



공학석사 학위논문

# Understanding the Trap Characteristics of Perovskite Solar Cells via Drive-Level Capacitance Profiling

DLCP 분석을 이용한 페로브스카이트 광전소자 내 전기적 결함의 공간 분포 변화 연구

2023년 8월

서울대학교 공과대학원 재료공학부

류 석 주

# Understanding the Trap Characteristics of Perovskite Solar Cells via Drive-Level Capacitance Profiling

DLCP 분석을 이용한 페로브스카이트 광전소자 내 전기적 결함의 공간 분포 변화 연구

## 지도 교수 박 병 우

# 이 논문을 공학석사 학위논문으로 제출함 2023년 8월

서울대학교 공과대학원 재료공학부 류 석 주

# 류석주의 공학석사 학위논문을 인준함 2023년 8월

위 역	원장.	장 호 원	(인)
부위	원장	박 병 우	(인)
위	원	이 명 재	(인)
위	원	김 진 현	(인)

## Abstract

Perovskite solar cells (PSCs) are gaining significant interest as the future of photovoltaics owing to their superior performance and cost-effectiveness. Nonetheless, the commercialization of perovskite solar cells faces significant hurdles due to the susceptibility to degradation from moisture, light, and heat, as well as the adverse impact of traps on device efficiency and stability.

Therefore, trap suppression through the passivation process is important for implementing perovskite solar cells with high efficiency and stability. It is also important to track trap changes inside perovskite solar cells to confirm the effectiveness of the passivation process. In this study, methylammonium chloride (MACI) additive and phenyltrimethylammonium iodide (PTMAI) posttreatment were applied to passivate bulk and surface defects. Furthermore, variations of the traps' quantitative spatial arrangement have been monitored using the drive-level capacitance profiling (DLCP) analysis.

A similar magnitude of trap reduction was observed for the bulk perovskite layer and two interfaces (electron transport layer (ETL)/perovskite and hole transport layer (HTL)/perovskite) when employing an optimal concentration of MACl additive. However, the effect of perovskite posttreatment in reducing the trap density was much more noticeable at the HTL/perovskite interface, compared to the bulk and ETL/perovskite regions. This observation was reinforced by the outcomes of the 500 h thermal stability tests at 60 °C from seven independent batches, which demonstrated a substantial suppression of trap accumulation, particularly at the HTL/perovskite interface by an order of magnitude.

**Keyword:** Perovskite Solar Cell, Organometal Halide Perovskite, Defect Passivation, Trap Density of States, Additive Process, Posttreatment, Depth-Profile Defect Analysis.

#### Student Number: 2021-22257

## **Table of Contents**

Abstract

**List of Figures** 

Chapter 1. Development of Perovskite Solar Cells......1

- **1.1. Fundamental Working Principle of Photovoltaics**
- 1.2. Benefits of Perovskite as a Photovoltaic Material
- 1.3. Degradation and Defects in Perovskite Solar Cells
- 1.4. References

Chapter 2. Understanding the Trap Characteristics of Perovskite Solar Cells via Drive-Level Capacitance Profiling......17

- 2.1. Introduction
- 2.2. Experimental Section/Methods
- 2.3. Results and Discussion
- **2.4.** Conclusions
- 2.5. References

Abstract in Korean......40

## **List of Figures**

#### Chapter 1.

- Figure 1-1. The operation mechanism of p-n junction photovoltaic devices. From Ref. [1].
- Figure 1-2. *J-V* measurement to estimate the photovoltaic performance.
- Figure 1-3. The Shockley-Queisser limit and efficiency of the photovoltaic devi ces with various active materials. From Ref. [3].
- Figure 1-4. Schematic illustration of perovskite solar cell and ABX<sub>3</sub> perovski te crystal. From Ref. [9].
- Figure 1-5. Tunable band of perovskite with different elements in ABX<sub>3</sub> pero vskite crystal. From Ref. [13].
- **Figure 1-6.** Various layered structures of perovskite solar cells. From Ref. [16].
- Figure 1-7. Diverse pathways of ion defects migrations. From Ref. [21].
- Figure 1-8. Various defects in the perovskite layer. From Ref. [22].
- **Figure 1-9.** Perovskite layer internal and interface defect passivation process es. From Ref. [23].

#### Chapter 2.

Figure 2-1. The properties and performance of the PSC by the concentration of MACl additive. (a) Cross-sectional SEM images, (b) schematic illustration of perovskite solar cells, (c) XRD patterns, and (d) depth-profile trap density of the perovskite solar cells with varying MACl additive concentrations (10, 30, and 50 mol. %) by the drive-level capacitance profiling (DLCP). (e) Statistics of power-

conversion efficiency (PCE) with different concentrations of MACl additives (10, 30, and 50 mol. %)

- Figure 2-2. Schematic diagram and photovoltaic performance of PSC. (a) Illustration of the PTMAI posttreatment, (b) *J-V* curves, (c) steady-state current, and (d) the photovoltaic performance statistics of the PSCs without/with the PTMAI posttreatment.
- **Figure 2-3.** Crystalline phase change by the PTMAI posttreatment. XRD patterns with the PTMAI passivation on the perovskite film.
- Figure 2-4. Optical property changes by the PTMAI posttreatment. (a) Photoluminescence spectra, (b) time-resolved photoluminescence (TRPL) spectra, and (d) UV-vis absorption spectra of the PTMAI nonpassivated/passivated PSCs.
- Figure 2-5. Thermal degradation of the PSCs at 60 °C for 500 h, without/with the PTMAI passivation. (a) Cross-sectional SEM images, and (b) retention rate from ~30 batches of the PSCs.
- Figure 2-6. The depth profiles of the electronic trap densities by the drivelevel capacitance profiling (DLCP) at 60 °C for 500 h. Depthprofile trap density of the PSCs (batch  $\alpha$ ) analyzed by the drive-level capacitance profiling (DLCP).
- Figure 2-7. The statistics of the trap densities at 60 °C for 500 h. The statistics of the trap densities at  $V_{DC}$  of ~0, ~0.5, and ~1.0 V, respectively (for seven batches,  $\alpha \eta$ ).
- Figure 2-8. The depth profiles of the electronic trap densities by the drivelevel capacitance profiling (DLCP) at 60 °C for 500 h. Trap densities of the PSCs without/with the PTMAI treatment (for six batches,  $\beta - \eta$ ).

#### Chapter 1.

#### **Development of Perovskite Solar Cells**

#### **1.1. Fundamental Working Principle of Photovoltaics**

Solar cells that incorporate the union of n-type and p-type semiconductors, each possessing distinct electrical characteristics, offer affordability through their absence of mechanical components. Furthermore, the solar cell promotes environmental friendliness by producing no pollutants and exerting no strain on natural resources. As shown in Figure 1-1, the fundamental principle of solar power generation lies in the phenomenon known as the photoelectric effect.<sup>1</sup> In other words, it refers to the process of converting sunlight into electrical energy. When solar radiation interacts with a solar cell comprising an n-type and a p-type semiconductor, it generates electrons and holes within the cell due to the energy of the incident light. Consequently, the holes migrate towards the p-type semiconductor while the electrons move towards the n-type semiconductor, resulting in the flow of electric current due to the creation of a potential difference.<sup>2</sup> The electricity produced in this manner is collected in a storage battery and distributed through a power conversion device.

Solar power generation effectiveness in photovoltaic devices is commonly evaluated through current density-voltage (*J-V*) measurement. Power conversion efficiency (PCE) denotes the proportion between solar energy absorbed by the device and the electrical energy output (maximum power output) obtained from the solar cell's terminal. As shown in Figure 1-2, PCE can be expressed as the product of three factors: open circuit voltage ( $V_{OC}$ ), short-circuit current density (*Jsc*), and fill factor (FF). Solar cells encounter a constrained efficiency, commonly referred to as the Shockley-Quarter limit (presented in Figure 1-3).<sup>3</sup> The limitation arises due to the band gap of the absorbing material constraining the open circuit voltage ( $V_{OC}$ ) of the solar cells, thereby preventing the absorption of photons with energies lower than the band gap. In other words, an elevated band gap of material leads to an increased  $V_{OC}$ , whereas a reduced band gap results in a higher  $J_{SC}$ . Consequently, there exists a threshold for enhancing power output, represented by the product of  $V_{OC}$  and  $J_{SC}$ . Therefore, an optimization of the bandgap is essential for high-efficiency solar cell implementation.<sup>4,5</sup> In general, it is known that a material with a band gap between 1.2 and 1.5 eV has a high photovoltaic performance.



**Figure 1-1.** The operation mechanism of p-n junction photovoltaic devices. From Ref. [1].



Figure 1-2. *J-V* measurement to estimate the photovoltaic performance.



**Figure 1-3.** The Shockley-Queisser limit and efficiency of the photovoltaic devices with various active materials. From Ref. [3].

#### **1.2. Benefits of Perovskite as a Photovoltaic Material**

Perovskite solar cells (PSCs) have garnered interest due to their costeffective production methods involving low temperatures and straightforward solution processes, in contrast to conventional silicon solar cells.<sup>6,7</sup> As a result, continuous research efforts have led to PCE exceeding 25% which surpasses the efficiency typically observed in polycrystalline silicon solar cells.<sup>8</sup>

The ABX<sub>3</sub> structure of organic metal halide perovskite, commonly used in solar cells, is characterized by the presence of organic molecules such as methylammonium (MA) and formamide (FA) at the A cation site, atoms such as Pb<sup>2+</sup> and Sn<sup>2+</sup> at the B cation site, and halides including I<sup>-</sup>, Br<sup>-</sup>, and Cl<sup>-</sup> at the X cation site (Figure 1-4).<sup>9</sup> Perovskite materials possess the ability to form intricate alloys by incorporating diverse molecules or elements at the A, B, and X positions. This allows for the introduction of inorganic elements such as Cs or Rb at the A position, in addition to MA and FA. Also, synthesis methods involve combining I and Br at the X position. Perovskite alloys, with their diverse compositions, can exhibit a wide range of bandgap.<sup>10,11,12</sup> The corresponding variations in bandgap can be observed in Figures 1-5.<sup>13</sup> Furthermore, organometallic halide perovskites, which are organic-inorganic hybrid compounds, possess distinct properties such as high absorption coefficients and long carrier diffusion lengths.<sup>14,15</sup> In addition to these advantages, as shown in 1-6, the fact that various structures such as a p-i-n planar structure that can fabricate flexible devices, n-i-p mesoscopic, and n-i-p planar structures can be manufactured is raising greater interest in perovskite solar cells.16



**Figure 1-4.** Schematic illustration of perovskite solar cell and ABX<sub>3</sub> perovskite crystal. From Ref. [9].



**Figure 1-5.** Tunable band of perovskite with different elements in ABX<sub>3</sub> perovskite crystal. From Ref. [13].



**Figure 1-6.** Various layered structures of perovskite solar cells. From Ref. [16].

#### **1.3. Degradation and Defects in Perovskite Solar Cells**

The organic metal halide perovskite is promising as an active area material for next-generation solar cells due to various advantages. Nevertheless, one of the hurdles faced by the development of perovskite solar cells is their deterioration, impacting the long-term stability and overall functionality of the device.<sup>17,18</sup>

Moisture, oxygen, heat, and light are the main causes of perovskite degradation. These factors cause soluble species formation, perovskite crystal structure change, defects formation, and ion migration.<sup>19,20</sup> The process of ion migration, as shown in Figure 1-7, leads to chemical reactions, the formation of electrical defects, and alterations in the composition of the perovskite material.<sup>21</sup> In addition, the perovskite layer contains defects in different forms, including bulk point defects, uncoordinated ions, anti-sites, and dangling bonds, as depicted in Figure 1-8.<sup>21,22</sup> These defects not only accelerate degradation but also have adverse impacts on the performance of the devices.

The defect passivation process is one of the effective approaches for mitigating degradation and enhancing the performance of perovskite devices. As shown in Figure 1-9, post-treatment, interlayer, dopant, and composition engineering are representative processes of defect passivation.<sup>23,24</sup> The aim of these processes is to reduce the adverse effects of defects by inhibiting recombination and enhancing charge transport properties.<sup>25</sup> Until now, cases of improving the PCE and stability of the device through various defect passivation processes have been reported. Furthermore, the exploration of new approaches and materials for defect passivation engineering is expected to implement more efficient and reliable perovskite solar cells.

10



Figure 1-7. Diverse pathways of ion defects migrations. From Ref. [21].



Figure 1-8. Various defects in the perovskite layer. From Ref. [22].



**Figure 1-9. Perovskite layer internal and interface defect passivation processes.** From Ref. [23].

#### **1.4. References**

- Shanawani, M.; Masotti, D.; Costanzo, A. THz Rectennas and Their Design Rules. *Electronics* 2017, *6*, 99.
- [2] Arnaoutakis, G. E. Novel Up-Conversion Concentrating Photovoltaic Concepts (Doctoral dissertation, Heriot-Watt University). 2015.
- [3] Ehrler, B.; Alarcón-Lladó, E.; Tabernig, S. W.; Veeken, T.; Garnett, E. C.; Polman, A. Photovoltaics Reaching for the Shockley–Queisser Limit. ACS Energy Lett. 2020, 5, 3029–3033.
- [4] 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. *Nat. Mater.* 2014, *13*, 897-903.
- [5] Liu, X.; Wu, Z.; Fu, X.; Tang, L.; Li, J.; Gong, J.; Xiao, X. Highly Efficient Wide-Band-Gap Perovskite Solar Cells Fabricated by Sequential Deposition Method. *Nano Energy* 2021, 86, 106114.
- [6] Sajid, S.; Elseman, A. M.; Huang, H.; Ji; J.; Dou, S.; Jiang, H.; Liu, X.; Wei, D.; Cui, P.; Li, M. Breakthroughs in NiO<sub>x</sub>-HTMs Towards Stable, Low-Cost and Efficient Perovskite Solar Cells. *Nano Energy* 2018, *51*, 408-424.
- Ye, T.; Hou, Y.; Nozariasbmarz, A.; Yang, D.; Yoon, J.; Zheng, L.; Wang, K.; Ramakrishna, S.; Priya, S. Cost-Effective High-Performance Charge-Carrier-Transport-Layer-Free Perovskite Solar Cells Achieved by Suppressing Ion Migration. ACS Energy Lett. 2021, 6, 3044-3052.
- [8] Todorov, T.; Gunawana, O.; Guha, S. A Road Towards 25% Efficiency and Beyond: Perovskite Tandem Solar Cells. *Mol. Syst. Des. Eng.* 2016, 1, 370-376.
- [9] Zhou, Y.; Herz, L. M.; Jen, A. K.; Saliba, M. Advances and Challenges in Understanding the Microscopic Structure–Property–Performance Relationship in Perovskite Solar Cells. *Nat. Energy* 2022, 7, 794-807.
- [10] Li, Y.; Meng, J.; Duan, P.; Wu, R.; Shi, Y.; Zhang, L.; Chunxia, Y.; Deng J.; Zhang, X. Transport Layer Engineering by Hydrochloric Acid for Efficient

Perovskite Solar Cells with a High Open-Circuit Voltage. *ACS Appl. Mater. Interfaces* **2023**, *15*, 23208-23216.

- [11] Liu, X.; Wu, Z.; Fu, X.; Tang, L.; Li, J.; Gong, J.; Xiao, X. Highly Efficient Wide-Band-Gap Perovskite Solar Cells Fabricated by Sequential Deposition Method. *Nano Energy* 2021, 86, 106114.
- Tao, J.; Liu, X.; Shen, J.; Han, S.; Guan, L.; Fu, G.; Kuang, D. B.; Yang, S.
   F-Type Pseudo-Halide Anions for High-Efficiency and Stable Wide-Band-Gap Inverted Perovskite Solar Cells with Fill Factor Exceeding 84%. ACS Nano 2022, 16, 10798-10810.
- [13] Wu, Y.; Chen, W.; Chen, G.; Liu, L.; He, Z.; Liu, R. The Impact of Hybrid Compositional Film/Structure on Organic–Inorganic Perovskite Solar Cells. *Nanomaterials* 2018, 8, 356.
- [14] De Wolf, S.; Holovsky, J.; Moon, S. J.; Loper, P.; Niesen, B.; Ledinsky, M.; Haung, F. J.; Yum, J. H.; Ballif, C. Organometallic Halide Perovskites: Sharp Optical Absorption Edge and Its Relation to Photovoltaic Performance. J. Phys. Chem. Lett. 2014, 5, 1035-1039.
- [15] Rehman, W.; Milot, R. L.; Eperon, G. E.; Wehrenfennig, C.; Boland, J. L.; Snaith, H. J.; Johnston, M. B.; Herz, L. M. Charge-Carrier Dynamics and Mobilities in Formamidinium Lead Mixed-Halide Perovskites. *Adv. Mater.* 2015, 27, 7938-7944.
- [16] Song, J. X.; Yin, X. X.; Li, Z. F.; Li, Y. W. Low-Temperature-Processed Metal Oxide Electron Transport Layers for Efficient Planar Perovskite Solar Cells. *Rare Met.* 2021, 40, 2730-2746.
- [17] Meng, L.; You, J.; Yang, Y. Addressing the Stability Issue of Perovskite Solar Cells for Commercial Applications. *Nat. Commun.* 2018, 9, 5265.
- [18] Rong, Y.; Hu, Y.; Mei, A.; Tan, H.; Saidaminov, M. I.; Seok, S. I.; Mcgehee, M. D.; Sargent, E. H.; Han, H. Challenges for Commercializing Perovskite Solar Cells. *Science* 2018, *361*, eaat8235.
- [19] 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*, 739-744.

- [20] Kim, M. C.; Ham, S. Y.; Cheng, D.; Wynn, T. A.; Jung, H. S.; Meng, Y. S. Advanced Characterization Techniques for Overcoming Challenges of Perovskite Solar Cell Materials. *Adv. Energy Mater.* 2021, *11*, 2001753.
- [21] Yuan, Y.; Huang, J. Ion Migration in Organometal Trihalide Perovskite and Its Impact on Photovoltaic Efficiency and Stability. Acc. Chem. Res. 2016, 49, 286-293.
- [22] Chen, B.; Rudd, P. N.; Yang, S.; Yuan, Y.; Huang, J. Imperfections and Their Passivation in Halide Perovskite Solar Cells. *Chem. Soc. Rev.* 2019, 48, 3842-3867.
- [23] Fu, L.; Li, H.; Wang, L.; Yin, R.; Li, B.; Yin, L. Defect Passivation Strategies in Perovskites for an Enhanced Photovoltaic Performance. *Energy Environ. Sci.* 2020, 13, 4017-4056.
- [24] Kim, J. Y.; Lee, J. W.; Jung, H. S.; Shin, H.; Park, N. G. High-Efficiency Perovskite Solar Cells. *Chem. Rev.* 2020, 120, 7867-7918.
- [25] Yun, A.J.; Kim, J.; Hwang, T.; Park, B. Origins of Efficient Perovskite Solar Cells with Low-Temperature Processed SnO<sub>2</sub> Electron Transport Layer. ACS Appl. Energy Mater. 2019, 2, 3554-3560.

### Chapter 2.

# Understanding the Trap Characteristics of Perovskite Solar Cells via Drive-Level Capacitance Profiling

#### **2.1. Introduction**

The trap-states are a type of defect in the crystal structure that can trap and immobilize charge carriers like electrons and holes, resulting in reduced efficiency by decreasing current and voltage output.<sup>1-12</sup> Additionally, these defects can provoke device degradation, leading to lower stability and a shorter lifespan.<sup>13-14</sup> To mitigate this issue, researchers are exploring ways to decrease the concentration of trap-states in the perovskite layer.<sup>6,10,14-21</sup>

With extensive research, additives and posttreatment methods were suggested to resolve the defect issues in the perovskite solar cells (PSCs). Particularly, the utilization of additives during perovskite precursor preparation and interface passivation with various agents have been widely studied, which are well-known methods for enhancing the device performance and stability.<sup>22-33</sup> Nevertheless, the mechanisms of the trap distributions throughout the perovskite layer (from the HTL and up to the ETL interfaces) are not been fully investigated yet. Even though electrochemical impedance spectroscopy (EIS) or x-ray photoelectron spectroscopy (XPS) can be conducted to understand the defect concentration, the depth profiling of electronic traps in the perovskite layer should be further researched to comprehend the behavior of defects.

The drive-level capacitance profiling (DLCP) is a method that can analyze the electronic properties of materials such as perovskites by examining changes in DC bias and AC voltage ranges at a given frequency.<sup>34-40</sup> The DLCP analysis is a potent tool for optimizing materials for electronic applications due to its high sensitivity in detecting even low levels of defects and traps in materials.<sup>34-36</sup> Moreover, the technique allows researchers to conduct depth profiling of electronic properties throughout the materials thickness (depth), thus providing valuable insights into their variations.<sup>34,35,36,39</sup> Specifically, the DLCP analysis can quantify the spatial distributions of charge traps throughout PSCs by analyzing the capacitance-voltage characteristics, and this information aids in understanding the mechanisms responsible for the carrier recombination and degradation in PSCs.<sup>14,37,39</sup>

Herein, the DLCP analysis is performed to investigate the impact of various experimental factors (additive and posttreatment agent) on the trap state density of the formamidinium lead triiodide (FAPbI3) PSCs. Based on the DLCP analysis, with a 30 mol. % MACl additive, the minimum density of trap states throughout the profiling regions of the perovskite layer is identified. Interestingly, unlike surface passivation, the reduction of trap densities in the perovskite bulk and interfaces with charge-transport layers is approximately equivalent. In addition, the application of further PTMAI posttreatment to the PSC resulted in not only the decrease of trap densities throughout the perovskite layer but also the suppression of trap formation during the heat-induced degradation. Although the decrease in trap density within the bulk region is relatively small, the most significant control effect is observed at the interface between the HTL and perovskite layer, where the posttreatment agent is applied. A reduced trap concentration signifies the inhibition of ion migration, slowing the degradation rate and activating carrier movement.<sup>4,10</sup> In line with the trap characteristics, the PSCs incorporating 30 mol. % additive and the PTMAI surface passivation exhibit an efficiency retention rate over 10% higher after the 60 °C thermal stability test compared to PSCs without these modifications. This study suggests the influence of different processes on the characteristics of the PSC by effectively mitigating trap generation within PSCs.

18

#### **2.2. Experimental Section/Methods**

**Preparation for FAPbI**<sup>3</sup> **Perovskite:** The precursor of the FAPbI<sup>3</sup> perovskite solution was prepared by 1.3 M formamidinium iodide (FAI, Great Cell Solar), lead iodide (PbI<sub>2</sub>, TCI) was blended with N, N-dimethylformamide (DMF, Sigma-Aldrich) and dimethyl sulfoxide (DMSO, Sigma-Aldrich). Dissolved in IPA (Sigma-Aldrich), phenyltrimethylammonium iodide (PTMAI, TCI) forms the PTMAI solution while the volume ratio of DMF to DMSO is 4:1. After being prepared in the N<sub>2</sub>-filled glovebox and stirred for 90 min, the solution was spin-coated.

Solar Cell Fabrication: After performing UV-ozone treatment for 15 min on the ITO substrate (AMG), a 4:1 volume ratio mixture of deionized water and SnO<sub>2</sub> nanoparticle dispersion in H<sub>2</sub>O (Alfa-Aesar) was deposited at 3000 rpm using 30 s spin-coating for electron transport layer (ETL), which was then heated at 150 °C for 30 min. Once the heated substrate was cooled to room temperature, another round of UV-ozone treatment was performed for 15 min. Next, the perovskite film was deposited onto the SnO<sub>2</sub> film by spin-coating the precursor solution in a two-step program consisting of 30 s at 500 rpm, followed by 10 s at 3000 rpm. The 1mL of diethyl ether (DaeJung) antisolvent was dropped onto the spinning substrate 10 s before the end of the program during the second step. Finally, the substrate was annealed in air at 150 °C for 10 min. For hole transport layer (HTL) solution, 17.5 mg of PTAA (117 kDa, MS Solutions) was dissolved in 1 mL of chlorobenzene (Sigma-Aldrich) with the addition of 6 µL of 4-tertbutylpyridine (tBP, Sigma-Aldrich), and 4  $\mu$ L of bis(trifluoromethane)sulfonimide lithium salt (Li-TFSI, Sigma-Aldrich) solution (520 mg/mL in acetonitrile). After stirring for 1 h, the HTL solution was deposited using spin-coating at 3000 rpm for 30 s. Thermal evaporation was used to deposit gold contact onto the device as the final step.

*Characterization*: To measure the current-voltage (*J-V*) characteristics and steady-state power output of the PSCs with an active area of  $0.09 \text{ cm}^2$ , the solar simulator (K3000, McScience) was utilized. The measurements were conducted under the standard AM 1.5 G (1 sun illumination: 100 mW/cm<sup>2</sup>). The

morphology of the perovskite films was examined using a field-emission scanning electron microscope (Merlin Compact, Zeiss). Using an x-ray diffractometer (New D-8 Advance, Bruker), the crystallinity of both the perovskite films and devices was examined. The PL analyzer (Fluotime 300, Picoquant) was used to perform photoluminescence (PL) spectra and time-resolved photoluminescence (TRPL) spectra measurements. A UV-visible spectrophotometer (V-770, JASCO) was employed to analyze the optical band gap and absorption of the film. An LCR meter (E4980A, Keysight) was utilized to perform the drive-level capacitance profiling (DLCP) on the solar cells. The capacitance of the cells was measured at a given 20 kHz frequency by changing DC and AC voltages from 0 to 1.0 V and 5 to 50 mV, respectively. In an N<sub>2</sub>-filled glove box, the thermal stability of the devices was tested by storing them at 60 °C. After cooling to room temperature for more than 2 h, analyses were performed.

#### **2.3. Results and Discussion**

To determine the optimal MACl additive concentration, surface, crystallinity, and capacitance of FAPbI<sub>3</sub> perovskites were investigated. The crosssectional scanning electron microscope (SEM) image of Figure 2-1(a) shows uniform and enlarged grain in the perovskite layer with 30 mol. % MACl additive. Figure 2-1(b) is a schematic diagram showing the movement of electron/hole carriers in perovskite layers according to the various MACl additive concentrations. X-ray diffraction (XRD) analysis in Figure 2-1(c) also confirms that the phase transition from  $\delta$ -FAPbI<sub>3</sub> (hexagonal structure) to  $\alpha$ -FAPbI<sub>3</sub> (cubic structure) is not carried out smoothly in the perovskite layer with 10 mol. % MACl additive. On the other hand,  $\alpha$ -FAPbI<sub>3</sub> is well formed in the perovskite layer with 30 and 50 mol. % of additives. However, in order to confirm the exact effect of the additive, observing the energetic and spatial variation of trap states that affect the efficiency and stability of the device is necessary.

Figure 2-1(d) shows the trap density distributions from the ETL to HTL of the perovskite layer at each MACl additive concentration analyzed by the DLCP. The measurement of the perovskite layer reveals high trap density in all profiling regions in ranks of 10, 50, and 30 mol. %, which indicates that the magnitude and distributions of trap density throughout the perovskite layer change depending on the concentration of the MACl additive. The PSC containing 30 mol. % MACl additive, which exhibits the lowest density of trap states throughout the measured profiling regions, achieves the highest efficiency of 20.5% (Figure 2-1(e)). Characteristically, when the concentrations of MACl additive are varied, a reduction in trap densities inside of the perovskite bulk is observed, similar to trap densities reduction near the interface of the perovskite layer. The effective involvement of the additive in trap behavior throughout the profiling regions can be inferred due to its inclusion in the precursor prior to the deposition of the perovskite layer, unlike posttreatment methods. Therefore, the DLCP analysis allows us to gather solid evidence for the effect of MACl additive on the trap density in various regions of the perovskite layer, including interfaces and bulk, and its direct contribution to the device's performance.



**Figure 2-1.** The properties and performance of the PSC by the concentration of MACI additive. (a) Cross-sectional SEM images, (b) schematic illustration of perovskite solar cells, (c) XRD patterns, and (d) depth-profile trap density of the perovskite solar cells with varying MACI additive concentrations (10, 30, and 50 mol. %) by the drive-level capacitance profiling (DLCP). (e) Statistics of power-conversion efficiency (PCE) with different concentrations of MACI additives (10, 30, and 50 mol. %).

Despite the MACl additive effectively enhancing the phase stabilization of the perovskite and reducing defects, an additional passivation step is required to remove any residual defects. To this end, the PSCs without/with the PTMAI surface passivation were compared to identify the magnitude of the initial trap and the reduction of heat-induced trap generation. Figure 2-2(a) schematically shows how the PTMAI passivation behaves on the surface and grain boundaries of the perovskite layer. Figure 2-2(b) compares the *J*-*V* curve of the devices' best PCE without/with the PTMAI posttreatment. The PSC with the PTMAI posttreatment shows the best PCE of 21.2% with an improvement in open-circuit voltage ( $V_{oc}$ ) of ~10% compared to the nonpassivated PSC. This implies that the passivation of existing defects is achieved by posttreatment. In addition, the current stability during light exposure for 500 s shown in Figure 2-2(c) is better and the  $J_{SC}$  is slightly improved due to the impact of the PTMAI passivation. Figure 2-2(d) shows the PCE statistics according to the PTMAI passivation, confirming that posttreated PSCs exhibit higher efficiencies in general.

To verify further passivation effects in the device, the optical properties and crystallinity of the perovskite layer are investigated. Through XRD analysis, higher  $\alpha$ -FAPbI<sub>3</sub> (001) peak intensity and lower PbI<sub>2</sub> (001) peak intensity can be observed in devices with the PTMAI posttreatment (Figure 2-3). This indicates that the crystallinity of the cubic  $\alpha$ -FAPbI3 structure is enhanced due to the PTMAI posttreatment effect. It also denotes that the PTMAI posttreatment suppresses the formation of PbI<sub>2</sub> (hexagonal structure) which acts as defects that cause nonradiation recombination and reduce the performance of the PSCs.



**Figure 2-2.** Schematic diagram and photovoltaic performance of PSC. (a) Illustration of the PTMAI posttreatment, (b) *J-V* curves, (c) steady-state current, and (d) the photovoltaic performance statistics of the PSCs without/with the PTMAI posttreatment.



**Figure 2-3.** Crystalline phase change by the PTMAI posttreatment. XRD patterns with the PTMAI passivation on the perovskite film.

Photoluminescence (PL) and ultraviolet-visible (UV-vis) absorption analyses were conducted to determine how the PTMAI posttreatment affects the optical properties of the device. PL analyses were performed with the ETL and HTL carrier-transport layers to determine the transport characteristics of charge carriers. Figure 2-4(a) confirms that the luminescence intensity of the device with the PTMAI passivation is lower, implying that the movement of charge carriers toward the transport layer is more efficient. In addition, in the time-resolved PL analysis (Figure 2-4(b)), the fast decay time of the posttreatment device can be identified, implying that the PTMAI passivates defects on the surface, inhibiting nonradiative recombination and helping charge carriers to be extracted quickly. The UV-absorption analysis shown in Figure 2-4(c) suggests the lack of difference in bandgap energy, as expected.

To observe various characteristics of the posttreated PSC by thermal degradation, especially the behavior of the trap states throughout the perovskite layer, a thermal stability test was performed at 60 °C, 500 h in an inert condition. Figure 2-5(a) shows the cross-sectional SEM of devices without/with the PTMAI posttreatment, before and after a 500 h heat stability test. Before the thermal stability test (0 h), the morphology difference of the film according to passivation is insignificant. Interestingly, after a 60 °C thermal stability test for 500 h, devices without the PTMAI posttreatment show poor morphological properties, where pinholes are also observed. On the other hand, the PTMAI posttreatment looks to alleviate the heat-induced degradation after 500 h. The degradation suppression effect can also be inspected through the retention rate statistics (Figure 2-5(b)). Posttreated PSCs have an average retention rate of more than 80%, and the highest device has a retention rate of  $\sim$ 94%.



**Figure 2-4. Optical property changes by the PTMAI posttreatment.** (a) Photoluminescence spectra, (b) time-resolved photoluminescence (TRPL) spectra, and (d) UV-vis absorption spectra of the PTMAI nonpassivated/passivated PSCs.



**Figure 2-5.** Thermal degradation of the PSCs at 60 °C for 500 h, without/with the PTMAI passivation. (a) Cross-sectional SEM images, and (b) retention rate from ~30 batches of the PSCs.

To confirm the spatial variations/evolutions of trap densities quantitatively within the perovskite layer under the thermal stress, the DLCP analyses were effectively employed.<sup>14,34-39</sup> The spatial distribution of trap density (at a low AC frequency,  $f \le 100$  kHz or  $E_{\omega} \ge 0.25$  eV) comes from a carrier density:  $N_t^C(x,\omega) =$  $N^C(x,\omega) - N_0^C(x,_{MHz})$ , where  $N_t^C(x,\omega)$  is the trap density,  $N^C(x,\omega)$  is total carrier concentration, and  $N_0^C(x,_{MHz})$  is a free-carrier concentration at high AC frequency ( $f \ge 1$  MHz).<sup>34-39</sup>

Figure 2-6, shows the variations of trap densities in the perovskite layer after a 500 h thermal stability test without/with the PTMAI posttreatment. Apparent profiling distance represents information from 0 nm (HTL/perovskite interface) to 500 nm (ETL/perovskite interface), measured by changing the DC voltage from 0 V to 1.0 V. First, all the devices exhibit a higher trap density at the interfaces than the bulk. In addition, regardless of the heat treatment, it can be confirmed that the trap density of the devices with the PTMAI posttreatment is lower throughout the profiling regions. In particular, the difference in the increases of trap densities after the thermal stability clearly indicates that the PTMAI posttreatment inhibits the heat-induced degradation and trap generation of devices.

To closely investigate the behavior of trap density near the interfaces and bulk after the thermal stability test, the DLCP analysis results from 7 different batches (7 solar cells without passivation plus 7 solar cells with passivation) accumulated under the same conditions are divided into the HTL/perovskite interface, bulk, and the ETL/perovskite interface (Figure 2-7). Figure 2-8 (for six batches,  $\beta - \eta$ ) represents the DLCP results, as measured under the same conditions as Figure 2-6 (batch  $\alpha$ ). Seven different batches (Figure 2-7) exhibit that higher trap densities are typically observed at the interfaces than at the bulk, which means that the trap states negatively affecting the efficiency and stability of the devices are mainly distributed between the charge-transport and perovskite interfaces. In particular, the trap densities after 500 h differs by up to an order of magnitude due to the posttreatment, clearly indicating that the suppression of degradation is particularly noticeable at the HTL/perovskite interface, as expected from the posttreatment. By conducting the detailed capacitance analyses through the DLCP during the thermal degradation process, changes in the trap densities can be observed quantitatively along the depth, confirming that the stability improvement of PSCs is directly influenced by the PTMAI posttreatment.



Figure 2-6. The depth profiles of the electronic trap densities by the drivelevel capacitance profiling (DLCP) at 60 °C for 500 h. Depth-profile trap density of the PSCs (batch  $\alpha$ ) analyzed by the drive-level capacitance profiling (DLCP).



**Figure 2-7.** The statistics of the trap densities at 60 °C for 500 h. The statistics of the trap densities at  $V_{DC}$  of ~0, ~0.5, and ~1.0 V, respectively (for seven batches,  $\alpha - \eta$ ).



Figure 2-8. The depth profiles of the electronic trap densities by the drivelevel capacitance profiling (DLCP) at 60 °C for 500 h. Trap densities of the PSCs without/with the PTMAI treatment (for six batches,  $\beta - \eta$ ).

#### 2.4. Conclusions

In this study, we have investigated how surface passivation and additive incorporation affect the trap distributions in the perovskite layer from the ETL and up to the HTL interfaces through the DLCP analysis. Under the 30 mol. % additive of MACl, the PSC device exhibited the minimum trap density throughout the profiling regions in the perovskite layer. The result of the thermal stability test conducted at 60 °C for 500 h on the PTMAI posttreated PSCs, demonstrated the effectiveness of surface passivation in not only reducing the initial trap formation but also mitigating further trap generation in both the perovskite interfaces and bulk. Specifically, these phenomena were most evident at the interface between the perovskite layer and HTL, where the posttreated layer is The findings suggest that the application of passivation agents positioned. inhibits ion migration and thereby reduces the vacancy generation in the perovskite layer, which means promoting the mobility of charge carriers and impeding the degradation. Despite identifying the precise sources of the detected traps remains a challenge, the observed changes in the trap behavior at different depths provide a significant step toward understanding the fundamental science behind the PSCs' performance and characteristics.

#### 2.5. References

- Wang, R.; Xue, J.; Wang, K. L.; Wang, Z. K.; Luo, Y.; Fenning, D.; Xu, G.; Nuryyeva, S.; Huang, T.; Zhao, Y.; Yang, J. L.; Zhu, J.; Wang, M.; Tan, S.; Yavuz, I.; Houk, K. N.; Yang, Y. Constructive Molecular Configurations for Surface-Defect Passivation of Perovskite Photovoltaics. *Science* 2019, *366*, 1509-1513.
- [2] Yun, A. J.; Gil, B.; Ryu, S.; Kim, J.; Park, B. Evolution of the Electronic Traps in Perovskite Photovoltaics during 1000 h at 85 °C. ACS Appl. Energy Mater. 2022, 5, 7192-7198.
- [3] Yuan, Y.; Huang, J. Ion Migration in Organometal Trihalide Perovskite and Its Impact on Photovoltaic Efficiency and Stability. *Acc. Chem. Res.* 2016, 49, 286-293.
- [4] Sun, Y.; Zhang, J.; Yu, H.; Huang, C.; Huang, J. Several Triazine-Based Small Molecules Assisted in the Preparation of High-Performance and Stable Perovskite Solar Cells by Trap Passivation and Heterojunction Engineering. ACS Appl. Mater. Interfaces 2022, 14, 6625-6637.
- [5] Cho, J.; Kim, B.; Ryu, S.; Yun, A. J.; Gil, B.; Lim, J.; Kim, J.; Kim, J.; Park,
  B. Multifunctional Green Solvent for Efficient Perovskite Solar Cells. *Electron. Mater. Lett.* 2023. [DOI:10.1007/s13391-023-00410-x]
- [6] Azmi, R.; Nurrosyid, N.; Lee, S. H.; Al Mubarok, M.; Lee, W.; Hwang, S.; Yin, W.; Ahn T. K.; Kim, T. W.; Ryu, D. Y.; Do, Y. R.; Jang, S. Y. Shallow and Deep Trap State Passivation for Low-Temperature Processed Perovskite Solar Cells. ACS Energy Lett. 2020, 5, 1396-1403.
- [7] Stolterfoht, M.; Wolff, C.M.; Márquez, J.A.; Zhang, S.; Hages, C.J.; Rothhardt, D.; Albrecht, S.; Burn, P.L.; Meredith, P.; Neher, D. Visualization and Suppression of Interfacial Recombination for High-Efficiency Large-Area *p-i-n* Perovskite Solar Cells. *Nat. Energy* 2018, *3*, 847-854.
- [8] Hwang, T.; Yun, A. J.; Kim, J.; Cho, D.; Kim, S.; Hong, S.; Park, B. Electronic Traps and Their Correlations to Perovskite Solar Cell

Performance via Compositional and Thermal Annealing Controls. *ACS Appl. Mater. Interfaces.* **2019**, *11*, 6907-6917.

- [9] Sherkar, T. S.; Momblona, C.; Gil-Escrig, L.; Bolink, H. J.; Koster, L. J. A. Improving Perovskite Solar Cells: Insights from a Validated Device Model. *Adv. Energy Mater.* 2017, 7, 1602432.
- [10] Zheng, X.; Wang, X.; Li, W.; Liu, Z.; Ming, W.; Wang, H.; Wang, H.; Li, D.; Liu, B.; Yang, C. Correlations of Ionic Migration and Deep-Level Traps Leads to Surface Defect Formation in Perovskite Solar Cells. *J. Phys. Chem. C* 2021, *125*, 19551–19559.
- [11] Kim, J.; Yun, A. J.; Park, B.; Kim, J. Minimizing the Transport Loss and Degradation of Perovskite Optoelectronics via Grain Dimerization Technique. *EcoMat* 2023, 5, e12314.
- [12] Slotcavage, D. J.; Karunadasa, H. I.; McGehee, M. D. Light-Induced Phase Segregation in Halide Perovskite Absorbers. ACS Energy Lett. 2016, 1, 1199-1205.
- [13] Domanski, K.; Roose, B.; Matsui, T.; Saliba, M.; Turren-Cruz, S. H.; Correa-Baena, J. P.; Carmona, C. R.; Richardson, G.; Foster, J. M.; Angelis, F. D.; Ball, J. M.; Petrozza, A.; Mine, N.; Nazeeruddin, M. K.; Tress, W.; Grätzel, M.; Steiner, U.; Hagfeldt, A.; Abate, A. Migration of Cations Induces Reversible Performance Losses Over Day/Night Cycling in Perovskite Solar Cells. *Energy Environ. Sci.* 2017, *10*, 604-613.
- [14] Ni, Z.; Jiao, H.; Fei, C.; Gu, H.; Xu, S.; Yu, Z.; Yang, G.; Deng, Y.; Jiang, Q.; Liu, Y.; Yan, Y.; Huang, J. Evolution of Defects during the Degradation of Metal Halide Perovskite Solar Cells Under Reverse Bias and Illumination. *Nat. Energy* 2022, *7*, 65-73.
- [15] Park, B.; Stephenson, G.B.; Allen, S.M.; Ludwig Jr., K.F. Development of Fluctuations into Domains during Ordering in Fe<sub>3</sub>Al. *Phys. Rev. Lett.* 1992, 68, 1742-1745.
- [16] Chen, B.; Rudd, P. N.; Yang, S.; Yuan, Y.; Huang, J. Imperfections and Their Passivation in Halide Perovskite Solar Cells. *Chem. Soc. Rev.* 2019, 48, 3842-3867.

- [17] Hwang, T.; Lee, B.; Kim, J.; Lee, S.; Gil, B.; Yun, A. J.; Park, B. From Nanostructural Evolution to Dynamic Interplay of Constituents: Perspectives for Perovskite Solar Cells. *Adv. Mater.* 2018, *30*, 1704208.
- [18] Jia, P.; Qin, L.; Zhao, D.; Tang, Y.; Song, B.; Guo, J.; Li, X.; Li, L.; Cui, Q.; Hu, Y.; Lou, Z.; Teng, F.; Hou, Y. The Trapped Charges at Grain Boundaries in Perovskite Solar Cells. *Adv. Funct. Mater.* 2021, *31*, 2107125.
- [19] Wang, F.; Bai, S.; Tress, W.; Hagfeldt, A.; Gao, F. Defects Engineering for High-Performance Perovskite Solar Cells. *npj Flex. Electron.* 2018, 2, 22.
- [20] Lee, J. W.; Kim, S. G.; Bae, S. H.; Lee, D. K.; Lin, O.; Yang, Y.; Park, N. G. The Interplay between Trap Density and Hysteresis in Planar Heterojunction Perovskite Solar Cells. *Nano Lett.* 2017, *17*, 4270-4276.
- [21] Sherkar, T. S.; Momblona, C.; Gil-Escrig, L.; Avila, J.; Sessolo, M.; Bolink, H. J.; Koster, L. J. A. Recombination in Perovskite Solar Cells: Significance of Grain Boundaries, Interface Traps, and Defect Ions. *ACS Energy Lett.* 2017, *2*, 1214-122.
- [22] Lee, S. H.; Jeong, S.; Seo, S.; Shin, H.; Ma, C.; Park, N. G. Acid Dissociation Constant: a Criterion for Selecting Passivation Agents in Perovskite Solar Cells. ACS Energy Lett. 2021, 6, 1612-1621.
- [23] Jiang, Q.; Zhao, Y.; Zhang, X.; Yang, X.; Chen, Y.; Chu, Z.; Ye, Q.; Li, X.; Yin, Z.; You, J. Surface Passivation of Perovskite Film for Efficient Solar Cells. *Nat. Photonics* 2019, *13*, 460-466.
- [24] Yun, A. J.; Kim, J.; Gil, B.; Woo, H.; Park, K.; Cho, J.; Park, B. Incorporation of Lithium Fluoride Restraining Thermal Degradation and Photodegradation of Organometal Halide Perovskite Solar Cells. ACS Appl. Mater. Interfaces 2020, 12, 50418-50425.
- [25] Wu, G.; Liang, R.; Ge, M.; Sun, G.; Zhang, Y.; Xing, G. Surface Passivation Using 2D Perovskites Toward Efficient and Stable Perovskite Solar Cells. *Adv. Mater.* 2022, *34*, 2105635.
- [26] Song, S.; Yang, S. J.; Choi, J.; Han, S. G.; Park, K.; Lee, H.; Min, J.; Ryu, S.; Cho, K. Surface Stabilization of a Formamidinium Perovskite Solar Cell Using Quaternary Ammonium Salt. ACS Appl. Mater. Interfaces 2021, 13, 37052-37062.

- [27] Gao, F.; Zhao, Y.; Zhang, X.; You, J. Recent Progresses on Defect Passivation Toward Efficient Perovskite Solar Cells. *Adv. Energy Mater.* 2020, 10, 1902650.
- [28] Kim, M.; Kim, G. H.; Lee, T. K.; Choi, I. W.; Choi, H. W.; Jo, Y.; Yoon, Y. J.; Kim, J. W.; Lee, J.; Huh, D.; Lee, H.; Kwak, S. K.; Kim, J. Y.; Kim, D. S. Methylammonium Chloride Induces Intermediate Phase Stabilization for Efficient Perovskite Solar Cells. *Joule* 2019, *3*, 2179-2192.
- [29] Pham, H. T.; Yin, Y.; Andersson, G.; Weber, K. J.; Duong, T.; Wong-Leung, J. Unraveling the Influence of CsCl/MACl on the Formation of Nanotwins, Stacking Faults and Cubic Supercell Structure in FA-Based Perovskite Solar Cells. *Nano Energy* 2021, 87, 106226.
- [30] Lim, J.; Gil, B.; Yun, A. J.; Kim, J.; Park, B. Micro/Nanostructural Analyses of Efficient and Stable Perovskite Solar Cells via KF Doping. ACS Appl. Energy Mater. 2023, 6, 371-377.
- [31] Zhu, T.; Zheng, D.; Liu, J.; Coolen, L.; Pauporté, T. PEAI-Based Interfacial Layer for High-Efficiency and Stable Solar Cells Based on a MACI-Mediated Grown FA<sub>0.94</sub>MA<sub>0.06</sub>PbI<sub>3</sub> Perovskite. ACS Appl. Mater. Interfaces 2020, 12, 37197-37207.
- [32] Kang, D. H.; Lee, S. U.; Park, N. G. Effect of Residual Chloride in FAPbI<sub>3</sub>
   Film on Photovoltaic Performance and Stability of Perovskite Solar
   Cell. ACS Energy Lett. 2023, 8, 2122-2129.
- [33] Zhang, F.; Zhu, K. Additive Engineering for Efficient and Stable Perovskite Solar Cells. *Adv. Energy Mater.* 2020, *10*, 1902579.
- [34] Heath, J. T.; Cohen, J. D.; Shafarman, W. N. Bulk and Metastable Defects in CuIn<sub>1-x</sub>Ga<sub>x</sub>Se<sub>2</sub> Thin Films Using Drive-Level Capacitance Profiling. *J. Appl. Phys.* 2004, 95, 1000-1010.
- [35] Warren, C. W.; Roe, E. T.; Miller, D. W.; Shafarman, W. N.; Lonergan, M. C. An Improved Method for Determining Carrier Densities via Drive Level Capacitance Profiling. *Appl. Phys. Lett.* 2017, *110*, 203901.
- [36] Michelson, C. E.; Gelatos, A. V.; Cohen, J. D. Drive-Level Capacitance Profiling: Its Application to Determining Gap State Densities in

Hydrogenated Amorphous Silicon Films. Appl. Phys. Lett. 1985, 47, 412-414.

- [37] Yun, A. J.; Ryu, S.; Lim, J.; Kim, J.; Park, B. Thermal Degradation of the Bulk and Interfacial Traps at 85 °C in Perovskite Photovoltaics. *Nanoscale* 2023, 15, 4334-4343.
- [38] Ni, Z.; Bao, C.; Liu, Y.; Jiang, Q.; Wu, W. Q.; Chen, S.; Dai, X.; Chen, B.; Hartweg, B.; Yu, Z.; Holman, Z.; Huang, J. Resolving Spatial and Energetic Distributions of Trap States in Metal Halide Perovskite Solar Cells. *Science* 2020, 367, 1352-1358.
- [39] Wu, W. Q.; Rudd, P. N.; Ni, Z.; Van Brackle, C. H.; Wei, H.; Wang, Q.; Ecker, B. R.; Gao, Y.; Huang, J. Reducing Surface Halide Deficiency for Efficient and Stable Iodide-Based Perovskite Solar Cells. J. Am. Chem. Soc. 2020, 142, 3989-3996.
- [40] Bi, D.; Yi, C.; Luo, J.; Décoppet, J. D.; Zhang, F.; Zakeeruddin, S. M.; Li, X.; Hagfeldt, A.; Grätzel, M. Polymer-Templated Nucleation and Crystal Growth of Perovskite Films for Solar Cells with Efficiency Greater than 21%. *Nat. Energy* 2016, *1*, 1-5.

#### **Abstract in Korean**

학번: 2021-22257

페로브스카이트 태양전지는 우수한 성능 및 낮은 제작비용으로 인해 차세대 태양전지로 주목 받고 있다. 하지만 수분, 빛, 열 등에 의해 쉽게 열화가 일어난다는 점과, 장치의 효율과 안정성에 악영향을 미치는 내부 결함은 페로브스카이트 태양전지의 상용화에 큰 문제점으로 여겨진다.

이러한 문제를 해결하고 높은 효율 및 안정성을 갖는 페로브스카이트 태양전지를 구현하기 위해, 부동태 공정을 통한 결함 억제가 중요하다. 또한 부동태 공정의 효과 확인 및 효율성 판단을 위해, 페로브스카이트 태양전지 내부 결함의 밀도 및 분포를 추적하는 연구 역시 함께 논의되어야 한다. 본 연구에서는 페로브스카이트 층 내부 및 표면 결함을 부동태화 하기 위하여 MACI 첨가제 및 PTMAI 후처리 공정을 적용하였다. 더 나아가, 페로브스카이트 층 내부 결함의 분포 및 밀도 변화 추이를 DLCP 분석을 통해 정량화 하였다.

최적화된 MACI 농도로 첨가제 공정을 진행한 소자의 경우, 페로브스카이트 층 내부와 전자전달층 및 정공전달층과 맞닿아 있는 두 계면에서 유사한 크기의 전자적 결함 밀도 감소가 관찰되었다. 그러나 PTMAI 후처리 공정을 진행한 소자의 경우, 결함 밀도 감소 효과가 페로브스카이트 층 내부 및 전자전달층/페로브스카이트 계면에 비해 정공전달층/페로브스카이트 계면에서 두드러지게 나타났다. 이러한 결과는 60 °C, 500시간 열 안정성 시험을 거친 독립적인 7번의 배치에 의해 강화되었으며, 특히 정공전달층/페로브스카이트 계면에서 온도에 의한 열화 이후 결함 축적이 상당히 억제되었음을 확인하였다.

**주요어:** 페로브스카이트 태양전지, 유기금속 할라이드 페로브스카이트, 결함 부동태화, 결함 상태 밀도, 첨가제 공정, 후처리 공정.

40