temperatures is necessary.

1.2 Outline of this work

To better understand the working principle of solar cells, semiconductor physics and physical processes in photovoltaic devices are introduced in Chapter 2. The device architecture based on planar structured solar cells as well as the physical processes such as photo-generation, carrier transport, charge collection, and recombination will be the focus of the discussion. With a basic understanding of the mechanism of photovoltaics, *J-V* characteristics are introduced, and the factors that impact the device performance are discussed.

After getting acquainted with solar cell physics, perovskite solar cells and OPVs are introduced in Chapter 3. First, the physical properties of perovskite materials and their contributions to the device performance are discussed. Also, the current status of perovskite solar cells is reviewed to assess the challenges and problems to be addressed. Different fabrication methods are also described since they determine the film quality. The second part focuses on the device architecture and physical processes in OPVs. The BHJ based OPVs are described and compared with planar perovskite solar cells. The critical role of the electrode/active layer interface is then discussed, and different methods to tune the interface properties are demonstrated. At last, ZnO and its application in OPVs are illustrated as well as the challenges of tuning its electrical property.

Before reaching the experimental results and conclusions, the device fabrication processes and experimental techniques that help to address the physical properties of solar cells are described in Chapter 4. The fabrication process is important as it determines the quality of each part in the devices and thus the efficiency. Details about the working principle of AFM, EIS, and EBSD and how to interpret the data are described.

Chapter 5 discusses the impact of microstructure in perovskite thin films on the device performance. The texture structure and morphology of perovskite thin films are tuned by ramp annealing treatment, which includes a two-step annealing profile. The correlation between device performance and the thin film crystallinity/texture is investigated. To elucidate the impact of the texture structure on the carrier dynamic processes in perovskite solar cells, EIS, which is able to disentangle the convoluted charge transport and collection processes, is performed on devices with different thickness and under different light intensities and applied biases.

To further understand how the microstructures, specifically grains and grain boundaries, impact the device performance, AFM techniques are utilized to investigate the correlation between microstructure and nano-scale device performance in Chapter 6. The discrete photocurrent levels across crystalline grains and the anti-correlation of  $J_{sc}$  and  $V_{oc}$  of each grain are identified by pc-AFM and point *J*-*V* spectra on perovskite thin films. With the aid of electron backscattering diffraction (EBSD) measurement, the crystal orientations of grains are revealed. Additionally, GBs in perovskite thin films demonstrate heterogeneous behaviors with low-angle GBs showing a higher power output than the adjacent grains. KPFM is utilized to investigate the energetics at grain boundaries.

Chapter 7 discusses the application of ZnO as a buffer layer between the cathode material, i.e., indium tin oxide (ITO) and the active layer of P3HT and PCBM. The work function of ZnO thin film is tuned, and its impact on the device performance is attributed to the efficient charge collection at the interface. Modulations on the interface energetics are analyzed by KPFM.

In Chapter 8, the thesis studies are summarized, together with future work from the perspectives of device engineering and instrumentation development.

### Chapter 2

### Solar cell physics

In this chapter, the semiconductor physics is introduced in the first part. The band structures, the doping of semiconductors and the formation of junctions between metals and semiconductors are discussed, as well as their applications in photovoltaics. The difference between organic and inorganic semiconductors is also described. In the second part, the configuration of planar structured solar cell is used as an example to illustrate the physical process occurring in the devices under illumination. The processes from the generation of excitons to the formation of photocurrent are detailed. Lastly, the *J-V* characterization of solar cells are described. The device performance parameters are defined and the factors impacting the characteristic parameters are deliberated.

#### 2.1 Introduction to semiconductors

#### 2.1.1 Basics of semiconductors

Semiconductors as the core of semiconductor devices are widely used in our daily life owing to the unique electrical properties compared with insulators and conductors. Generally, semiconductors demonstrate certain crystal structures: a cluster of repetitive atom arrangements. When two atoms are brought together, the atomic orbitals would split into two new orbitals with higher and lower energy than that of the original orbitals. With more and more atoms forming a cluster, the split orbitals form bands as shown in Figure 2.1. If the material shows continuous electronic states without a gap, it is a conductor. For semiconductors and insulators, there is a bandgap in the energy diagram. The band above the gap is defined as conduction band (CB) and the one below is the valence band (VB). The bandgap of semiconductors is around 0.5 to 3.0 eV. Materials with bandgaps larger than 3 eV are called insulators. At the low temperature and under the dark condition, semiconductors are barely conductive since not many electrons can be excited to the CB. However, when enough energy is provided to the semiconductor, such as incident photons and thermal energy, electrons in the VB can be excited to the CB and the material becomes "conductive". For the organic semiconductors, which are  $\pi$ -bonded molecules or polymers, they form relatively dense but discrete levels instead of continuous bands. The highest occupied level is called HOMO, similar to the concept of valence band maximum (VBM) in inorganic semiconductors. The lowest unoccupied level is called LUMO, corresponding to the conduction band minimum (CBM). The difference between LUMO and HOMO equals the bandgap of the material. Compared with inorganic semiconductors, organic semiconductors demonstrate smaller dielectric constants because of the diminished charge screening capability.



Figure 2.1: **Band formation of semiconductors**: as the number of atoms increases, the atomic orbitals split into multiple levels and thus form the conduction band and the valence band.

To investigate the carrier population in semiconductors, the density of states and Fermi level function are two key parameters. The density of states is a prerequisite for determining the carrier concentration and energy distributions of carriers in semiconductors. It equals the number of allowed electron states per energy per volume. Through the approximation of a particle in a 3-D box, the density of states (D(E)) is expressed by:

$$D_e(E) = \frac{1}{2\pi} \left(\frac{2m_e^*}{\hbar^2}\right)^{3/2} \left(E - E_c\right)^{1/2}$$
(2.1)

$$D_h(E) = \frac{1}{2\pi} \left(\frac{2m_h^*}{\hbar^2}\right)^{3/2} \left(E_V - E\right)^{1/2}$$
(2.2)

Here,  $m_e^*$  and  $m_h^*$  are the effective mass of electron and hole, respectively, which is related to the band structure of the semiconductor. In addition to the density of states, the Fermi function is also crucial to calculate the number of electrons occupying certain electronic states. The Fermi function f(E), as a function of energy, is equal to the ratio of filled states over all allowed states at a given energy. It can be described by the following equation:

$$f(E) = \frac{1}{1 + e^{(E - E_f)/kT}}$$
(2.3)

 $E_f$  is called the Fermi level as shown in Figure 2.1 which lies within the bandgap. For intrinsic semiconductors, the Fermi level is close to the center of the bandgap. If the material is doped, its Fermi level would shift upwards or downwards accordingly.

#### 2.1.2 Intrinsic and extrinsic semiconductors

Semiconductors containing an insignificant number of impurity atoms are referred as intrinsic semiconductors. Since the only way to generate electrons and holes is to excite electrons in the VB to the CB in intrinsic semiconductors, the population of electrons and holes are always equal. However, semiconductors with a high electron (n-type) or hole (p-type) concentration are widely used in semiconductor devices. These types of semiconductors are termed as extrinsic semiconductors and show different electrical properties than intrinsic ones. In order to manipulate the carrier concentration, the specific impurity atoms are added into the semiconductor, which is described as doping.



Figure 2.2: Schematic of semiconductor doping. (a) n- and p-type doping of silicon with phosphorous and boron atoms; (b) the influence of donor states ( $E_D$ ) and acceptor states ( $E_A$ ) on the position of Fermi level.

Figure 2.2 depicts the semiconductor bonding model of Si, which helps us understand the mechanism of the doping process. As an IV column semiconductor, there are four valence

electrons and four neighbors for each Si. By sharing the valence electrons, the covalent bonds are formed between Si atoms. When a silicon atom is replaced by a phosphorous atom, five valence electrons are available for bonding with the adjacent Si atoms. However, there are only four Si neighbors and each of them needs only one electron to form the covalent bond. The extra electron is loosely bound to the phosphorous atom and can be easily freed from it by the thermal energy provided at room temperature. In this case, the phosphorous atom is called donor. In the energy band diagram (Figure 2.2), it can be seen that the energy level  $(E_D)$  introduced by replacing Si with P is very close to the conduction band edge and the electrons can be excited to the CB at room temperature. Correspondingly, the Fermi level is shifted upwards (closer to CB) compared with the intrinsic case. Vice versa, the replacement of Si with a Boron atom which only provides three valence electrons would result in an electron vacancy (hole). The adding of Boron atoms (acceptor) introduces the energy levels close to VB ( $E_A$ ) which are able to accept electrons excited by the thermal energy at room temperature from the valence band. Thus, the Fermi level shifts downwards to the VB. The doping source can be intrinsic and extrinsic. The example shown above is the extrinsic doping of Si. For solution-processed perovskite materials, both n-type and p-type doping have been identified depending on the fabrication process and the types of intrinsic defects, such as the vacancy/interstitial of I<sup>-</sup> or MA<sup>+</sup>.

#### 2.1.3 Equilibrium distribution of carriers

The density of states and the Fermi function have been introduced previously. The carrier concentration in the intrinsic semiconductors can then be calculated by the following equations:

$$n = \int_{E_c}^{\infty} D_e(E) f(E) dE$$
(2.4)

$$p = \int_{-\infty}^{E_V} D_h(E) (1 - f(E)) dE$$
(2.5)

Here, n and p are the concentration of electrons in conduction band and holes in valence band, respectively. According to Boltzmann approximation, if the Fermi level is far enough from both band edges, the Fermi function can be simplified by:

$$f(E) \approx e^{\left(E_f - E\right)/k_B T} \tag{2.6}$$

And n and p can thus be written by:

$$n = N_c \exp(-(E_c - E_f)/k_B T)$$
(2.7)

$$N_C = 2\left(\frac{m_e^* k_B T}{2\pi\hbar^2}\right)^{3/2} \tag{2.8}$$

$$p = N_V \exp(-(E_f - E_V)/(k_B T))$$
 (2.9)

$$N_V = 2\left(\frac{m_h^* k_B T}{2\pi\hbar^2}\right)^{3/2} \tag{2.10}$$

 $N_C$  and  $N_V$  are termed as the effective density of states of the conduction band and the valence band, respectively. According to the above equations, the product of n and p equals:

$$n \cdot p = N_c N_V \exp\left(-E_g/k_B T\right) = n_i^2 \tag{2.11}$$

$$n_i = \sqrt{N_c N_V} \exp(-E_g/2k_B T) \tag{2.12}$$

Here, we introduce the intrinsic carrier concentration  $(n_i)$ : the electron and hole concentration in intrinsic semiconductors, which is related to the bandgap and the density of states. For example, in Si, the intrinsic carrier concentration at room temperature is  $1.05 \times 10^{10}$  cm<sup>-3</sup>.

For the extrinsic semiconductors, the above equations still hold. However, the electron and hole concentrations are not equal anymore. For n-type semiconductors, the electron density in the conduction band is given by:

$$n = n_i + N_D^+ \tag{2.13}$$

where  $N_D^+$  is the density of ionized donors. At 0 K, all donor states are full so n = 0. As the temperature increases, donor electrons are excited to CB and  $n \approx N_D^+$  since  $N_D^+ \gg n_i$ . As equation (2.11) still holds, the hole density in the valence band is written by:

$$p \approx n_i^2 / N_D^+ \tag{2.14}$$

At even high temperatures, a large number of electrons in the valence band are excited to the conduction band  $(n_i \gg N_D)$  and *n* equals  $n_i$  again.



Figure 2.3: Temperature dependence of carrier concentrations in n-type semiconductors.

2.1.4 Junctions

Some basic physical properties of semiconductors have been introduced in the previous content. Photovoltaic devices consist of multiple layers of materials in order to generate photocurrent. A junction forms when two materials are in contact, which could facilitate the charge transport and collection in the devices. Thus, it is necessary to talk about the scenario when a semiconductor is in contact with materials such as metals and semiconductors.

#### 2.1.4.1 Metal-semiconductor junction

Suppose that there is an n-type semiconductor with the work function of  $\Phi_n$  and a metal with the work function of  $\Phi_m$  ( $\Phi_n < \Phi_m$ ) as shown in Figure 2.4. Before they are in contact, the vacuum levels align indicating that CB, VB and  $E_f$  of the semiconductor and the metal are independent. However, when these two materials are in contact, the Fermi levels level up to reach the equilibrium, leading to the shift of the vacuum level. Electrons in the semiconductor flow to the metal and leave the positive charges in the region close to the metal which is called the space charge region. The width of the space charge region depends on the dielectric constant of the semiconductor ( $\varepsilon_s$ ), the doping level of the semiconductor ( $N_D$ ), the vacuum level change at the junction ( $V_{bi}$ ) and the applied bias ( $V_A$ ), as described by:

$$W = \sqrt{\frac{2\varepsilon_s(V_{bi} - V_A)}{qN_D}} \tag{2.15}$$

The n-type semiconductor with a high doping level, for example, demonstrates a narrow depletion region due to the high concentration of electrons. On the other side of the junction, the corresponding negative charges in the metal is limited to the interface owing to its high dielectric constant. The separation of electrons and holes forms an electric field which suppresses the charge transfer at the contact. The intensity of the electric field increases as more charges are separated. Ultimately, the electric field would stop the charge flow at the junction. Though the space charge region in the semiconductor is positively charged, the conduction and the valence band positions relative to the vacuum level are the same as the regions away from the junction. As the vacuum level in the space charge region changes, the CB and VB change accordingly, the process of which is described as the band bending. This junction formed between the n-type semiconductor and the metal is referred as the Schottky barrier which shows a rectifying characteristic.



Figure 2.4: Formation of Schottky barriers: (a) n-type semiconductor and metal junction when  $\Phi_n < \Phi_m$ ; (b) p-type semiconductor and mental junction when  $\Phi_p > \Phi_m$ .

Figure 2.5 illustrates the rectifying characteristic of the Schottky barrier formed between the n-type semiconductor and the metal. As mentioned before, at the thermal equilibrium there is not net current flow (the number of electrons flowing to the metal equals the number of holes to the semiconductor). Under a reverse bias, a positive voltage is applied to the semiconductor which enlarges the band bending and further suppresses the electrons from flowing to the metal. Consequently, the net current is determined by the leakage current resulting from the movement of holes to the metal. In n-type semiconductors, holes are the minority carriers, so the current level is quite small. Under a forward bias, a negative voltage is applied to the semiconductor, and Schottky barrier is reduced. Thus, the flow of electrons to the metal is enhanced. As the barrier height decreases, the current level increases approximately exponentially with the bias. Similarly, Schottky barrier is observed at the junction of the p-type semiconductor and the metal when  $\Phi_p > \Phi_m$  as shown in Figure 2.4b.



Figure 2.5: Rectifying characteristics of the metal/semiconductor junction.

The situation is different if the work function of the metal is higher than that of the n-type semiconductor. As shown in Figure 2.6, the electrons flow from the metal to the semiconductor in order to reach the thermal equilibrium. This type of junction does not show the rectifying characteristics and is called Ohmic contact since the majority carriers is able to pass the junction in either direction with a low resistance. Similarly, for the p-type semiconductors and the metals, when  $\Phi_p < \Phi_m$ , an Ohmic contact forms at the junction. There are other ways to form an Ohmic contact in addition to the satisfaction of  $\Phi_n > \Phi_m$  or  $\Phi_p < \Phi_m$ . In the heavily doped semiconductors, for example, the space charge region could be quite narrow (several nanometers) and thus the majority carriers are able to tunnel through the barrier.

At the organic semiconductor/metal junction, the situation is different. The formation of the junction, in this case, is described by the Integer Charge-Transfer model.<sup>103</sup> The charge transfer

at the organic semiconductor/metal interface is dominated by the tunneling of electrons because of the negligible hybridization of  $\pi$ -electronic molecular orbitals and the substrate wavefunctions. The tunneling of the electrons indicates that the transfer process involves an integer amount of charge to the well-defined charge states located at the surface of the organic semiconductor.



Figure 2.6: Formation of Ohmic contacts at the metal/semiconductor junction. Between metal and (a) n-type semiconductors when  $\Phi_n > \Phi_m$ , (b) p-type semiconductors when  $\Phi_p < \Phi_m$ 

There are the positive and the negative integer charge-transfer states ( $E_{ICT+}$  and  $E_{ICT-}$ ). The energy of  $E_{ICT+}$  is defined as the energy required to take away one electron from the molecules, and the energy of  $E_{ICT-}$  is the energy gained by the molecule when adding an electron to it. The generation of the Integer Charge-Transfer states is caused by the formation of the self-localized states, also called polarons, when reducing or adding an electron to the organic molecules. As depicted in Figure 2.7, when the work function of the metal,  $\Phi_m$ , falls between the  $E_{ICT+}$  and  $E_{ICT-}$ , the vacuum level alignment is expected at the interface. If  $\Phi_m$  is larger than  $E_{ICT+}$ , electrons would be taken away from the organic molecules and the Fermi level is pinned to the  $E_{ICT+}$ . Similarly, the Fermi level would be pinned at the  $E_{ICT-}$  when the Fermi level of metal is above  $E_{ICT-}$  as a result of the addition of electrons to the organic molecules. It is worth mentioning that this also holds for the semiconducting organic/inorganic interfaces with negligible interactions.



Figure 2.7: Schematics of the formation of junctions at the semiconducting organics and metal interface: when (a)  $\Phi_m$  is smaller than  $E_{ICT-}$ , (b)  $\Phi_m$  is between  $E_{ICT-}$  and  $E_{ICT+}$ , and (c)  $\Phi_m$  is larger than  $E_{ICT-}$ .



Figure 2.8: Illustration of the band alignment at (a) p-n and (b) p-i-n junctions.

## 2.1.4.2 p-n junction and p-i-n junction

The p-n junction is the most widely adopted structure in photovoltaic devices. When an ntype and a p-type semiconductor are in contact, the junction formed is called the p-n junction. As mentioned before, the Fermi levels level up if two materials are in contact and an electric field is introduced at the junction. As shown in Figure 2.8, electrons in the n-type material flow to the ptype material and holes in the p-type material flow to the n-type material. Thus, the space charge regions exist on both sides of the junction. The junction always behaves as a barrier for the majority carriers and a high conductivity path for the minority carriers, which is beneficial for the charge separation. In solar cells, the separation of electrons and holes is crucial to the formation of photocurrent.

If the carrier diffusion length in the semiconductor is short and photo-generated carriers in p- or n-type materials are not likely to contribute to the photocurrent, the p-i-n junction is advantageous. The junction is formed by inserting a layer of the intrinsic semiconductor between

n- and p-type materials. The built-in electric field is extended to a wider region as shown in Figure2.8b and drives electrons and holes generated in the intrinsic layer to the opposite directions.



Figure 2.9: **Planar structured solar cells: active layer, anode and cathode**. Under illumination, the active layer absorbs photons and generates excitons which are then dissociated into free carriers.

#### 2.2 Planar structured solar cells

In this part, planar structured solar cells are used as an example to illustrate the working principle of photovoltaic devices. Planar structured solar cells consist of three parts: active layer, cathode and anode as shown in Figure 2.9. The active layer, which is made of semiconductors, absorbs light and converts it into electrons and holes via the photovoltaic effect. The generated electrons and holes are then transported to the electrodes. As a result of the selectivity of electrode materials, the cathode and anode collect electrons and holes, respectively. Then, the free carriers form an electrical current and contribute to the external circuit.

#### 2.2.1 Light absorption and exciton dissociation

The active layer absorbs photons and generates charge carriers. The number of photons that the active layer is able to absorb is determined by many factors. First, the active layer can only

absorb the photons with the energy higher than its bandgap. Semiconductors with low bandgap utilize more of the solar spectrum and thus generate more photocarriers and output a higher current. Second, the quantity of the light absorption depends on the absorption coefficient which is wavelength dependent. Photons with the energy just above the bandgap only excite electrons around the valence band edge to the CB edge, while high energy photons can excite electrons deep in the VB. In addition, the absorption coefficient depends on the density of states in the conduction and valence band of semiconductors. A higher density of states provides more "parking lots" for the excited electrons in the conduction band. Last, the thickness of the active layer influences the absorption of photons. More photons can be absorbed in thicker films. However, if the film is too thick, photocarriers must travel a long distance to the electrode, which increases the possibility of being nullified by the counter charges (more details are shown in the latter part of this chapter). An optimized film thickness is essential to balance between the light absorption and carrier transport process in photovoltaic devices.

After the absorption of photons, it generates the electron-hole pairs, which are called excitons, in the semiconductor as shown in Figure 2.9. There is a binding force between the electron and hole in the exciton. Consequently, it requires an external force to dissociate excitons into free carriers. The bound of the electron and the hole is similar to the coulombic interaction between the positive and negative charges. According to Coulomb's law, the force is reversely proportional to the dielectric constant:

$$F = \frac{q^2}{4\pi\varepsilon\varepsilon_0 r^2} \tag{2.16}$$

where r is the distance between the two charges. The energy required to dissociate the exciton is called the binding energy, which is also related to the dielectric constant of the active layer
material.<sup>36, 104</sup> Semiconductors with high dielectric constants, such as organic-inorganic hybrid perovskites, demonstrate low exciton binding energy: tenths of meV. For organic semiconductors with small dielectric constants, the binding energy could be as high as hundreds of meV. Consequently, in OPVs, the donor-acceptor system is introduced to create an energy offset at the interface of the donor and the acceptor to dissociate excitons.<sup>19, 105</sup> More details on the donor-acceptor system will be discussed in next chapter.

#### 2.2.2 Charge transport

With the excitons being dissociated into free carriers, the next step is charge transport. Electrons and holes must travel across the active layer to the cathode and anode, respectively. The mechanism of charge transport process in the active layer is the drift and diffusion.

## 2.2.2.1 Drift

Drift is defined as the motion of the charged particle in response to an electric field. When an electric field is applied to the device, it drives holes moving towards the direction of the electric field and the electrons in the direction opposite to the electric field. Thus, the drift current is given by:

$$i_{n,drift} = q\mu_n nE \tag{2.17}$$

$$i_{p,drift} = q\mu_p pE \tag{2.18}$$

*E* is the electric field in the device, and  $\mu_n$  and  $\mu_p$  are the carrier mobility for the electron and hole, respectively, with the unit of cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. The origin of *E*-field could be an external bias applied to the device or a built-in electric field established between materials of different work functions. For example, in photovoltaic devices, the cathode and anode consist of different materials. The anode material which collects holes demonstrates a low work function. For the cathode, materials

with high work functions are employed to collect electrons. When the cathode, the anode and the active layer are in contact, a built-in electric field forms due to the alignment of Fermi-levels, as illustrated in Figure 2.8. When solar cells are under illumination, the built-in electric field draws the photo-generated electrons to the cathode and holes to the anode, forming the photocurrent. The carrier mobility is the key parameter in determining the performance of solar cells. Carriers with a high mobility suppress the recombination of electrons and holes and improve the charge transport and collection efficiency. One factor that influences the carrier mobility is the scattering process taken place in the active layer. For semiconductors, the phonon scattering and the ionized impurity scattering processes tend to be dominant. The phonon scattering refers to the collision between the carriers and the vibrating lattice atoms. The ionized impurity scattering is related to the coulombic interaction (attraction or repulsion) between the carriers and the ionized donors/acceptors, especially in the highly doped semiconductors. In addition, for polycrystalline materials, like organic-inorganic hybrid perovskite thin films, the defect scattering must be taken into consideration due to the break of crystal symmetry at the grain boundaries. The carrier mobilities for electrons and holes could also be different in the same material owing to the different effective mass. The imbalanced carrier mobility requires more efficient charge collection at the electrode which collects the carriers with the lower mobility.

## 2.2.2.2 Diffusion

Diffusion is the process in which particles tend to redistribute to reach a concentration equilibrium as a result of the random thermal motion. Consequently, a net movement of carriers goes from the areas of the high concentration to the areas of the low concentration in solar cells. The corresponding currents are expressed by the following equations:

$$i_{n,diff} = q D_n \nabla_n \tag{2.19}$$

$$i_{p,diff} = -qD_p \nabla_p \tag{2.20}$$

where  $D_n$  and  $D_q$  are the diffusion coefficient of electrons and holes with the unit of cm<sup>2</sup> s<sup>-1</sup>;  $\nabla_n$  and  $\nabla_p$  are the concentration gradient of electrons and holes. The diffusion coefficient, similar to the carrier mobility in the drift process, is crucial in determining the carrier diffusion process. The relationship between the diffusion coefficient and the carrier mobility has been built by Einstein:

$$\frac{D}{\mu} = \frac{kT}{q} \tag{2.21}$$

In the studies of solar cells, many techniques, such as Hall measurement, PL quenching and time of flight, have been employed to extract the carrier mobility information in order to characterize the transport properties of devices.

### 2.2.3 Charge Collection

After the photo-generated electrons and holes arrive at the electrode, they must be selectively collected by the electrodes in order to contribute to the external circuit, instead of being "nullified" by the counter charges. The selectivity of cathodes and anodes is enhanced by a selective contact layer inserted between the active layer and the electrodes, named by the electron or hole transport layer (ETL/HTL). Generally, materials used in the selective contact layer are highly doped n-type and p-type semiconductors for ETL and HTL, respectively, with a high carrier mobility. For example, n-type materials employed as ETL usually show high selectivity and conductivity of electrons and a deep VB to block holes.<sup>106-107</sup> Another factor to consider here is the energy level alignment at the contact. The interface energetics is critical since it directly impacts the collection efficiency. Ideally, an Ohmic contact is expected at the active layer/selective contact and the selective contact/electrode interfaces to avoid the energy loss. However, the

formation of the Schottky barrier is the common case in solar cells. Meanwhile, at the interfaces, there exists a high density of defects which leads to severe recombination. More details about surface recombination will be discussed in the next section.



Figure 2.10: **Schematic of charge transport driven by the built-in electric-field**. (a) Illustration of the carrier transport process in the active layer; (b) the built-in electric field induced by the work function difference of electrodes drives electrons and holes to the cathode and the anode, respectively.



Figure 2.11: Schematic of charge collection at the interface. (a) The free carriers are collected by the cathode and the anode due to the selectivity of the electrode materials, (b) both interfaces between the active layer and ETL as well as ETL and cathode impact the charge collection efficiency.

## 2.2.4 Recombination, carrier lifetime and diffusion length

#### 2.2.4.1 Recombination in photovoltaic devices

Recombination is the loss mechanism of photovoltaic devices which refers to the loss of free carriers. For example, an electron annihilates a hole instead of contributing to the photocurrent. There are different ways of recombination, such as radiative recombination, Auger recombination and trap-assisted recombination.

Radiative recombination is the dominant loss mechanism in the direct bandgap semiconductors. As shown in Figure 2.12, an electron in the conduction band relaxes to the valence band and recombines with a hole while releasing a photon. This loss mechanism is related to the

intrinsic property of the material and is inevitable. Though the radiative recombination is damaging the performance of photovoltaic devices, the light emitting diode device is a good example of utilizing the radiative recombination mechanism.



Figure 2.12: **Schematics of the loss mechanisms**. (a) Band to band radiative recombination, (b) Auger recombination, (c) trap-assisted recombination, and (d) surface recombination

The other unavoidable loss mechanism is the Auger recombination which involves three charge carriers. Figure 2.12b depicts the Auger recombination process. When an electron in the CB decays to the VB, instead of releasing the energy in the form of heat or photons, it transfers the amount of energy, which equals the bandgap, to the other electron in the CB which eventually goes back to the CB edge via thermal relaxation. The above process involves the interaction among the carriers, so Auger recombination is dominant in the low bandgap materials with high carrier densities.

Recombination via trap states, also called Shockley-Read-Hall (SRH) recombination, denotes the recombination of electrons and holes via an electronic state within the bandgap. For the perfect single-crystal semiconductors, SRH recombination does not occur due to the lack of mid-gap states. As shown in Figure 2.12c, SRH recombination includes two steps. First, an electron (or hole) is trapped in the mid-gap state which is introduced by the defects of the crystal structures. The trapping and de-trapping processes are reversible since the trapped charges can be re-emitted to the CB or VB by thermal excitation. However, if a hole (or electron) is also captured by the mid-gap state before the electron (or hole) is thermally re-emitted to the CB, recombination would happen. For defect states deep into the bandgap, the thermal energy required to de-trap the charge is relatively high and it is likely to induce recombination since the trapped charge has a high chance to recombine with a counter charge than being re-emitted. Vice versa, if the defect state is close to the band edge, the trapped charges can be easily de-trapped instead of recombining with the counter charges.

Surface recombination is another critical loss mechanism for photovoltaic devices. The semiconductor surface is an area with a high density of defects as the crystal symmetry is interrupted and a large number of dangling bonds exist there. As the carriers recombine, a concentration gradient would form which drives more carriers to the surface. However, the surface recombination can be suppressed by passivating the defect sites, such as neutralizing the charged sites by doping or forming bonds with the unpaired electrons by introducing small molecules or interfacial layers at the contact.

#### 2.2.4.2 Carrier lifetime and diffusion length

Recombination process, as discussed before, is a loss mechanism in photovoltaic devices. It determines how long the carriers survive, how far they travel before recombining, and eventually the number of carriers contributing to the external circuit. The average amount of time which the carrier can survive in an excited state is called the carrier lifetime. The diffusion length is the distance that carriers are able to travel after photogeneration and before recombination. It determines the thickness of the active layer in solar cells. For example, the thickness of the active layer in OPVs is around 100 nm as a result of the low carrier diffusion length. The active layer in perovskite solar cells is around 300-500 nm thick since the perovskite materials demonstrate a carrier diffusion length as long as hundreds of nanometers. Overall, the carrier lifetime and carrier diffusion length are the key factors that impact the efficiency of photovoltaic devices. Semiconductor devices with short carrier lifetime and diffusion length would suffer from severe recombination and demonstrate low efficiency.

Carrier lifetime ( $\tau$ ) depends on the total recombination rate of the three recombination mechanisms mentioned above. Therefore, it can improve the lifetime of photogenerated carriers by employing semiconductors with insignificant radiative/Auger recombination and manipulating the density of defect states to suppress the SRH recombination. Obviously, carriers with a longer lifetime are able to diffuse a further distance, and the correlation between carrier lifetime and diffusion length (*L*) is written by:

$$L = \sqrt{\tau D} \tag{2.22}$$

*D* is the diffusion coefficient and related to the intrinsic property of the semiconductor.

#### 2.3 J-V characteristics of photovoltaic devices

*J-V* characteristics are measured in order to determine the device performance of solar cells. In the dark, photovoltaic devices behave as diodes and the corresponding *J-V* curve is shown in Figure 2.13. The dark current ( $I_D$ ) is written by:

$$I_D = -I_o \left[ \exp\left(\frac{qV}{nkT}\right) - 1 \right]$$
(2.23)

 $I_o$  is called the saturation current which equals the leakage current of the device in the dark condition. *n* (usually larger than 1) is the ideality factor as the behavior of real devices deviates from an ideal diode. Under illumination, the flow of photo-generated carriers in the device forms the photocurrent ( $I_{ph}$ ). Therefore, the total current (I) of the device is given by:

$$I = I_{ph} - I_o\left[\exp\left(\frac{qV}{nkT}\right) - 1\right]$$
(2.24)

The efficiency of photovoltaic devices ( $\eta$ ) equals the maximum power output ( $P_{max}$ ) over the power input ( $P_{in}$ ).  $P_{in}$  is determined by the incident light intensity. From the *J*-*V* characteristics shown in Figure 2.13, the power output is calculated by the product of total current and the corresponding voltage. Therefore, the maximum power output is extracted, and the efficiency is written by:

$$\eta = \frac{P_{max}}{P_{in}} = \frac{I_{sc}V_{oc}FF}{P_{in}}$$
(2.25)

Here,  $I_{sc}$  and  $V_{oc}$  are directly read from the *J*-*V* curves. At zero bias, the current is named as the short-circuit current ( $I_{sc}$ ). When the photocurrent is canceled out by the dark current, the correspondingly applied bias is called the open-circuit voltage. Then, fill factor can be expressed in terms of  $I_{sc}$  and  $V_{oc}$ :

$$FF = \frac{P_{max}}{I_{sc}V_{oc}}$$
(2.26)

The current density is generally used when talking about the device performance since the current depends on the device area. Hence, in the following discussions, we use term  $J_{sc}$  (short-circuit current density) instead of  $I_{sc}$ .



Figure 2.13: Illustration of *J-V* curves and the characteristic parameters of photovoltaic devices under dark and illumination conditions.

2.3.1 Short-circuit current  $(J_{sc})$ 

Mathematically,  $J_{sc}$  can be written by:

$$J_{sc} = \int_{E_{gap}}^{\infty} flux(E) EQE(E) dE$$
(2.27)

where flux(E) is the photon flux of the incident light, and EQE (the external quantum efficiency) is defined by the number of electrons contributing to the photocurrent over the number of incident photons. First,  $J_{sc}$  depends on the incident light intensity. The photocurrent increases when the device is under the illumination of a higher intensity. EQE, which also determines the photocurrent level, equals:

$$EQE = \eta_{LH} \times \eta_{CT} \times \eta_{CC} \tag{2.28}$$

 $\eta_{LH}$ ,  $\eta_{CT}$  and  $\eta_{CC}$  refer to the efficiency of light harvesting, carrier transport, and charge collection processes as described before. Consequently, the active layer material, the selective contacts, the electrode materials, and their interactions collaboratively impact the photocurrent and the device performance.

# 2.3.2 Open-circuit voltage (Voc)

The value of  $V_{oc}$  depends on the bandgap of the active layer semiconductor as well as the Fermi-level splitting under illumination. In semiconductors with large bandgaps, the excited electrons and holes possess more energy leading to a higher open-circuit voltage. Under the strong illumination, the extent of the Fermi level splitting increases and thus the  $V_{oc}$ . Since the photogenerated carriers are then collected by the electrodes, the interface energetics also impact the value of  $V_{oc}$ . For example, if an injection barrier presents or severe recombination happens at the interface, the  $V_{oc}$  decreases drastically. As the  $V_{oc}$  equals the voltage when the corresponding total current is zero, we obtain:

$$V_{oc} = \frac{nkT}{q} \ln(\frac{l_{ph}}{l_o} + 1)$$
(2.29)

Since  $I_{ph} \gg I_o$  and  $I_{ph}$  depends on the light intensity, the light intensity dependence of  $V_{oc}$  can be simplified as follows:

$$V'_{oc} = V_{oc} + \frac{nkT}{q} \ln X$$
 (2.30)

*X* is the relative light intensity with the unit of 1. By plotting  $V_{oc}$  versus *X*, the ideality factor can be calculated, which shines light on the recombination mechanism in the devices.

2.3.3 Fill factor, shunt resistance and series resistance

According to Figure 2.13, FF representing the squareness of the *J*-*V* curve is related to the shunt resistance ( $R_{sh}$ ) and the series resistance ( $R_s$ ). The introduction of  $R_{sh}$  and  $R_s$  modifies the total current equation by:

$$I = I_{ph} - I_o \exp \frac{q(V - IR_s)}{nkT} - \frac{V - IR_s}{R_{sh}}$$
(2.31)

The series resistance refers to the total resistance of the device to the movement of photocarriers. Thus, the resistances coming from the active layer, the electrodes and the interfaces between different layers contribute to  $R_s$ .  $R_s$  impacts the squareness of the *J*-*V* curve close to the open-circuit condition because of the resulting voltage drop across the device.



Figure 2.14: Equivalent circuit of photovoltaic devices including series and shunt resistances.

The shunt resistance impacts FF and the device performance since it provides an alternative path for the photocurrent as shown in Figure 2.14. For example, when the active layer is not compact, the contact of ETL and HTL acts as a leakage path for photocurrent with the electrons in ETL recombining with holes in HTL. Therefore,  $R_{sh}$  mainly affects the shape of the *J*-*V* curve closer to the short-circuit condition.

In this chapter, the semiconductor physics and the working principle of photovoltaic devices as well as the *J*-*V* characteristics are introduced. The discussion over the factors that impact the photo-generation, charge transport and collection, and recombination processes is helpful to understand the strategies of boosting the device performance. In the next chapter, the focus is introducing the physical processes in perovskite solar cells and OPVs.

### Chapter 3

#### Perovskite solar cells and organic photovoltaics

In this chapter, the physical processes in perovskite solar cells and OPVs are introduced. First, the physical properties of perovskite materials and their contributions to the remarkable device performance of perovskite solar cells are discussed. In addition, the current stage, as well as the challenges of perovskite solar cells, are reviewed. The working principle of organic photovoltaics is described in the second part. Especially, the critical role of the interfacial layer in OPVs is illustrated together with the methods to improve the charge collection at the interface. The physical properties of ZnO and its application in OPVs are presented at last.

### 3.1 Organic-inorganic hybrid perovskite solar cells

In 2009, organic-inorganic hybrid perovskite materials were first applied in dye-sensitized solar cells by Kojima *et al.*, yielding an efficiency of 3.8 %.<sup>108</sup> Three years later, Snaith *et al.* employed the perovskite materials in solid state photovoltaic devices, which increased the efficiency to over 10%.<sup>28</sup> By the year of 2017, the highest certified efficiency of perovskite solar cells has reached 22.7%.<sup>109</sup> The drastic improvement of the device performance, together with the low-cost and facile fabrication of perovskite materials, has drawn tremendous attention to this type of materials in the past few years. Perovskite solar cells have been considered as one of the most promising candidates for the next generation photovoltaic technology.

#### 3.1.1 Basics of perovskite materials

The most well-studied organic-inorganic hybrid perovskite material is methylammonium lead iodide (MAPbI<sub>3</sub>) which adopts an ABX<sub>3</sub> formula and the perovskite structure as shown in Figure 3.1. In MAPbI<sub>3</sub> perovskite, A site is composed of methylammonium (MA) cation. The lead (B site) and iodide (X site) form an octahedral cage with lead in the center and iodide at the corners. There are many other options to fill A, B and X positions of the perovskite materials. For A site, formamidinium (FA),  $Cs^+$  and  $Rb^+$  have been used to replace or partially substitute MA.  $Sn^{2+}$  has been found to be a possible substitute for  $Pb^{2+}$  at B site. As to X site,  $Cl^-$  and  $Br^-$  were mixed with iodide. Perovskite materials with different compositions demonstrate varied physical properties. For example, according to Shockley-Queisser limit, the optimal bandgap of a single junction photovoltaic device is around 1.1 to 1.4 eV which is smaller than the bandgap of MAPbI<sub>3</sub>. By replacing or mixing the cations or anions of the perovskite material, the bandgap can be effectively tuned. So far, the major concerns about the commercialization of perovskite solar cells are the toxicity of lead, the stability and hysteretic *J-V* characteristics of devices. The above concerns can be addressed by modifying the composition of perovskite materials. In this study, the focus is to investigate the electrical property of the microstructures in MAPbI<sub>3</sub> and its contribution to the associated device performance.

The crystal structure of MAPbI<sub>3</sub> is tetragonal at room temperature with the octahedral PbI<sub>6</sub> cage corner-connected and MA cations filling the openings.<sup>110</sup> At 330 K, the tetragonal phase undergoes a phase transition to the cubic phase.<sup>111</sup> In photovoltaic devices, perovskite materials are employed in the form of polycrystalline thin films. The bandgap is about 1.5 to 1.6 eV for the polycrystalline MAPbI<sub>3</sub> thin films. According to the density functional theory (DFT) calculation, the conduction band minimum (around 3.9 eV) is composed of the non-bonding state of the 6*p* orbitals of Pb and 5*p* orbitals of iodide, while the valence band maximum (around 4.5 eV) consists of the anti-bonding of 6*s* orbitals of Pb and 5*p* orbitals of polycrystal the formation of band structures, the orientation of MA cation still impacts the electronic properties of perovskite materials.<sup>114-115</sup>



Figure 3.1: Crystal structure and band diagram of organic-inorganic hybrid perovskites. (a) Crystal structure of organic-inorganic hybrid perovskites (ABX<sub>3</sub>) with a tetragonal phase and (b) the band diagram of MAPbI<sub>3</sub>. In the perovskite structure, A site: MA, FA; B site: Pb, Sn; X site: Cl, Br, I.



inverted planar structure

conventional planar structure

Figure 3.2: Illustration of the device architectures of perovskite solar cells: meso-porous structure, inverted (p-i-n) structure and conventional (n-i-p) structure.

### 3.1.2 Structure of solid-state perovskite solar cells

As mentioned above, the efficiency of perovskite solar cells took off after the electrolyte was replaced by solid-state materials. In general, there are two different types of perovskite solar cells: meso-porous structured and planar structured as shown in Figure 3.2.<sup>27-28, 31-32, 40-41, 44, 107</sup> The meso-porous structure is usually composed of meso-porous titanium oxide (TiO<sub>2</sub>) as the electron transport layer and the scaffold of the perovskite layer.<sup>28, 31, 44, 48</sup> By filling into the porous structure, it is more likely to form a continuous and compact film which is essential for high efficiency devices. One has discovered that perovskite materials exhibit an excellent carrier diffusion length (> 100 nm for MAPbI<sub>3</sub>) and the ambipolar charge transport properties, indicating that photogenerated electrons and holes are able to travel hundreds of nanometers within the perovskite material before they recombine.<sup>116-120</sup> Therefore, the planar structured perovskite solar cells have drawn an increasing amount of attention.<sup>27, 32, 40-41, 107, 120</sup>

According to the configuration of planar structured solar cells, there are two types of planar devices: conventional and inverted structured solar cells as shown in Figure 3.2. The inverted structured (p-i-n) perovskite solar cells usually employ a thin layer of conducting metal oxide, such as indium tin oxide (ITO) or fluorine doped tin oxide (FTO) coated glass as the cathode to collect electrons. The selectivity of the electrode is modified by inserting an n-type material (ETL), such as TiO<sub>2</sub> and ZnO.<sup>27, 41, 107</sup> The most widely used HTL in perovskite solar cells is 2,2(7,7(tetrakis-(N,N-di-pmethoxyphenylamine)9,9(-spirobifluorene))) (spiro-OMeTAD) which is first dissolved in chlorobenzene with additives to improve the conductivity and then spin-coated on top of the perovskite layer. Other inorganic and organic hole transport materials have also been employed in perovskite solar cells such as copper thiocyanate (CuSCN), nickel oxide (NiO<sub>x</sub>), P3HT, poly-triarylamine (PTAA).<sup>121-124</sup> The disadvantage of the inverted structure is that the

ETLs require a high processing temperature, which increases the complexity and cost of the device fabrication and limits the application on the flexible substrates. In contrast to the inverted structure, the conventional structured solar cells employ the n-i-p configuration. The most widely used hole transport material is PEDOT:PSS which is spin-coated onto ITO or FTO from water solution and requires a low annealing temperature (around 100 °C). Due to the organic nature of PEDOT:PSS, it can also be coated onto soft substrates in order to fabricate flexible devices. As for ETLs,  $C_{60}$  fullerene and its derivatives, like phenyl- $C_{61}$ -butyric acid methyl ester (PC<sub>61</sub>BM), are commonly used in the conventional structured solar cells. These organic molecules are dissolved in chlorobenzene and then cast on top of perovskite layer.

# 3.1.3 Fabrication of polycrystalline perovskite thin films

Prior to discussing the physical process in perovskite solar cells, it is necessary to introduce the fabrication of perovskite layers since the film quality is significantly impacted by the processing methods. The simplest way to make MAPbX<sub>3</sub> perovskite thin films is spin-coating the precursor solution, which is composed of lead iodide/chloride (PbI<sub>2</sub>/PbCl<sub>2</sub>) and methylammonium halide (MAX) with certain ratios in dimethylformamide (DMF)/dimethyl sulfoxide (DMSO), onto the substrate followed by annealing at 100 °C as shown in Figure 3.3.<sup>28, 31, 125</sup> To prepare MAPbI<sub>3</sub>, the ratio of MAI and PbI<sub>2</sub> is 1.0. The incorporation of Cl in the perovskite material requires the mixture of MAI and PbCl<sub>2</sub> with a ratio of 3:1. This method works fine for meso-porous structured devices but not the planar structured devices with respect to the morphology and surface coverage of perovskite layers. It is challenging to form a continuous and pin-hole free perovskite film on the planar substrates. As mentioned in the previous chapter, it is critical to prepare a compact film without any pinholes in order to achieve high efficiencies. One way to improve the film quality is adjusting the precursor solution. The influences of the concentration of precursor solution, the

types of lead precursor, and the ratio of lead precursor and organic cation on film quality have been studied by several groups.<sup>125-129</sup> One has reported that a higher concentration leads to a compact thin film and the larger grain size with improved crosslinking of grains, which contribute to the enhanced characteristic parameters of device performance.<sup>128</sup> Meanwhile, it has been proposed that the first step of the crystallization process involves the removal of organic molecules which are the product of the reaction between lead source and organic salt.<sup>126</sup> Thus, lead acetate was employed, instead of lead iodide, to form methylammonium acetate (MAAc). Since MAAc requires a lower temperature to decompose, the fast nucleation and crystallization are induced during the annealing treatment resulting in an ultra-smooth thin film. The ratio of lead precursor and organic salt is another factor that impacts the quality of perovskite thin films. An excess amount of PbI<sub>2</sub> influences not only the grain size but also the electronic structure of perovskite thin films.<sup>129</sup> In addition, anti-solvent methods, washing the generic film during spin-coating process to introduce over-saturation, have also been reported to effectively improve the film quality by inducing the fast nucleation and crystallization.<sup>130-131</sup> A similar but simpler way to oversaturate the perovskite layer and induce the homogeneous nucleation is applying a vacuum-flash treatment which pumps away the remaining solvent molecules in the film right after spin-coating.<sup>30</sup>

While the one-step methods evolve, two-step fabrication, also called sequential deposition, starts to draw more and more attention since it generates a compact film on the planar substrates. In this method, the first step is to deposit a compact PbI<sub>2</sub> layer. The PbI<sub>2</sub> is dissolved in DMF/DMSO and then cast onto the substrate. On top of the compact PbI<sub>2</sub> layer, MAI is subsequently deposited, followed by the thermal annealing process to allow the inter-diffusion of PbI<sub>2</sub> and MAI to form the perovskite phase. There are several different ways to deposit the MAI layer. Burschka *et al.* and Liu *et al.* dipped the PbI<sub>2</sub> coated sample into MAI contained isopropanol

(IPA) solution.<sup>107, 132</sup> Another approach to incorporate MAI into the active layer is spin-coating the MAI solution onto the PbI<sub>2</sub> layer.<sup>133-134</sup> In this scheme, the critical part is to find an orthogonal solvent, which dissolves MAI but not PbI<sub>2</sub>. The most commonly used candidate is IPA. Due to the low melting point of MAI, Chen *et al.* developed a vapor-assisted solution process which introduces the organic part into the perovskite layer by vaporizing MAI.<sup>135</sup>



Figure 3.3: **Illustration of preparing perovskite thin films by one-step method**. A few drops of the precursor solution are dripped onto the substrate, and then the substrate is spun at a high speed. The thin film is annealed at about 100 °C leading to the formation of the perovskite structure.

Generally, the challenges of two-step methods are to fully convert PbI<sub>2</sub> into the perovskite structure and control the grain size. The concerns mentioned above are related to the fast crystallization of PbI<sub>2</sub> which leads to randomly sized crystallites.<sup>134</sup> It is difficult for MAI to penetrate into the large crystallites due to the edge-on nature of PbI<sub>2</sub> crystals. Therefore, it is critical to control the grain size of the PbI<sub>2</sub> layer. One has discovered that the crystallization process can be effectively controlled through retarding the crystallization of PbI<sub>2</sub> via its strong coordination with solvent molecules, such as DMSO.<sup>134, 136</sup> The solvent molecules interact with Pb by donating a pair of electrons, which slow down the crystallization of PbI<sub>2</sub> and stretch the PbI<sub>2</sub> lattice for the incorporation of MAI. The other way to control the grain size is the solvent annealing process.<sup>137</sup> After depositing the MAI layer, the sample is transferred to the hotplate. A petri-dish with a few

microliters of DMF covers the sample. During the annealing process, DMF molecules are vaporized and fill the petri-dish. The diffusivity of  $PbI_2$  and MAI are enhanced in the solvent atmosphere leading to a large grain size in micron scale and high film quality.



Figure 3.4: **Illustration of preparing perovskite thin films by two-step methods**. The first step is to spin-coat a layer of PbI<sub>2</sub>. The introduction of the MAI layer can be achieved in different ways, such as (1) immersing in the MAI/IPA solution, (2) spin-coating the MAI/IPA solution on top of PbI<sub>2</sub>, and (3) thermal evaporation of MAI.

As mentioned at the beginning of this chapter, the efficiency of single junction perovskite solar cells has reached over 20%. The thin film preparation processes, which control the film quality, play a critical role in determining the device performance. Large-area devices with highquality perovskite films are required in order to commercialize perovskite solar cells. However, the majority of the methods mentioned above result in low film quality and increase the complexity of the fabrication process when it comes to the fabrication of large devices. Several techniques have been developed to make large-area perovskite thin films with high quality so far.<sup>30, 138-139</sup> The devices with the area around 1 cm<sup>2</sup> have achieved an efficiency close to 20%.<sup>30</sup> Kim *et al.* have reported an even larger device (16 cm<sup>2</sup>) with an efficiency of 12%.<sup>139</sup> Still, it is imperative to keep boosting the device performance and simplifying the fabrication processes of large-area perovskite photovoltaic devices.

Overall, photovoltaic devices employing perovskite materials demonstrate excellent capabilities for the commercialized solar cells. In the following part of this section, the outstanding optical and electrical properties of perovskite solar cells, as well as the remaining challenges, will be discussed.



Figure 3.5: **Absorption coefficient of ITO/PEDOT:PSS/MAPbI**<sup>3</sup> **sample**. Even though ITO and PEDOT:PSS layers contribute to the calculated value, the high absorption coefficient, which is comparable to that of GaAs, is still dominated by the perovskite material. Inset: an image of ITO/PEDOT:PSS/MAPbI<sub>3</sub>.

3.1.4 Light absorption and carrier generation in perovskite solar cells

The perovskite thin films with a bandgap of ~ 1.5 eV show a dark brown color. Most of the high-efficiency perovskite solar cells obtain a 300-600 nm thick perovskite film which is able to absorb 90% of the visible light.<sup>32-33, 140</sup> One has reported that polycrystalline MAPbI<sub>3</sub> perovskites demonstrate a sharp absorption onset around 800 nm, a high absorption coefficient (around  $10^5$  cm<sup>-1</sup>) and the Urbach energy as small as 15 meV.<sup>52, 141</sup> Figure 3.5 depicts the absorption coefficient of ITO/PEDOT:PSS/MAPbI<sub>3</sub> sample. The high absorption coefficient of perovskite material is related to its direct bandgap nature and the stronger *p*-*p* orbitals interaction of the conduction band compared with *s*-*p* interactions and indirect bandgap semiconductors.<sup>52</sup> The unoccupied *p*-orbitals of lead contribute to the high density of states at the conduction band minimum and the sharp absorption onset.<sup>142</sup> The small Urbach energy indicates a well-ordered structure of perovskite thin films and a low density of mid-gap states. The high absorption coefficient coefficient contributes to not only the high photocurrent but the small *V*<sub>oc</sub> loss. With a high light harvesting efficiency, perovskite solar cells require a thin active layer which reduces the recombination-induced saturated dark current.<sup>140</sup>

After photons are absorbed by the perovskite layer, excitons are generated. It has been reported that the exciton binding energy is around a few tenths of meV in perovskite materials which is comparable to the thermal energy provided at room temperature, implying that majority of the excitons are spontaneously dissociated into free carriers upon light absorption.<sup>36, 143</sup> The efficient free carrier generation under illumination also contributes to the remarkable device performance of perovskite solar cells through avoiding the recombination within the excitons. It is worth mentioning that the co-existence of excitons and free carriers has also been observed,

especially under a high incident photon density, by D'Innocenzo *et al.* and Nah *et al.*, indicating the wide perspective of perovskite materials in different types of optoelectronic devices.<sup>34, 144</sup>

## 3.1.5 Carrier transport and collection in perovskite solar cells

The transport of holes and electrons is critical in determining the device performance as discussed before. So far, MAPbI<sub>3</sub> and MAPbI<sub>3-x</sub>Cl<sub>x</sub> have demonstrated superior charge transport properties with ambipolar characteristics, balanced charge transport of electrons and holes.<sup>117, 119-</sup>  $^{120, 145-146}$  One has reported the carrier diffusion length to be over 100  $\mu$ m for both types of carriers, and the mobilities of electrons and holes are around 100 and 20 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> in MAPbI<sub>3</sub> single crystals, measured by time-of-flight (TOF) and space charge limited current (SCLC).<sup>117</sup> In polycrystalline perovskite thin films, the carrier diffusion length is over 100 nm for MAPbI<sub>3</sub> and  $1\mu$ m for MAPbI<sub>3-x</sub>Cl<sub>x</sub>,<sup>119, 146</sup> and the carrier mobilities drop to below 20 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for both electrons and holes.<sup>119, 145</sup> The superior charge transport and ambipolar characteristic of perovskite materials have been attributed to the similarly small effective mass of electrons and holes as discovered by DFT calculations.<sup>118, 147</sup> In addition, the low doping level of perovskite materials (weakly p-type) explains the excellent carrier mobility and diffusion length with the diminished carrier scattering and recombination.<sup>117</sup> It is worth mentioning that the reported carrier mobilities vary in a considerable range due to not only the utilization of different measurements but also the diverse film quality, since the carrier mobility is potentially influenced by grain sizes, crystallinity, grain boundaries and electronic traps in the perovskite films.<sup>148</sup>

It has been reported that devices with larger grain sizes yield a higher efficiency due to the improved quality of the film and the reduced density of grain boundaries (GBs) since GBs act as not only recombination centers but the carrier scattering centers.<sup>149-151</sup> Nevertheless, the concern here is that the increase of grain size is also accompanied by the change of the texture structure,

the degree of preferential crystal orientation. Docampo *et al.* have found that the crystal orientation plays a more significant role than the grain size in determining the film quality and thus the charge transport property. <sup>43, 54</sup> Besides, one has reported that the electron mobility varies along different crystal orientations.<sup>152</sup> Therefore, it is necessary to take grain sizes, crystal orientations and GBs into consideration when investigating the charge transport in perovskite thin films, and employ techniques with high spatial resolutions in order to distinguish the role of GBs from grain interiors.

The charge collection process at the interface between the active layer and ETL/HTL is another critical factor that impacts the device performance. The carrier injection barrier at the interfaces has been identified in perovskite solar cells.<sup>40, 153-154</sup> To effectively collect carriers, it is essential to form an Ohmic contact via the matching energy levels between ETL/HTL and perovskite materials. Additionally, the conductivity of ETL/HTL materials influences FF and thus the device performance by contributing to  $R_s$ . One has reported that the charge injection from perovskite materials to spiro-OMeTAD is more efficient than to polymeric HTLs due to the matching energy levels and the high carrier mobility in the former.<sup>155</sup> The insertion of an interface layer between TiO<sub>2</sub> and MAPbI<sub>3</sub> and doping of ETL are also employed to enhance the charge collection by tuning the injection barrier and the conductivity of ETL.<sup>156-157</sup>

At the surface of perovskite materials, there also exist defect states due to the broken symmetry and the dangling bonds. The trapping of electrons and holes at the surface would result in recombination, which hampers the charge collection process.<sup>158-159</sup> More details about surface recombination and the passivation of surface defects will be discussed in next session.

## 3.1.6 Non-radiative recombination in perovskite solar cells

In this section, the discussion focuses on the non-radiative recombination in perovskite solar cells. Typically, non-radiative recombination happens via trap states within the bandgap. The

trap states, induced by the crystal structure defects, are able to trap and de-trap electron/hole. If the carrier cannot be de-trapped from the mid-gap state before encountering an opposite charge, recombination happens. Thus, the density of trap states, trap/de-trap kinetics and carrier concentrations impact the non-radiative recombination process.

The structural defects exist in the bulk of the perovskite thin films, as well as at the surface and grain boundaries. As mentioned before, the small Urbach energy (~15 meV) indicates a wellordered structure and the low density of mid-gap states in the polycrystalline perovskite thin films. It has been reported that the polycrystalline perovskite thin film demonstrates a bulk trap density around 10<sup>15</sup> - 10<sup>16</sup> cm<sup>-3</sup> which is comparable to the solution-processed CIGS films.<sup>51, 160</sup> Several theoretical studies have revealed the unusual defect physics in perovskite thin films. One has discovered that the defects generate shallow levels close to CB or VB.<sup>52, 161-162</sup> Consequently, these defect states act as unintentional doping sources instead of recombination centers. In addition, it has been pointed out that the defects in MAPbI<sub>3</sub> that create deep levels require high formation energy and barely exist in low-temperature processed perovskite films.<sup>162</sup> The low density of trap states in perovskite thin films is also ascribed to the low crystallization activation energy (less than 100 kJ mol<sup>-1</sup>) compared with that of amorphous silicon, which is as high as 400 kJ mol<sup>-1</sup>.<sup>127</sup> Though the polycrystalline perovskite thin films show a low density of trap states, it has been suggested that the trap-assisted recombination in the bulk perovskite still impacts the power output of devices.<sup>51, 140, 163-164</sup> By comparing with single crystals, it is evident that polycrystalline perovskite thin films demonstrate a short diffusion length, a low carrier mobility and a high defect density. And these characteristics collectively impact to the device performance of perovskite solar cells.

Besides the point defects, the defects located at grain boundaries also impact the density of trap states in the bulk perovskite thin films. Different from point defects, GBs possess more

complicated structural defects, 2-dimensional planar defects. It is likely that there are various stoichiometries at GBs. Guo et al. have carried out DFT calculations to investigate the electronic structure of GBs in MAPbI<sub>3</sub> thin films.<sup>53</sup> The same conclusion as point defects has been made that 2D planar defects at GBs do not generate deep level electronic states. Experimentally, the nondetrimental, even beneficial, role of grain boundaries has been observed by employing the techniques with spatial resolutions such as AFM, microwave impedance microscopy (MIM) and KPFM.<sup>48, 165-167</sup> However, de Quilettes et al. and Mamun et al. have employed confocal and widefield fluorescence microscopy and discovered the lower PL intensity and faster PL decay at GBs compared to grain interiors in perovskite thin films, suggesting the GB-induced non-radiative recombination.<sup>51, 168-169</sup> Meanwhile, one has found the heterogeneous behaviors of GBs: some GBs act as the "highway" of lateral carrier transport while others possess an energy barrier for charge transport across grains.<sup>49, 170</sup> More interestingly, MacDonald *et al.* have found the depth-dependent electrical behaviors of GBs due to the faster degradation of MAPbI<sub>3</sub> close to the top surface.<sup>170</sup> Though most of the techniques mentioned above provide a high resolution, the characterization of the power output of the microstructures in perovskite thin films, which provides direct evidence on their contributions to the device performance, has not been performed due to the challenges brought by the roughness of perovskite thin films and the stacking of grains and GBs.

Contrary to the controversial role of GBs, non-radiative recombination at the interface has been criticized as the dominant carrier loss mechanism in perovskite solar cells. The broken symmetry at the perovskite surface introduces trap states and thus result in severe recombination. Trap-mediated recombination has been identified in both perovskite/ETL and perovskite/HTL interfaces. A large portion of recombination occurs at the interface of perovskite/PEDOT:PSS in n-i-p planar structured devices. The adoption of nickel oxide nanoparticles or poly[N,N'-bis(4butylphenyl)-N,N'-bis(phenyl)- benzidine (poly-TPD) enhances the passivation of surface states and thus reduces the  $V_{oc}$  loss.<sup>171-172</sup> Also, Correa-Baena *et al.* discovered that in p-i-n structured perovskite solar cells the recombination dynamics are strongly correlated with the dopant concentration in spiro-OMeTAD layer, and a  $V_{oc}$  as high as 1.22 V has been achieved by controlling the amount of dopants.<sup>173</sup>

The passivation of perovskite/ETL interfaces has been accomplished by employing tin oxide (SnO<sub>2</sub>), chlorine-capped TiO<sub>2</sub>, magnesium oxide (MgO) coated ZnO nanoparticles as ETL, or inserting an ultrathin polymer-fullerene film.<sup>173-176</sup> Similarly, Yang *et al.* have inserted an organic self-assembled monolayer (Si-bearing 3-aminopropyltriethoxysilane) to introduce an interfacial dipole, which boosts the interaction of perovskite materials and ETL and tunes the band energy alignment to enhance the charge extraction.<sup>177</sup> In addition, due to the interfacial charge transfer anisotropy of perovskite films, tuning the texture structure and preferential crystal orientation improves the charge collection and suppresses the recombination at the interface. Overall, the passivation of interface recombination is especially beneficial to reduce the  $V_{oc}$  loss and improve the efficiency of perovskite solar cells.

#### 3.1.7 Remaining challenges in perovskite solar cells

Though the device performance of perovskite solar cells has reached over 20 %, there are still some challenges in the commercialization process, such as the J-V hysteresis characteristics and device stability.

The hysteresis characteristics of perovskite solar cells refer to the discrepancy of J-V curves when sweeping the voltage in the forward and reverse diractions.<sup>178</sup> Therefore, the existence of the hysterical phenomenon poses challenges in accurately determining the device performance of the devices. The hysteresis behavior stems from the devices themselves and is impacted by the

scanning conditions. From the inside, the hysteresis behavior depends on the perovskite materials and the selective transport layers.<sup>172, 179-182</sup> It has been discovered that inverted structured perovskite solar cells demonstrate a negligible hysteresis due to the passivation effect of PCBM.<sup>183</sup> On the outside, the scanning conditions such as the scan rate, the external electric field, and the pre-conditioning of devices also impact the hysteresis of J-V curves.<sup>184-186</sup> Since the discovery of the hysteresis behavior in perovskite solar cells, many mechanisms have been proposed, such as the ferroelectricity of MAPbI<sub>3</sub>, the trapping/de-trapping process, and ion migrations.<sup>179-180, 187-189</sup> Several studies have revealed that ion migration is the dominant mechanism of the hysteresis behavior in perovskite solar cells.<sup>179-180, 186, 190</sup>

The ion migration is driven by the built-in and/or external electric field, resulting in the ionic accumulation at the interface. Consequently, the built-in electric field in the bulk perovskite is enhanced or diminished depending on the species of the accumulated ions and the interface. When sweeping the voltage in different directions, even under the same bias, the effective electric field in the device would be different due to the slow response of the ion migration, leading to the mismatch of the photo-response. The time-scale of the ionic movement also matches with the observed hysteresis response to the scan rate in perovskite solar cells. Figure 3.6 describes the ion migration process due to the built-in electric field and its impact on the distribution of the electric field. The accumulated ions at the interfaces form an electric field in the opposite direction to the built-in electric field, which diminishes the intensity of the effective electric field in the bulk perovskite layer. As discussed before, the electric field causes a less efficient charge separation in perovskite solar cells. The ions at the interface modify the charge extraction barrier as well, as depicted in Figure 3.6. The species of ions migrating in the perovskite material are likely to be I

and MA<sup>+</sup> ions due to the low activation energy of migration comparing with that of Pb<sup>2+</sup> ion, as calculated by Meloni *et al.* and Eamea *et al.*<sup>180, 190</sup> Experimentally, the concentration contrast of MA<sup>+</sup> ions before and after poling the device has been observed by Yuan *et al.*, indicating the migration of MA<sup>+</sup> under the external electric field.<sup>191</sup> Also, Li *et al.* have observed the I<sup>-</sup> migration and characterized the migration kinetics in perovskite solar cells with the aid of wide-field PL microscopy.<sup>192</sup>



Figure 3.6: Schematic of the ion migration in the perovskite material. Illustration of (a) the existence of mobile ions in perovskite layers and their moving directions (negative ions: blue arrow, positive ions: red arrow) under the built-in electric field when sandwiched between the anode and the cathode with different work functions; (b) the accumulation of ions at the interface and the modified (diminished) built-in electric field in the bulk of perovskite layer.

In order to suppress the ion migration, it is necessary to understand ion migration paths in the perovskite photovoltaic devices. According to DFT study, the ions migrate along the defects in the perovskite layer by hopping between neighbor sites.<sup>180, 190</sup> Additionally, Shao *et al.* and Yun *et al.* have reported a faster ion migration along GBs and attributed it to the high density of defects with the aid of c-AFM and KPFM techniques.<sup>193-194</sup> Therefore, it is important to improve the

crystallinity, reduce the concentration of mobile ions, and grow large grains to decrease the density of mobile ions and grain boundaries in perovskite thin films.<sup>183, 195-196</sup> Likewise, it is important to passivate the perovskite surface to suppress the ion migration.<sup>172, 197</sup>

The device stability is the other challenge that perovskite solar cells are facing on the way to the market of photovoltaic devices. It is well-known that MAPbI<sub>3</sub> is sensitive to moisture and heat.<sup>198-201</sup> The moisture in the air accelerates the decomposition of perovskite materials into HI, MA and PbI<sub>2</sub>. The encapsulation of perovskite solar cells has successfully protected the devices from the humid environment and improved the device stability.<sup>202-203</sup> The other external factor that impacts the stability is the heat induced by illumination under working condition. The low thermal stability leads to the decomposition of MAPbI<sub>3</sub> under constant illumination. In addition, as discussed above, a transition from the tetragonal to the cubic phase of MAPbI<sub>3</sub> happens around 50 <sup>o</sup>C which is within the range of the operation temperature for photovoltaic devices. The organic part (MA) in the perovskite materials has been accused of hampering the thermal stability. Several studies have demonstrated that by introducing organic or even inorganic cations, such as FA and Cs, the stability of the corresponding perovskite materials is greatly improved as well as the phase transition temperature.<sup>30, 204-205</sup> Recently, one has reported the migration of the electrode metals, such as Au, to the active layer through small molecule HTLs under thermal stress, leading to the decomposition of MAPbI<sub>3</sub>.<sup>173, 206</sup> To suppress the migration of Au, novel and stable hole transport materials have been employed to replace spiro-OMeTAD and the thermal stability is improved.<sup>205,</sup> 207

In order to compete with silicon solar cells, perovskite solar cells have to demonstrate a degradation rate of 0.5 % per year for up to 20 years and comparable or even lower costs.<sup>200</sup>

Accordingly, more efforts are needed to make high-quality perovskite materials with excellent stability, and cost-effective ETL/HTLs in order to commercialize perovskite photovoltaic devices.

3.2 Organic photovoltaics and the application of ZnO as a buffer layer

This part focuses on the application of ZnO nanoparticles in organic photovoltaics. Before talking about ZnO, it is necessary to briefly talk about organic photovoltaics. OPVs demonstrate a low cost, facile manufacturing, and the mechanical flexibility.<sup>57-58</sup> Majority of the OPVs are using polymers as light absorbers which offer a high absorption coefficient (usually  $\geq 10^{5}$ cm<sup>-1</sup>). The chemical flexibility of the modifications facilitates the tuning of optoelectrical properties in organic semiconductors. Here, the P3HT:PCBM blend, one of the most widely studied active layer in OPVs, is used as an example.





P3HT is a p-type polymer based on polythiophene, demonstrating an extended delocalized  $\pi$ -electron system with the bandgap around 2.0 eV. PCBM is an n-type small molecule based on C60.<sup>106</sup> The general physical processes in OPVs are illustrated in Figure 3.7. Compared with perovskite materials, the dielectric constants of P3HT and other organic semiconductors are small. Consequently, upon illumination, the excitons generated in P3HT show a high binding energy (0.3 eV-0.7eV) and thus cannot be spontaneously dissociated at room temperature.<sup>208-211</sup> One way to efficiently separate the photogenerated electron and hole pairs is to introduce a potential drop, for example, the P3HT and PCBM interface as discussed in Chapter 2. At the heterojunction of P3HT:PCBM, electrons and holes are separated via the transfer of electrons to PCBM. Accordingly, P3HT and PCBM are called the donor and the acceptor, respectively. There are many ways to create the donor-acceptor interface. For example, it can be achieved in a layered structure: one layer of P3HT followed by one layer of PCBM. However, the concern is that the excitons must diffuse to the heterojunction and then be dissociated. The average distance that excitons travel before recombination, also called exciton diffusion length, is usually less than 20 nm in organic materials.<sup>212</sup> Therefore, it requires the thickness of P3HT layer to be around the same range to efficiently dissociate excitons, which is obviously not thick enough to make the most out of the incident photons. The bulk heterojunction (BHJ) configuration solves the rivalry of the exciton diffusion length and the film thickness by intimately mixing the donor and acceptor. In order to form the BHJ, P3HT and PCBM are dissolved together in organic solvents, such as chlorobenzene, followed by spin-coating onto the substrate. As illustrated in Figure 3.7, donors and acceptors form segregated domains in the active layer. Under illumination, excitons are generated in the donor, and then they diffuse to the interface and get separated. In this scenario, as long as the domain size is within the same range of the exciton diffusion length, excitons can be efficiently dissociated at the donor/acceptor interface. The challenges for this structure are controlling the domain size and forming the percolated path for both donors and acceptors. If the domain size is much larger than the carrier diffusion length, the excitons that are generated deep within the domains recombine within the acceptor before reaching the interface. Without the percolated path, the free carriers dissociated at the interface would be spatially confined inside the domain and cannot be collected by the electrodes, as illustrated in Figure 3.7.

After the exciton dissociation process, free electrons and holes are transported within donors and acceptors separately. The carrier mobilities of organic semiconductors are generally low, ranging from 10<sup>-5</sup> to 1 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, which limit the thickness of the active layer and pose certain requirements on the length of the percolated pathways.<sup>213</sup> For example, if the percolated path of P3HT is longer than the hole diffusion length, it increases the possibility in the recombination of separated electrons and holes at P3HT/PCBM interface.

The interfacial layers play a significant role in determining the device performance of OPVs. First, interfacial layers act as selective contacts. As depicted in Figure 3.7, the P3HT:PCBM blend would directly contact the electrodes without the assistance of interfacial layers. Electrons in PCBM and holes collected by the anode are likely to recombine at PCBM/anode contact. A similar situation holds for the P3HT/cathode contact. Therefore, an interfacial layer is necessary to form a selective contact and suppress the recombination at the contact. In OPVs, the commonly used electron selective materials include ZnO, TiO<sub>2</sub>, fullerene-based molecules. And p-type materials, such as PEDOT:PSS, molybdenum oxide (MoO<sub>3</sub>) and NiO, are employed as the interfacial layer at the anode/active layer interface. Second, the interfacial layers optimize the contact by tuning the working function of the electrode and reducing the injection barrier. From the perspective of energetics, in OPVs, the built-in electric field, which depends on the work

function difference of the anode and cathode materials, not only assists the dissociation of excitons but facilitates the charge transport. The existence of injection barriers at the active layer/electrode interfaces has been observed and attributed to the energy level mis-alignment.<sup>214-216</sup> By inserting an interfacial layer, it has been demonstrated to effectively tune the work function of electrodes and thus optimize the contact, resulting in high device performance.<sup>59, 62, 106, 217-220</sup> An alternative way to tune the work function is via the formation of a dipole layer at the contact. Figure 3.8 depicts the impact of the interfacial dipole on the work function of the electrode. When an interfacial dipole points out of the electrode, it reduces the work function and vice versa. In addition, materials, like bathocuproine (BCP) and MoO<sub>3</sub>, with bandgaps larger than that of the donor and the acceptor act as the exciton blocking material since it requires extra energy to transfer the exciton to the interfacial layer.<sup>221-224</sup>

ZnO is a direct bandgap material with the bandgap around 3.4 eV.<sup>225</sup> The CBM and VBM of ZnO are 4.3 and 7.7 eV, respectively.<sup>225</sup> ZnO frequently exhibits the n-type conductivity due to the existence of intrinsic defects in the material.<sup>226-227</sup> The intrinsic defects include zinc vacancy/interstitial, oxygen vacancy/interstitial, and antisites of Zn and oxygen. One has found that the zinc vacancies, which result in deep acceptor states with low formation energy under n-type conditions, are likely to be the compensating defects in n-type samples. And the deep VBM enables ZnO acting as an effective hole blocking material. In addition, the application of ZnO interfacial layer in OPVs has been proved to improve the stability of the devices.<sup>85, 228-229</sup> However, the control over the electrical conductivity of ZnO is still challenging, which hinders the application of ZnO in electronic devices.<sup>81</sup> In order to tune the conductivity, it is critical to control the intrinsic and extrinsic defects, which is still a major issue for ZnO materials.



Figure 3.8: Schematics of work function tuning via the formation of interface dipole. The interface dipole ( $\mu$ ) pointing out of the surface induces a vacuum level shift and thus reduces the work function of ITO.
## Chapter 4

# Device fabrication and experimental methods

To characterize the photovoltaic devices and investigate the dynamic processes, many techniques have been employed in this study. It is necessary to understand the principles of the experimental instruments in order to interpret the results. In this chapter, first, the detailed procedures of sample preparation are described. Different preparation methods have been developed and resulted in different film quality, especially for perovskite thin films. Hence, it is important to know the fabrication process of the devices. Second, the experimental conditions and instrument settings are illustrated for cross-referencing the experimental results between different studies. Particularly, the working principles of AFM, EIS and EBSD measurements are introduced in the last session for a better understanding of the experimental results.

#### 4.1 Device fabrication

#### 4.1.1 Fabrication of perovskite solar cells

In this study, the conventional planar structured (n-i-p) perovskite solar cells were fabricated and investigated. In this architecture, the MAPbI<sub>3</sub> layer is sandwiched between ITO/PEDOT:PSS (anode) and PCBM/BCP/Ag (cathode). The fabrication process involves multiple deposition techniques, such as solution processes and physical vapor depositions.

# 4.1.1.1 Anode preparation

The anode preparation was done in the cleanroom. ITO/Glass substrates from Xinyan Technology Ltd. were pre-cleaned in alconox, deionized (DI) water, acetone and IPA, respectively, with sonication for 10 min. Then, the substrates were blown dry with nitrogen. In order to tune the work function of ITO and remove the organic molecules adsorbed on the surface, the substrates

were transferred to the vacuum chamber and processed with oxygen plasma for 5 min at 150 W (PX-250, March Instruments).

The spin-coating of PEDOT:PSS layer was done in the air. PEDOT:PSS solution (Heraeus Technology Group) was filtered and sonicated for 30 min before used for spin-coating. The solution was kept in the fridge (around 5 °C) when not in use. 50 uL of PEDOT:PSS solution was dripped on top of ITO/glass and then spin-coated at 6000 RPM for 20s. A highly transparent film with light blue color was formed on the substrate. Right after spin-coating, the substrate was transferred onto a hotplate which was pre-heated to 150 °C. After 5 min, the residual water from the solution was completely removed from PEDOT:PSS films. The samples were immediately transferred into the glovebox where the water and oxygen levels were below 0.1 ppm for the next step: the deposition of the perovskite layer.

#### 4.1.1.2 Preparation of MAPbI<sub>3</sub> thin film

In this study, both one-step and two-step methods were employed to fabricate the pure MAPbI<sub>3</sub> thin film of different thickness and grain sizes. The formation of the perovskite phase is through combining the lead source and CH<sub>3</sub>NH<sub>3</sub>I with the aid of thermal annealing. The perovskite layers were prepared in the glovebox due to its sensitivity to the ambient condition. Details of the fabrication process are described below.

To synthesize CH<sub>3</sub>NH<sub>3</sub>I, 10 mL of hydroiodic acid (57wt% in water, Sigma) was added to 24 mL of methylamine (33 wt.% in ethanol, Sigma) dropwise into a round-bottom flask which was immersed in ice/water bath (0 °C). After completing the adding of acid, the solution turned dark brown and was stirred for another 2 hr at 0 °C, Then, the solution was transferred to a rotary evaporator in a water bath at 50 °C. The water and ethanol were gradually removed from the solution leaving the yellow precipitate in the flask. Next, the raw product was dissolved in the

minimum amount of ethanol and then precipitated by adding diethyl ether. The precipitate with light yellow color was then filtered. The recrystallization process was repeated two more times to purify the CH<sub>3</sub>NH<sub>3</sub>I product into white crystallites.



Figure 4.1: Images of the spin-coater and the hotplate ensembled in the glovebox.

In one-step method, both lead source and MAI were dissolved in DMF and/or DMSO. To make MAPbI<sub>3</sub>, 2.88 g of PbI<sub>2</sub> (Sigma) and 0.636 g of CH<sub>3</sub>NH<sub>3</sub>I were dissolved in 5 mL mixture of dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) and stirred at 60 °C for 12 hr in the glovebox. The solids gradually dissolved, forming a light-yellow solution.

The precursor solution prepared above was then spun onto the PEDOT:PSS/ITO substrate at 1000 RPM for 15 s and 5000 rpm for another 30 s. A light-yellow film was formed on the substrate. The samples were then annealed at 100 °C for 10 min, which was referred as fast annealed samples. The films turned into dark brown after heated for 5 s. As to ramp annealing process, the samples were first annealed at a lower temperature  $T_0$  for 10 min, and then the temperature was ramped up to 100 °C at different ramp rates, followed by 10 min annealing at 100 °C. The color of the film gradually turned into dark brown and the film became highly reflective. The thickness of  $MAPbI_3$  thin films was tuned by adjusting the concentration of the precursor solution as listed in Table 4.1.

Solution Concentration	Solution temperature	Film thickness
mol L <sup>-1</sup>	°C	nm
0.63	25	110
1.25	25	200
1.87	25	290
2.50	70	450

Table 4.1: Precursor concentration and film thickness.

In Chapter 6, the samples were prepared by two-step method followed by the solvent annealing process in order to grow columnar-structured grains. First, 230 mg of PbI<sub>2</sub> and 15 mg of MAI were dissolved in 1 mL of DMF and MAI, respectively. The solutions were stirred at room temperature in the glovebox for 2 hr. The as-prepared  $PbI_2$  solution was spun onto PEDOT:PSS/ITO substrate at 4000 RPM for 30 s. Then, MAI was spun on top of PbI<sub>2</sub> at 4000 RPM for 20 s. A smooth film with light brown color was formed immediately after spin-coating. The samples were immediately transferred to a hotplate which was preheated at 100 °C. A petridish coated with 10 µL DMF was then put on top of the sample, forming a solvent environment during the annealing (30 min). The resulting film thickness was around 110 nm as measured by AFM. In order to increase the film thickness to 300 nm and characterize the film quality, the concentration of PbI<sub>2</sub> and MAI were increased to 500 mg mL<sup>-1</sup> and 40 mg mL<sup>-1</sup>, respectively, with the annealing duration extended to one hour. To prepare the sample for EBSD measurement, the same procedure was adopted while using a higher concentration of PbI<sub>2</sub> (1000 mg mL<sup>-1</sup>, 100 °C) and MAI (40 mg mL<sup>-1</sup>, 70 °C). And the solvent annealing condition was adjusted to 2 hr with the aid of 20 µL DMF. All the processes were carried out in a nitrogen-filled glovebox.

# 4.1.1.3 Cathode preparation

The preparation of cathode involves the solution process and the thermal evaporation. PCBM (2 wt% in chlorobenzene) was spun onto the perovskite film at 1500 RMP for 30 s. The resulting samples were transferred to a vacuum deposition chamber (Angstrom Engineering). First, 5 nm of BCP was thermally evaporated and deposited on top of perovskite at the rate of 0.5 Å s<sup>-1</sup>. The sample stage was rotating during the deposition to guarantee the full coverage of BCP. Then, Ag (100 nm) was thermally evaporated at increasing rates (0.5, 1.0 and 2.0 Å s<sup>-1</sup>) with a patterned shadow mask covering the samples. The stage was still to avoid the shadow effect which could potentially enlarge the device area. The deposition of BCP and Ag was under a pressure of ~ 3.0 × 10<sup>-6</sup> Torr.





Figure 4.2: Images of the thermal evaporator used for deposition of MoO<sub>3</sub>, C60, BCP and Ag layers.

#### 4.1.2 Fabrication of organic photovoltaics

To make ZnO thin film, zinc acetate solution (0.1 mol L<sup>-1</sup>) was prepared in 2methoxyethanol (MXL) and monoethanolamine (MEA) with a molar ratio of 1:1 between zinc acetate dihydrate and MEA.<sup>230</sup> All materials were purchased from Sigma-Aldrich. The addition of MEA is to increase the solubility of zinc acetate in MXL by the chelation between -OH/-NH<sub>2</sub> group and zinc. The solution was spin-coated at 4000 RPM for 40 s onto ITO/Glass substrates (Xinyan Technology Ltd.) which were pre-cleaned with sonication in acetone and isopropanol. The samples were then annealed for 10 min at different temperatures to decompose the acetate precursor and crystallize the ZnO film. These films were subsequently rinsed in DI water and ethanol, followed by annealing at 150 °C for 10 min to dry the sample.<sup>90</sup>

ZnO film preparation was followed by spin-coating a P3HT and PCBM blend (1: 0.8 in weight) in chlorobenzene (27 mg ml<sup>-1</sup> in total) at 800 RPM for 30 s. P3HT and PCBM were purchased from Rieke Metal and American Dye Sources Inc., respectively. The samples were then heated to 105 °C at a rate of 20 °C min<sup>-1</sup> and annealed at this temperature for 20 min, followed by cooling at a ramping rate of 10 °C min<sup>-1</sup> to room temperature. The entire process was carried out in a glove box where the oxygen and water impurity levels were below 0.1 ppm. The resulting samples were transferred to a vacuum deposition chamber (Angstrom Engineering), where 10 nm MoO<sub>3</sub> and 100 nm Ag were thermally deposited with shadow masks under a deposition pressure of  $3.0 \times 10^{-6}$  Torr.

#### 4.2 Experimental conditions of characterizing tools

# 4.2.1 *J*-*V* and EQE measurements

Solar cell efficiencies were characterized in air using a Keithley 2420 source-meter and a Newport solar simulator under 100 mW cm<sup>-2</sup> illumination measured with an NREL calibrated mc-

Si detector with KG5 filter. Filters were applied to adjust the light intensities from 0.0092 to 1 sun for the *J-V* measurements at varied light intensities. The scan rate of the *J-V* characteristics of perovskite solar cells was 50 mV s<sup>-1</sup>. The EQE measurements were carried out on a setup comprising a Xe lamp, a monochromator, a current-voltage preamplifier, and a lock-in amplifier. The light spectrum was determined with a monocrystalline photodetector calibrated by the National Institute of Standard and Technology (NIST). Devices were corrected for the spectral mismatch (M) with values of approximately 0.98 <M< 1.01.

# 4.2.2 SEM and EBSD measurements

The film topology and cross-section morphology of MAPbI<sub>3</sub>/PEDOT:PSS/ITO samples were studied by Hitachi S-4700II field emission scanning electron microscope with the acceleration voltage of 15kV. In order to get a sharp edge for cross-sectional SEM, the sample was immersed in liquid nitrogen for 2 min before cleavage. Then, a 5-nm Pt was sputtered on the cross-section cleaved sample to avoid charging effect.

EBSD measurement was carried out using a TESCAN Mira 3field-emission SEM equipped with OIM data collection (version 6.1.3); Kikuchi patterns were collected using 15 kV accelerating voltage and indexed in the "interactive" mode of the data collection software.

#### 4.2.3 X-ray diffraction measurement

X-ray diffraction pattern of the polycrystalline perovskites was characterized by Bruker Davinci Diffractometer using Cu Kα radiation (Rigaku D-max operating at 40 kV and 40 mA) with rotational sample stage. The XRD measurement of ZnO film was carried out on Bruker D8 X-ray Diffractometer.

#### 4.2.4 AFM measurement

AFM, pc-AFM and KPFM measurements were carried out on the MFP-3D-AFM from Asylum Research in a nitrogen-filled cell. The illumination condition was established by a green laser (532nm) shining from the bottom of the sample that sits above an inverted optical microscope. The light intensity was around 200 mW cm<sup>-2</sup>. The infrared laser for the cantilever detection (860nm) was below the absorption edge of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>, not interfering with the photo-response measurements. A Pt/Ir coated tip with the spring constant of 0.2 N m<sup>-1</sup> was used in the pc-AFM measurements, while 20 nN force was applied between tip and sample. As the tip moved across the surface, the topology and current were measured simultaneously at the scan rate of 0.5 Hz. In the point J-V measurements, the AFM tip was fixed while a bias connected to the bottom ITO electrode was swept and current between the tip and ITO were recorded. The fitting of the point J-V curves was done in Origin software. For AFM (tapping mode) and KPFM, a Ti/Pt coated tip with a spring constant of 2 N m<sup>-1</sup> was used. In KPFM, first, the topology of the sample was measured in the tapping mode. Then, the tip was lifted by 30 nm and followed the topography of the first scan. Meanwhile, a bias was applied to the tip (sample grounded) to nullify the electrostatic force between the tip and sample.

# 4.2.5 EIS measurement

Electrochemical impedance spectroscopy was conducted on an Autolab potentiostat coupled with Nova electrochemical software using a 50 mV amplitude perturbation and sweeping frequencies from 0.5 to 400 kHz. The light source was a 450 W Xe arc lamp. An AM 1.5 solar filter was used to simulate sunlight at 100 mW cm<sup>-2</sup>. Capacitance and resistance data were fitted using ZView software (Scribner Associates). More details about the fitting and equivalent circuit are provided in Chapter 5.

#### 4.2.6 UV-vis spectroscopy

Absorbance spectra were calculated from the transmission and reflection measured using a dual-beam Lambda 800 UV/vis spectrometer. The transmittance and reflectance of both PEDOT:PSS/ITO (substrate) and MAPbI<sub>3</sub>/PEDOT:PSS/ITO (sample) were measured. The absorbance of perovskite films is calculated by the following equation:<sup>231</sup>

$$A_{film} = -\ln(\frac{T_{sample}/T_{substrate}}{1 - \frac{R_{sample} - R_{substrate}}{T_{substrate}^2}})$$
(4.1)

# 4.3 Working principles of experimental methods

# 4.3.1 Atomic force microscopy

As a type of scanning probe microscopy, AFM demonstrates a high spatial resolution on the order of less than a nanometer. It was first invented by IBM scientist, Binnig, Quate and Gerber in 1986 to investigate the surfaces of insulating materials at the atomic scale.<sup>232</sup> After over 30 years, AFM has developed into one of the leading techniques for investigating the nano-scale properties, such as the morphology, the local conductivity and the surface potential, of different kinds of materials. AFM experiments in this study are performed on MFP-3D AFM manufactured by Asylum Research. Figure 4.3 shows the basic setup of AFM.

AFM consists of a cantilever with a sharp tip at the end, which is also called probe. The probe is mounted to the cantilever holder as shown in Figure 4.4. The movement of the tip is controlled by the z-piezo assembled in the cantilever holder. A sharp laser produced by a laser diode is aligned with the end of the cantilever. The laser is deflected by the cantilever, and the deflection is detected by a position sensitive photodetector. The detected signal is then transferred to the feedback loop, which generates topography information and controls the AFM probes by controlling the z-piezoelectric element.



Figure 4.3: Illustration of the basic setup of AFM and tip-sample force ( $F_{ts}$ ).

# 4.3.1.1 Tip-sample interactions

The working principle of AFM is based on the interaction of atoms: atomic force. During the scan, the probe is brought close to the sample surface. The interaction between the probe and sample leads to the bending of the probe and changes the deflection of the cantilever which is detected by the photodetector. There exist the short-range chemical, van der Waals, electrostatic and magnetic forces, as well as meniscus forces formed by the adhesion layer when the sample is exposed to the ambient condition with surface contaminations.<sup>233</sup> It is necessary to introduce the tip-sample interaction for a better understanding of the working principle of AFM.



Figure 4.4: Images of AFM (MFP-3D) and the cantilever holder.

The short-range interaction between the tip and the sample described by Lennard-Jones potential,  $U_{LJ}$ , is given by:

$$U_{LJ} = \varepsilon \left[ \left( \frac{r_m}{r} \right)^{12} - 2 \left( \frac{r_m}{r} \right)^6 \right]$$
(4.2)

where  $\varepsilon$  is the depth of the potential wall, r is the distance between particles, and  $r_m$  is the distance at which the potential reaches its minimum, as depicted in Figure 4.5. The tip-sample force ( $F_{ts}$ ) is then given by:

$$F_{ts} = -\frac{\partial U_{LJ}}{\partial z} \tag{4.3}$$

where *z* is the distance between the tip and the sample surface. The corresponding force curve is shown in Figure 4.5b. It is evident that the interaction between the tip and the sample is attractive when the distance is larger than  $r_m$ . However, when the tip and the sample get too close to each other (*z* <  $r_m$ ), this interaction becomes repulsive due to the Pauli exclusion principle which restricts the overlapping of the electron orbitals.<sup>233</sup>



Figure 4.5: **Examples of Lennard-Jones potential curve and the tip/sample force curve**. (a) Lennard-Jones potential curve describing the interaction of two atoms; (b) the force between the tip and the sample based on Lennard-Jones potential.

# 4.3.1.2 Contact mode and tapping mode

AFM operates in different modes, such as the contact mode and the tapping mode. Figure 4.6 illustrates the operation of the contact and tapping mode. The contact mode refers to the mode in which the probe is touching the sample with a gentle force applied to the probe as marked in Figure 4.5b. The applied force would lead to the upward bending of the cantilever and thus the change of the deflection. In order to control the force, the response of the photodetector with reference to the applied force and the spring constant of the probe need to be extracted from the force curve and the thermal spectrum. An example of the force curve is shown in Figure 4.6b. When the probe approaches the sample but still away from the surface, there is barely any interaction between them (i). As the probe gets closer to the surface, it starts to "feel" the attractive interaction with the sample and bend down (ii). Due to the instability of the interaction, when the probe reaches a certain distance, it would snap into the contact with the sample (iii). As the probe is further pressed against the surface, it reaches the repulsive region with the probe bending upward

(iv). When retracting the probe, it requires a larger force to pull the probe off the surface due to the adhesive interaction as mentioned before (v).



Figure 4.6: Schematics of the contact and tapping modes, and an example of the tip-sample force curve. (a) Operation principle of the contact mode and the tapping mode; (b) a typical force curve between the tip and the sample when the tip approaches and is withdrawn from the sample.

According to the force curve (part iv and v), the parameter called Defl InvOLs ( $\alpha$ ) with the unit of nm V<sup>-1</sup> is extracted, which builds a correlation between the displacement of the probe with the applied bias to the z-piezo. A thermal spectrum is performed with the room temperature thermal

motion driving the cantilever. By fitting the peak in the thermal spectrum with a single harmonic oscillator model, the natural resonance frequency ( $\omega_o$ ) can be extracted. The spring constant (k), in the unit of nN nm<sup>-1</sup>, can be calculated by the following equation:

$$\omega_0 = 2\pi f_0 = \sqrt{\frac{k}{m^*}} \tag{4.4}$$

where  $m^*$  is the effective mass which accounts for the tip-cantilever geometry. Therefore, according to Hook's law, the correlation between the applied force ( $F_{app}$ ) and bias is given by:

$$F_{app} = k\Delta z = k\alpha\Delta V \tag{4.5}$$

Using the above equation, the applied force can be tuned by changing the applied bias ( $\Delta V$ ) to the z-piezo. Generally, the soft probes are used in the contact mode since the probes get contaminated easily by grabbing the dirt when being dragged across the surface. The consequences of probe contamination are 1) the reduced spatial resolution due to the blunt tip and 2) the change of tip and sample interaction. For example, pc-AFM is also operated in contact mode, and the current flow through the probe would be diminished by the insulating dirt attached to the probe.

The other important operation mode is the tapping mode, also called AC mode, which avoids the lateral dragging force caused by the continuous contact between the tip and the sample. In the tapping mode, the probe is driven by the z-piezo at or near its resonance frequency over the surface, as shown in Figure 4.6a, and the change in the oscillatory behavior is monitored to map the topography. The motion of the probe is described by the following equation:

$$m\ddot{z} + \frac{m\omega_o}{o}\dot{z} + kz = F_{ts} + F_d\cos(\omega_d t)$$
(4.6)

where *m* is the mass of the probe, *Q* is the quality factor of the cantilever as a result of both the lever and the environment, and  $F_d$  and  $\omega_d$  are the drive amplitude and frequency, respectively.

Under a small perturbation, the tip is under the influence of a parabolic tip-surface interaction potential. And the total force (*F*) acting on the tip, the effective spring constant ( $k_e$ ), and the effective resonance frequency ( $\omega_e$ ) are expressed by:

$$F = F_d + \left(\frac{dF}{dz}\right)_{z_o} \left(z - z_o\right) \tag{4.7}$$

$$k_e = -\frac{dF}{dz} = \left(k - \frac{dF_{ts}}{dz}\right)_{z_o} \tag{4.8}$$

$$\omega_e = \left(\frac{k - (dF_{ts}/dz)}{m}\right)^{1/2} \tag{4.9}$$

It is evident that the interaction between the probe and the sample would result in the shift of the resonance frequency. As shown in Figure 4.5, even in the tapping mode, AFM is operated in the attractive or repulsive regime depending on the distance between the tip and the sample. In the attractive regime, the tip is farther away from the sample, which is an even safer situation for the probe. While in the repulsive regime, the probe is closer to the sample surface and there is a higher chance that the tip touches the sample, especially for rough surfaces. But it is worth pointing out that the scanning in the repulsive regime provides a higher resolution than that in the attractive regime.

The impact of the attractive and repulsive interaction is depicted in Figure 4.7. In the attractive regime, the term  $dF_{ts}/dz > 0$ , thus the resonance frequency decreases. It is obvious that when the tip is driven at the free resonance frequency ( $\omega_0$ ), the amplitude decreases. The phase of the oscillatory behavior of the cantilever is 90 ° when driven at  $\omega_0$ . However, in the attractive mode, the phase would be larger than 90°, which is an important indicator of the operating regime. In the repulsive mode, the amplitude would also be diminished as well as the phase (<90°). During the measurement, it is critical to maintain the operation in the same regime. If the tip toggles between

the two modes, the image quality would be affected due to the tip jumping into and out of the sample surface, which is called "phase jump".



Figure 4.7: **Illustration of the resonance frequency shift when the tip-sample interaction falls into attractive and repulsive regimes**.

#### 4.3.1.3 Photo-conducting AFM

Pc-AFM is a useful tool to study the photoresponse of the microstructures. The schematic of pc-AFM is illustrated in Figure 4.8. Pc-AFM operates in the contact mode while adopting a probe with a conductive coating in order to flow current. During the scan, the tip is grounded while a bias is applied to the sample if needed. The light source is a laser coming from the bottom of the sample and aligned with the probe. Thus, the setup requires the bottom of the sample to be transparent so that the laser can pass through. The topology and current information are collected simultaneously while the probe moves across the sample. In order to achieve a high-quality current map, it is crucial to make sure that it forms a good contact between the tip and sample by applying a proper force without damaging the sample surface or contaminating the probe.



Figure 4.8: **Schematic of pc-AFM setup**. The topology and current are measured spontaneously as the tip moves across the sample. The current signal is tracked and amplified by the current amplifier.

# 4.3.1.4 Kelvin probe force microscope

KPFM is a useful tool to study the energetics since it measures the contact potential difference (CPD) which is reflecting the surface potential of the sample. The setup of KPFM is illustrated in Figure 4.9. It operates in the tapping mode with the topology and CPD information acquired separately. First, the tip moves across the sample and collects the topography information. Then, it is lifted by several tenths of nanometers and moves above the sample while maintaining

the same height relative to the sample by following the trace of the topography. Meanwhile, CPD is measured by a nullifying mechanism.



Figure 4.9: **Schematics of KPFM setup and the operation mode**. (a) Illustration of the setup of KPFM: the lock-in amplifier tracks the oscillatory term with the same frequency as the applied AC bias, and then the potential feedback loop adjusts the DC bias to nullify the CPD; (b) an example of the operation of KPFM.



Figure 4.10: Illustration of the working principle of KPFM.

Figure 4.10 depicts the nullifying mechanism of KPFM. The AFM tip and the sample with different work functions demonstrate the vacuum level alignment while they are away from each other. When they get close enough for tunneling or make an electrical contact, the Fermi levels tend to level up, resulting in a current flow from the sample to the tip as shown in Figure 4.10b. The alignment of Fermi levels causes the vacuum level shift. The magnitude of the energy level shift is equal to CPD. Then, a DC bias is applied to the tip to nullify the CPD and thus stops the current flow. With the vacuum levels lining up, the DC bias applied to the tip equals the CPD between the tip and sample. This is the nullifying mechanism of KPFM.

In the KPFM measurement, an AC bias is applied between the tip and sample, together with the DC bias. If the tip and sample are treated as a parallel plate capacitor, the electrostatic force (F) between them is described by:

$$F = \frac{1}{2} \frac{\partial C}{\partial z} V^2 \tag{4.10}$$

where *V* is the total potential difference, and *C* and *z* are the capacity and distance between the tip and the sample, respectively. The total potential difference including the AC bias ( $V_{AC} sin(\omega t)$ ), DC bias ( $V_{DC}$ ), and the CPD ( $V_{CPD}$ ) is given by:

$$V = V_{AC}\sin(\omega t) + V_{DC} + V_{CPD}$$
(4.11)

Substituting the *V* in equation 4.10, *F* is given by:

$$F = \frac{1}{2} \frac{\partial C}{\partial z} \left\{ \left[ (V_{DC} - V_{CPD})^2 + \frac{1}{2} V_{AC}^2 \right] + 2 \left[ (V_{DC} - V_{CPD}) V_{AC} \sin(\omega t) \right] - \frac{1}{2} V_{AC}^2 \cos(2\omega t) \right\} (4.12)$$

To determine CPD, the second term is critical. By applying a DC bias with the same value of CPD, the oscillatory force at the frequency of the drive would be nullified. The lock-in amplifier tracks the second term and sends the information to the potential feedback loop which controls the

DC bias. This is how KPFM works based on AFM setup. Stiffer probes with the conductive coating are applied in KPFM. However, CPD measured from KPFM is a relative value. In order to extract the surface potential and work function information, a reference material with a well-defined work function is needed. In this study, the highly ordered pyrolytic graphite (HOPG, WF of 4.6 eV), a typical calibration sample, is employed in KPFM measurement.

# 4.3.2 Electrochemical impedance spectroscopy

Impedance refers to the resistance of circuit elements to the current flow, such as resistors and capacitors.

$$Z = \frac{v}{l} \tag{4.13}$$

Measuring the impedance with only DC bias barely provides information of the total resistance of the system, while the impedance measurement with an AC perturbation enables us to differentiate impedance components, including resistance and capacitance related to various charge transfer, transport, storage, etc. processes, and therefore de-convolute different physical processes. For example, EIS measurement is widely applied in the study of the carrier dynamic processes in solar cells and is able to disentangle them via the frequency dependent behaviors of different processes.

#### 4.3.2.1 Impedance of capacitors and combination of resistor and capacitor

When an AC bias is applied to the capacitor, the current flows during the charging and discharging processes. The AC bias (V) and capacitive current ( $i_c$ ) are given by:

$$V = V_o \cos(\omega t) \tag{4.14}$$

$$i_c = C \frac{dV}{dt} = \omega C V_o \cos\left(\omega t + \frac{\pi}{2}\right)$$
(4.15)

where  $V_o$  is the amplitude of AC bias, and  $\omega$  is the angular frequency. The correlation of V and  $i_c$  is described in a phasor diagram as shown in Figure 4.11. The current is always ahead of the bias by  $\pi/2$ , which is called the phase angle ( $\emptyset$ ), and their values equal to their projections on the x-axis. In this case, the y-axis is the imaginary axis. This stems from the Euler equation:

$$\exp(j\Delta) = \cos\Delta + j\sin\Delta \tag{4.16}$$

where j is the square root of -1. It is easier to do calculations with exponents in terms of multiplication and derivation. Then, V and  $i_c$  is described with exponents by:

$$V = V_o \exp(j(\omega t)) \tag{4.17}$$

(4.19)

$$i_c = C \frac{dV}{dt} = C j \omega V_o \exp(j(\omega t)) = j \omega C V$$
(4.18)

The impedance of capacitor  $(\dot{Z}_c)$  can then be written as:



Figure 4.11: Cosine-based phasor diagram for a purely capacitive circuit.

Next, the system with more than one electrical element is discussed. The total impedance is calculated in the same way as the resistors in systems with elements in series or parallel. For example, a circuit consists of a capacitor and a resistor in parallel, RC parallel circuit, which is commonly seen in the equivalent circuit of photovoltaic devices. It is similar to the classical Randle's circuit with the negligible diffusional impedance and series resistance, in which the capacitance is associated with Helmholtz layer formed at the electrode/solution interface and the resistance represents the charge transfer resistance. The total impedance of the parallel circuit ( $\dot{Z}_{tot}$ ) is given by:

$$\frac{1}{\dot{z}_{tot}} = \frac{1}{\dot{z}_c} + \frac{1}{R}$$
(4.20)

Substituting equation (4.19) into the above one, one can get:

$$\dot{Z}_{tot} = \frac{R}{1 + \omega^2 C^2 R^2} - j \frac{\omega C R^2}{1 + \omega^2 C^2 R^2}$$
(4.21)

Consequently, the absolute value of impedance and phase angle ( $\emptyset$ ) equal:

$$\left| \dot{Z}_{tot} \right| = \frac{R}{\sqrt{1 + \omega^2 C^2 R^2}}$$
 (4.22)

$$\emptyset = \tan^{-1}(\omega CR) \tag{4.23}$$

Generally, the impedance data can be plotted in two ways: Nyquist plot and Bode plot. In the Nyquist plot, the x-axis is the real part of the impedance ( $Z_{real}$ ) and y-axis represents the imaginary part ( $-Z_{im}$ ). Log|Z| and  $\emptyset$  are plotted against log frequency in Bode plot. Figure 4.12 depicts an example of Nyquist and Bode plots of an RC parallel circuit. It is not difficult to notice that it shows a semicircle feature in the Nyquist plot. The semicircle intercepts with the x-axis at x=0 and R. The capacitance can be extracted from the maximum point of  $-Z_{im}$ :

(a) high 
$$f$$
  
 $N_{r}$  low  $f$   
 $Z_{real}$   
(b)  $\overline{Z} = \overline{DO}$  log  $f$   
(c)  $\overline{D} = \overline{DO}$  log  $f$ 

 $C=\frac{1}{\omega R}$ 

(4.24)

log f

Figure 4.12: Examples of Nyquist (a) and Bode (b), (c) plots of a RC parallel circuit.

#### 4.3.2.2 Application of EIS in solar cells

In the first part of this session, the basics of impedance have been introduced. The impedance spectroscopy measures the impedance response of the systems composed of capacitors, resistors etc. Then, the question is what the origin of the capacitor and resistor behaviors is in solar cells.

Capacitances, including geometric, chemical and contact capacitances, have been identified in solar cells. And resistors always accompany with the capacitors, either in series or parallel. The existence of geometric capacitance ( $C_g$ ) is related to the geometry of the design and the dielectric property of the device. For example, in perovskite solar cells, the capacitance measured at high frequency has been attributed to the perovskite material, and the calculated dielectric constant from the capacitance of EIS measurement matches well with that of the perovskite materials.<sup>234-235</sup> The geometric capacitance is described by:

$$C_g = \frac{\varepsilon_0 \varepsilon}{L} \tag{4.25}$$

where  $\varepsilon$  and  $\varepsilon_0$  are the dielectric constant of the sample and the vacuum permittivity, respectively, and *L* is the film thickness.

Chemical capacitance is attributable to the displacement of the Fermi level with respect to the band edge as a result of the accumulation of carriers.<sup>234, 236-237</sup> Consequently, the chemical capacitance is correlated with the carrier concentration. At the interfaces, the spatial separation of electrons and holes also contributes to the capacitor behaviors. For example, at the cathode, electrons are collected by the selective contact while holes remain in the bulk. Therefore, the spatial separated electrons and holes contribute to the capacitance at the contact.

In DSSCs, for instance, a capacitor forms at the mesoscopic cathode (electron reservoirs in TiO<sub>2</sub>) interface and the electrolyte connected with Pt electrode. The change of the electrochemical potential at the cathode leads to the variation of Fermi level as well as the concentration of electrons. Hence, the capacitance is dominated by the chemical capacitance which is related to the chemical potential of electrons in TiO<sub>2</sub> plates.<sup>237</sup> The carriers in the two "plates" tend to recombine as mentioned in Chapter 2. Therefore, a resistor called recombination resistance ( $R_{rec}$ ) is in parallel with the chemical capacitor, which represents the resistance to the current resulted from the recombination of electrons and holes. Therefore, a larger  $R_{rec}$  indicates a better charge separation in the devices. The other resistance commonly observed in solar cells is  $R_s$  as discussed in Chapter 2. The transport of carriers in the bulk, as well as the barriers presented at the interface contribute to  $R_s$ .

The essential part of understanding the EIS data is to adopt an accurate equivalent circuit to describe the physical processes in the devices. Solar cells demonstrate different capacitive behaviors due to the configuration of the device and materials properties. One way to figure out the origin of the capacitive behavior is investigating its dependency on the device structure, illumination conditions and applied bias. For example, the geometric capacitance is reversely proportional to the distance between two capacitor plates, i.e., the thickness of the absorber layer, while the chemical capacitance increases with the light intensity and the thickness of the absorber layer.<sup>234</sup> More details about the equivalent circuit used in this study are discussed in Chapter 5.

# 4.3.3 Electron backscattering diffraction measurement

EBSD measurement is a useful tool for materials analysis, such as characterizing the crystal orientation, misorientation, grain and grain boundary, and phases. The mechanism behind EBSD measurement is the backscattered electron diffraction process. When an electron beam hits the

sample, the interaction between electron beams and the sample atoms extends from nanometer to a few microns within a teardrop-shaped volume, called interaction volume. The inelastic scattering would generate secondary electrons close to the surface, which yields high-resolution images of morphology. This is the mechanism of SEM imaging process.

The elastic scattering happens deeper in the sample. The backscattered electrons are generated as shown in Figure 4.13b. The diffraction of the backscattered electrons between certain crystal planes in the sample provides the local crystal orientation information. Since heavy atoms demonstrate a stronger interaction with the backscattered electrons, samples with large atomic numbers show stronger EBSD signals. In this study, EBSD measurement is employed to measure the crystal orientation of grains in the polycrystalline perovskite thin film.



Figure 4.13: **Schematics of the inelastic and elastic scattering of electrons**. When the electron beam (yellow) interacts with the atoms, for inelastic scattering, the electron beam would knock out electrons from the atoms as secondary electrons (a), while the electrons are backscattered in the elastic scattering (b).

# 4.3.3.1 EBSD setup and electron diffraction process

The schematic layout of EBSD system is shown in Figure 4.14. Experimentally, EBSD is assembled in SEM. The sample is tilted by 70° with respect to the horizontal direction in order to increase the signal contrast and the interaction volume. With the electron beam focusing on the sample, the backscattered electrons are ejected from the sample surface and detected by the phosphor detector. Some of the backscattered electrons exit the sample at the Bragg angle and diffract according to Bragg's law. The diffraction of backscattered electrons forms Kikuchi lines on the phosphor detector. The patterns are then captured by the camera mounted behind the detector. Since the EBSD measurement is assembled in the SEM, the secondary electrons provide morphology information during the measurement.



Figure 4.14: Schematic layout of EBSD system.



Figure 4.15: Illustration of the backscattered electrons diffraction and the formation of Kikuchi bands on the phosphor detector.

Figure 4.15 depicts the diffraction of backscattered electrons in EBSD measurement. Though the scattering process is chaotic, some of the scattered electrons in the sample satisfy the Bragg's law when exiting the surface. Consequently, the diffracted electrons form two cones, called Kossel cones. As the detector is close to the sample, the Kossel cones are intercepted by the detector and appear as two "parallel" lines in the phosphor screen, which are called Kikuchi lines. Each line forms an angle of  $\theta$  with the crystal plane. The Kikuchi lines together with the space in between are termed as Kikuchi bands. The bandwidth is proportional to the *d*-spacing of diffraction planes. As the diffraction can happen at multiple crystal planes, many Kikuchi bands are observed in the EBSD measurement. And the electron diffraction at the same plane can show up at different locations of the detector depending on the crystal orientations.



Figure 4.16: **Illustration of Hough transform: transform** (a) a dot and (b) a line into Hough space. In real space, infinite lines can pass through the same dot at different angles. Draw dotted lines perpendicular to the lines passing the dot from the same origin and record the distance from the origin to the intersect of the lines ( $\rho$ ) and the angle ( $\theta$ ) which are the axes in Hough space. And a dot in real space corresponds to a wave in Hough space. As shown in (b), a line in the real space consists of infinite dots and each dot correspond a wave in Hough space. However, all the waves intersect at the same dot in the Hough space. Thus, a dot in the Hough space can represent a line in the real space.

Electrons in the bulk of the sample suffer from inelastic events instead of elastic backscattering. Combined with the high tilt angle, only scattered electrons within several tenths to

a few hundred nanometers away from the surface contribute to the diffraction pattern. Therefore, the crystal lattice should be strain-free and without contamination within the same range in order to enhance the electron diffraction. Also, factors such as the surface roughness, grain sizes and atomic numbers impact the scattered electrons and thus the pattern quality. For example, at the valley of the sample surface, the tall features block the scattered electrons from reaching the detector resulting in none detectable signal, as observed in the EBSD measurement of polycrystalline perovskite thin films.

# 4.3.3.2 Indexing process and band identification

Hough transform is employed in indexing process of EBSD measurement, which reduces the amount of data in the image while maintaining the characteristic information. In Figure 4.16, the mechanism of Hough transform is illustrated. The Kikuchi lines are first transformed into points in Hough space. By locating the peak positions in Hough transform, the Kikuchi bands are identified. With the basic crystal information uploaded in the system, the possible Kikuchi bands are then simulated. By comparing the calculated look-up table of interplanar angles with the band information from the Hough space, the crystal orientation information is extracted. More details about the data processing are described in Chapter 6.

# Chapter 5

# Elucidating the impact of thin film texture on charge transport and collection in perovskite solar cells

In this chapter, electrochemical impedance spectroscopy is utilized, which has the potential to disentangle the bulk and contact processes, to pinpoint the effects of the thin film texture on the performance of perovskite solar cells. By adapting ramp annealing treatment to rationally tailor the crystallinity of the perovskite layer, it is demonstrated that the texture of the perovskite thin film not only influences the surface recombination kinetics and thus the charge carrier collection at the contacts but also affects the carrier diffusion length and charge transport in the bulk. Lastly, it is shown that ramp annealing is a well-controlled process that can result in highly reproducible device performance as detailed in this Chapter. This methodology could aid in the simple design and fabrication of high-efficiency organic-inorganic hybrid perovskite solar cells.

5.1 Ramp annealing treatment and crystalline structure of perovskite thin films

Figure 5.1 shows the SEM images of the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> thin film deposited on PEDOT:PSS/ITO using the conventional one-step solution process,<sup>32</sup> where the annealing is performed at 100 °C for 10 min which is termed as the fast-annealing treatment. Beyond the relatively high density of cracks, the  $\theta$ -2 $\theta$  X-ray diffraction scan of such prepared films in the Bragg-Brentano configuration (blue curve in Figure 5.2b) further reveals the polycrystalline nature of the film with perovskite grains oriented along the (110), (310), (112) planes, etc. To improve the surface morphology and to gain a better control over the film crystallinity and texture (meaning the degree of preferential crystal orientation in this dissertation), the ramp-annealing treatment is adapted in the fabrication process.



Figure 5.1: **SEM images of perovskite films processed under different conditions**. SEM images of perovskite films (~ 110 nm thick): (a) fast annealed at 100 °C for 10 min; annealed at 40 °C then ramped up to 100 °C at (b) 1 °C min<sup>-1</sup>, (c) 10 °C min<sup>-1</sup> and (d) 100 °C min<sup>-1</sup>, followed by annealing at 100 °C for 10 min; cross-sectional SEM images of optimized ramp-annealed sample (e) and fast annealed sample (f).

The schematic of the ramp annealing profile is sketched in Figure 5.3a, which consists of three steps, that is, low temperature annealing, ramping, and final annealing at 100 °C. The rationale behind this treatment is twofold: (i) to induce heterogeneous nucleation of the perovskite phase at the interface between film (solvent-solute) and substrate and (ii) to remove solvent molecules when the film is still largely amorphous, thus minimizing cracking. The microstructure of the perovskite thin film is determined by the nucleation and growth processes. The heterogeneous nucleation is generally induced at the film/substrate interface, while the homogeneous nucleation occurs within the bulk film. The activation barrier is inversely proportional to the thermodynamic driving force for the transformation of amorphous film into

crystalline films. Therefore, the nucleation at the interface requires a lower activation energy than the homogeneous case due to the reduced surface area of the nucleus and minimized interface energy. In our case, comparing to the homogeneous nucleation that occurs in the bulk of the perovskite film, nucleation at the perovskite/PEDOT: PSS interface can potentially lead to columnar structures with preferentially oriented grains guided by the interaction between the perovskite and the substrate (see Figure 5.3b for schematics). Because the activation energy of homogeneous nucleation is larger than that of the heterogeneous nucleation, it is desirable to first perform the thermal annealing at a relatively low temperature where only heterogeneous nucleation can occur,<sup>238-239</sup> followed by the ramping up of the temperature to 100 °C to complete the crystallization/growth process.

In order to obtain rationally tuned texture structure in perovskite thin films, the parameters of the ramp-annealing procedure are further analyzed. First, the low temperature annealing step is explored. Figure 5.2a shows the XRD patterns of the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/PEDOT:PSS/ITO samples annealed for 10 min at 40, 50, and 60 °C. Grains oriented along the (110) plane are the most predominant, followed by those along the (310) plane. Then, the ratio of the (110) and (310) peak intensities is analyzed to illustrate the texture of the film. The largest ratio is achieved in samples annealed at 40 °C, suggesting that the film processed at this condition has developed a more textured structure with a preferred grain orientation. In contrast, at higher annealing temperatures (50 or 60 °C), it is likely that the nucleation is induced both inside the film and at the interface, leading to a more randomly oriented crystal structure. The other critical parameter that influences the film quality is the ramping rate of the temperature from 40 to 100 °C. As shown in Figure 5.2b, the optimized value is 10 °C min<sup>-1</sup>, which is attributed to the balance between the kinetic-limited and thermodynamic-limited processes. If the rate is too low, that is, 1 °C min<sup>-1</sup>, homogeneous

nucleation may be induced during the long duration of the temperature ramping up process, whereas at the high rate (100 °C min<sup>-1</sup>), the growth of the interface-nucleated grains can be hindered by mass transport.



Figure 5.2: **XRD patterns and** *J-V* **characteristics of perovskite devices with different annealing treatments**. XRD patterns of perovskite thin films (110 nm) annealed (a) at different low temperatures and (b) at 40 °C followed by different ramping rates to 100 °C. The ratios of the (110) and (310) peak intensities are listed on the side for comparison. *J-V* characteristics of the devices with the perovskite layer (c) annealed at temperatures corresponding to those in (a) during the low temperature step followed by 100 °C annealing (with a fixed ramping rate of 10 °C min<sup>-1</sup>), and (d) processed at the selected conditions from those presented in (b). For comparison, XRD and device performance of the fast-annealed sample are also included in (b) and (d), respectively.

#### 5.2 Correlation between device performance and the thin film texture

To examine how the crystalline quality and texture of the perovskite film impact the device performance, J-V curves are measured on devices constructed of ITO/PEDOT:PSS/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> (110nm)/PCBM/BCP/Ag. In this structure, CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> film is the active layer which absorbs light and creates the photocarriers that are subsequently collected by the anode (ITO) and cathode (Ag) through the hole-transport (PEDOT:PSS) and electron-transport (PCBM/BCP) layers, respectively. Figure 5.2c, d and Table 5.1 show the J-V characteristics of the devices with the perovskite layer processed at the varying annealing temperatures or ramping rates corresponding to those exploited in the films displayed in Figure 5.2a, b, respectively. These data strongly suggest that the trend of the device performance closely follows that of the active layer crystallinity as revealed in the XRD patterns, demonstrating that the texture of the perovskite film is essential in determining the device efficiency.

It is worth mentioning that for films that are not thermally treated (black curve in Figure 5.2a), an intermediate phase emerges at small  $2\Theta$  angles (<10°), corresponding to a large lattice spacing along the out-of-plane direction. This intermediate phase is likely to consist of CH<sub>3</sub>NH<sub>3</sub>I-PbI<sub>2</sub>-DMSO (solvent molecule).<sup>130, 240-241</sup> Although solvent molecules can be removed during the fast-annealing treatment, the volume shrinkage in films that are rapidly undergoing the transition to the crystalline phase will result in cracks as those observed in the SEM image in Figure 5.1a. Ramp-annealed samples, on the other hand, exhibit smooth and compact morphology with minimized density of cracks, as shown in Figure 5.1b-d. This is presumably owing to the removal of solvent molecules during the low temperature annealing step when the film is still largely amorphous.<sup>242</sup> Nevertheless, even though the cracks present on the fast-annealed sample increase
the surface roughness, the film is still continuous without deep pinholes or shunting paths, as shown in the cross-sectional SEM images in Figure 5.1f.



Figure 5.3: Schematics of annealing profiles and nucleation/crystallization processes. (a) Schematics of the thermal annealing profile for the fast- (left) and ramp- (right) annealing treatments. (b) Schematics of the homogeneous nucleation induced in the bulk (top) and the heterogeneous nucleation at the interface (bottom), and their impacts on the crystallinity/texture of the thin film.

In the following discussion, the focus is on the analysis and comparison between the fastannealed sample and the ramp-annealed one treated under the optimized annealing condition (unless specified), corresponding to the blue and red curves in Figure 5.2b, d, respectively, as they represent the two ends of the spectrum in terms of film crystallinity/texture and device performance. The ramp-annealed samples outperform the fast-annealed ones in both the  $J_{sc}$  and the FF, which leads to an improved PCE from 6.3 to 8.7 %. The typical *J-V* curves under the forward and reverse scans are plotted in Figure 5.4, demonstrating a negligible hysteresis for both types of the devices. The histogram displayed in Figure 5.5 further summarizes the performance of more than 40 devices from 10 batches of samples prepared on different days, where the enhancement of  $J_{sc}$  and FF, and therefore improved PCE are consistently observed in ramp-annealed samples.

Table 5.1: Characteristic parameters of perovskite solar cells processed under different conditions. Parameters of the devices constructed of ITO/PEDOT:PSS/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> (110nm)/ PCBM/BCP /Ag with the perovskite layer processed at different  $T_0$  and ramping rates.

To	ramp rate °C min <sup>-1</sup>	J <sub>sc</sub> mA cm <sup>-2</sup>	$V_{oc}  onumber V$	FF	PCE %
	Fast annealing	10.2±1.0	0.93±0.01	0.66±0.01	6.3±0.6
40 °C	10	13.1±1.3	0.91±0.01	0.73±0.01	8.7±0.9
50 °C	10	12.2±1.2	0.90±0.01	0.70±0.02	7.7±0.8
60 °C	10	12.0±1.2	0.90±0.01	0.73±0.01	7.9±0.8
40 °C	100	10.4±1.0	0.93±0.01	0.67±0.01	6.5±0.6
40 °C	1	10.8±1.1	0.92±0.01	0.69±0.03	7.0±0.7



Figure 5.4: Plot of *J-V* curves scanned in forward and reverse directions. *J-V* characteristics of the fast- and ramp-annealed devices (perovskite active layer of 110 nm thick) under the forward and reverse scans with a scan rate of 50 mV s<sup>-1</sup>. Hysteresis is negligible on both samples.

The  $J_{sc}$  can also be calculated from the spectral response of the cell using the equation  $J_{sc} = q \int \phi(\lambda) \times EQE(\lambda) d\lambda$ , where  $\phi(\lambda)$  is the photon flux, and EQE, the external quantum efficiency, represents the ratio between the number of collected charge carriers and the number of incident photons at a given wavelength. Because EQE measures how efficiently the cell converts incident light into electrical energy, it is determined by the product of the light harvesting efficiency, the carrier transport efficiency, and the charge collection efficiency, that is,  $\eta_{LH}(\lambda) \times \eta_{CT}(\lambda) \times \eta_{CC}(\lambda)$ . Figure 5.6a displays the corresponding EQE data of the two devices, where the rampannealed one shows consistently higher quantum efficiency over the entire wavelength range. However, as illustrated in Figure 5.6b, the absorbance spectrum obtained from the UV-vis measurement does not show any noticeable difference between the fast- and ramp-annealed

CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/ PEDOT:PSS/ITO samples, indicating that  $\eta_{LH}(\lambda)$  is not the origin of the EQE enhancement.



Figure 5.5: **Histograms of device characteristics of perovskite solar cells**.  $J_{sc}$ ,  $V_{oc}$ , FF and PCE for fast- (blue) and ramp-annealing (red) processed samples with perovskite layer's thickness of 110 nm. Optimized parameters, that is, low temperature treatment at 40 °C and ramping rate at 10 °C min<sup>-1</sup> are adapted in the latter. More than 40 devices fabricated from 10 batches of samples made on different days are analyzed.



Figure 5.6: Plots of EQE and absorbance spectra of perovskite devices. (a) EQE curves corresponding to the fast- and ramp-annealed devices with the 110 nm thick perovskite active layer, and the calculated  $J_{sc}$  from EQE (12.8 and 10.1 mA cm<sup>-2</sup>) matches well with the  $J_{sc}$  extracted from J-V curves (13.1 and 10.2 mA cm<sup>-2</sup>). (b) Absorbance spectra of the fast- and ramp-annealed CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> (110nm)/PEDOT:PSS/ITO samples.



Figure 5.7: Plots of EIS results measured under illumination at varied bias. (a) An example of Nyquist plot measured under short-circuit condition at 1 sun, where a high frequency arc (left) and a low frequency one (right) can be clearly observed (inset: the equivalent circuit); (b)  $R_s$  fitted from the EIS data at varied bias and under 1 sun illumination using the equivalent circuit shown in (a). The total time of the measurement is about 1.5 hours. (c) and (d) Dependence of resistances and capacitances on bias under 1 sun.

# 5.3 Impact of thin film texture on charge collection and transport

It is important to point out that the textured-structure of the perovskite layer may impact the carrier transport efficiency ( $\eta_{CT}(\lambda)$ ) because of the enhancement of the long-range structural coherence in the film.<sup>39, 243</sup> The textured structure could also improve the charge collection efficiency ( $\eta_{CT}(\lambda)$ ) because energy level alignment and charge transfer at the contacts can be highly dependent on the surface orientation/termination of the perovskite layer.<sup>39, 55</sup>



Figure 5.8: **Plots of capacitances, resistances and recombination time constants at the opencircuit condition versus the light intensity**. The dependence of capacitances (a) and resistances (b) on the light intensity under the open-circuit condition; (c) calculated interface recombination time constants under the short and open circuit conditions, respectively, at different light intensities for both fast- and ramp-annealed devices (110 nm perovskite layer).

To clarify the underlying mechanism of the improved EQE and  $J_{sc}$  in the ramp-annealed devices and to pinpoint the effects of the thin film texture, EIS measurements are further performed, which can potentially disentangle processes occurring in the bulk and at the contact. As shown in

the Nyquist plot under 1 sun illumination (Figure 5.7a), two arcs are present which are wellseparated in frequency. The associated capacitance and resistance of each arc are extracted by fitting the impedance data to the equivalent circuit shown in the inset of Figure 5.7a. In order to assign the physical processes that correspond to the two arcs, EIS measurements are performed as a function of applied bias and under different light intensities at both short and open circuit conditions.



Figure 5.9: Plots of  $V_{oc}$  and  $J_{sc}$  versus the light intensity. Light intensity dependence of (a)  $V_{oc}$  and (b)  $J_{sc}$  for fast- and ramp-annealed devices (110 nm perovskite).

The high frequency arc is associated with a capacitance,  $C_2$ , on the order of  $1 \times 10^{-7}$  F cm<sup>-2</sup>, for both ramp annealed and fast annealed samples (Figure 5.8a). The magnitude of  $C_2$  is fairly constant with respect to applied bias (Figure 5.7d) and incident light intensities (Figure 5.8a), consistent with prior reports which have established this capacitance as the bulk dielectric capacitance of the perovskite layer.<sup>234-235</sup> The other equivalent circuit commonly used in perovskite solar cells consists of two RC circuits in series. However, the nature of  $C_1$ , a geometric capacitance due to the dielectric perovskites, supports the equivalent circuit adopted in the study. The

capacitance,  $C_I$ , which is associated with the low frequency arc, has previously been assigned to ionic or electrical accumulation layers at the perovskite interface with charge selective contacts, for example, accumulated holes at the cathode.<sup>235, 244</sup> While  $C_I$  is generally found to increase with light intensity, the value of  $C_I$  for the ramp annealed samples is approximately 2 orders of magnitude larger than the fast annealed ones (Figure 5.8a).

As shown in Figure 5.8b, the resistance associated with the bulk capacitance,  $R_2$ , can be a few times larger than the resistance associated with the interface capacitance,  $R_1$ , for both rampannealed and fast-annealed samples. Both resistances exhibit a similar behavior of deceasing with the increasing light intensity (Figure 5.8b) as well as with applied bias (Figure 5.7c), which is opposite to the trend observed for the interface capacitance  $(C_1)$ . As noted by Bisquert and coworkers,<sup>244</sup> these observations suggest that the resistances are connected to a common process of recombination at the interface. In this case, the interface recombination kinetics are described by the time constant given by  $\tau_s = (R_1 + R_2)C_1$ . Figure 5.8c shows that at open circuit,  $\tau_{s,oc}$  is consistently 2 orders of magnitude larger for the ramp-annealed samples, indicating significantly faster recombination at the interface for the fast annealed samples. Given this fact, it seems surprising that the fast-annealed cells produce the same open circuit photovoltage,  $V_{oc}$ , as the ramp annealed samples. There has been a recent debate centered on the physical meaning of the low frequency response ( $R_1$  and  $C_1$ ).<sup>244-246</sup> Therefore, to test the connection of  $\tau_{s,oc}$  and  $V_{oc}$ , *J*-*V* curves are also measured as a function of incident light intensity. Figure 5.9a shows a plot of  $V_{oc}$  versus intensity for both ramp-annealed and fast-annealed samples. Fits of these trends to the diode equation reveal a nearly ideal diode quality factor,  $\gamma$ , of 1.4 for the ramp annealed samples, whereas  $\gamma$  is 5.6 for the fast-annealed samples, suggesting that they are controlled by different recombination mechanisms. A close examination of the  $V_{oc}$  versus intensity relation for the fastannealed sample further reveals that the quality factor decreases with light intensity, and a  $\gamma$  of 5.6 is a simple average. This can be attributed to the filling of trap states or recombination centers associated with the interfaces by photogenerated carriers, resulting in the gradual drop of the quality factor to a value close to that of the ramp annealed sample under sufficient illumination (>0.2 sun).<sup>164</sup> The diode quality factors further accounts for the larger FF which is consistently measured for the ramp-annealed compared to the fast annealed-samples.



Figure 5.10: **Plots of resistances and capacitances at the short-circuit condition versus the light intensity**. Dependence of (a) resistances and (b) capacitances on the light intensity at the short-circuit condition. The measurements are taken on samples with the perovskite layer thickness of 110 nm.

The  $J_{sc}$  is found to increase linearly with light intensity for both samples (Figure 5.9b). The interfacial recombination time constants are also determined at short circuit, where  $\tau_{s,sc}$  is found to be larger than  $\tau_{s,oc}$  for both samples at all light intensities (Figure 5.8c). Unlike at open circuit, however, the time constants of the ramp-annealed and fast annealed samples are fairly close at short circuit (see Figure 5.10 for resistances and capacitances at varying intensity under the short circuit). This suggests that interfacial recombination may not account for charge collection losses.

It was suggested that the collection efficiency can be calculated from the ratio of the recombination resistance  $(R_1 + R_2)$  at the open circuit and the short circuit according to  $\eta_{cc} = 1 - R_{oc}/R_{sc}$ .<sup>244</sup> This analysis produces nominally identical values of  $\eta_{cc} = 0.985$  for the ramp-annealed samples and  $\eta_{cc} = 0.978$  for the fast-annealed samples. Thus, differences in charge collection efficiencies cannot completely account for the discrepancy in  $J_{sc}$  observed. Instead, if this photocurrent discrepancy mainly originates from the bulk diffusion / recombination processes through differences in the carrier diffusion length, it should be reflected in the device performance as a function of the perovskite layer thickness.<sup>19, 119, 146</sup>

Table 5.2: Characteristic parameters of perovskite solar cells with different thickness. The devices are constructed of ITO/PEDOT:PSS/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/PCBM/BCP/Ag with the varying thickness of the perovskite layer processed at the fast- or ramp-annealing conditions. The optimized  $T_0$  and ramping rate are adapted in the latter.

Annealing	film thickness	$J_{sc}$	Voc	FF	РСЕ
process	nm	mA cm <sup>-2</sup>	V		%
Fast	110	10.6±1.1	$0.84 \pm 0.02$	0.58±0.03	5.1±0.5
Fast	200	15.0±1.5	$0.90 \pm 0.01$	$0.52 \pm 0.01$	$7.0\pm0.7$
Fast	290	8.9±0.9	$0.88 \pm 0.01$	$0.70 \pm 0.01$	$5.4 \pm 0.5$
Fast	450	8.8±0.9	$0.85 \pm 0.01$	$0.67 \pm 0.02$	$5.0 \pm 0.5$
Ramp	110	13.7±1.4	$0.89 \pm 0.01$	$0.66 \pm 0.01$	$8.0{\pm}0.8$
Ramp	200	17.2±1.7	$0.87 \pm 0.01$	$0.65 \pm 0.01$	9.7±1.0
Ramp	290	22.0±2.2	0.83±0.01	$0.66 \pm 0.01$	12.1±1.2
Ramp	450	16.5±1.7	$0.88 \pm 0.01$	$0.67 \pm 0.01$	9.7±1.0



Figure 5.11: Plot of *J<sub>sc</sub>* and PCE dependence on the perovskite layer thickness.



Figure 5.12: Plots of capacitances, resistances and recombination time constants of devices with thick perovskite films at the short-circuit condition versus the light intensity. Dependence of capacitances (a) and resistances (b) on light intensity under the short-circuit condition for both ramp- and fast-annealed devices with the 290 nm thick perovskite layer. (c) Calculated interface recombination time constants under the short and open circuit conditions at different light intensities.

By varying the concentration of the precursor solution, film thickness can be controlled between 110 nm and 450 nm as listed in Table 5.2. Indeed, the highest PCE for the fast- and rampannealed samples is achieved at the thickness of 200 nm (7.0 %) and 290 nm (12.1%), respectively, as illustrated in Figure 5.11, suggesting a longer carrier diffusion length associated with the latter.

Because the  $J_{sc}$  and PCE variations between the ramp- and fast-annealed samples are most pronounced at the perovskite layer thickness of 290 nm, corresponding EIS measurements are performed at this thickness which might provide more information on the recombination parameters under the short-circuit condition. The associated capacitances and resistances, as well as the derived recombination time constants are plotted in Figure 5.12. In contrast to the comparable  $\tau_{s,sc}$  in thin devices,  $\tau_{s,sc}$  of the 290 nm thick ramp- and fast-annealed samples differs by 2 orders of magnitude, as shown in Figure 5.12c, which originates from the larger  $R_1$  and  $R_2$  in the former (Figure 5.12b). It has been argued that the applied bias in EIS measurements can lead to ionic transport and polarization of the interfaces in devices with the regular structure, which consequently interferes with the EIS measurements and changes the mechanism of recombination from bulk- to surface-dominant.<sup>247</sup> The same ionic processes will also lead to a gradual increase of  $R_s$  (defined in Figure 5.7b) over time and introduce hysteresis in J-V curves.<sup>247-248</sup> Nevertheless, as shown in Figures 5.4 and 5.7b, no obvious J-V hysteresis or change in  $R_s$  is observed in our experiments, indicating that the ion migration/polarization issue is not as severe in our invertedstructured devices. This can be attributed to the surface passivation effect of fullerene molecules, 183 as well as the avoidance of chemical reactions as those occur at the interfaces between perovskite and TiO<sub>2</sub>/Spiro-OMeTAD in devices with the regular structure.<sup>247</sup> Therefore, the larger  $R_1$  and  $R_2$ as measured in the ramp-annealed sample under the short-circuit condition (Figure 5.12b) provide a strong indication that beyond the surface recombination at contacts, bulk recombination process

is also suppressed in the ramp-annealed devices, which ultimately leads to the longer carrier diffusion length, as illustrated in Figure 5.11. Note that similar to the thin devices, significant variation in  $\tau_{s,oc}$ , mainly contributed by the modulation in  $C_I$ , that is, interface capacitance, is also observed between the ramp- and fast-annealed 290 nm thick samples, as illustrated in Figure 5.13.



Figure 5.13: **Plots of capacitances and resistances of devices with thick perovskite films at the open-circuit condition versus the light intensity.** Dependence of resistances (a) and capacitances (b) on light intensity under the open-circuit condition measured on samples with the 290 nm thick perovskite layer, the trend of which is similar to that of the devices with 110 nm thick perovskite.

Although there are theoretical predictions that defects in the perovskite layer mainly contribute to the shallow traps and thus are not detrimental to the device performance,<sup>52, 161, 249</sup> our study suggests that it is still crucial to improve the crystallinity and texture of the perovskite layer to boost the device performance. On the one hand, the recombination at the contacts is expected to be the dominant loss mechanism in perovskite solar cells.<sup>38, 172, 250</sup> Instead of introducing interfacial layer at the contact<sup>172, 250-251</sup> or passivating the surface trap states with small molecules<sup>158-159</sup> which could complicate the device fabrication process, our study demonstrates

that the recombination kinetics at the interfaces can be effectively suppressed simply by the rampannealing treatment via controlling the surface orientations or terminations of perovskite grains. On the other hand, it is likely that the preferential crystal orientation in the ramp-annealed sample yields an increase in the density of low-angle grain boundaries in the polycrystalline perovskite thin film, which, as compared to the large-angle grain boundaries, exhibit better carrier transport properties with minimized bulk carrier recombination.

### 5.4 Conclusion

In this chapter, it is demonstrated that the texture of perovskite thin film influences both the surface recombination at the contacts and the carrier diffusion length in the bulk. The combination of the two effects leads to enhanced performance in devices constructed of preferentially oriented perovskite thin films. These findings could aid in the simple design and fabrication of planar-structured high-efficiency perovskite solar cells. However, it is still not clear how the texture structure enhances the charge transport and suppresses the surface recombination. As mentioned above, one possibility is that the low-angle grain boundaries are beneficial in perovskite films compared with high-angle grain boundaries. Also, the carrier mobility along different grain orientation could be different. Since CBM of perovskite mainly consists of *p*orbitals of lead and iodide, different crystal orientation would impact the distribution of electron cloud and therefore the charge transport. Therefore, it is critical to investigate the correlation between crystal orientation and carrier mobility as well as the role of grain boundaries in perovskite thin films, which is the focus of next chapter.

### **Chapter 6**

# Crystalline orientation dependent photoresponse and heterogeneous behaviors of grain boundaries in perovskite solar cells

In this chapter, photoconductive atomic force microscopy and Kelvin probe force microscopy are employed to study the photoresponse of microstructures in perovskite thin films. The discrete photocurrent levels across crystalline grains along with the anti-correlated behavior between the local  $J_{sc}$  and  $V_{oc}$  are identified in perovskite thin films for the first time, revealing an orientation-dependent transport. Additionally, the photoelectrical properties of low-angle grain boundaries from that of large-angle boundaries are distinguished, with the former even displaying higher  $J_{sc}$  and  $V_{oc}$  than adjacent grain interiors. It is worth mentioning that the high-resolution photocurrent mapping and diode-shaped point J-V curves established in this study allow the extraction of local device parameters, thus providing new insights into the correlation between microstructures of the film and properties/performance of the device. Unraveling such correlation will aid the fabrication of high-efficiency hybrid perovskite solar cells.

# 6.1 Photocurrent mapping of perovskite thin films with columnar structures

Figure 6.1a, b show the top view and cross-sectional view SEM images, respectively, of the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/PEDOT:PSS/ITO sample prepared with sequential deposition followed by solvent annealing.<sup>137</sup> One-step spin-coating induces small perovskite grains due to the fast crystallization of perovskite films. Compared with one-step method, the sequential deposition retards the crystallization process, which facilitates the mass transport and the growth of perovskite grains. The DMF vapors during the solvent annealing process further promote the ion diffusivity and contribute to the improved grain sizes. Therefore, films processed under such condition are constructed of single grains along the perpendicular direction with the lateral grain size varying

between 100 and 500 nm. For studies aiming at unraveling the photoresponse of individual grain or GB, such column-structured thin film is a prerequisite which ensures that the photocurrent measured on the top surface is not convoluted by the stacking of grains or GBs underneath. Additionally, instead of a thicker film (300 nm) as in the device configuration (see Figure 6.1c), a thinner film (110 nm) is employed in the pc-AFM studies as the roughness of the film increases with the thickness which can cause artifacts in photocurrent mapping.



Figure 6.1: **SEM images of perovskite thin films and** *J-V* **characteristics of perovskite devices**. (a) Top view and (b) cross-sectional SEM images of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/PEDOT:PSS/ITO sample; (c) *J-V* characteristics of devices with the structure of ITO/PEDOT:PSS/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>(~300nm)/C60/ BCP/Ag, yielding a device performance of 13.0 % under 1 sun illumination.



Figure 6.2: **Photocurrent map and line profile of perovskite thin films**. Simultaneously obtained (a) topology and (b) photocurrent map of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> /PEDOT:PSS/ITO under the illumination of a green laser while applying a -2V bias to the sample. The three discrete photocurrent levels correspond to grains of different types, as marked by A, B, and C in (b). (c) and (d) show the line profile along the red mark in (b). Note that the streaky features on the bottom of (b) indicates a slight tip change during the scan.

Figure 6.2 shows the photocurrent map along with the simultaneously taken topography image of the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/PEDOT:PSS/ITO sample, while -2V bias is applied to the ITO bottom electrode with the tip grounded. This imaging condition is chosen because the work functions (measured by KPFM using highly ordered pyrolytic graphite (HOPG) as the reference) of the ITO electrode and the Pt/Ir coated AFM tip are ~5.0 eV and ~4.6 eV, respectively, indicating that the built-in electric field for collecting photo-generated holes by ITO through the hole transport layer (PEDOT:PSS) and electrons by the AFM tip is rather weak. Photocarriers are thus more effectively extracted with the aid of an external electric field. It can be seen in Figure 6.2 that the grain and GB features are more distinguishable in the photocurrent map than in the topography image. Line profiles as depicted in Figure 6.2c, d further illustrate that the photocurrent contrast does not originate from the height variation.

It is worth pointing out that in the pc-AFM setup even though the tip makes a nano-contact with the film surface, the current spreads out beneath the tip due to the electric field distribution.<sup>252</sup> There are studies suggesting that more carriers will be collected in larger grains simply due to the larger volumes.<sup>253</sup> In order to explore the correlation between the grain area and the photocurrent, the photocurrent levels are plotted against grain areas for the six type A grains, ten type B grains, and ten type C grains (Figure 6.3a). The Pearson correlation coefficient (*R*) is -0.67, and  $R^2$  equals 0.45. It is not surprising that there is a weak correlation between the grain area/volume and the photocurrent level, attributable to the confinement of photoexcited carriers due to the energy barriers for the lateral transport imposed by the grain boundaries.<sup>253</sup> However, if the photocurrent level is predominantly determined by the grain area, one would expect a broadly distributed photocurrent for each grain type since the areas of the grains vary significantly within each type.



Figure 6.3: **Illustration of the correlation between the grain area and the photocurrent of different types of grains**. (a) Scatter plot of photocurrent levels versus grain areas, with the Pearson correlation coefficient of -0.67; (b) ranges of photocurrent (black solid dots) and grain area (gray floating columns) for different types of grains.

As shown in Figure 6.3, the photocurrents are overall more narrowly distributed in comparison with the grain areas, such that the discrete photocurrent levels can be discerned in the pc-AFM image (Figure 6.2b). Meanwhile, the photocurrent levels associated with grain A, B, and

C barely overlap to each other despite the considerable overlapping of their grain areas (Figure 6.3b). Note that AFM is not an ensemble averaging technique. Thus, it is important to consider the distribution, instead of just the averaged value, of the measured parameters. The distribution of the photocurrent levels observed among the different grain types leads to the conclusion that the grain area is not the predominant factor in determining the grain photoconductivity. The superior spatial resolution of the photocurrent map, as evidenced by the uniform photocurrent on each grain and the sharp photocurrent contrast across grains of different types, is likely attributable to the photoinduced giant dielectric constant in CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> that constraints the electric field distribution.<sup>254</sup>

Table 6.1: **Parameters of fitted point** *J-V* **curves.** Fitted parameters of the averaged point *J-V* curves corresponding to grain A, B, C and grain boundary AA

Туре	$egin{array}{c} J_{sc} \ \mathbf{A} \end{array}$	$V_{oc}  onumber V$	FF	Power W
А	-4.67×10 <sup>-10</sup>	0.61	0.32	9.13×10 <sup>-11</sup>
В	-2.28×10 <sup>-10</sup>	0.70	0.38	6.05×10 <sup>-11</sup>
С	-2.95×10 <sup>-11</sup>	0.75	0.30	6.65×10 <sup>-12</sup>
GB AA	-1.50×10 <sup>-9</sup>	0.83	0.34	4.29×10 <sup>-10</sup>

Based on the magnitude of the photocurrent, perovskite grains can be categorized into three types as shown in Figure 6.4a: type A (-2 ~ -3 nA), type B (-1 ~ -2 nA), and type C (less than -1 nA). To further investigate the contribution of grains to the overall device performance, point *J*-*V* spectrum measurements are performed to extract the parameters of nanoscale  $J_{SC}$ ,  $V_{OC}$  and FF. Figure 6.4b displays the characteristic *J*-*V* spectra collected on the different grain types. Since these spectra exhibit diode behaviors, similar to the macroscopic *J*-*V* curves measured on functional perovskite solar cells (Figure 6.1c), the diode equation,  $J = J_{SC} - J_0 \left(e^{qV/mK_BT} - 1\right)$  is applied to the fitting, where  $J_{SC}$ ,  $J_0$ , q and M represent photocurrent, dark current, elemental charge, and ideality factor of the diode, respectively. The extracted parameters are listed in Table 6.1. Note that the dependence of  $J_{SC}$  on the grain type is consistent with that observed in the photocurrent mapping, despite the overall smaller values because of the absence of applied external field at the short-circuit condition.



Figure 6.4: **Plots of averaged photocurrents and point** *J-V* **curves of grains**. (a) Average and standard deviation of photocurrent measured on the grains of different types, summarized from the photocurrent map shown in Figure 6.2b; (b) averaged point *J-V* curves at ten different locations for each grain type under illumination.

The most striking feature revealed in Figure 6.4b and Table 6.1 is the anti-correlation behavior between  $J_{SC}$  and  $V_{OC}$  among the grains of different types, that is, ones of larger  $J_{SC}$  are associated with lower  $V_{OC}$ . This observation is counterintuitive at first because if it is the bulk recombination that limits the device performance, one would expect a correlating trend between

the sample layout in the pc-AFM the parameters. Nevertheless, studies. two CH<sub>3</sub>NH<sub>3</sub>PEDOT:PSS/ITO, lacks an electron transport layer as compared to the complete device architecture (Figure 6.1c). Without the selective contact layer, severe recombination would occur at the tip (cathode) and sample interface under the open-circuit condition. Indeed, fit of the device J-V curve to the diode equation reveals a significantly enhanced FF compared to those obtained from the pc-AFM point spectra (Table 6.1), suggesting that surface recombination at the contact plays a more dominant role in the latter.<sup>255</sup> Since surface recombination is determined by the minority carrier density, the recombination current at the tip-sample contact can be described as:  $J_R = q \Delta p S$ , where q is the elemental charge,  $\Delta p$  is the excess hole carrier density at the contact, and S is the effective recombination velocity which is proportional to the capture coefficient for holes and the surface density of recombination centers.<sup>164</sup> Because of the large magnitude of S expected at the non-selective tip-perovskite contact, the surface recombination will be limited by the diffusion of holes to the contact interface via its impact on  $\Delta p$ .<sup>256</sup> Thus, the higher the carrier mobility is, the more significant the surface recombination and the smaller the Voc will be. On the other hand, higher carrier mobility will lead to enhanced  $J_{SC}$  under the short-circuit condition. Thereby, the anti-correlation behavior between  $J_{SC}$  and  $V_{OC}$  of the pc-AFM point spectra is attributed to diffusion-limited surface recombination, where grain A carries the highest mobility followed by grains B and C.

### 6.2 Identification of grain orientations in perovskite thin films by EBSD

The mobility variation is likely associated with the distinct crystal orientation of each grain type. It has been predicted that the charge carrier mobility is a function of the crystal orientation,<sup>152</sup> which ultimately leads to varied carrier migration path along different perovskite grains.<sup>257</sup> In order to pinpoint the crystalline orientation of each grain, electron backscatter diffraction (EBSD)

measurements are conducted on columned perovskite thin films.<sup>258</sup> Due to the damage of the sample by electron beam and the impact of surface topography on the detection of backscattered electrons, EBSD typically yields extremely diminished signals on perovskite samples. To alleviate the challenge, perovskite films with the thickness of ~ 1 $\mu$ m is employed in order to allow a larger interaction volume with the electron beam. It is worthwhile to point out that the cross-sectional SEM image (Figure 6.5) confirms the columnar structure of the perovskite layer, like the thin film case.



Figure 6.5: Cross-sectional SEM image of the perovskite film with ~1 um thickness.

Figure 6.6 presents the EBSD patterns taken at different locations of the same grain. These patterns show the same Kikuchi bands but with slight shift and contrast variation, indicating that each grain is a single crystalline domain. The shift and contrast variation can be attributed to the surface topography effect. For instance, when the electron beam strikes on the valley features of the surface, no EBSD signals can be detected as a result of the blocking of backscattered electrons. During the EBSD experiment, the damage of the sample by electron beam is observed, as evidenced by the presence of pits next to the red markers shown on the top grain of the SEM image (Figure 6.6).



Figure 6.6: **Images of EBSD patterns on the same grain**. EBSD patterns taken at three different locations within one grain, as marked on the top-view SEM image.

In Figure 6.7, the distinct EBSD patterns taken on three grains are depicted. The indexed orientations of these grains are presented in Euler angles ( $\varphi_1$ ,  $\emptyset$ ,  $\varphi_2$ ), that is, a triplet of rotations that describe the grain crystalline orientation with respect to a reference coordinate system, as specified on the bottom of the indexed patterns.



Figure 6.7: **Images of EBSD patterns and indexing taken on different grains**. EBSD patterns (middle panels, with and without line markers), along with their indexes (right), taken on the three different grains as marked by green cross and circled by dotted line on the top-view SEM images (left). To guide the comparison between the EBSD patterns and their indexes, main features of the EBSD patterns are outlined with the same color as the corresponding indexed lines. Due to the weak backscattered electron intensity from the sample, not all Kikuchi lines can be observed experimentally. Euler angles of each grain are listed on the bottom of the indexes.

From the Euler angles, the Miller indices of the perovskite grains can be calculated using the following equations:

$$\cos \phi = \frac{\frac{l}{c}}{\sqrt{\frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}}}$$
(6.1)

$$\cos\varphi_2 = \frac{k}{\sqrt{h^2 + k^2}} \tag{6.2}$$

where  $\emptyset$  and  $\varphi_2$  are Euler angles, *a*, *b* and *c* are lattice constants (*a* = *b* in this case), and *h*, *k* and *l* are miller indices.<sup>259</sup>  $\varphi_1$  represents the in-plane rotation and thus will not impact the miller indices. The Miller indices derived from the EBSD measurements (Table 6.2) match with the (110), (310) and (202) diffraction peaks observed in the XRD pattern (Figure 6.8). Note that the angles formed between the corresponding crystalline planes are around 10°. This experimental uncertainty is comparable with that of the EBSD measurement performed on a single crystal CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> with a much smoother surface.<sup>258</sup>



Figure 6.8: **XRD pattern of perovskite thin film with columnar structures**. The diffraction pattern demonstrates its polycrystalline nature. Peaks labelled with grey stars correspond to the x-ray diffraction of ITO/glass substrate.

Table 6.2: **Miller indices derived from Euler angles.** The extracted Miller indices of perovskite grains match with the predominant diffraction peaks observed in the XRD pattern. The angles between the corresponding crystalline planes are included.

Euler angles (φ <sub>1</sub> , Ø, φ <sub>2</sub> )	Miller indices (calculated)	Miller indices (XRD patterns)	Angle between corresponding crystalline planes
183.3°, 55.8°, 353.2°	(1.00 0.68 0.17)	(110)	13.4°
167.4°, 77.0°, 345.3°	(3.00 1.16 0.72)	(310)	12.9°
353.3°, 85.2°, 296.0°	(2.00 0.19 1.42)	(202)	10.6°



Figure 6.9: **Images of similar EBSD patters taken on different grains**. Different grains (marked by green cross and circled by dotted line on the top-view SEM images, left) can exhibit similar EBSD patterns (right panels, with and without line markers) with slight shift, indicating that the film has a textured structure with certain preferred crystalline orientations. To guide the view, common features between the two EBSD patterns are outlined. These patterns correspond to (202) crystalline orientation of the perovskite grains.

Lastly, similar EBSD patterns can also be identified among various grains (Figure 6.9), indicating that the as-prepared film demonstrates a textured structure with certain preferred crystalline orientations. In conjunction with XRD and SEM data, EBSD results convincingly support the proposed mechanism of diffusion-limited surface recombination, which correlates the discrete photoconductivity levels with the crystalline orientation of each grain. Unfortunately, due to the roughness of the perovskite film and the damage caused by the electron beam, EBSD mapping could not be performed on such films, which could potentially elucidate the distribution of preferential crystal orientations as observed in the XRD data. Novel preparation methods are needed in order to achieve smooth surfaces on perovskite films. The other way to investigate the local crystal orientation is transmission electron microscopy (TEM). The primary way to prepare the thin films for TEM tests is using focused ion beam (FIB). However, the damage caused by the FIB could be even worse than that of the electron beams. If the perovskite film could directly grow on the TEM grid, the TEM measurement is also able to elucidate the crystal orientation information of perovskite domains. In this case, it is important to choose the TEM grid with proper coating materials in order to achieve a compact thin film, similar to the film grown on the glass substrates.

#### 6.3 Photoresponse of low-angle and high angle grain boundaries

Next, the photo-response of GBs that are categorized based on the relative photoconductivity level of the adjacent grains is examined. For instance, GBs formed between adjacent grains of the same photoconductivity level are termed as boundaries AA, BB, and CC. The other types of GBs, including types AB, AC, and BC, emerge between grains of different photoconductivity levels. The photocurrents of more than seventy GBs and five data points for each GB are extracted from the photocurrent map (Figure 6.2) with the statistics of the analysis presented in Figure 6.10a. It can be seen that AA, BB and CC types of GBs carry higher

photocurrents than that of the adjacent grains, whereas AB, BC or AC GBs yield a photocurrent that lies between the levels of the adjacent grains. To further illustrate the impacts of GBs, point J-V measurement is performed on the AA type boundary as shown in Figure 6.10b. Compared with grain A, the AA boundary exhibits a higher  $J_{SC}$ , consistent with the observation in the photocurrent map. More interestingly,  $V_{OC}$  is also larger than that of the grain interior. With a similar FF, the maximum power output of AA boundary is around five times of the grain A, suggesting a beneficial role of such GB to the overall photovoltaic performance. Parameters extracted from the fit to the diode equation are listed in Table 6.1. According to the previous discussion, it is likely that AA, BB and CC boundaries are low-angle GBs formed between two perovskite domains of the same crystalline orientation. And AB, BC and AC boundaries are highangle GBs located between grains that exhibit different crystalline orientations.

There is one concern, which is a common issue in AFM techniques, about the tip artifact. The contact area between tip and sample influenced by the surface topography and the spread-out of the electric field would both impact the current measured in pc-AFM. For instance, if a side contact is established, for example, at steep valley features, more photocarriers would be collected to the tip. Here, pc-AFM measurement is conducted on perovskite thin films (110 nm) with relatively smooth surface in order to avoid the contact issue. A typical line profile of the surface is shown in Figure 6.2, where a rising angle of ~10° is observed at the boundary between B-B grains (also illustrated in Figure 6.11). Owing to the smoothness of the surface, the contact area does not vary much when tip lands on top of GBs as compared to that landing on the grain interior (Figure 6.3). Regarding the spread-out of the electric field, the field is well confined in the perovskite layer as evidenced by the uniform photocurrent on each grain and the sharp photocurrent contrast across grains of different types. To be more quantitative, it is estimated that

the field spread-out is around 30 nm based on the spatial resolution of the photocurrent map (Figure 6.2b).



Figure 6.10: **Plots of averaged photocurrents and point** *J-V* **curves of grain boundaries**. (a) Average and standard deviation of photocurrent measured at GBs of different types, summarized from the photocurrent map shown in Figure 6.2b. The averaged photocurrents of grain interiors are marked on the graph as reference. (b) Point *J-V* curves of type AA GBs in comparison with that of grain A (the same curve as displayed in Figure 6.4b).



Figure 6.11: Schematic of the tip-sample contact and the electric field distribution at grain boundaries and grain interiors.

6.4 Electronic structure of grain boundaries investigated by KPFM

To elucidate the electronic structures at GBs, KPFM characterization is performed on CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/PEDOT:PSS/ITO samples. KPFM measures the work function difference between tip and sample, which is also termed as contact potential difference, i.e., CPD=W<sub>tip</sub>-W<sub>sample</sub>. The spatial variation of CPD indicates inhomogeneous sample work function which could be associated with the local bending of band structures and thus impacts the charge separation/transport processes.<sup>165, 260-261</sup> Figure 6.12 illustrates the topography and simultaneously obtained KPFM image of the same area (except some drift) before and after light illumination. The shift of the averaged CPD from -110 to -320 mV is likely induced by the spatial separation of photo-generated carriers in the perovskite film, that is, the built-up of electrons on the top surface and holes on the bottom interface (CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/PEDOT:PSS/ITO is hole selective).

The purpose of KPFM studies here is to illustrate the behavior of grain boundaries, where the adjacent grains act as the reference. It can be seen in Figure 6.12a that the majority of the GBs show a lower CPD (more negative) in comparison with that of the grains under the dark condition; however, this contrast is reversed upon illumination. First, this observation indicates that the artifact associated with the topography convolution is negligible. Otherwise, the contrast between grains and GBs should remain consistent regardless of light illumination. Second, a downward bending of the band structure at the GBs, as illustrated in Figure 6.12b, can be inferred from the CPD contrast observed under illumination. This band bending will facilitate charge separation as photo-generated electrons are attracted to the GBs, and holes are repelled from them. Because electrons and holes are spatially separated, the recombination process is suppressed at the GBs, potentially leading to an improvement in  $V_{OC}$  and  $J_{SC}$ . Moreover, a reduced surface recombination is also expected at the tip-GB contact because of the lower concentration of photo-generated holes, which could further contribute to enhancing  $V_{OC}$ . Last, it must be mentioned that pc-AFM and KPFM cannot be performed at the same location as the setups for these two measurements are different.

Although KPFM is not capable of distinguishing the low-angle from the large-angle GBs, it elucidates that the GBs, in general, may not be detrimental to the device performance of perovskite solar cells. The origin of the downward band bending at GBs, however, is not clear at the moment. One possibility is the unintentional doping of GBs by defects.<sup>161, 262-263</sup> It has been predicted that the intrinsic defects at surfaces and grain boundaries of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> do not produce deep level states, because of the anti-bonding coupling between Pb lone-pair *s* and I *p* orbitals, as well as the high ionicity and large lattice constants of the material.<sup>50, 161, 264-265</sup> Rather, the energy levels of these structural defects are positioned close to the band edge of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>. Thus, they act as unintentional doping sources instead of trapping/non-radiative recombination centers, owing to the delocalization nature of their wave functions. It is necessary to point out that even though

grains with similar photocurrent levels are likely correlated to the same crystal orientation as illustrated in the EBSD and XRD results, the mis-orientation between adjacent grains of similar photocurrent could be large due to the difference in-plane rotations. Therefore, further studies on the in-plane azimuthal orientations of the grains are necessary in order to elucidate the detailed structures of the grain boundaries.



Figure 6.12: **Images of KPFM results and schematic of band bending at GBs**. (a) Topology (left) and CPD (right) images obtained on CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/PEDOT:PSS/ ITO under dark (top) and illumination (bottom) conditions. (b) Proposed band alignment between grains and GBs based on the KPFM measurements.

Nevertheless, some studies have suggested that GBs play a detrimental role in the device performance since devices with larger grains demonstrate higher efficiency.<sup>149-151</sup> It's speculated that whether GBs play a beneficial or detrimental role in the PV performance should heavily rely on the layout of the GB network in the perovskite film. According to the band alignment picture (Figure 6.12b), GBs, on the one hand, facilitate charge separation and act as electron transport channels; on the other hand, they pose energy barriers for the lateral charge transport across different grains. Therefore, in perovskite thin films composed of small grains stacking on top of each other, horizontally positioned GBs will impede the flow of charge between the top and bottom electrodes. As the grain size increases together with the enhanced crystallinity and texture of the film, grain stacking will be suppressed, and grain boundaries will align mainly along the perpendicular direction, leading to improved device performance. Lastly, future investigations into the atomic structures, chemical and electronic states of the different types of GBs, that is, low-angle vs. large-angle, are warranted to obtain a mechanistic understanding of the impacts of these GBs on the PV performance.

# 6.5 Conclusion

Pc-AFM and KPFM are performed to study the local electrical properties of grains and GBs in organic-inorganic hybrid perovskite thin films. Three discrete photoconductivity levels are identified among perovskite grains, likely corresponding to the crystal orientation of each grain. Local *J-V* curves recorded on these grains further suggest an anti-correlation behavior between  $J_{SC}$  and  $V_{OC}$ , which can be attributed to diffusion-limited surface recombination at the non-selective perovskite-tip contact. In addition, the photo-response of perovskite films displays a pronounced heterogeneity across the grain boundaries, with the boundaries formed between grains of the same photoconductivity level displaying even enhanced photocurrent and open circuit voltage compared

to those of the adjacent grain interiors. These observations demonstrate that the texture structure impact the charge transport process due the orientation-dependent carrier mobility and the beneficial role of low-angle grain boundaries in perovskite thin film. Overall, the results in Chapter 5 and 6 highlight the significance of controlling the microstructure of perovskite thin films in order to push the efficiencies to the limit.
#### **Chapter 7**

#### High-performance inverted solar cells with a controlled ZnO buffer layer

In this chapter, the impact of the processing temperature of ZnO cathode buffer layers on the device performance of OPVs is investigated. Using the sol–gel method, it is found that the processing temperature of ZnO cathode buffer layers significantly influences the device performance of inverted polymer OPVs composed of blended films of P3HT and PCBM. In particular, ZnO processed at relatively low temperatures results in better device performance than those processed at higher temperatures despite the improved crystallinity and electron mobility of the latter. This finding is attributed to the tuning of the ZnO work function with the annealing temperature, which determines the interface energetics at the cathode and thus influences the open-circuit voltage, series resistance and fill factor.

7.1 Impact of ZnO preparation temperature on device performance of organic photovoltaics

Figure 7.1(a) illustrates the electronic structure of the inverted solar cells.<sup>266</sup> In this electrically inverted structure, electrons are transported in PCBM to the ITO/ZnO cathode and holes in P3HT toward the MoO<sub>3</sub>/Ag anode. The concentration of zinc acetate (0.1 M), the thickness of ZnO (8 nm) and MoO<sub>3</sub> (10 nm) films, and the annealing temperature of the P3HT/PCBM active layer (105 °C) were all optimized. The *J*-*V* characteristic curves for devices with a single layer of ZnO buffer prepared at 300 and 450 °C are shown in Figure 7.1(b). The average power conversion efficiency, and the corresponding  $J_{sc}$ ,  $V_{oc}$ , and FF are included in Table 7.1. The low-temperature annealing results in significant improvements of  $V_{oc}$ , FF, and device performance. Figure 7.1(b) also suggests that  $R_{series}$  increases with the temperature, leading to a smaller slope of the *J*-*V* curve at the open-circuit condition. Indeed,  $R_{series}$  which is extracted by fitting the photocurrent *J*-*V* 

curves to the Shockley diode equation<sup>267</sup> is 10  $\Omega$  cm<sup>2</sup> for the 300 °C case and 16  $\Omega$  cm<sup>2</sup> for the 450 °C case.



Figure 7.1: **Band diagram and** *J-V* **curves of inverted OPVs with ZnO processed at different conditions**. (a) Layout of the inverted organic solar cell with ZnO as the cathode buffer layer and the schematics of energy levels before reaching the equilibrium (vacuum level alignment). (b) *J-V* characteristics for devices based on a single layer ZnO cathode buffer prepared at 300 °C and 450 °C, respectively. (c) *J-V* characteristics for two devices based on a single layer ZnO cathode buffer prepared at 300 °C and 450 °C, at 300 °C with one piece of the ITO substrate was preheated at 450 °C.

It is well known that the optical and electrical properties of the ITO substrate can be sensitive to high temperature annealing. Accordingly, to eliminate the impact of ITO at higher annealing temperatures, control experiments were performed with zinc acetate spun on preannealed (450 °C) and pristine ITO substrates, followed by 300 °C annealing of both to create ZnO thin films. The *J-V* curves of the two devices are plotted in Figure 7.1(c), which show nearly identical performance, suggesting that any changes in the optical and electronic properties of ITO from the higher temperature annealing do not play a significant role here, distinct from an earlier report.<sup>102</sup>

Table 7.1: Summary of the average solar cell performance parameters.  $J_{sc}$ ,  $V_{oc}$ , FF, and PCE for devices made of 0 layer (0L), 1 layer (1L), 2 layers (2L) and 3 layers (3L) ZnO buffer prepared at 300 and 450 °C, respectively. The performance parameters for 1L–3L samples are averaged over more than 10 devices at each condition, and the parameters for 0L samples are averaged over 4 devices (the device area is 4.84 mm<sup>2</sup>), with the standard deviations included.

ZnO buffer layer	$J_{sc}$	$V_{oc}$	T	PCE
	mA cm <sup>-2</sup>	V	ГГ	%
0L at 300 °C	$9.7\pm0.2$	$0.33\pm0.01$	$0.43\pm0.01$	$1.4 \pm 0.1$
1L at 300 °C	$10.5\pm0.8$	$0.62\pm0.01$	$0.60\pm0.02$	$3.9\pm0.3$
2L at 300 °C	$10.4 \pm 1.0$	$0.61\pm0.02$	$0.58\pm0.04$	$3.7\pm0.6$
3L at 300 °C	$10.2 \pm 1.1$	$0.61\pm0.02$	$0.59\pm0.06$	$3.8\pm0.8$
0L at 450 °C	$9.6 \pm 0.2$	$0.32\pm0.01$	$0.41\pm0.01$	$1.3 \pm 0.1$
1L at 450 °C	$9.7 \pm 1.0$	$0.53\pm0.04$	$0.52\pm0.03$	$2.7\pm0.5$
2L at 450 °C	$9.7\pm0.3$	$0.53\pm0.03$	$0.52\pm0.01$	$2.7\pm0.2$
3L at 450 °C	$9.6\pm0.4$	$0.51\pm0.04$	$0.51\pm0.02$	$2.5\pm0.3$
1L at 300 °C/ITO at 450 °C	$10.1 \pm 0.7$	$0.60\pm0.02$	$0.58\pm0.03$	$3.6\pm0.3$

To further distinguish the contributions of the interface quality and the ZnO thin film conductivity, inverted devices with the ZnO buffer layer of various thickness were fabricated via multiple spin-coatings followed by thermal annealing at each step. As presented in Figure 7.2 and

Table 7.1, devices without ZnO buffer layer show diminished performance, likely due to the enhanced recombination at the cathode which decreases the shunt resistance, leading to reduced  $V_{oc}$  and FF. Additionally, devices with the ZnO buffer layer processed at 300 °C consistently outperform those processed at 450 °C at each corresponding buffer layer thickness, where the different ZnO film thicknesses under a given annealing condition show similar performance in  $V_{oc}$  and FF. This limited thickness dependence suggests that interface properties at the cathode are markedly influenced by the ZnO processing temperature, and the resistance of the ZnO thin film plays a lesser role in determining the performance of the inverted devices.



Figure 7.2: *J-V* characteristics for devices with varied ZnO film thickness. 0 layer, 1 layer, 2 layers and 3 layers of ZnO buffer prepared at 300 and 450 °C, respectively.

## 7.2 Origin of the temperature dependence

To clarify the underlying mechanisms of the improved device performance in inverted solar cells with the ZnO buffer annealed at 300 °C, comprehensive experiments were performed to investigate the potential effects of thermal annealing on the properties of ZnO thin films, including

optical transmittance, thin film crystallinity, surface morphology, and work function. After examining all these factors, it is discovered that interface energetics at the cathode plays the most dominating factor in determining the device performance.



Figure 7.3: **Transmittance and XRD spectra of ITO/ZnO films annealed at different temperatures**. (a) Optical transmittance for bare ITO annealed at 450 °C and ZnO/ITO prepared at 300 and 450 °C, respectively. The thickness of ZnO layer is about 8 nm. (b) XRD  $2\theta$ – $\omega$  spectra for ZnO films prepared at 300 and 450 °C on glass. The peak near 34.4 degree is characteristic for the diffraction of ZnO wurtzite phase. Inset: TGA curve of the zinc acetate gel. The significant mass loss near 300 °C corresponds to the complete thermal decomposition of zinc acetate precursor.

The optical transmittance of ITO/ZnO substrates is depicted in Figure 7.3(a) where the low-temperature annealed substrate yields a higher transmittance than the high-temperature annealed one in the visible range. However, such a difference mainly originates from the ITO substrate, as illustrated by the similar transmittance between the bare ITO and the ITO/ZnO substrates annealed at 450 °C, respectively. This observation implies a limited impact of the ZnO optical properties on the OPV device performance as the films are very thin.

It has been well established that higher annealing temperatures lead to improved thin film crystallinity and enhanced electron mobility.<sup>97, 230, 268</sup> As presented in the XRD data of ZnO thin films in Figure 7.3(b), samples annealed at 300 °C show amorphous structures, whereas a pronounced ZnO (002) peak is observed in thin films processed at 450 °C. One may expect to obtain better electron transport, reduced  $R_{series}$  and therefore enhanced fill factors in devices with high-temperature processed ZnO films. However, the devices processed at 300 °C show better performance, including fill factor which suggests that there are other dominant factors compensating the crystallinity and mobility effect. It is worth noting that annealing the ZnO buffer layer below 300 °C results in significantly reduced device performance, which likely stems from the incorporation of residue zinc acetate in the ZnO film as indicated by the thermogravimetric analysis (TGA) of zinc acetate (inset of Figure 7.3(b)).

The roughness and homogeneity of ZnO thin films are also investigated with AFM. Figure 7.4(a) and (b) are AFM images of the single layer ZnO film prepared at 300 and 450 °C. The film prepared at 450 °C is rougher with a root mean square (rms) roughness of 2.2 nm as compared to the film prepared at 300 °C (rms of 1.7 nm), which might result in a higher leakage current (smaller  $R_{shunt}$ ) and enhanced recombination between injected holes and photo-generated electrons at the cathode. However, this difference in roughness is unlikely to be the driving force for the

performance difference observed between various annealing conditions since the OPV device performance is not strongly dependent on the ZnO film thickness, as suggested in Figure 7.2, even though the multiple layer coating is expected to improve the compactness of the ZnO film and thus reduces the leakage paths.



Figure 7.4: **AFM images of ZnO films processed under different conditions**. (a) and (b) are tapping-mode AFM morphology images of single layer ZnO thin film deposited on the ITO substrate and subsequently annealed at 300 °C and at 450 °C, respectively. The image size is  $1 \times 1 \mu m^2$ .

7.3 Tuning of the ZnO work function and interface energetics at the cathode

In the inverted bulk heterojunctions where the exciton dissociation occurs predominantly at the P3HT/PCBM interface, the capability of ZnO as the cathode buffer layer to collect photogenerated electrons from the PCBM directly determines the charge collection efficiency. Thus, the energy alignment (or rather, collection barriers) at the ITO/ZnO and ZnO/PCBM interfaces is crucial to the device performance.

KPFM is a useful tool to measure the work function of electrodes and the interface energetics in solar cells.<sup>61, 269-270</sup> It is worth mentioning that oxygen molecules adsorbed on ZnO grain boundaries can trap free electrons and cause a depletion layer near the surface.<sup>271-273</sup> Accordingly, the interface energetics between ZnO and photoactive materials and the resultant transport properties (in dark) in solar cell devices can be impacted. It is found that light soaking using the solar illuminator is effective at removing these surface states, after which the dark current and the photocurrent merge together in the forward bias. The work functions obtained at such conditions are summarized in Table 7.2.

Table 7.2: Work functions (in eV) of ITO, ITO/ZnO, and ITO/ZnO/PCBM measured by KPFM. The ITO and ITO/ZnO are annealed at 300 and 450 °C, respectively. A representative error bar is ±0.04 eV

ZnO preparation temperature	ΙΤΟ	ITO/ZnO	ITO/ZnO/PCBM
300 °C	4.77	4.36	4.34
450 °C	4.76	4.53	4.38

The energy level alignments between ITO, ZnO and PCBM from KPFM are shown in Figure 7.5, where the depletion widths and band bending are inferred. One can see that the ZnO

work function has been tuned by thermal treatment where the Fermi level in the 300 °C annealed film is positioned in closer proximity to the conduction band edge, as compared to the one annealed at 450 °C. This implies that the former sample is more heavily n-doped by native defects, including Zn interstitials and oxygen vacancies, that have been partially annihilated by annealing at higher temperatures because of the improved thin film crystallinity.<sup>268, 274</sup> Consequently, the width of the Schottky barrier formed at the ITO/ZnO interface may be significantly reduced in the samples annealed at 300 °C, as shown in Figure 7.5.



Figure 7.5: **Schematic of the interface energy level alignment at different interfaces**. (a) and (b) are schematic band diagrams to illustrate the energy level alignment at the interfaces for devices based on the 300 and 450 °C processed ZnO films, respectively, as deduced from KPFM measurements.

In addition, it is found that the Fermi level of the ITO/ZnO cathode is pinned at the negative integer charge transfer state ( $E_{ICT}$ ) of PCBM for both samples within the experimental error. As shown in Figure 7.5(a), in the 300 °C case, a neutral contact is formed at the ZnO/PCBM interface

as a result of the alignment of energy levels between the cathode and PCBM. While for the ZnO film annealed at 450 °C, although its work function falls well within the transport gap of PCBM so that one may expect the vacuum level alignment at the interface,<sup>68</sup> KPFM results suggest that the Fermi level is still pinned at the  $E_{ICT}$  of PCBM, leading to the formation of an interface dipole. Two possibilities are proposed to reconcile the discrepancy. First, the charge transfer behavior between ZnO and PCBM may be disturbed by the existence of interface gap states.<sup>67</sup> Second, if the PCBM film is unintentionally doped by impurities, the imbalance in work functions upon contact with the ITO/ZnO cathode (450 °C) can be compensated by the electron flow from PCBM to the cathode.<sup>269-270</sup>

Finally, the impact of the interface energetics on the solar cell device performance is discussed. As presented in Table 7.1, the devices made of the 300 °C annealed ZnO cathode buffer display a higher FF, a larger PCE and an optimal  $V_{oc}$  as obtained in the P3HT:PCBM systems with ohmic contacts.<sup>72, 275</sup> On the contrary,  $V_{oc}$ , FF, and PCE are reduced by about 15 %, 13 %, and 31 %, respectively, in the devices composed of the 450 °C annealed ZnO film. These findings suggest that there are several factors contributing to the enhanced performance in devices composed of the ZnO buffer layer processed at 300 °C. (1) Charge collection at the ITO/ZnO interface may be improved by electron tunneling through the Schottky barrier of reduced width; (2) the Fermi level of the ITO/ZnO cathode lines up with the  $E_{ICT}$  of PCBM which enhances the electronic coupling at the interface and minimizes the  $V_{oc}$  loss. In contrast, the extraction barrier at the ZnO (450 °C)/ PCBM interface may result in a significant charge accumulation and the consequent recombination loss at the interface; (3) these two effects also contribute to the low contact resistance, thereby a smaller  $R_{series}$  and a larger FF in the 300 °C case.

# 7.4 Conclusion

The inverted solar cells with controlled ZnO cathode buffer layers in the ITO/ZnO/ P3HT:PCBM/MoO<sub>3</sub>/Ag structure are fabricated, which are comparable to the best conventional cells. Through comprehensive characterization of the surface morphology, thin film crystallinity and optical and electrical properties, it is discovered that the tuning of the ITO/ZnO work function and the interface energetics play a dominant role in determining the device performance for sol– gel processed ZnO. These findings could aid in the design and interface engineering of high quality OPVs incorporating ZnO buffer layers on low temperature, flexible substrates

## **Chapter 8**

#### **Conclusions and future work**

#### 8.1 Summary of results

To boost the device performance of photovoltaic devices, it is critical to understand the impact of microstructures, such as the thin film texture, grains and grain boundaries, on the device performance, especially for devices composed of polycrystalline films. A strong correlation between the efficiency and microstructure is demonstrated in organic-inorganic hybrid perovskite solar cells, which is one of the most promising candidates for the next generation of commercialized photovoltaic devices.

As shown in Chapter 5, by adopting the ramp annealing process, both the morphology and the texture structure of polycrystalline perovskite thin films can be effectively tailored. Compared with the complicated two-step or solvent/vapor annealing methods as introduced in Chapter 4, the ramp annealing treatment reduces the complexity during the thin film processing yet still enables high-quality perovskite devices, which is advantageous for the large-scale manufacturing processs. By employing EIS measurements, the impact of texture structure on the carrier dynamic processes, such as carrier transport in the bulk and charge collection at the interface, is elucidated. Though the interface, instead of the bulk, has been argued to render severe recombination in perovskite thin films. Also, the enhanced texture structure in perovskite thin films is accompanied by an increase in the number of low-angle grain boundaries. It is well-known that there is a higher density of defects at GBs due to the broken symmetry of the crystal planes. The defects in perovskite thin films have been theoretically investigated, and the results show that they do not generate mid-gap states or act as recombination centers. However, the detrimental role of them has been observed

experimentally. Taking these factors into consideration, it is necessary to investigate the impacts of different types of grain boundaries on the performance of perovskite solar cells.

Pc-AFM and KPFM, which provide nano-scale resolution on charge transport, are employed to investigate the contributions of grains and grain boundaries to the overall efficiency of perovskite devices. For the perovskite thin film consisting of multiple grains stacked in the vertical direction, the measured current would be convoluted by grains and grain boundaries in the film. Unfortunately, the issue of grain and grain boundary stacking has been largely neglected in most of the previous AFM studies on perovskite thin films. To isolate the contributions of different types of grains and grain boundaries, it is crucial to employ perovskite thin films with columnar structures, where the orientation dependent photoresponse of grains and the heterogeneous behaviors of grain boundaries are observed. In details, the discrete photocurrent levels and anticorrelation behavior between the photocurrent and photovoltage measured by the local J-V curves on different grains indicate that the crystalline orientation of grains (extracted separately by the EBSD measurement) impacts carrier transport properties. These observations support the proposition of the correlation between crystal orientation and carrier mobility. In addition, pc-AFM results indicate the non-detrimental role of grain boundaries in perovskite thin films with low-angle grain boundaries showing improved photocurrent and photovoltage. The downward band bending at GB, as revealed by KPFM, serves to attract electrons and repel holes. Consequently, GBs enhance the carrier transport and suppress the recombination. These discoveries point out the importance of controlling the grain orientation and low-angle grain boundaries in perovskite thin films for achieving efficient devices.

In addition to perovskite solar cells, OPVs have also drawn a significant amount of attention due to the low cost and mechanical flexibility. Besides the active layer, the interface is

also crucial in determining the device performance. In bulk heterojunction solar cells, it requires a high selectivity at the electrodes due to the existence of both donor and acceptor at the interface. By tuning the post-annealing temperature of sol-gel processed ZnO film, the work function of the cathode is tuned. The mechanism of work function tuning is the variation in the density of intrinsic defects, which acts as the dopant, with annealing temperature. By controlling the defect density, a sharp Schottky barrier is formed between ITO (cathode) and ZnO (electron transport layer), which electrons can tunnel through. Accordingly, the charge injection efficiency is improved. These findings not only aid in the design of OPVs but demonstrate the importance of interfacial engineering process which helps reduce the energy loss and improve the device performance.

Overall, the carrier transport and charge collection processes have been investigated in different types of solar cells. For devices composed of polycrystalline films, like perovskite solar cells, it is critical to understand the influence of microstructures on device performance. In Chapter 5, the correlation between device performance and texture structure of perovskite thin film is discovered in MAPbI<sub>3</sub> based perovskite solar cells. The ramp annealing treatment is an effective way to tune the crystallinity. Nevertheless, in order to largely enhance the texture structure of perovskite thin films, many methods can be conducted such as doping the material with chloride. For GBs, only low-angle GBs in perovskite thin films demonstrate a beneficial role as revealed in this work, which is likely related to the varied defect chemistry. By modifying the defect chemistry, such as adding extra CH<sub>3</sub>NH<sub>3</sub>I, the majority of the GBs may be activated and show a higher conductivity.<sup>276</sup> Additionally, interfacial engineering can effectively enhance the charge collection at the interface and thus contribute to the device performance. Ideally, the formation of Ohmic contacts at the interfaces is expected for efficient charge collection. In our study in Chapter 7, though a Schottky barrier is formed at the interface, by controlling the width of the barrier, an

effective charge collection is enabled with electrons tunneling through the barrier. These discoveries provide deep physical insights into the impact of microstructures on the physical processes in photovoltaic devices and offer new strategies of device engineering to improve the overall efficiency.

## 8.2 Future work

As we have extensively discussed, AFM measurements are capable of providing nanoscale information. However, taking the c-AFM or pc-AFM measurements as an example, the transport properties measured locally are convoluted between the surface/contact and the bulk. On one hand, as discussed in Chapter 5, EIS is capable of disentangling the physical process occurring in the bulk and at the contact of solar cell devices at the macroscopic scale. Thus, the incorporation of EIS into AFM will be powerful at revealing the relevant physical processes at the nanoscale, offering unprecedent insights into the operation of solar cells and the limiting factors of the device efficiency.

As mentioned in Chapter 3, one of the challenges faced in perovskite solar cells is the hysteresis issue which is likely associated with the ionic migration. It has been suggested that the ions move faster along grain boundaries due to the high density of local defects.<sup>193, 277</sup> Beyond the  $R_s$  which would increase upon the accumulation of ions at the interface, the interfacial capacitance  $(C_I)$  in the equivalent circuit as shown in Chapter 5 is also likely impacted by the ion accumulation at the interface. Therefore, by performing EIS measurements at grain interiors and grain boundaries, the potential impacts of grain boundaries on the ion migration could be revealed. In addition, similar to the carrier transport, the migration path of ions could also depend on the crystal orientation. By comparing the impedance responses on various grains of the different (hkl) orientation, information on the orientation-dependency of ion migration could be illustrated.

To commercialize perovskite solar cells, it is essential to improve the stability of the devices. Due to the broken symmetry, the moisture in the ambient atmosphere is more likely to diffuse into the perovskite film at GBs. The consequence of the decomposition is the formation of volatile CH<sub>3</sub>NH<sub>2</sub> and hydroiodic acid (HI), leaving PbI<sub>2</sub> in the film. PbI<sub>2</sub> demonstrates a large bandgap and poor carrier transport properties. Therefore, the decomposition of perovskite materials would diminish the conductivity resulting in the increase of  $R_s$ . Furthermore, the dielectric constant of PbI<sub>2</sub> and perovskite materials is different, and the  $C_2$  as defined in the equivalent circuit would be affected. By comparing the impedance response of grain and grain boundary, the decomposition process in the perovskite thin films could be spatially resolved.

It is worth pointing out that it is difficult to determine the "device" area in EIS measurement performed with AFM due to the point-contact between tip and sample and the spread-out of the electric field. Thus, it might be challenging to solely analyze the capacitance and resistance since their values depend on the effective "device" area. However, parameters, such as time constant, would be more characteristic since the variation in the effective area is canceled out by the multiplication of resistance and capacitance. APPENDIX

### APPENDIX

This part would focus on the spin-coating method and the fabrication process of perovskite solar cells. The film quality, such as morphology, surface coverage, crystallinity and defect density, impacts the device performance. Therefore, it is essential to prepare films with high quality. The most widely used method for the fabrication of perovskite films and devices is the spin-coating deposition. Spin-coating deposition is one of the most widely used techniques to prepare thin films with the thickness ranging from a few nanometers to microns on a flat substrate. The advantages of spin-on deposition are the easy setup and the high uniformity.

Generally, two steps are involved in the spin-coating process. The first step is to dispense the precursor solution onto the substrates. To ensure the surface coverage and uniformity, it requires the solution to fully cover the substrate, which is determined by the surface tension of the solution and the surface energy o the substrates. Precursors with a low surface tension tend to spread-out well over the substrates. Also, when the surface energy is high, it is more favorable to cover the substrate with precursors to minimize the surface energy. A good example to illustrate the dispensing issue is the preparation of PEDOT:PSS layer. PEDOT:PSS (organic salt) is dissolved in water. The solution demonstrates a high surface tension, which poses the challenge in the dispensing process. To overcome this issue, ITO substrates are treated with oxygen plasma which increases the surface energy by adding -OH groups to the surface. Yet, it enhances the interaction of the solvent (H<sub>2</sub>O) and the ITO surface via the formation of hydrogen bond. Therefore, the PEDOT:PSS film with high surface coverage is achieved.

The second step is spinning which includes two stages. At first, most of the precursor solution is removed when the spinning starts. Then, the remaining solute and solvent start to

densify with further removal of the solvent molecules. In this step, the film quality such as surface coverage and crystallinity is further impact by the solvent used in the precursor solution. When the boiling point of the solvent is low, it evaporates fast during the spin-coating, leading to films with high surface coverage but low crystallinity. On the contrary, the long time is required to remove the solvent molecules with a high boiling point, which promotes the order of the molecular arrangement (crystallinity). However, due to the strong interaction between precursor molecules compared with precursor and substrates, the solute molecules tend to grow into islands, which reduces the surface coverage. To achieve thin films with both high surface coverage and crystallinity, the mixture of solvents with high and low boiling points could be adopted. The densification of the film is completed while the solvent with a low boiling point is removed. The remaining solvent molecules with a high boiling point would assist the arrangement of the precursor molecules.



mixture of solvents

Figure A. 1: Solvent engineering of spin-coating method preparing halide perovskite thin film: the impact of the boiling point of the solvents.

For perovskite materials, the commonly used solvents are DMF, DMSO and  $\gamma$ butyrolactone (GBL). In this work, PbI<sub>2</sub> and CH<sub>3</sub>NH<sub>3</sub>I are first dissolved in DMF to fabricate the planar-structured perovskite solar cells. But the surface coverage is quite low when spin-coated onto PEDOT:PSS substrates. Two strategies are developed to improve the surface coverage. The first way is by adding toluene (2%) to DMF. The boiling point of toluene is 110.6 °C which is lower than that of DMF, which accelerates the evaporation of the solvent. Also, the solubility of PbI<sub>2</sub> in toluene is very low, leading to the fast densification of precursors on the substrates. The SEM images of perovskite films prepared with different precursor solutions are illustrated in Figure A.2. In addition to the improvement of surface coverage, the grain size also increases. A further study on the impact of toluene on the film quality of perovskite, such as grain size and crystallinity, is necessary in the future.



Figure A. 2: **SEM images of perovskite films prepared from precursors with different solvents.** (a) and (b) are the top-view and cross-section SEM images of perovskite films prepared from DMF. (c) and (d) are the top-view SEM images of perovskite film prepared from DMF/Toluene and DMF/DMSO solvents.

The other way is by using the mixture of DMF and DMSO. Though the boiling point of DMSO is higher than DMF, it is discovered that DMSO reduces the surface tension of the precursor solution and induces the formation of intermediate phase. As discussed in Chapter 5, the intermediate phase demonstrates a large *d*-spacing compared with PbI<sub>2</sub>, which facilitate the formation of perovskite phase by promoting the incorporation of organic cations (CH<sub>3</sub>NH<sub>3</sub><sup>+</sup>). Consequently, the addition of DMSO improves the dispensing of precursor solution and accelerates the crystallization of perovskite materials. The corresponding SEM images are shown in Figure A.2. The smaller grain size of perovskite films processed with DMF/DMSO is likely due to the fast crystallization induced by the intermediate phase, which limits the mass transport and growth of perovskite grains.

In Chapter 6, to grow perovskite films with columnar structures, two-step spin-coating is adopted together with solvent annealing. The purpose of using two-step instead of one-step is to retard the crystallization of perovskite films. As shown in Figure A.2, the accelerated nucleation results in small grain sizes. Therefore, by spin-coating PbI<sub>2</sub> and CH<sub>3</sub>NH<sub>3</sub>I separately, it requires  $Pb^{2+}$ ,  $\Gamma$ , and CH<sub>3</sub>NH<sub>3</sub><sup>+</sup> to diffuse across the film in order to form the perovskite phase. To further increase the grain size, the solvent annealing is employed. By annealing the perovskite film in the DMF vapor, the diffusivity of ions is improved which enhance the growth of each grain. It is worth mentioning that the perovskite film is very sensitive to the DMF vapor. Too much DMF would lead to the decompose of perovskite phase into PbI<sub>2</sub>. Therefore, the amount of DMF depends on the sample size (area and thickness) and the volume of the "chamber". For example, when preparing the film of 100 nm, 10 microliters DMF is enough to make columnar grains. However, when preparing films with 1-micron thickness, 20-30 microliter DMF is needed. In addition, the annealing time extends from 30 min to 5 hours. Other solvents, such as DMSO and GBL, are also used in the solvent annealing. But the film quality is not comparable to that of DMF. It is likely due to their higher boiling point which requires a higher annealing temperature. And the perovskite film would decompose at elevated temperatures. Another factor that would impact the film quality is the morphology of PbI<sub>2</sub> layer. We have observed that the film quality is better when the PbI<sub>2</sub> layer is annealing for 1-5 min. Further systematic studies on the impact of PbI<sub>2</sub> (morphology and crystallinity) on the final film quality in the solvent annealing is necessary.

In this work, the thickness of perovskite films has also been tuned by controlling the concentration of the precursor solution. The film thickness increases linearly with the concentration within a certain range. However, the concentration is also limited by the solubility. When depositing perovskite films of 1 micron, the precursor solution is heated at 80 °C. The preheat treatment of precursor may also reduce the viscosity of the solution which benefits the dispensing of the precursor. The other approach is to adjust the spin-speed. The film thickness is reversely proportional to the square root of spin-speed. So, the film thickness varies 3 times when the spin-speed varies 10 times. The concern is that spin-coating at low speed could reduce the uniformity of the film. Consequently, it is recommended to tune the film thickness via adjusting the concentration.

The film quality is critical in determining the efficiency of photovoltaic devices. Compared with other deposition methods, the spin-coating method is simple and facile. And the thin film properties such as morphology and crystallinity can be effectively engineered by solvent formulation and process control.

152

BIBLIOGRAPHY

# BIBLIOGRAPHY

1. Hoel, M.; Kverndokk, S., Depletion of fossil fuels and the impacts of global warming. *Resource and Energy Economics* **1996**, *18* (2), 115-136.

2. Hall, C. A. S., Fossil Fuels. In *Energy Return on Investment: A Unifying Principle for Biology, Economics, and Sustainability*, Springer International Publishing: Cham, 2017; 95-105.

3. Bolin, B.; Doos, B.; WARRICK, R.; JAEGER, J., The greenhouse effect, climatic change, and ecosystems((Book)). *Chichester, England and New York, John Wiley and Sons(SCOPE* **1986**, (29).

4. Schneider, S. H., The greenhouse effect- Science and policy. *Science* **1989**, *243* (4892), 771-781.

5. Le Quéré, C.; Andres, R. J.; Boden, T.; Conway, T.; Houghton, R. A.; House, J. I.; Marland, G.; Peters, G. P.; van der Werf, G. R.; Ahlström, A.; Andrew, R. M.; Bopp, L.; Canadell, J. G.; Ciais, P.; Doney, S. C.; Enright, C.; Friedlingstein, P.; Huntingford, C.; Jain, A. K.; Jourdain, C.; Kato, E.; Keeling, R. F.; Klein Goldewijk, K.; Levis, S.; Levy, P.; Lomas, M.; Poulter, B.; Raupach, M. R.; Schwinger, J.; Sitch, S.; Stocker, B. D.; Viovy, N.; Zaehle, S.; Zeng, N., The global carbon budget 1959–2011. *Earth Syst. Sci. Data* **2013**, *5* (1), 165-185.

6. Arneth, A.; Sitch, S.; Pongratz, J.; Stocker, B. D.; Ciais, P.; Poulter, B.; Bayer, A. D.; Bondeau, A.; Calle, L.; Chini, L. P.; Gasser, T.; Fader, M.; Friedlingstein, P.; Kato, E.; Li, W.; Lindeskog, M.; Nabel, J. E. M. S.; Pugh, T. A. M.; Robertson, E.; Viovy, N.; Yue, C.; Zaehle, S., Historical carbon dioxide emissions caused by land-use changes are possibly larger than assumed. *Nature Geosci* **2017**, *10* (2), 79-84.

7. Administration, U. S. E. I. U.S. Energy Consumption by Energy Source, 2016. <u>https://www.eia.gov/energyexplained/?page=us\_energy\_home</u> (accessed October).

8. Lewis, N. S.; Nocera, D. G., Powering the planet: Chemical challenges in solar energy utilization. *Proceedings of the National Academy of Sciences* **2006**, *103* (43), 15729-15735.

9. *Global Energy Statistical Yearbook 2017, Accessed November 2017.* 

10. Zhao, J.; Wang, A.; Green, M. A.; Ferrazza, F., 19.8% efficient "honeycomb" textured multicrystalline and 24.4% monocrystalline silicon solar cells. *Applied Physics Letters* **1998**, *73* (14), 1991-1993.

11. Fabre, E.; Baudet, Y. In *Polycrystalline silicon solar cells*, Photovoltaic Solar Energy Conference, 1978; 178-186.

12. Schropp, R. E.; Carius, R.; Beaucarne, G., Amorphous silicon, microcrystalline silicon, and thin-film polycrystalline silicon solar cells. *MRS bulletin* **2007**, *32* (3), 219-224.

13. Pillai, S.; Catchpole, K.; Trupke, T.; Green, M., Surface plasmon enhanced silicon solar cells. *Journal of applied physics* **2007**, *101* (9), 093105.

14. Carlson, D. E.; Wronski, C. R., Amorphous silicon solar cell. *Applied Physics Letters* **1976**, 28 (11), 671-673.

15. Derkacs, D.; Lim, S.; Matheu, P.; Mar, W.; Yu, E., Improved performance of amorphous silicon solar cells via scattering from surface plasmon polaritons in nearby metallic nanoparticles. *Applied Physics Letters* **2006**, *89* (9), 093103.

16. Repins, I.; Contreras, M. A.; Egaas, B.; DeHart, C.; Scharf, J.; Perkins, C. L.; To, B.; Noufi, R., 19.9% efficient ZnO/CdS/CuInGaSe2 solar cell with 81.2% fill factor. *Progress in Photovoltaics: Research and applications* **2008**, *16* (3), 235-239.

17. Contreras, M. A.; Egaas, B.; Ramanathan, K.; Hiltner, J.; Swartzlander, A.; Hasoon, F.; Noufi, R., Progress toward 20% efficiency in Cu (In, Ga) Se2 polycrystalline thin film solar cells. *Progress in Photovoltaics: Research and applications* **1999**, *7* (4), 311-316.

18. Ramanathan, K.; Contreras, M. A.; Perkins, C. L.; Asher, S.; Hasoon, F. S.; Keane, J.; Young, D.; Romero, M.; Metzger, W.; Noufi, R., Properties of 19.2% efficiency ZnO/CdS/CuInGaSe2 thin film solar cells. *Progress in Photovoltaics: research and applications* **2003**, *11* (4), 225-230.

19. Nelson, J., Polymer:fullerene bulk heterojunction solar cells. *Materials Today* **2011**, *14* (10), 462-470.

20. Günes, S.; Neugebauer, H.; Sariciftci, N. S., Conjugated polymer-based organic solar cells. *Chemical reviews* **2007**, *107* (4), 1324-1338.

21. Hoppe, H.; Sariciftci, N. S., Organic solar cells: An overview. *Journal of materials research* **2004**, *19* (7), 1924-1945.

22. O'Regan, B.; Gratzel, M., A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO2 films. *Nature* **1991**, *353* (6346), 737-740.

23. Hagfeldt, A.; Boschloo, G.; Sun, L.; Kloo, L.; Pettersson, H., Dye-sensitized solar cells. *Chem. Rev* **2010**, *110* (11), 6595-6663.

24. Grätzel, M., Dye-sensitized solar cells. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* **2003**, *4* (2), 145-153.

25. Grätzel, M., Conversion of sunlight to electric power by nanocrystalline dye-sensitized solar cells. *Journal of Photochemistry and Photobiology A: Chemistry* **2004**, *164* (1), 3-14.

26. Green, M. A.; Ho-Baillie, A.; Snaith, H. J., The emergence of perovskite solar cells. *Nat Photon* **2014**, *8* (7), 506-514.

27. Liu, M.; Johnston, M. B.; Snaith, H. J., Efficient planar heterojunction perovskite solar cells by vapour deposition. *Nature* **2013**, *501* (7467), 395-398.

28. Lee, M. M.; Teuscher, J.; Miyasaka, T.; Murakami, T. N.; Snaith, H. J., Efficient hybrid solar cells based on meso-superstructured organometal halide perovskites. *Science* **2012**, *338* (6107), 643-647.

Hodes, G., Applied physics. Perovskite-based solar cells. *Science* 2013, *342* (6156), 317-8.

30. Li, X.; Bi, D.; Yi, C.; Décoppet, J.-D.; Luo, J.; Zakeeruddin, S. M.; Hagfeldt, A.; Grätzel, M., A vacuum flash–assisted solution process for high-efficiency large-area perovskite solar cells. *Science* **2016**.

31. Ball, J. M.; Lee, M. M.; Hey, A.; Snaith, H. J., Low-temperature processed mesosuperstructured to thin-film perovskite solar cells. *Energy & Environmental Science* **2013**, *6* (6), 1739.

32. Docampo, P.; Ball, J. M.; Darwich, M.; Eperon, G. E.; Snaith, H. J., Efficient organometal trihalide perovskite planar-heterojunction solar cells on flexible polymer substrates. *Nat Commun* **2013**, *4*, 2761.

33. Sun, S.; Salim, T.; Mathews, N.; Duchamp, M.; Boothroyd, C.; Xing, G.; Sum, T. C.; Lam, Y. M., The origin of high efficiency in low-temperature solution-processable bilayer organometal halide hybrid solar cells. *Energy Environ. Sci.* **2014**, *7* (1), 399-407.

34. D'Innocenzo, V.; Grancini, G.; Alcocer, M. J. P.; Kandada, A. R. S.; Stranks, S. D.; Lee, M. M.; Lanzani, G.; Snaith, H. J.; Petrozza, A., Excitons versus free charges in organo-lead trihalide perovskites. *Nat Commun* **2014**, *5*, 3586.

35. Galkowski, K.; Mitioglu, A.; Miyata, A.; Plochocka, P.; Portugall, O.; Eperon, G. E.; Wang, J. T.-W.; Stergiopoulos, T.; Stranks, S. D.; Snaith, H. J.; Nicholas, R. J., Determination of the exciton binding energy and effective masses for methylammonium and formamidinium lead trihalide perovskite semiconductors. *Energy & Environmental Science* **2016**, *9* (3), 962-970.

36. Miyata, A.; Mitioglu, A.; Plochocka, P.; Portugall, O.; Wang, J. T.-W.; Stranks, S. D.; Snaith, H. J.; Nicholas, R. J., Direct measurement of the exciton binding energy and effective masses for charge carriers in organic-inorganic tri-halide perovskites. *Nat Phys* **2015**, *11* (7), 582-587.

37. Zhao, T.; Shi, W.; Xi, J.; Wang, D.; Shuai, Z., Intrinsic and Extrinsic Charge Transport in CH3NH3PbI3 Perovskites Predicted from First-Principles. *Scientific Reports* **2016**, *7*, 19968.

38. Lee, Y. H.; Luo, J.; Son, M.-K.; Gao, P.; Cho, K. T.; Seo, J.; Zakeeruddin, S. M.; Grätzel, M.; Nazeeruddin, M. K., Enhanced Charge Collection with Passivation Layers in Perovskite Solar Cells. *Advanced Materials* **2016**, *28* (20), 3966-3972.

39. Bae, S.; Park, J.-S.; Han, I. K.; Shin, T. J.; Jo, W. H., CH3NH3PbI3 crystal orientation and photovoltaic performance of planar heterojunction perovskite solar cells. *Solar Energy Materials and Solar Cells* **2017**, *160*, 77-84.

40. Correa Baena, J. P.; Steier, L.; Tress, W.; Saliba, M.; Neutzner, S.; Matsui, T.; Giordano, F.; Jacobsson, T. J.; Srimath Kandada, A. R.; Zakeeruddin, S. M.; Petrozza, A.; Abate, A.; Nazeeruddin, M. K.; Gratzel, M.; Hagfeldt, A., Highly efficient planar perovskite solar cells through band alignment engineering. *Energy & Environmental Science* **2015**, *8* (10), 2928-2934.

41. Li, S.-S.; Chang, C.-H.; Wang, Y.-C.; Lin, C.-W.; Wang, D.-Y.; Lin, J.-C.; Chen, C.-C.; Sheu, H.-S.; Chia, H.-C.; Wu, W.-R.; Jeng, U. S.; Liang, C.-T.; Sankar, R.; Chou, F.-C.; Chen, C.-W., Intermixing-seeded growth for high-performance planar heterojunction perovskite solar cells assisted by precursor-capped nanoparticles. *Energy & Environmental Science* **2016**, *9* (4), 1282-1289.

42. Bi, D.; Yi, C.; Luo, J.; Décoppet, J.-D.; Zhang, F.; Zakeeruddin, Shaik M.; Li, X.; Hagfeldt, A.; Grätzel, M., Polymer-templated nucleation and crystal growth of perovskite films for solar cells with efficiency greater than 21%. *Nature Energy* **2016**, *1*, 16142.

43. Giesbrecht, N.; Schlipf, J.; Oesinghaus, L.; Binek, A.; Bein, T.; Muller-Buschbaum, P.; Docampo, P., Synthesis of Perfectly Oriented and Micrometer-Sized MAPbBr3 Perovskite Crystals for Thin-Film Photovoltaic Applications. *Acs Energy Letters* **2016**, *1* (1), 150-154.

44. Chen, H.; Zheng, X.; Li, Q.; Yang, Y.; Xiao, S.; Hu, C.; Bai, Y.; Zhang, T.; Wong, K. S.; Yang, S., An amorphous precursor route to the conformable oriented crystallization of CH3NH3PbBr3 in mesoporous scaffolds: toward efficient and thermally stable carbon-based perovskite solar cells. *Journal of Materials Chemistry A* **2016**, *4* (33), 12897-12912.

45. Niu, G.; Yu, H.; Li, J.; Wang, D.; Wang, L., Controlled orientation of perovskite films through mixed cations toward high performance perovskite solar cells. *Nano Energy* **2016**, *27*, 87-94.

46. Ye, J.; Zheng, H.; Zhu, L.; Zhang, X.; Jiang, L.; Chen, W.; Liu, G.; Pan, X.; Dai, S., Hightemperature shaping perovskite film crystallization for solar cell fast preparation. *Solar Energy Materials and Solar Cells* **2017**, *160*, 60-66.

47. Wu, B.; Nguyen, H. T.; Ku, Z.; Han, G.; Giovanni, D.; Mathews, N.; Fan, H. J.; Sum, T. C., Discerning the Surface and Bulk Recombination Kinetics of Organic–Inorganic Halide Perovskite Single Crystals. *Advanced Energy Materials* **2016**, *6* (14), 1600551.

48. Edri, E.; Kirmayer, S.; Henning, A.; Mukhopadhyay, S.; Gartsman, K.; Rosenwaks, Y.; Hodes, G.; Cahen, D., Why lead methylammonium tri-iodide perovskite-based solar cells require a mesoporous electron transporting scaffold (but not necessarily a hole conductor). *Nano Lett* **2014**, *14* (2), 1000-4.

49. Kutes, Y.; Zhou, Y.; Bosse, J. L.; Steffes, J.; Padture, N. P.; Huey, B. D., Mapping the Photoresponse of CH3NH3PbI3 Hybrid Perovskite Thin Films at the Nanoscale. *Nano Letters* **2016**, *16* (6), 3434-3441.

50. Yang, M.; Zeng, Y.; Li, Z.; Kim, D. H.; Jiang, C.-S.; van de Lagemaat, J.; Zhu, K., Do grain boundaries dominate non-radiative recombination in CH3NH3PbI3 perovskite thin films? *Physical Chemistry Chemical Physics* **2017**, *19* (7), 5043-5050.

51. deQuilettes, D. W.; Vorpahl, S. M.; Stranks, S. D.; Nagaoka, H.; Eperon, G. E.; Ziffer, M. E.; Snaith, H. J.; Ginger, D. S., Impact of microstructure on local carrier lifetime in perovskite solar cells. *Science* **2015**, *348* (6235), 683-686.

52. Yin, W.-J.; Shi, T.; Yan, Y., Unique Properties of Halide Perovskites as Possible Origins of the Superior Solar Cell Performance. *Advanced Materials* **2014**, *26* (27), 4653-4658.

53. Guo, Y.; Wang, Q.; Saidi, W. A., Structural Stabilities and Electronic Properties of High-Angle Grain Boundaries in Perovskite Cesium Lead Halides. *The Journal of Physical Chemistry C* **2017**, *121* (3), 1715-1722.

54. Docampo, P.; Hanusch, F. C.; Giesbrecht, N.; Angloher, P.; Ivanova, A.; Bein, T., Influence of the orientation of methylammonium lead iodide perovskite crystals on solar cell performance. *Apl Mater* **2014**, *2* (8), 081508.

55. Yin, J.; Cortecchia, D.; Krishna, A.; Chen, S.; Mathews, N.; Grimsdale, A. C.; Soci, C., Interfacial Charge Transfer Anisotropy in Polycrystalline Lead Iodide Perovskite Films. *J Phys Chem Lett* **2015**, *6* (8), 1396-1402.

56. Leblebici, S. Y.; Leppert, L.; Li, Y.; Reyes-Lillo, S. E.; Wickenburg, S.; Wong, E.; Lee, J.; Melli, M.; Ziegler, D.; Angell, D. K.; Ogletree, D. F.; Ashby, Paul D.; Toma, F. M.; Neaton, J. B.; Sharp, I. D.; Weber-Bargioni, A., Facet-dependent photovoltaic efficiency variations in single grains of hybrid halide perovskite. *Nature Energy* **2016**, *1*, 16093.

57. Brabec, C. J.; Sariciftci, N. S.; Hummelen, J. C., Plastic Solar Cells. *Advanced Functional Materials* **2001**, *11* (1), 15-26.

58. Coakley, K. M.; McGehee, M. D., Conjugated Polymer Photovoltaic Cells. *Chemistry of Materials* **2004**, *16* (23), 4533-4542.

59. Hau, S. K.; Yip, H.-L.; Acton, O.; Baek, N. S.; Ma, H.; Jen, A. K. Y., Interfacial modification to improve inverted polymer solar cells. *Journal of Materials Chemistry* **2008**, *18* (42), 5113-5119.

60. Kuwabara, T.; Kawahara, Y.; Yamaguchi, T.; Takahashi, K., Characterization of Inverted-Type Organic Solar Cells with a ZnO Layer as the Electron Collection Electrode by ac Impedance Spectroscopy. *ACS Applied Materials & Interfaces* **2009**, *1* (10), 2107-2110.

61. Davis, R. J.; Lloyd, M. T.; Ferreira, S. R.; Bruzek, M. J.; Watkins, S. E.; Lindell, L.; Sehati, P.; Fahlman, M.; Anthony, J. E.; Hsu, J. W. P., Determination of energy level alignment at interfaces of hybrid and organic solar cells under ambient environment. *Journal of Materials Chemistry* **2011**, *21* (6), 1721-1729.

62. Hau, S. K.; Yip, H.-L.; Ma, H.; Jen, A. K.-Y., High performance ambient processed inverted polymer solar cells through interfacial modification with a fullerene self-assembled monolayer. *Applied Physics Letters* **2008**, *93* (23), 233304.

63. Stubhan, T.; Salinas, M.; Ebel, A.; Krebs, F. C.; Hirsch, A.; Halik, M.; Brabec, C. J., Increasing the Fill Factor of Inverted P3HT:PCBM Solar Cells Through Surface Modification of Al-Doped ZnO via Phosphonic Acid-Anchored C60 SAMs. *Advanced Energy Materials* **2012**, *2* (5), 532-535.

64. Bai, S.; Wu, Z.; Xu, X.; Jin, Y.; Sun, B.; Guo, X.; He, S.; Wang, X.; Ye, Z.; Wei, H.; Han, X.; Ma, W., Inverted organic solar cells based on aqueous processed ZnO interlayers at low temperature. *Applied Physics Letters* **2012**, *100* (20), 203906.

65. Jie Luo, H. W., Chao He. Aiyuan Li, Wei Yang, and Yong Cao, Enhanced open-circuit voltage in polymer solar cells. *Applied Physics Letters* **2009**, *95* (4), 043301.

66. Chen, L.-M.; Xu, Z.; Hong, Z.; Yang, Y., Interface investigation and engineering - achieving high performance polymer photovoltaic devices. *Journal of Materials Chemistry* **2010**, 20 (13), 2575-2598.

67. Hwang, J.; Wan, A.; Kahn, A., Energetics of metal–organic interfaces: New experiments and assessment of the field. *Materials Science and Engineering: R: Reports* **2009**, *64* (1), 1-31.

68. Braun, S.; Salaneck, W. R.; Fahlman, M., Energy-Level Alignment at Organic/Metal and Organic/Organic Interfaces. *Advanced Materials* **2009**, *21* (14-15), 1450-1472.

69. Mihailetchi, V. D.; Blom, P. W. M.; Hummelen, J. C.; Rispens, M. T., Cathode dependence of the open-circuit voltage of polymer:fullerene bulk heterojunction solar cells. *Journal of Applied Physics* **2003**, *94* (10), 6849-6854.

70. Tress, W.; Leo, K.; Riede, M., Influence of Hole-Transport Layers and Donor Materials on Open-Circuit Voltage and Shape of I–V Curves of Organic Solar Cells. *Advanced Functional Materials* **2011**, *21* (11), 2140-2149.

71. He, C.; Zhong, C.; Wu, H.; Yang, R.; Yang, W.; Huang, F.; Bazan, G. C.; Cao, Y., Origin of the enhanced open-circuit voltage in polymer solar cells via interfacial modification using conjugated polyelectrolytes. *Journal of Materials Chemistry* **2010**, *20* (13), 2617-2622.

72. Hau, S. K.; O'Malley, K. M.; Cheng, Y.-J.; Yip, H.-L.; Ma, H.; Jen, A. K.-Y., Optimization of active layer and anode electrode for high-performance inverted bulk-heterojunction solar cells. *IEEE Journal of Selected Topics in Quantum Electronics* **2010**, *16* (6), 1665-1675.

73. Steim, R.; Kogler, F. R.; Brabec, C. J., Interface materials for organic solar cells. *Journal of Materials Chemistry* **2010**, *20* (13), 2499-2512.

74. Liang, Z.; Zhang, Q.; Wiranwetchayan, O.; Xi, J.; Yang, Z.; Park, K.; Li, C.; Cao, G., Effects of the Morphology of a ZnO Buffer Layer on the Photovoltaic Performance of Inverted Polymer Solar Cells. *Advanced Functional Materials* **2012**, *22* (10), 2194-2201.

75. Gadisa, A.; Liu, Y.; Samulski, E. T.; Lopez, R., Minimizing interfacial losses in inverted organic solar cells comprising Al-doped ZnO. *Applied Physics Letters* **2012**, *100* (25), 253903.

76. Steim, R.; Choulis, S. A.; Schilinsky, P.; Brabec, C. J., Interface modification for highly efficient organic photovoltaics. *Applied Physics Letters* **2008**, *92* (9), 093303.

77. Waldauf, C.; Morana, M.; Denk, P.; Schilinsky, P.; Coakley, K.; Choulis, S. A.; Brabec, C. J., Highly efficient inverted organic photovoltaics using solution based titanium oxide as electron selective contact. *Applied Physics Letters* **2006**, *89* (23), 233517.

78. Li, G.; Chu, C. W.; Shrotriya, V.; Huang, J.; Yang, Y., Efficient inverted polymer solar cells. *Applied Physics Letters* **2006**, *88* (25), 253503.

79. Liao, H.-H.; Chen, L.-M.; Xu, Z.; Li, G.; Yang, Y., Highly efficient inverted polymer solar cell by low temperature annealing of Cs2CO3 interlayer. *Applied Physics Letters* **2008**, *92* (17), 173303.

80. Zhao, D. W.; Liu, P.; Sun, X. W.; Tan, S. T.; Ke, L.; Kyaw, A. K. K., An inverted organic solar cell with an ultrathin Ca electron-transporting layer and MoO3 hole-transporting layer. *Applied Physics Letters* **2009**, *95* (15), 153304.

81. Janotti, A.; Van de Walle, C. G., Fundamentals of zinc oxide as a semiconductor. *Reports on progress in physics* **2009**, *72* (12), 126501.

82. Huang, J.; Yin, Z.; Zheng, Q., Applications of ZnO in organic and hybrid solar cells. *Energy & Environmental Science* **2011**, *4* (10), 3861-3877.

83. Hu, J.; Wu, Z.; Wei, H.; Song, T.; Sun, B., Effects of ZnO fabricating process on the performance of inverted organic solar cells. *Organic Electronics* **2012**, *13* (7), 1171-1177.

84. Umeda, T.; Hashimoto, Y.; Mizukami, H.; Shirakawa, T.; Fujii, A.; Yoshino, K., Improvement of characteristics on polymer photovoltaic cells composed of conducting polymer - fullerene systems. *Synthetic Metals* **2005**, *152* (1), 93-96.

85. Schumann, S.; Da Campo, R.; Illy, B.; Cruickshank, A. C.; McLachlan, M. A.; Ryan, M. P.; Riley, D. J.; McComb, D. W.; Jones, T. S., Inverted organic photovoltaic devices with high efficiency and stability based on metal oxide charge extraction layers. *Journal of Materials Chemistry* **2011**, *21* (7), 2381-2386.

86. Chang, C.-Y.; Tsai, F.-Y., Efficient and air-stable plastics-based polymer solar cells enabled by atomic layer deposition. *Journal of Materials Chemistry* **2011**, *21* (15), 5710-5715.

87. Kang, Y.-J.; Lim, K.; Jung, S.; Kim, D.-G.; Kim, J.-K.; Kim, C.-S.; Kim, S. H.; Kang, J.-W., Spray-coated ZnO electron transport layer for air-stable inverted organic solar cells. *Solar Energy Materials and Solar Cells* **2012**, *96* (Supplement C), 137-140.

88. Cheng, Y.-J.; Hsieh, C.-H.; He, Y.; Hsu, C.-S.; Li, Y., Combination of Indene-C60 Bis-Adduct and Cross-Linked Fullerene Interlayer Leading to Highly Efficient Inverted Polymer Solar Cells. *Journal of the American Chemical Society* **2010**, *132* (49), 17381-17383.

89. Chou, C.-H.; Kwan, W. L.; Hong, Z.; Chen, L.-M.; Yang, Y., A Metal-Oxide Interconnection Layer for Polymer Tandem Solar Cells with an Inverted Architecture. *Advanced Materials* **2011**, *23* (10), 1282-1286.

90. White, M. S.; Olson, D. C.; Shaheen, S. E.; Kopidakis, N.; Ginley, D. S., Inverted bulkheterojunction organic photovoltaic device using a solution-derived ZnO underlayer. *Applied Physics Letters* **2006**, *89* (14), 143517.

91. Sekine, N.; Chou, C.-H.; Kwan, W. L.; Yang, Y., ZnO nano-ridge structure and its application in inverted polymer solar cell. *Organic Electronics* **2009**, *10* (8), 1473-1477.

92. Takanezawa, K.; Tajima, K.; Hashimoto, K., Efficiency enhancement of polymer photovoltaic devices hybridized with ZnO nanorod arrays by the introduction of a vanadium oxide buffer layer. *Applied Physics Letters* **2008**, *93* (6), 063308.

93. Shin, K.-S.; Lee, K.-H.; Lee, H. H.; Choi, D.; Kim, S.-W., Enhanced Power Conversion Efficiency of Inverted Organic Solar Cells with a Ga-Doped ZnO Nanostructured Thin Film Prepared Using Aqueous Solution. *The Journal of Physical Chemistry C* **2010**, *114* (37), 15782-15785.

94. Hau, S. K.; Cheng, Y.-J.; Yip, H.-L.; Zhang, Y.; Ma, H.; Jen, A. K. Y., Effect of Chemical Modification of Fullerene-Based Self-Assembled Monolayers on the Performance of Inverted Polymer Solar Cells. *ACS Applied Materials & Interfaces* **2010**, *2* (7), 1892-1902.

95. Kyaw, A. K. K.; Sun, X. W.; Jiang, C. Y.; Lo, G. Q.; Zhao, D. W.; Kwong, D. L., An inverted organic solar cell employing a sol-gel derived ZnO electron selective layer and thermal evaporated MoO3 hole selective layer. *Applied Physics Letters* **2008**, *93* (22), 221107.

96. Yang, T.; Cai, W.; Qin, D.; Wang, E.; Lan, L.; Gong, X.; Peng, J.; Cao, Y., Solution-Processed Zinc Oxide Thin Film as a Buffer Layer for Polymer Solar Cells with an Inverted Device Structure. *The Journal of Physical Chemistry C* **2010**, *114* (14), 6849-6853.

97. Sun, Y.; Seo, J. H.; Takacs, C. J.; Seifter, J.; Heeger, A. J., Inverted Polymer Solar Cells Integrated with a Low-Temperature-Annealed Sol-Gel-Derived ZnO Film as an Electron Transport Layer. *Advanced Materials* **2011**, *23* (14), 1679-1683.

98. Sun, Y.; Gong, X.; Hsu, B. B. Y.; Yip, H.-L.; Jen, A. K. Y.; Heeger, A. J., Solution-processed cross-linkable hole selective layer for polymer solar cells in the inverted structure. *Applied Physics Letters* **2010**, *97* (19), 193310.

99. Hsieh, C.-H.; Cheng, Y.-J.; Li, P.-J.; Chen, C.-H.; Dubosc, M.; Liang, R.-M.; Hsu, C.-S., Highly Efficient and Stable Inverted Polymer Solar Cells Integrated with a Cross-Linked Fullerene Material as an Interlayer. *Journal of the American Chemical Society* **2010**, *132* (13), 4887-4893.

100. Amb, C. M.; Chen, S.; Graham, K. R.; Subbiah, J.; Small, C. E.; So, F.; Reynolds, J. R., Dithienogermole As a Fused Electron Donor in Bulk Heterojunction Solar Cells. *Journal of the American Chemical Society* **2011**, *133* (26), 10062-10065.

101. Liu, M.-Y.; Chang, C.-H.; Chang, C.-H.; Tsai, K.-H.; Huang, J.-S.; Chou, C.-Y.; Wang, I.-J.; Wang, P.-S.; Lee, C.-Y.; Chao, C.-H.; Yeh, C.-L.; Wu, C.-I.; Lin, C.-F., Morphological evolution of the poly(3-hexylthiophene)/[6,6]-phenyl-C61-butyric acid methyl ester, oxidation of the silver electrode, and their influences on the performance of inverted polymer solar cells with a sol–gel derived zinc oxide electron selective layer. *Thin Solid Films* **2010**, *518* (17), 4964-4969.

102. Zhang, C.; You, H.; Lin, Z.; Hao, Y., Inverted organic photovoltaic cells with solution-processed zinc oxide as electron collecting layer. *Japanese Journal of Applied Physics* **2011**, *50* (8R), 082302.

103. Braun, S.; Salaneck, W. R.; Fahlman, M., Energy Level Alignment at Organic/Metal and Organic/Organic Interfaces. *Advanced Materials* **2009**, *21* (14-15), 1450-1472.

104. Alvarado, S. F.; Seidler, P. F.; Lidzey, D. G.; Bradley, D. D. C., Direct Determination of the Exciton Binding Energy of Conjugated Polymers Using a Scanning Tunneling Microscope. *Physical Review Letters* **1998**, *81* (5), 1082-1085.

105. Liang, Y.; Xu, Z.; Xia, J.; Tsai, S.-T.; Wu, Y.; Li, G.; Ray, C.; Yu, L., For the Bright Future—Bulk Heterojunction Polymer Solar Cells with Power Conversion Efficiency of 7.4%. *Advanced Materials* **2010**, *22* (20), E135-E138.

106. Jiang, C.; Lunt, R. R.; Duxbury, P. M.; Zhang, P. P., High-performance inverted solar cells with a controlled ZnO buffer layer. *RSC Advances* **2014**, *4* (7), 3604-3610.

107. Liu, D.; Kelly, T. L., Perovskite solar cells with a planar heterojunction structure prepared using room-temperature solution processing techniques. *Nature Photonics* **2013**, *8*, 133.

108. Kojima, A.; Teshima, K.; Shirai, Y.; Miyasaka, T., Organometal halide perovskites as visible-light sensitizers for photovoltaic cells. *Journal of the American Chemical Society* **2009**, *131* (17), 6050-6051.

109. Best Research-Cell Efficiencies by National Renewable Energy Laboratory. http://www.nrel.gov/pv/assets/images/efficiency\_chart.jpg 2016.

110. Baikie, T.; Fang, Y.; Kadro, J. M.; Schreyer, M.; Wei, F.; Mhaisalkar, S. G.; Graetzel, M.; White, T. J., Synthesis and crystal chemistry of the hybrid perovskite (CH3NH3)PbI3 for solid-state sensitised solar cell applications. *Journal of Materials Chemistry A* **2013**, *1* (18), 5628-5641.

111. Quarti, C.; Mosconi, E.; Ball, J. M.; D'Innocenzo, V.; Tao, C.; Pathak, S.; Snaith, H. J.; Petrozza, A.; De Angelis, F., Structural and optical properties of methylammonium lead iodide across the tetragonal to cubic phase transition: implications for perovskite solar cells. *Energy & Environmental Science* **2016**, *9* (1), 155-163.

112. Brivio, F.; Walker, A. B.; Walsh, A., Structural and electronic properties of hybrid perovskites for high-efficiency thin-film photovoltaics from first-principles. *Apl Mater* **2013**, *1* (4), 042111.

113. Umebayashi, T.; Asai, K.; Kondo, T.; Nakao, A., Electronic structures of lead iodide based low-dimensional crystals. *Physical Review B* **2003**, *67* (15), 155405.

114. Motta, C.; El-Mellouhi, F.; Kais, S.; Tabet, N.; Alharbi, F.; Sanvito, S., Revealing the role of organic cations in hybrid halide perovskite CH3NH3PbI3. *Nature Communications* **2015**, *6*, 7026.

115. Hutter, E. M.; Gélvez-Rueda, M. C.; Osherov, A.; Bulović, V.; Grozema, F. C.; Stranks, S. D.; Savenije, T. J., Direct–indirect character of the bandgap in methylammonium lead iodide perovskite. *Nature Materials* **2016**, *16*, 115.

116. Shi, D.; Adinolfi, V.; Comin, R.; Yuan, M.; Alarousu, E.; Buin, A.; Chen, Y.; Hoogland, S.; Rothenberger, A.; Katsiev, K.; Losovyj, Y.; Zhang, X.; Dowben, P. A.; Mohammed, O. F.; Sargent, E. H.; Bakr, O. M., Low trap-state density and long carrier diffusion in organolead trihalide perovskite single crystals. *Science* **2015**, *347* (6221), 519-522.

117. Dong, Q.; Fang, Y.; Shao, Y.; Mulligan, P.; Qiu, J.; Cao, L.; Huang, J., Electron-hole diffusion lengths  $> 175 \mu m$  in solution-grown CH3NH3PbI3 single crystals. *Science* **2015**, *347* (6225), 967-970.

118. Giorgi, G.; Fujisawa, J.-I.; Segawa, H.; Yamashita, K., Small Photocarrier Effective Masses Featuring Ambipolar Transport in Methylammonium Lead Iodide Perovskite: A Density Functional Analysis. *The Journal of Physical Chemistry Letters* **2013**, *4* (24), 4213-4216.

119. Stranks, S. D.; Eperon, G. E.; Grancini, G.; Menelaou, C.; Alcocer, M. J. P.; Leijtens, T.; Herz, L. M.; Petrozza, A.; Snaith, H. J., Electron-Hole Diffusion Lengths Exceeding 1 Micrometer in an Organometal Trihalide Perovskite Absorber. *Science* **2013**, *342* (6156), 341-344.

120. Chen, Y.; Peng, J.; Su, D.; Chen, X.; Liang, Z., Efficient and Balanced Charge Transport Revealed in Planar Perovskite Solar Cells. *ACS Applied Materials & Interfaces* **2015**, *7* (8), 4471-4475.

121. Yin, X.; Chen, P.; Que, M.; Xing, Y.; Que, W.; Niu, C.; Shao, J., Highly Efficient Flexible Perovskite Solar Cells Using Solution-Derived NiOx Hole Contacts. *ACS Nano* **2016**, *10* (3), 3630-3636.

122. Qin, P.; Tanaka, S.; Ito, S.; Tetreault, N.; Manabe, K.; Nishino, H.; Nazeeruddin, M. K.; Grätzel, M., Inorganic hole conductor-based lead halide perovskite solar cells with 12.4% conversion efficiency. *Nature communications* **2014**, *5*, 3834.

123. Heo, J. H.; Im, S. H.; Noh, J. H.; Mandal, T. N.; Lim, C.-S.; Chang, J. A.; Lee, Y. H.; Kim, H.-j.; Sarkar, A.; Nazeeruddin, M. K.; Grätzel, M.; Seok, S. I., Efficient inorganic–organic hybrid heterojunction solar cells containing perovskite compound and polymeric hole conductors. *Nature Photonics* **2013**, *7*, 486.

124. Guo, Y.; Liu, C.; Inoue, K.; Harano, K.; Tanaka, H.; Nakamura, E., Enhancement in the efficiency of an organic–inorganic hybrid solar cell with a doped P3HT hole-transporting layer on a void-free perovskite active layer. *Journal of Materials Chemistry A* **2014**, *2* (34), 13827-13830.

125. Eperon, G. E.; Burlakov, V. M.; Docampo, P.; Goriely, A.; Snaith, H. J., Morphological Control for High Performance, Solution-Processed Planar Heterojunction Perovskite Solar Cells. *Advanced Functional Materials* **2014**, *24* (1), 151-157.

126. Zhang, W.; Saliba, M.; Moore, D. T.; Pathak, S. K.; Hörantner, M. T.; Stergiopoulos, T.; Stranks, S. D.; Eperon, G. E.; Alexander-Webber, J. A.; Abate, A.; Sadhanala, A.; Yao, S.; Chen, Y.; Friend, R. H.; Estroff, L. A.; Wiesner, U.; Snaith, H. J., Ultrasmooth organic–inorganic perovskite thin-film formation and crystallization for efficient planar heterojunction solar cells. *Nature Communications* **2015**, *6*, 6142.

127. Moore, D. T.; Sai, H.; Tan, K. W.; Smilgies, D.-M.; Zhang, W.; Snaith, H. J.; Wiesner, U.; Estroff, L. A., Crystallization kinetics of organic–inorganic trihalide perovskites and the role of the lead anion in crystal growth. *Journal of the American Chemical Society* **2015**, *137* (6), 2350-2358.

128. Liu, D.; Liu, C.; Wu, L.; Li, W.; Chen, F.; Xiao, B.; Zhang, J.; Feng, L., Highly reproducible perovskite solar cells with excellent CH3NH3PbI3-xClx film morphology fabricated via high precursor concentration. *RSC Advances* **2016**, *6* (56), 51279-51285.

129. Chang, J.; Zhu, H.; Xiao, J.; Isikgor, F. H.; Lin, Z.; Hao, Y.; Zeng, K.; Xu, Q.-H.; Ouyang, J., Enhancing the planar heterojunction perovskite solar cell performance through tuning the precursor ratio. *Journal of Materials Chemistry A* **2016**, *4* (20), 7943-7949.

130. Jeon, N. J.; Noh, J. H.; Kim, Y. C.; Yang, W. S.; Ryu, S.; Seok, S. I., Solvent engineering for high-performance inorganic–organic hybrid perovskite solar cells. *Nature Materials* **2014**, *13*, 897.

131. Xiao, M.; Huang, F.; Huang, W.; Dkhissi, Y.; Zhu, Y.; Etheridge, J.; Gray-Weale, A.; Bach, U.; Cheng, Y.-B.; Spiccia, L., A Fast Deposition-Crystallization Procedure for Highly Efficient Lead Iodide Perovskite Thin-Film Solar Cells. *Angewandte Chemie* **2014**, *126* (37), 10056-10061.

132. Burschka, J.; Pellet, N.; Moon, S.-J.; Humphry-Baker, R.; Gao, P.; Nazeeruddin, M. K.; Grätzel, M., Sequential deposition as a route to high-performance perovskite-sensitized solar cells. *Nature* **2013**, *499*, 316.

133. Xiao, Z.; Bi, C.; Shao, Y.; Dong, Q.; Wang, Q.; Yuan, Y.; Wang, C.; Gao, Y.; Huang, J., Efficient, high yield perovskite photovoltaic devices grown by interdiffusion of solution-processed precursor stacking layers. *Energy & Environmental Science* **2014**, *7* (8), 2619-2623.

134. Wu, Y.; Islam, A.; Yang, X.; Qin, C.; Liu, J.; Zhang, K.; Peng, W.; Han, L., Retarding the crystallization of PbI2 for highly reproducible planar-structured perovskite solar cells via sequential deposition. *Energy & Environmental Science* **2014**, *7* (9), 2934-2938.

135. Chen, Q.; Zhou, H.; Hong, Z.; Luo, S.; Duan, H.-S.; Wang, H.-H.; Liu, Y.; Li, G.; Yang, Y., Planar Heterojunction Perovskite Solar Cells via Vapor-Assisted Solution Process. *Journal of the American Chemical Society* **2014**, *136* (2), 622-625.

136. Yang, W. S.; Noh, J. H.; Jeon, N. J.; Kim, Y. C.; Ryu, S.; Seo, J.; Seok, S. I., Highperformance photovoltaic perovskite layers fabricated through intramolecular exchange. *Science* **2015**, *348* (6240), 1234-1237.

137. Xiao, Z.; Dong, Q.; Bi, C.; Shao, Y.; Yuan, Y.; Huang, J., Solvent Annealing of Perovskite-Induced Crystal Growth for Photovoltaic-Device Efficiency Enhancement. *Advanced Materials* **2014**, *26* (37), 6503-6509.

138. Chen, W.; Wu, Y.; Yue, Y.; Liu, J.; Zhang, W.; Yang, X.; Chen, H.; Bi, E.; Ashraful, I.; Grätzel, M.; Han, L., Efficient and stable large-area perovskite solar cells with inorganic charge extraction layers. *Science* **2015**, *350* (6263), 944-948.

139. Kim, J.; Yun, J. S.; Cho, Y.; Lee, D. S.; Wilkinson, B.; Soufiani, A. M.; Deng, X.; Zheng, J.; Shi, A.; Lim, S.; Chen, S.; Hameiri, Z.; Zhang, M.; Lau, C. F. J.; Huang, S.; Green, M. A.; Ho-Baillie, A. W. Y., Overcoming the Challenges of Large-Area High-Efficiency Perovskite Solar Cells. *ACS Energy Letters* **2017**, *2* (9), 1978-1984.

140. Huang, J.; Yuan, Y.; Shao, Y.; Yan, Y., Understanding the physical properties of hybrid perovskites for photovoltaic applications. *Nature Reviews Materials* **2017**, *2*, 17042.

141. De Wolf, S.; Holovsky, J.; Moon, S.-J.; Löper, P.; Niesen, B.; Ledinsky, M.; Haug, F.-J.; Yum, J.-H.; Ballif, C., Organometallic Halide Perovskites: Sharp Optical Absorption Edge and Its Relation to Photovoltaic Performance. *The Journal of Physical Chemistry Letters* **2014**, *5* (6), 1035-1039.

142. Adinolfi, V.; Peng, W.; Walters, G.; Bakr, O. M.; Sargent, E. H., The Electrical and Optical Properties of Organometal Halide Perovskites Relevant to Optoelectronic Performance. *Advanced Materials* **2018**, *30* (1), 1700764.

143. Lin, Q.; Armin, A.; Nagiri, R. C. R.; Burn, P. L.; Meredith, P., Electro-optics of perovskite solar cells. *Nature Photonics* **2014**, *9*, 106.

144. Nah, S.; Spokoyny, B.; Stoumpos, C.; Soe, C. M. M.; Kanatzidis, M.; Harel, E., Spatially segregated free-carrier and exciton populations in individual lead halide perovskite grains. *Nature Photonics* **2017**, *11*, 285.

145. Xing, G.; Mathews, N.; Sun, S.; Lim, S. S.; Lam, Y. M.; Grätzel, M.; Mhaisalkar, S.; Sum, T. C., Long-Range Balanced Electron- and Hole-Transport Lengths in Organic-Inorganic CH3NH3PbI3. *Science* **2013**, *342* (6156), 344-347.

146. Adhyaksa, G. W. P.; Veldhuizen, L. W.; Kuang, Y.; Brittman, S.; Schropp, R. E. I.; Garnett, E. C., Carrier Diffusion Lengths in Hybrid Perovskites: Processing, Composition, Aging, and Surface Passivation Effects. *Chemistry of Materials* **2016**, *28* (15), 5259-5263.

147. Feng, J.; Xiao, B., Effective Masses and Electronic and Optical Properties of Nontoxic MASnX3 (X = Cl, Br, and I) Perovskite Structures as Solar Cell Absorber: A Theoretical Study Using HSE06. *The Journal of Physical Chemistry C* **2014**, *118* (34), 19655-19660.

148. Herz, L. M., Charge-Carrier Mobilities in Metal Halide Perovskites: Fundamental Mechanisms and Limits. *ACS Energy Letters* **2017**, *2* (7), 1539-1548.

149. Shargaieva, O.; Lang, F.; Rappich, J.; Dittrich, T.; Klaus, M.; Meixner, M.; Genzel, C.; Nickel, N. H., Influence of the Grain Size on the Properties of CH3NH3PbI3 Thin Films. *ACS Applied Materials & Interfaces* **2017**, *9* (44), 38428-38435.

150. Watthage, S. C.; Song, Z.; Shrestha, N.; Phillips, A. B.; Liyanage, G. K.; Roland, P. J.; Ellingson, R. J.; Heben, M. J., Enhanced Grain Size, Photoluminescence, and Photoconversion Efficiency with Cadmium Addition during the Two-Step Growth of CH3NH3PbI3. *ACS Applied Materials & Interfaces* **2017**, *9* (3), 2334-2341.

151. Chen, J.; Song, J.; Huang, F.; Li, H.; Liu, S.; Wang, M.; Shen, Y., The Role of Synthesis Parameters on Crystallization and Grain Size in Hybrid Halide Perovskite Solar Cells. *The Journal of Physical Chemistry C* **2017**, *121* (32), 17053-17061.

152. Wang, Y.; Zhang, Y.; Zhang, P.; Zhang, W., High intrinsic carrier mobility and photon absorption in the perovskite CH3NH3PbI3. *Physical Chemistry Chemical Physics* **2015**, *17* (17), 11516-11520.

153. Handa, T.; Tex, D. M.; Shimazaki, A.; Wakamiya, A.; Kanemitsu, Y., Charge Injection Mechanism at Heterointerfaces in CH3NH3PbI3 Perovskite Solar Cells Revealed by Simultaneous Time-Resolved Photoluminescence and Photocurrent Measurements. *The Journal of Physical Chemistry Letters* **2017**, *8* (5), 954-960.

154. Shi, L. X.; Wang, Z. S.; Huang, Z.; Sha, W. E. I.; Wang, H.; Zhou, Z., The effects of interfacial recombination and injection barrier on the electrical characteristics of perovskite solar cells. *AIP Advances* **2018**, *8* (2), 025312.

155. Jiménez-López, J.; Cambarau, W.; Cabau, L.; Palomares, E., Charge Injection, Carriers Recombination and HOMO Energy Level Relationship in Perovskite Solar Cells. *Scientific Reports* **2017**, *7* (1), 6101.

156. Zhou, H.; Chen, Q.; Li, G.; Luo, S.; Song, T.-b.; Duan, H.-S.; Hong, Z.; You, J.; Liu, Y.; Yang, Y., Interface engineering of highly efficient perovskite solar cells. *Science* **2014**, *345* (6196), 542-546.

157. Li, Y.; Zhao, Y.; Chen, Q.; Yang, Y.; Liu, Y.; Hong, Z.; Liu, Z.; Hsieh, Y.-T.; Meng, L.; Li, Y.; Yang, Y., Multifunctional Fullerene Derivative for Interface Engineering in Perovskite Solar Cells. *Journal of the American Chemical Society* **2015**, *137* (49), 15540-15547.

158. Abate, A.; Saliba, M.; Hollman, D. J.; Stranks, S. D.; Wojciechowski, K.; Avolio, R.; Grancini, G.; Petrozza, A.; Snaith, H. J., Supramolecular Halogen Bond Passivation of Organic– Inorganic Halide Perovskite Solar Cells. *Nano Letters* **2014**, *14* (6), 3247-3254.
159. Noel, N. K.; Abate, A.; Stranks, S. D.; Parrott, E. S.; Burlakov, V. M.; Goriely, A.; Snaith, H. J., Enhanced Photoluminescence and Solar Cell Performance via Lewis Base Passivation of Organic–Inorganic Lead Halide Perovskites. *ACS Nano* **2014**, *8* (10), 9815-9821.

160. Xing, G.; Mathews, N.; Lim, S. S.; Yantara, N.; Liu, X.; Sabba, D.; Grätzel, M.; Mhaisalkar, S.; Sum, T. C., Low-temperature solution-processed wavelength-tunable perovskites for lasing. *Nature Materials* **2014**, *13*, 476.

161. Kim, J.; Lee, S.-H.; Lee, J. H.; Hong, K.-H., The Role of Intrinsic Defects in Methylammonium Lead Iodide Perovskite. *The Journal of Physical Chemistry Letters* **2014**, *5* (8), 1312-1317.

162. Yin, W.-J.; Shi, T.; Yan, Y., Unusual defect physics in CH3NH3PbI3 perovskite solar cell absorber. *Applied Physics Letters* **2014**, *104* (6), 063903.

163. Wetzelaer, G.-J. A. H.; Scheepers, M.; Sempere, A. M.; Momblona, C.; Ávila, J.; Bolink, H. J., Trap-Assisted Non-Radiative Recombination in Organic–Inorganic Perovskite Solar Cells. *Advanced Materials* **2015**, *27* (11), 1837-1841.

164. Stranks, S. D.; Burlakov, V. M.; Leijtens, T.; Ball, J. M.; Goriely, A.; Snaith, H. J., Recombination Kinetics in Organic-Inorganic Perovskites: Excitons, Free Charge, and Subgap States. *Physical Review Applied* **2014**, *2* (3), 034007.

165. Yun, J. S.; Ho-Baillie, A.; Huang, S.; Woo, S. H.; Heo, Y.; Seidel, J.; Huang, F.; Cheng, Y.-B.; Green, M. A., Benefit of Grain Boundaries in Organic–Inorganic Halide Planar Perovskite Solar Cells. *The Journal of Physical Chemistry Letters* **2015**, *6* (5), 875-880.

166. Chu, Z.; Yang, M.; Schulz, P.; Wu, D.; Ma, X.; Seifert, E.; Sun, L.; Li, X.; Zhu, K.; Lai, K., Impact of grain boundaries on efficiency and stability of organic-inorganic trihalide perovskites. *Nature Communications* **2017**, *8* (1), 2230.

167. Li, J.-J.; Ma, J.-Y.; Ge, Q.-Q.; Hu, J.-S.; Wang, D.; Wan, L.-J., Microscopic Investigation of Grain Boundaries in Organolead Halide Perovskite Solar Cells. *ACS Applied Materials & Interfaces* **2015**, *7* (51), 28518-28523.

168. deQuilettes, D. W.; Jariwala, S.; Burke, S.; Ziffer, M. E.; Wang, J. T. W.; Snaith, H. J.; Ginger, D. S., Tracking Photoexcited Carriers in Hybrid Perovskite Semiconductors: Trap-Dominated Spatial Heterogeneity and Diffusion. *ACS Nano* **2017**, *11* (11), 11488-11496.

169. Mamun, A. A.; Ava, T. T.; Jeong, H. J.; Jeong, M. S.; Namkoong, G., A deconvoluted PL approach to probe the charge carrier dynamics of the grain interior and grain boundary of a perovskite film for perovskite solar cell applications. *Physical Chemistry Chemical Physics* **2017**, *19* (13), 9143-9148.

170. MacDonald, G. A.; Yang, M.; Berweger, S.; Killgore, J. P.; Kabos, P.; Berry, J. J.; Zhu, K.; DelRio, F. W., Methylammonium lead iodide grain boundaries exhibit depth-dependent electrical properties. *Energy & Environmental Science* **2016**, *9* (12), 3642-3649.

171. Tvingstedt, K.; Gil-Escrig, L.; Momblona, C.; Rieder, P.; Kiermasch, D.; Sessolo, M.; Baumann, A.; Bolink, H. J.; Dyakonov, V., Removing Leakage and Surface Recombination in Planar Perovskite Solar Cells. *ACS Energy Letters* **2017**, *2* (2), 424-430.

172. Hou, Y.; Chen, W.; Baran, D.; Stubhan, T.; Luechinger, N. A.; Hartmeier, B.; Richter, M.; Min, J.; Chen, S.; Quiroz, C. O. R.; Li, N.; Zhang, H.; Heumueller, T.; Matt, G. J.; Osvet, A.; Forberich, K.; Zhang, Z.-G.; Li, Y.; Winter, B.; Schweizer, P.; Spiecker, E.; Brabec, C. J., Overcoming the Interface Losses in Planar Heterojunction Perovskite-Based Solar Cells. *Advanced Materials* **2016**, *28* (25), 5112-5120.

173. Correa-Baena, J.-P.; Tress, W.; Domanski, K.; Anaraki, E. H.; Turren-Cruz, S.-H.; Roose, B.; Boix, P. P.; Gratzel, M.; Saliba, M.; Abate, A.; Hagfeldt, A., Identifying and suppressing interfacial recombination to achieve high open-circuit voltage in perovskite solar cells. *Energy & Environmental Science* **2017**, *10* (5), 1207-1212.

174. Tan, H.; Jain, A.; Voznyy, O.; Lan, X.; García de Arquer, F. P.; Fan, J. Z.; Quintero-Bermudez, R.; Yuan, M.; Zhang, B.; Zhao, Y.; Fan, F.; Li, P.; Quan, L. N.; Zhao, Y.; Lu, Z.-H.; Yang, Z.; Hoogland, S.; Sargent, E. H., Efficient and stable solution-processed planar perovskite solar cells via contact passivation. *Science* **2017**, *355* (6326), 722-726.

175. Cao, J.; Wu, B.; Chen, R.; Wu, Y.; Hui, Y.; Mao, B.-W.; Zheng, N., Efficient, Hysteresis-Free, and Stable Perovskite Solar Cells with ZnO as Electron-Transport Layer: Effect of Surface Passivation. *Advanced Materials*, 1705596.

176. Peng, J.; Wu, Y.; Ye, W.; Jacobs, D. A.; Shen, H.; Fu, X.; Wan, Y.; Duong, T.; Wu, N.; Barugkin, C.; Nguyen, H. T.; Zhong, D.; Li, J.; Lu, T.; Liu, Y.; Lockrey, M. N.; Weber, K. J.; Catchpole, K. R.; White, T. P., Interface passivation using ultrathin polymer-fullerene films for high-efficiency perovskite solar cells with negligible hysteresis. *Energy & Environmental Science* **2017**, *10* (8), 1792-1800.

177. Yang, G.; Wang, C.; Lei, H.; Zheng, X.; Qin, P.; Xiong, L.; Zhao, X.; Yan, Y.; Fang, G., Interface engineering in planar perovskite solar cells: energy level alignment, perovskite morphology control and high performance achievement. *Journal of Materials Chemistry A* **2017**, *5* (4), 1658-1666.

178. Snaith, H. J.; Abate, A.; Ball, J. M.; Eperon, G. E.; Leijtens, T.; Noel, N. K.; Stranks, S. D.; Wang, J. T.-W.; Wojciechowski, K.; Zhang, W., Anomalous Hysteresis in Perovskite Solar Cells. *The Journal of Physical Chemistry Letters* **2014**, *5* (9), 1511-1515.

179. Calado, P.; Telford, A. M.; Bryant, D.; Li, X.; Nelson, J.; O'Regan, B. C.; Barnes, P. R. F., Evidence for ion migration in hybrid perovskite solar cells with minimal hysteresis. *Nature Communications* **2016**, *7*, 13831.

180. Eames, C.; Frost, J. M.; Barnes, P. R. F.; O'Regan, B. C.; Walsh, A.; Islam, M. S., Ionic transport in hybrid lead iodide perovskite solar cells. *Nature Communications* **2015**, *6*, 7497.

181. Levine, I.; Nayak, P. K.; Wang, J. T.-W.; Sakai, N.; Van Reenen, S.; Brenner, T. M.; Mukhopadhyay, S.; Snaith, H. J.; Hodes, G.; Cahen, D., Interface-Dependent Ion

Migration/Accumulation Controls Hysteresis in MAPbI3 Solar Cells. *The Journal of Physical Chemistry C* **2016**, *120* (30), 16399-16411.

182. Tao, C.; Neutzner, S.; Colella, L.; Marras, S.; Srimath Kandada, A. R.; Gandini, M.; Bastiani, M. D.; Pace, G.; Manna, L.; Caironi, M.; Bertarelli, C.; Petrozza, A., 17.6% stabilized efficiency in low-temperature processed planar perovskite solar cells. *Energy & Environmental Science* **2015**, *8* (8), 2365-2370.

183. Shao, Y.; Xiao, Z.; Bi, C.; Yuan, Y.; Huang, J., Origin and elimination of photocurrent hysteresis by fullerene passivation in CH3NH3PbI3 planar heterojunction solar cells. *Nature Communications* **2014**, *5*, 5784.

184. Kim, H.-S.; Park, N.-G., Parameters Affecting I–V Hysteresis of CH3NH3PbI3 Perovskite Solar Cells: Effects of Perovskite Crystal Size and Mesoporous TiO2 Layer. *The Journal of Physical Chemistry Letters* **2014**, *5* (17), 2927-2934.

185. Tress, W.; Marinova, N.; Moehl, T.; Zakeeruddin, S. M.; Nazeeruddin, M. K.; Gratzel, M., Understanding the rate-dependent J-V hysteresis, slow time component, and aging in CH3NH3PbI3 perovskite solar cells: the role of a compensated electric field. *Energy & Environmental Science* **2015**, *8* (3), 995-1004.

186. De Bastiani, M.; Dell'Erba, G.; Gandini, M.; D'Innocenzo, V.; Neutzner, S.; Kandada, A. R. S.; Grancini, G.; Binda, M.; Prato, M.; Ball, J. M.; Caironi, M.; Petrozza, A., Solar Cells: Ion Migration and the Role of Preconditioning Cycles in the Stabilization of the J–V Characteristics of Inverted Hybrid Perovskite Solar Cells (Adv. Energy Mater. 2/2016). *Advanced Energy Materials* **2016**, *6* (2), 1501453.

187. Frost, J. M.; Butler, K. T.; Walsh, A., Molecular ferroelectric contributions to anomalous hysteresis in hybrid perovskite solar cells. *Apl Mater* **2014**, *2* (8), 081506.

188. Sherkar, T. S.; Jan Anton Koster, L., Can ferroelectric polarization explain the high performance of hybrid halide perovskite solar cells? *Physical Chemistry Chemical Physics* **2016**, *18* (1), 331-338.

189. Chen, B.; Yang, M.; Priya, S.; Zhu, K., Origin of J–V Hysteresis in Perovskite Solar Cells. *The Journal of Physical Chemistry Letters* **2016**, *7* (5), 905-917.

190. Meloni, S.; Moehl, T.; Tress, W.; Franckevičius, M.; Saliba, M.; Lee, Y. H.; Gao, P.; Nazeeruddin, M. K.; Zakeeruddin, S. M.; Rothlisberger, U.; Graetzel, M., Ionic polarizationinduced current-voltage hysteresis in CH3NH3PbX3 perovskite solar cells. *Nature Communications* **2016**, *7*, 10334.

191. Yuan, Y.; Chae, J.; Shao, Y.; Wang, Q.; Xiao, Z.; Centrone, A.; Huang, J., Photovoltaic Switching Mechanism in Lateral Structure Hybrid Perovskite Solar Cells. *Advanced Energy Materials* **2015**, *5* (15), 1500615.

192. Li, C.; Guerrero, A.; Zhong, Y.; Gräser, A.; Luna, C. A. M.; Köhler, J.; Bisquert, J.; Hildner, R.; Huettner, S., Real-Time Observation of Iodide Ion Migration in Methylammonium Lead Halide Perovskites. *Small* **2017**, *13* (42), 1701711.

193. Shao, Y.; Fang, Y.; Li, T.; Wang, Q.; Dong, Q.; Deng, Y.; Yuan, Y.; Wei, H.; Wang, M.; Gruverman, A.; Shield, J.; Huang, J., Grain boundary dominated ion migration in polycrystalline organic-inorganic halide perovskite films. *Energy & Environmental Science* **2016**, *9* (5), 1752-1759.

194. Yun, J. S.; Seidel, J.; Kim, J.; Soufiani, A. M.; Huang, S.; Lau, J.; Jeon, N. J.; Seok, S. I.; Green, M. A.; Ho-Baillie, A., Critical Role of Grain Boundaries for Ion Migration in Formamidinium and Methylammonium Lead Halide Perovskite Solar Cells. *Advanced Energy Materials* **2016**, *6* (13), 1600330.

195. Wu, F.; Yue, X.; Song, Q.; Zhu, L., Replacing PbI2 by MAPbI3 to Realize Large Grain Size and Reduced Hysteresis for Highly Efficient Perovskite Solar Cells. *Solar RRL* **2018**, *2* (1), 1700147.

196. Ke, W.; Xiao, C.; Wang, C.; Saparov, B.; Duan, H.-S.; Zhao, D.; Xiao, Z.; Schulz, P.; Harvey, S. P.; Liao, W.; Meng, W.; Yu, Y.; Cimaroli, A. J.; Jiang, C.-S.; Zhu, K.; Al-Jassim, M.; Fang, G.; Mitzi, D. B.; Yan, Y., Employing Lead Thiocyanate Additive to Reduce the Hysteresis and Boost the Fill Factor of Planar Perovskite Solar Cells. *Advanced Materials* **2016**, *28* (26), 5214-5221.

197. Yang, D.; Zhou, X.; Yang, R.; Yang, Z.; Yu, W.; Wang, X.; Li, C.; Liu, S.; Chang, R. P. H., Surface optimization to eliminate hysteresis for record efficiency planar perovskite solar cells. *Energy & Environmental Science* **2016**, *9* (10), 3071-3078.

198. Petrus, M. L.; Schlipf, J.; Li, C.; Gujar, T. P.; Giesbrecht, N.; Müller-Buschbaum, P.; Thelakkat, M.; Bein, T.; Hüttner, S.; Docampo, P., Capturing the Sun: A Review of the Challenges and Perspectives of Perovskite Solar Cells. *Advanced Energy Materials* **2017**, *7* (16), 1700264.

199. Yang, S.; Fu, W.; Zhang, Z.; Chen, H.; Li, C.-Z., Recent advances in perovskite solar cells: efficiency, stability and lead-free perovskite. *Journal of Materials Chemistry A* **2017**, *5* (23), 11462-11482.

200. Correa-Baena, J.-P.; Saliba, M.; Buonassisi, T.; Grätzel, M.; Abate, A.; Tress, W.; Hagfeldt, A., Promises and challenges of perovskite solar cells. *Science* **2017**, *358* (6364), 739-744.

201. Han, Y.; Meyer, S.; Dkhissi, Y.; Weber, K.; Pringle, J. M.; Bach, U.; Spiccia, L.; Cheng, Y.-B., Degradation observations of encapsulated planar CH3NH3PbI3 perovskite solar cells at high temperatures and humidity. *Journal of Materials Chemistry A* **2015**, *3* (15), 8139-8147.

202. Dong, Q.; Liu, F.; Wong, M. K.; Tam, H. W.; Djurišić, A. B.; Ng, A.; Surya, C.; Chan, W. K.; Ng, A. M. C., Encapsulation of Perovskite Solar Cells for High Humidity Conditions. *ChemSusChem* **2016**, *9* (18), 2597-2603.

203. Bush, K. A.; Palmstrom, A. F.; Yu, Z. J.; Boccard, M.; Cheacharoen, R.; Mailoa, J. P.; McMeekin, D. P.; Hoye, R. L. Z.; Bailie, C. D.; Leijtens, T.; Peters, I. M.; Minichetti, M. C.; Rolston, N.; Prasanna, R.; Sofia, S.; Harwood, D.; Ma, W.; Moghadam, F.; Snaith, H. J.; Buonassisi, T.; Holman, Z. C.; Bent, S. F.; McGehee, M. D., 23.6%-efficient monolithic perovskite/silicon tandem solar cells with improved stability. *Nature Energy* **2017**, *2*, 17009.

204. Sun, Y.; Peng, J.; Chen, Y.; Yao, Y.; Liang, Z., Triple-cation mixed-halide perovskites: towards efficient, annealing-free and air-stable solar cells enabled by Pb(SCN)2 additive. *Scientific Reports* **2017**, *7*, 46193.

205. Saliba, M.; Matsui, T.; Seo, J.-Y.; Domanski, K.; Correa-Baena, J.-P.; Nazeeruddin, M. K.; Zakeeruddin, S. M.; Tress, W.; Abate, A.; Hagfeldt, A.; Gratzel, M., Cesium-containing triple cation perovskite solar cells: improved stability, reproducibility and high efficiency. *Energy & Environmental Science* **2016**, *9* (6), 1989-1997.

206. Domanski, K.; Correa-Baena, J.-P.; Mine, N.; Nazeeruddin, M. K.; Abate, A.; Saliba, M.; Tress, W.; Hagfeldt, A.; Grätzel, M., Not All That Glitters Is Gold: Metal-Migration-Induced Degradation in Perovskite Solar Cells. *ACS Nano* **2016**, *10* (6), 6306-6314.

207. Abate, A.; Paek, S.; Giordano, F.; Correa-Baena, J.-P.; Saliba, M.; Gao, P.; Matsui, T.; Ko, J.; Zakeeruddin, S. M.; Dahmen, K. H.; Hagfeldt, A.; Gratzel, M.; Nazeeruddin, M. K., Silolothiophene-linked triphenylamines as stable hole transporting materials for high efficiency perovskite solar cells. *Energy & Environmental Science* **2015**, *8* (10), 2946-2953.

208. Gregg, B. A.; Hanna, M. C., Comparing organic to inorganic photovoltaic cells: Theory, experiment, and simulation. *Journal of Applied Physics* **2003**, *93* (6), 3605-3614.

209. Clarke, T. M.; Durrant, J. R., Charge Photogeneration in Organic Solar Cells. *Chemical Reviews* **2010**, *110* (11), 6736-6767.

210. Richter, T. V.; Braun, C. H.; Link, S.; Scheuble, M.; Crossland, E. J. W.; Stelzl, F.; Würfel, U.; Ludwigs, S., Regioregular Polythiophenes with Alkylthiophene Side Chains. *Macromolecules* **2012**, *45* (14), 5782-5788.

211. Deibel, C.; Mack, D.; Gorenflot, J.; Schöll, A.; Krause, S.; Reinert, F.; Rauh, D.; Dyakonov, V., Energetics of excited states in the conjugated polymer poly(3-hexylthiophene). *Physical Review B* **2010**, *81* (8), 085202.

212. Tamai, Y.; Ohkita, H.; Benten, H.; Ito, S., Exciton Diffusion in Conjugated Polymers: From Fundamental Understanding to Improvement in Photovoltaic Conversion Efficiency. *The Journal of Physical Chemistry Letters* **2015**, *6* (17), 3417-3428.

213. Dimitrakopoulos, C. D.; Mascaro, D. J., Organic thin-film transistors: A review of recent advances. *IBM Journal of Research and Development* **2001**, *45* (1), 11-27.

214. Yan, L.; Gao, Y., Interfaces in organic semiconductor devices. *Thin Solid Films* **2002**, *417* (1), 101-106.

215. Cahen, D.; Kahn, A., Electron Energetics at Surfaces and Interfaces: Concepts and Experiments. *Advanced Materials* **2003**, *15* (4), 271-277.

216. Veenstra, S. C.; Jonkman, H. T., Energy-level alignment at metal–organic and organic–organic interfaces. *Journal of Polymer Science Part B: Polymer Physics* **2003**, *41* (21), 2549-2560.

217. Cravino, A.; Schilinsky, P.; Brabec, C. J., Characterization of Organic Solar Cells: the Importance of Device Layout. *Advanced Functional Materials* **2007**, *17* (18), 3906-3910.

218. Hu, Z.; Zhang, J.; Hao, Z.; Zhao, Y., Influence of doped PEDOT:PSS on the performance of polymer solar cells. *Solar Energy Materials and Solar Cells* **2011**, *95* (10), 2763-2767.

219. Konios, D.; Kakavelakis, G.; Petridis, C.; Savva, K.; Stratakis, E.; Kymakis, E., Highly efficient organic photovoltaic devices utilizing work-function tuned graphene oxide derivatives as the anode and cathode charge extraction layers. *Journal of Materials Chemistry A* **2016**, *4* (5), 1612-1623.

220. Stratakis, E.; Savva, K.; Konios, D.; Petridis, C.; Kymakis, E., Improving the efficiency of organic photovoltaics by tuning the work function of graphene oxide hole transporting layers. *Nanoscale* **2014**, *6* (12), 6925-6931.

221. Peumans, P.; Bulović, V.; Forrest, S. R., Efficient photon harvesting at high optical intensities in ultrathin organic double-heterostructure photovoltaic diodes. *Applied Physics Letters* **2000**, *76* (19), 2650-2652.

222. Lee, J.; Park, S.; Lee, Y.; Kim, H.; Shin, D.; Jeong, J.; Jeong, K.; Cho, S. W.; Lee, H.; Yi, Y., Electron transport mechanism of bathocuproine exciton blocking layer in organic photovoltaics. *Physical Chemistry Chemical Physics* **2016**, *18* (7), 5444-5452.

223. Zhang, F. J.; Zhao, D. W.; Zhuo, Z. L.; Wang, H.; Xu, Z.; Wang, Y. S., Inverted small molecule organic solar cells with Ca modified ITO as cathode and MoO3 modified Ag as anode. *Solar Energy Materials and Solar Cells* **2010**, *94* (12), 2416-2421.

224. Wang, M.; Li, Y.; Huang, H.; Peterson, E. D.; Nie, W.; Zhou, W.; Zeng, W.; Huang, W.; Fang, G.; Sun, N.; Zhao, X.; Carroll, D. L., Thickness dependence of the MoO3 blocking layers on ZnO nanorod-inverted organic photovoltaic devices. *Applied Physics Letters* **2011**, *98* (10), 103305.

225. Mang, A.; Reimann, K.; Rübenacke, S., Band gaps, crystal-field splitting, spin-orbit coupling, and exciton binding energies in ZnO under hydrostatic pressure. *Solid State Communications* **1995**, *94* (4), 251-254.

226. Özgür, Ü.; Alivov, Y. I.; Liu, C.; Teke, A.; Reshchikov, M. A.; Doğan, S.; Avrutin, V.; Cho, S.-J.; Morkoç, H., A comprehensive review of ZnO materials and devices. *Journal of Applied Physics* **2005**, *98* (4), 041301.

227. Look, D. C., Recent advances in ZnO materials and devices. *Materials Science and Engineering: B* 2001, 80 (1), 383-387.

228. MacLeod, B. A.; Tremolet de Villers, B. J.; Schulz, P.; Ndione, P. F.; Kim, H.; Giordano, A. J.; Zhu, K.; Marder, S. R.; Graham, S.; Berry, J. J.; Kahn, A.; Olson, D. C., Stability of inverted organic solar cells with ZnO contact layers deposited from precursor solutions. *Energy & Environmental Science* **2015**, *8* (2), 592-601.

229. Chang, Y.-M.; Leu, C.-Y., Conjugated polyelectrolyte and zinc oxide stacked structure as an interlayer in highly efficient and stable organic photovoltaic cells. *Journal of Materials Chemistry A* **2013**, *1* (21), 6446-6451.

230. Ohyama, M.; Kouzuka, H.; Yoko, T., Sol-gel preparation of ZnO films with extremely preferred orientation along (002) plane from zinc acetate solution. *Thin solid films* **1997**, *306* (1), 78-85.

231. Klahr, B. M.; Martinson, A. B. F.; Hamann, T. W., Photoelectrochemical Investigation of Ultrathin Film Iron Oxide Solar Cells Prepared by Atomic Layer Deposition. *Langmuir* **2011**, *27* (1), 461-468.

232. Binnig, G.; Quate, C. F.; Gerber, C., Atomic Force Microscope. *Physical Review Letters* **1986**, *56* (9), 930-933.

233. Jalili, N.; Laxminarayana, K., A review of atomic force microscopy imaging systems: application to molecular metrology and biological sciences. *Mechatronics* **2004**, *14* (8), 907-945.

234. Almora, O.; Zarazua, I.; Mas-Marza, E.; Mora-Sero, I.; Bisquert, J.; Garcia-Belmonte, G., Capacitive Dark Currents, Hysteresis, and Electrode Polarization in Lead Halide Perovskite Solar Cells. *The Journal of Physical Chemistry Letters* **2015**, *6* (9), 1645-1652.

235. Guerrero, A.; Garcia-Belmonte, G.; Mora-Sero, I.; Bisquert, J.; Kang, Y. S.; Jacobsson, T. J.; Correa-Baena, J.-P.; Hagfeldt, A., Properties of Contact and Bulk Impedances in Hybrid Lead Halide Perovskite Solar Cells Including Inductive Loop Elements. *The Journal of Physical Chemistry C* **2016**, *120* (15), 8023-8032.

236. Bisquert, J.; Bertoluzzi, L.; Mora-Sero, I.; Garcia-Belmonte, G., Theory of Impedance and Capacitance Spectroscopy of Solar Cells with Dielectric Relaxation, Drift-Diffusion Transport, and Recombination. *The Journal of Physical Chemistry C* **2014**, *118* (33), 18983-18991.

237. Bisquert, J., Chemical capacitance of nanostructured semiconductors: its origin and significance for nanocomposite solar cells. *Physical Chemistry Chemical Physics* **2003**, *5* (24), 5360-5364.

238. Bassiri-Gharb, N.; Bastani, Y.; Bernal, A., Chemical solution growth of ferroelectric oxide thin films and nanostructures. *Chemical Society Reviews* **2014**, *43* (7), 2125-2140.

239. Schwartz, R. W.; Schneller, T.; Waser, R., Chemical solution deposition of electronic oxide films. *Comptes Rendus Chimie* **2004**, *7* (5), 433-461.

240. Zuo, L.; Dong, S.; De Marco, N.; Hsieh, Y.-T.; Bae, S.-H.; Sun, P.; Yang, Y., Morphology Evolution of High Efficiency Perovskite Solar Cells via Vapor Induced Intermediate Phases. *Journal of the American Chemical Society* **2016**, *138* (48), 15710-15716.

241. Rong, Y.; Venkatesan, S.; Guo, R.; Wang, Y.; Bao, J.; Li, W.; Fan, Z.; Yao, Y., Critical kinetic control of non-stoichiometric intermediate phase transformation for efficient perovskite solar cells. *Nanoscale* **2016**, *8* (26), 12892-12899.

242. Kang, R.; Kim, J.-E.; Yeo, J.-S.; Lee, S.; Jeon, Y.-J.; Kim, D.-Y., Optimized Organometal Halide Perovskite Planar Hybrid Solar Cells via Control of Solvent Evaporation Rate. *The Journal of Physical Chemistry C* **2014**, *118* (46), 26513-26520.

243. Choi, J. J.; Yang, X.; Norman, Z. M.; Billinge, S. J. L.; Owen, J. S., Structure of Methylammonium Lead Iodide Within Mesoporous Titanium Dioxide: Active Material in High-Performance Perovskite Solar Cells. *Nano Letters* **2014**, *14* (1), 127-133.

244. Zarazua, I.; Han, G.; Boix, P. P.; Mhaisalkar, S.; Fabregat-Santiago, F.; Mora-Seró, I.; Bisquert, J.; Garcia-Belmonte, G., Surface Recombination and Collection Efficiency in Perovskite Solar Cells from Impedance Analysis. *The Journal of Physical Chemistry Letters* **2016**, *7* (24), 5105-5113.

245. Pockett, A.; Eperon, G. E.; Sakai, N.; Snaith, H. J.; Peter, L. M.; Cameron, P. J., Microseconds, milliseconds and seconds: deconvoluting the dynamic behaviour of planar perovskite solar cells. *Physical Chemistry Chemical Physics* **2017**, *19* (8), 5959-5970.

246. Contreras-Bernal, L.; Salado, M.; Todinova, A.; Calio, L.; Ahmad, S.; Idígoras, J.; Anta, J. A., Origin and Whereabouts of Recombination in Perovskite Solar Cells. *The Journal of Physical Chemistry C* **2017**, *121* (18), 9705-9713.

247. Correa-Baena, J.-P.; Turren-Cruz, S.-H.; Tress, W.; Hagfeldt, A.; Aranda, C.; Shooshtari, L.; Bisquert, J.; Guerrero, A., Changes from Bulk to Surface Recombination Mechanisms between Pristine and Cycled Perovskite Solar Cells. *ACS Energy Letters* **2017**, *2* (3), 681-688.

248. Richardson, G.; O'Kane, S. E. J.; Niemann, R. G.; Peltola, T. A.; Foster, J. M.; Cameron, P. J.; Walker, A. B., Can slow-moving ions explain hysteresis in the current-voltage curves of perovskite solar cells? *Energy & Environmental Science* **2016**, *9* (4), 1476-1485.

249. Walsh, A.; Scanlon, D. O.; Chen, S.; Gong, X. G.; Wei, S. H., Self-Regulation Mechanism for Charged Point Defects in Hybrid Halide Perovskites. *Angewandte Chemie International Edition* **2015**, *54* (6), 1791-1794.

250. Marin-Beloqui, J. M.; Lanzetta, L.; Palomares, E., Decreasing Charge Losses in Perovskite Solar Cells Through mp-TiO2/MAPI Interface Engineering. *Chemistry of Materials* **2016**, *28* (1), 207-213.

251. Wang, L.; Moghe, D.; Hafezian, S.; Chen, P.; Young, M.; Elinski, M.; Martinu, L.; Kéna-Cohen, S.; Lunt, R. R., Alkali Metal Halide Salts as Interface Additives to Fabricate HysteresisFree Hybrid Perovskite-Based Photovoltaic Devices. *ACS Applied Materials & Interfaces* **2016**, 8 (35), 23086-23094.

252. Sun, J.; Pimcharoen, K.; Wagner, S. R.; Duxbury, P. M.; Zhang, P., Nanoscale imaging of dense fiber morphology and local electrical response in conductive regioregular poly(3-hexylthiophene). *Organic Electronics* **2014**, *15* (2), 441-448.

253. Tian, W.; Cui, R.; Leng, J.; Liu, J.; Li, Y.; Zhao, C.; Zhang, J.; Deng, W.; Lian, T.; Jin, S., Limiting Perovskite Solar Cell Performance by Heterogeneous Carrier Extraction. *Angewandte Chemie International Edition* **2016**, *55* (42), 13067-13071.

254. Juarez-Perez, E. J.; Sanchez, R. S.; Badia, L.; Garcia-Belmonte, G.; Kang, Y. S.; Mora-Sero, I.; Bisquert, J., Photoinduced Giant Dielectric Constant in Lead Halide Perovskite Solar Cells. *The Journal of Physical Chemistry Letters* **2014**, *5* (13), 2390-2394.

255. Kim, J.; Kim, G.; Kim, T. K.; Kwon, S.; Back, H.; Lee, J.; Lee, S. H.; Kang, H.; Lee, K., Efficient planar-heterojunction perovskite solar cells achieved via interfacial modification of a solgel ZnO electron collection layer. *Journal of Materials Chemistry A* **2014**, *2* (41), 17291-17296.

256. Sandberg, O. J.; Sundqvist, A.; Nyman, M.; Österbacka, R., Relating Charge Transport, Contact Properties, and Recombination to Open-Circuit Voltage in Sandwich-Type Thin-Film Solar Cells. *Physical Review Applied* **2016**, *5* (4), 044005.

257. Zhang, B.; Zhang, M. J.; Pang, S. P.; Huang, C. S.; Zhou, Z. M.; Wang, D.; Wang, N.; Cui, G. L., Carrier Transport in CH3NH3PbI3 Films with Different Thickness for Perovskite Solar Cells. *Advanced Materials Interfaces* **2016**, *3* (17), 1600327.

258. Khoram, P.; Brittman, S.; Dzik, W. I.; Reek, J. N. H.; Garnett, E. C., Growth and Characterization of PDMS-Stamped Halide Perovskite Single Microcrystals. *The Journal of Physical Chemistry C* **2016**, *120* (12), 6475-6481.

259. Dingley, D. J.; Randle, V., Microtexture determination by electron back-scatter diffraction. *Journal of Materials Science* **1992**, *27* (17), 4545-4566.

260. Kronik, L.; Cahen, D.; Schock, H. W., Effects of Sodium on Polycrystalline Cu(In,Ga)Se2 and Its Solar Cell Performance. *Advanced Materials* **1998**, *10* (1), 31-36.

261. Fuertes Marrón, D.; Sadewasser, S.; Meeder, A.; Glatzel, T.; Lux-Steiner, M. C., Electrical activity at grain boundaries of Cu(In,Ga)Se2 thin films. *Physical Review B* **2005**, *71* (3), 033306.

262. Persson, C.; Zunger, A., Compositionally induced valence-band offset at the grain boundary of polycrystalline chalcopyrites creates a hole barrier. *Applied Physics Letters* **2005**, 87 (21), 211904.

263. Yan, Y.; Jiang, C. S.; Noufi, R.; Wei, S.-H.; Moutinho, H. R.; Al-Jassim, M. M., Electrically Benign Behavior of Grain Boundaries in Polycrystalline CuInSe2 Films. *Physical Review Letters* **2007**, *99* (23), 235504.

264. Haruyama, J.; Sodeyama, K.; Han, L.; Tateyama, Y., Termination Dependence of Tetragonal CH3NH3PbI3 Surfaces for Perovskite Solar Cells. *The Journal of Physical Chemistry Letters* **2014**, *5* (16), 2903-2909.

265. Shi, T.; Yin, W.-J.; Hong, F.; Zhu, K.; Yan, Y., Unipolar self-doping behavior in perovskite CH3NH3PbBr3. *Applied Physics Letters* **2015**, *106* (10), 103902.

266. Meyer, J.; Shu, A.; Kröger, M.; Kahn, A., Effect of contamination on the electronic structure and hole-injection properties of MoO3/organic semiconductor interfaces. *Applied Physics Letters* **2010**, *96* (13), 133308.

267. Bouzidi, K.; Chegaar, M.; Bouhemadou, A., Solar cells parameters evaluation considering the series and shunt resistance. *Solar Energy Materials and Solar Cells* **2007**, *91* (18), 1647-1651.

268. Nunes, P.; Fortunato, E.; Martins, R., Influence of the post-treatment on the properties of ZnO thin films. *Thin Solid Films* **2001**, *383* (1), 277-280.

269. Ishii, H.; Hayashi, N.; Ito, E.; Washizu, Y.; Sugi, K.; Kimura, Y.; Niwano, M.; Ouchi, Y.; Seki, K., Kelvin probe study of band bending at organic semiconductor/metal interfaces: examination of Fermi level alignment. *physica status solidi (a)* **2004**, *201* (6), 1075-1094.

270. Lange, I.; Blakesley, J. C.; Frisch, J.; Vollmer, A.; Koch, N.; Neher, D., Band Bending in Conjugated Polymer Layers. *Physical Review Letters* **2011**, *106* (21), 216402.

271. Kim, J.; Kim, G.; Choi, Y.; Lee, J.; Park, S. H.; Lee, K., Light-soaking issue in polymer solar cells: Photoinduced energy level alignment at the sol-gel processed metal oxide and indium tin oxide interface. *Journal of Applied Physics* **2012**, *111* (11), 114511.

272. Verbakel, F.; Meskers, S. C. J.; Janssen, R. A. J., Electronic memory effects in diodes from a zinc oxide nanoparticle-polystyrene hybrid material. *Applied Physics Letters* **2006**, *89* (10), 102103.

273. Ke, C.; Gang, C.; Shujie, W.; Linsong, L.; Shuxi, D.; Xingtang, Z.; Bingsuo, Z.; Zuliang, D., Surface states dominative Au Schottky contact on vertical aligned ZnO nanorod arrays synthesized by low-temperature growth. *New Journal of Physics* **2007**, *9* (7), 214.

274. Natsume, Y.; Sakata, H., Zinc oxide films prepared by sol-gel spin-coating. *Thin Solid Films* **2000**, *372* (1), 30-36.

275. Reese, M. O.; White, M. S.; Rumbles, G.; Ginley, D. S.; Shaheen, S. E., Optimal negative electrodes for poly(3-hexylthiophene): [6,6]-phenyl C61-butyric acid methyl ester bulk heterojunction photovoltaic devices. *Applied Physics Letters* **2008**, *92* (5), 053307.

276. Son, D.-Y.; Lee, J.-W.; Choi, Y. J.; Jang, I.-H.; Lee, S.; Yoo, P. J.; Shin, H.; Ahn, N.; Choi, M.; Kim, D.; Park, N.-G., Self-formed grain boundary healing layer for highly efficient CH3 NH3 PbI3 perovskite solar cells. *Nature Energy* **2016**, *1*, 16081.

277. Yuan, Y.; Huang, J., Ion Migration in Organometal Trihalide Perovskite and Its Impact on Photovoltaic Efficiency and Stability. *Accounts of Chemical Research* **2016**, *49* (2), 286-293.