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The Effect of Nanostructure Control on the Performance of Organic-Inorganic Hybrid Perovskite Solar Cells

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The Effect of Nanostructure Control on the Performance of Organic-Inorganic Hybrid Perovskite Solar Cells

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Abstract

Solar cell is one of most promising renewable energy harvesting devices which directly converts solar light into electrical power. Among various materials used as a light absorber in solar cell, organic-inorganic hybrid perovskite (OIHP) has outstanding physical properties including low exciton binding energy (< 50 meV), high carrier mobility (> 10 cm²/V·s), long carrier diffusion length (> 1 μm), high absorption coefficient, and tunable energy band gap. Owing to these merits, the OIHP solar cell has exhibited rapid enhancement in power conversion efficiency (PCE) compared to other types of solar cells since it is applied as all solid-state device in 2012. In addition, the OIHP solar cell can be fabricated by low-cost solution process which is beneficial to commercialization.

The main research issues for commercialization of OIHP solar cell are improving the PCE to reduce energy production cost, and ensuring long-term stability under various environment such as humid condition, oxygen, light, and heat. In this thesis, the effects of grain size of perovskite film on the photovoltaic performance are studied to enhance the PCE of solar cell. Also, large grain evolution of perovskite film for Cl-containing perovskite precursor is investigated in detail. Furthermore, development of inorganic hole transporting materials to enhance thermal stability of device are discussed.

In Chapter 1, basic operation principles of photovoltaic devices and the structure of perovskite unit cell and perovskite solar cells are briefly introduced. Fundamentals to deposit uniform perovskite films with film formation mechanisms from nucleation to grain growth are also discussed. Various strategies to enhance optoelectronic performances of solar cell are reviewed, especially focusing on the mitigation of trap density of states.
In Chapter 2, the correlation between grain size of perovskite film and photovoltaic performances are investigated. CH$_3$NH$_3$PbI$_3$ (MAPbI$_3$) perovskites are synthesized by applying second solvent dripping to nonstoichiometric precursors containing excess CH$_3$NH$_3$I. The resulting perovskite films exhibit a larger average grain size with a better crystallinity compared to that from stoichiometric precursors. As a result, the performance of planar perovskite solar cells is significantly improved, achieving an efficiency of 14.3%. Furthermore, perovskite films are effectively analyzed using a conductive AFM and noise spectroscopy. Comparing the topography and photocurrent maps, the variation of photocurrents in nanoscale is systematically investigated, and a linear relationship between the grain size and photocurrent is revealed. Also, noise analyses with a conductive probe enable examination of the defect density of perovskites at specific grain interiors by excluding the grain-boundary effect, and reduced defects are clearly observed for the perovskites using CH$_3$NH$_3$I-rich precursors.

In Chapter 3, MAPbI$_3$(Cl) perovskite films is synthesized by using excess MACl-containing precursors, which exhibit approximately an order of magnitude larger grain size with higher $<110>$-preferred orientation compared with that from stoichiometric precursors. Comprehensive mechanisms for the large grain evolution by Cl incorporation are elucidated in detail by correlating the changes in grain orientation, distribution of grain size, and the remaining Cl in the perovskite during thermal annealing. In the presence of Cl, $<110>$- and $<001>$-oriented grains grow faster than other grains at the initial stage of annealing. Further annealing leads to the dissipation of Cl, resulting in the shrinkage of $<001>$ grains while $<110>$ grains continuously grow, as analyzed by x-ray rocking curve and diffraction. As a result of reduced grain boundaries and enhanced $<110>$ texture, the trap density of perovskite solar cells diminishes by ~10% by incorporating MACl in the
precursor, resulting in a fill factor more than 80%.

Finally in Chapter 4, CuGaO$_2$ nanoparticles are used with CuSCN for the hole-transporting layer (HTL) of a perovskite solar cell, and the effects on photovoltaic property and long-term thermal stability are analyzed. Uniform films of CuGaO$_2$ are prepared by treating CuGaO$_2$ nanoparticles with amino-silane that leads to well-dispersed CuGaO$_2$ solution followed by spin-coating of the suspension. Subsequent spin-coating of CuSCN solution onto the CuGaO$_2$ forms a smooth HTL with excellent coverage and electrical conductivity. Comparing to the reference device with CuSCN HTL, the CuGaO$_2$/CuSCN device improves carrier extraction and reduces trap density by ~40%, as measured by photoluminescence and capacitance analysis. Excellent thermal stability is also demonstrated: ~80% of the initial efficiency of the perovskite solar cells with the CuGaO$_2$/CuSCN HTL is retained after 400 h under 85°C/85% relative humidity environment.

**Keywords:** perovskite solar cells, power conversion efficiency, excess CH$_3$NH$_3$I, conductive AFM, noise spectroscopy, excess CH$_3$NH$_3$Cl, trap density, grain size, texture, CuGaO$_2$, CuSCN, long-term stability

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Chapter 1. Overview

1.1. Operational Principle and Characterization of Photovoltaic Performance

The basic working principle of solar cell is photovoltaic effect. When solar radiation reached on the materials, the valence band electron excites into higher energy state (conduction band) by absorbing photon energy larger than the energy bandgap of materials leaving the hole in the valence band (Fig. 1-1). If these photon energy absorbing occurs in the space charge region of p-n junction, excited electron and hole are spatially separated by the built in field causing net current through the junction. The charge carriers (electron and hole) moving away from the depletion region are extracted to external circuit by diffusion. In open-circuit condition, the separated charges pile up at each type of materials changing initial majority carrier density, and photovoltage are generated from the separation of quasi-Fermi level of p- and n-type materials. The carriers excited by photon energy larger than the bandgap of materials cool down to the states near the bandedge through phonon interaction called thermalization. Excited carriers can recombine with the carriers having opposite charges before extracting to external circuit. Defect sites such as point defect, dislocation, surface, and grain boundary generate intra band states acting as traps for charge carrier, and increase non-radiative recombination. From the above working principle, following factors should be considered to fabricate efficient solar cells.

1. Sufficient light absorption using materials having adequate bandgap (1.3 – 1.4 eV for single junction solar cell) and high absorption coefficient.
2. Efficient separation of excited charge carriers to each side of electrode by drift and diffusion.
3. Minimization of non-radiative recombination pathway by reducing defect density.
Performance of the solar cell can be quantified by four parameters obtained from current density ($J$) – applied voltage ($V$) curve (Fig. 1-2). The short circuit current ($J_{SC}$) is the generated photocurrent without any load on the device (fermi level at equilibrium). The open-circuit voltage ($V_{OC}$) is the applied voltage at zero output current. The power-conversion efficiency (PCE) is the ratio of maximum power output of device to the incident light power (100 mW/cm$^2$ at 1 sun). The fill factor is the ratio of PCE to the product of $J_{SC}$ and $V_{OC}$. The fill factor closer to 1 means that the device is more likely operate with ideal diode.
Fig. 1-1. (Color) Working process of $p$-$n$ junction solar cells.
Fig. 1-2. A schematic of $J$-$V$ curve and photovoltaic parameters.
1.2. Organic-Inorganic Hybrid Perovskite (OIHP) Solar Cells

Organic-inorganic hybrid perovskites (OIHPs) usually have a ABX$_3$ structure containing monovalent organic or inorganic cations (CH$_3$NH$_3^+$ (MA), (NH$_2$)$_2$CH$^+$ (FA), Cs$^+$, or Rb$^+$) in A-site, divalent inorganic cations (Pb$^{2+}$ or Sn$^{2+}$) in B-site, and halide anions (Cl$^-$, Br$^-$, or I$^-$) in X-site. Since the 2012 when all solid-state OIHP solar cell has been reported firstly, improvement of record PCE is most drastic compared to the other-type solar cells, and the PCE is now closely reached to the theoretical Shockley-Queisser limit (Fig. 1-3).[1] The remarkable points of OIHP solar cells are solution processability of almost all deposition process for device fabrication and the outstanding physical properties of OIHP films including a high absorption coefficient, a low exciton binding energy (< 50 meV), a superior carrier mobility, electrically benign nature of defect states, and tunable bandgap by alloying. The main research issues for the commercialization of OIHP solar cells can be classified into four categories. First, improving the PCE is of importance to reduce the power production cost for competitive advantage as a renewable energy system. Second, long-term stability of device should be guaranteed. OIHP films are vulnerable to the water, oxygen, light, heat, and electric field, and the electron/hole transport layers also affect the device stability, especially under illumination condition. Commercial Si-based solar panels are generally guaranteed for at least 10 years, thus detailed researches on each parts of OIHP device are necessary to achieve a competitive stability. Third, fabrication techniques for large area production should be developed. Spin coating process which is most widely applied to deposit OIHP films has limitation for large area uniformity, and technologies such as roll-to-roll or blade coating have been studied. Lastly, replacing Pb in perovskite composition with other non-hazard element is required in terms of
environmental concerns.

The carrier concentration of OIHP films have been reported in the range between $10^9$ – $10^{14}$ with $p$-type characteristics.[2] The junction configuration is constructed as $n$-$i$-$p$ (TCO/ETL/perovskite/HTL/metal electrode) or $p$-$i$-$n$ (TCO/HTL/perovskite/ETL/metal electrode) depending on the stacking sequence, where ETL is a $n$-type electron transporting layer and HTL is a $p$-type hole transporting layer, and perovskite is considered as an intrinsic semiconductor due to the much lower carrier concentration compared to the ETL and HTL (Fig. 1-4). For $n$-$i$-$p$ configuration, TiO$_2$ blocking layer and mesoporous TiO$_2$ are most widely used as an ETL, and various $n$-type metal oxides like SnO$_2$, ZnO, or BaSnO$_3$ are also applied.[3] $p$-type organic materials including spiro-OMeTAD, PTAA, and P3HT are commonly used for HTL.[3] However, due to the high cost and thermal stability issue, $p$-type metal oxides such as CuO, CuGaO$_2$, CuCrO$_2$, or NiO$_x$ have been tried to replace these organic HTL.[3] For $p$-$i$-$n$ configuration, aforementioned $p$-type metal oxide or PEDOT:PSS are used as a HTL, and $n$-type organic materials like PCBM or C60 are applied as an ETL.[3] The excited electron and hole in the perovskite layer under illumination are transferred into ETL and HTL, respectively, by built in field, and eventually extracted to the external circuit.
Fig. 1-3. (Color) Theoretical Shockley-Queisser efficiency limit as a function of band gap, and experimental efficiencies of solar cells using various light absorber.

From Ref. [1]
Fig. 1-4. (Color) A schematic device architecture and energy band diagram of $n$-$i$-$p$ type OIHP solar cell.
1.3. Deposition of Perovskite Films: Evolution of the Microstructure

Various processing conditions can be altered to deposit an OIHP thin film including precursor composition, additive, deposition method, and annealing protocols due to its solution processability. Lots of methods have been applied for achieving high quality thin film, and despite large tuning in the process condition, desirable perovskite structure are obtained.[4-13] M. J. Heben et al. proposed the pseudobinary temperature-phase processing diagram depending on the composition of PbI$_2$ and MAI (Fig. 1-5(a)).[14] In this phase diagram, MAPbI$_3$ has tetragonal I4/mcm perovskite phase (β phase) at room temperature, and tetragonal P4mm phase (α phase) becomes stable above 60°C owing to reduction of the degree of distortion in the unit cell in stoichiometric composition. In the case of PbI$_2$-rich precursor, perovskite phase is stable with a presence of PbI$_2$ up to the MAI composition reaching ~0.2. With MAI-rich composition, as intercalated species (MA$^+$ and I$^-$) increase in the metal halide layer (corner sharing PbI$_6^+$ octahedrons), transitional phase between 2D and 3D perovskites termed “stacked perovskite sheets” (SPSs) appears near stoichiometric composition. Increment in MAI contents gives rise to “low-dimensional perovskites” (LDPs) due to further insertion of MA$^+$ between the metal halide layers.[15] As can be seen in a phase diagram, the perovskite phase is stable for a wide range of composition under 190°C enabling a variety of deposition approaches to synthesize a OIHP thin film.

To achieve high photovoltaic efficiency, OIHP thin films having optimal microstructural morphology without pin-holes are necessary in the given phase equilibrium nature. Therefore, understanding the fundamental mechanisms for film formation from nucleation and growth to coalescence is of significant importance during spin-coating and
annealing to control the evolution process. In typical one-step solution process, perovskite film is known to grow by Volmer-Weber mode in which condensed phase is formed on substrate surface into not a continuous epitaxial layer but a separate islands due to the more toughly bounded atoms to each other than to the substrate, thus high density of nucleation is essential for uniform film morphology.[16,17] According to LaMer model, solute in precursor solution is expended competitively by nucleation and growth, and increasing supersaturation accelerates the nucleation rate compared to growth rate enabling dense nucleation (Fig. 1-5(b)).[18,19] However, slow evaporation of the solvent having high boiling point like DMF, DMSO, and GBL used in perovskite precursors suppresses nucleation density causing non-uniform rod-shape film morphology. To overcome this intrinsic problem, external approaches have been applied to augment supersaturation in solution such as introducing anti-solvent which cannot dissolve PbI₂ and MAI, for immediate precipitation,[5,20] increasing substrate temperature over solvent boiling point,[12,21] flowing the heated air during spin-coating,[22] and using vacuum pump for rapid solvent evaporation.[23-25] Such various approaches enable the formation of pin-hole free and uniform OIHP thin films.

After spin-coating process adopting techniques to induce compact morphology, annealing is conducted to as-deposited film which activates transformation of intermediate phase into perovskite phase or grain coarsening promoted by increment in atomic diffusivity at high temperature. Migration of thermally activated grain boundary for developing meta-stable equilibrium at grain boundary junction and Ostwald ripening occurring by difference in free energy ascribed to each boundary curvatures in a liquid mediator are two main mechanisms of coalescence.[26] As shown in Fig. 1-5(c), if we assume that grain boundary energy is independent on orientation, the equilibrium angles
between three neighboring grains in 2D configuration are 120°. Therefore, a grain having 6 neighboring grains is stable, while inward net force is induced at boundary for a grain less than 6 neighbors which is shrink, and outward force is applied for a grain more than 6 neighbors which is grow. Such solid-state grain coarsening proceeds rapidly until an average grain size is smaller than film thickness, and growth is slow down and eventually stop when grain size comparable with film thickness.[27,28] This phenomenon is known as “specimen thickness effect”, and the stagnation of grain growth is attributed to grain boundary grooves at the surface inducing drag force which restrains boundary motion. Albeit grain growth is obstructed by dragging force, abnormal and secondary grain growth can occur for further coalescence.[28] Some specific oriented grains which have low surface energy or interface energy with substrate can additionally grow with expense of neighboring grains after normal grain growth is stagnated. During the intermediate stage of this process, bimodal distribution of grain size is distinctively observed, and subsequently unimodal distribution of lateral grain size exceeding film thickness is obtained.

An OIHP thin film exhibits <110>-texture on a typical TiO₂ or PEDOT:PSS substrate due to thermodynamically favored interfaces thus, secondary growth could be expected to occur.[29,30] Abnormal grain growth in perovskite film has been reported for the process adopting Cl containing precursor, and bimodal distribution of grain size at the intermediate stage with resultant large grain morphology was observed.[31] Ostwald ripening which is another coarsening mechanism have been also studied in an OHP thin film through liquid mediated post process. In these reports, compact MAPbI₃ film was obtained by anti-solvent dripping method then, MAI or MABr-dissolved isopropanol solution was spin-coated onto the film resulting enlarged grain morphology.[32,33]
Components in tiny grains with steep boundary curvature have high chemical potential and are dissolved in isopropanol while large grains with gentle curvature grow further due to the low chemical potential. Solvent annealing method is also reminiscent of Ostwald ripening. Significant coalescence took place during annealing under DMF and DMSO vapor, whereas grain growth was limited in typical thermal annealing.[34,35] It can be thought that solvent enabling to dissolve OIHPs acts as a liquid mediator promoting grain growth process for Ostwald ripening.

In the two-step process, high coverage of perovskite film can be attained by dipping the uniformly coated PbI\textsubscript{2} film into organo-halide solution.[11,36] There are also competition between nucleation and growth in two-step deposition, and concentration of MAI dipping solution controls the degree of supersaturation with resultant nucleation density.[37] Therefore, from the relation between nucleation density and crystal volume which is inversely proportional, final grain size can be estimated as follows:

\[
\ln Y = \frac{32\sigma_{sl}^3}{3kT V_m \left( \frac{kT}{V_m} \left( \ln X - \ln C_0(T) \right) \right)^2} + C'
\]

where \(Y\) is grain size, \(\sigma_{sl}\) is average surface tension, \(k\) is Boltzmann constant, \(V_m\) is the volume of nuclei, \(X\) is the MAI concentration, and \(C_0\) and \(C'\) are the equilibrium concentration of MAI and constant, respectively. The experimental grain sizes as a function of MAI concentration were well matched with fitting line (Fig. 1-5(d)). From the comprehensive insight of above contents, classical nucleation and growth mechanism enable to elucidate the microstructural evolution of OIHP thin films therefore, processing parameters which should be tuned to deposit desirable morphology can be judged.
Fig. 1-5. (Color) (a) Pseudobinary processing diagram of MAPbI$_3$ up to 190°C. From Ref. [14]. (b) Nucleation and growth rate as a function of supersaturation. (c) Schematic illustration of solid state grain growth in thin films. From Ref. [26]. (d) Theoretically derived and experimentally obtained grain size of MAPbI$_3$ as a function of MAI concentration. From Ref. [37].
1.4. General Strategies to Improve the Performance of OIHP Solar Cells

Non-radiative recombination of charge carriers is main detrimental loss for the photovoltaic efficiency, and trap states stemming from deep level defects act as recombination center.[38] Grain boundary one of major defects in thin film accompanies high density of trap states, and is commonly considered to degrade the performance of electronic device. Effects of grain boundary on the various properties of an OIHP solar cell have been widely studied, and there are two contrasting streams in which one is that grain boundary is inert and even helpful on the cell performance while, the other shows catastrophic ramification. Analysis results using theoretical calculations suggest that grain boundary does not generate intra bandgap states, and several groups demonstrate that local photocurrent obtained from conductive AFM (cAFM) at boundary region exhibits higher than that at the grain interior.[39-42] For example, L. J. Wan et al. suggested that a built-in potential at the grain boundaries, which attracts electrons and repels holes, confirmed by surface potential difference suppress the recombination of carriers. However, as will be seen in the chapter 2, the photocurrent at grain interior and grain size has a linear proportionality in photocurrent mapping by cAFM showing large grain size and high crystallinity positively affects photovoltaic performance. Also, most of the researches have shown that enlarging the grain size of OIHPs and passivating the grain boundary related defects by doping or post treatment improve the charge transport and recombination properties resulting in high efficiency of solar cell (Fig. 1-6).[4,8,11,12,31-34,43-47] Therefore, the efficacy of reducing grain boundary should be considered as positive for outstanding device performance.
Fig. 1-6. (Color) (a) Diffusion length (L) and power conversion efficiency (η) as a function of grain size (<x>) of perovskite films. From Ref. [47]. (b) Power conversion efficiency, electrical mobility, and short-circuit current density depending on the grain size of perovskite. From Ref. [12].
Diverse attempts to augment the grain size have been carried out with introducing additive to precursor solution,[48,49] controlling the annealing conditions such as temperature, time, and atmosphere,[4,34,35,50] post treatment after spin-coating,[32,33] and adopting non-wetting substrate.[51] Fig. 1-7(a) presents enlargement of grain size depending on various substrate having different wetting angle of water. Especially in the comparison between PEDOT:PSS and c-OTPD used as a substrate, grain growth on the non-wetting substrate is more significant than that of wetting substrate with extended annealing (Fig. 1-7(b)). When average grain size reaches film thickness, grain coarsening is limited by surface tension dragging force applying on the grain boundary. Growth on the non-wetting substrate however, can be further proceeded due to the reduction of this drag force. Trap density of state (tDOS) was extracted by admittance spectroscopy depending on each substrates, and 2-3 orders of magnitude lower value was observed for the OIHP film on c-OTPD substrate than that on PEDOT:PSS owing to larger perovskite grains and improved interface property (Fig. 1-7(c)).

The effect of grain size for the charge transport have been verified by comparing the carrier diffusion length of ~175 µm for single crystal OIHPs with ~1 µm for polycrystalline thin film.[52,53] Carrier mobilities of hole and electron for single crystal, which is ~105 and ~25 cm²/V·s, respectively, obtained from hall measurement, are also several times higher than that for the thin film.[52,54] These enhancements in charge transport could be ascribed to reduced trap density in single crystal which is a few orders of magnitude lower compared to polycrystal, as shown in Fig. 1-7(d). These results enlighten the potential room for improving optoelectronic quality of a polycrystalline OIHP thin film by applying trap passivating techniques.

In addition to increasing grain size, defects healing strategies to passivate shallow
and deep trap states have been vastly researched. Alloying or doping of A-site with monovalent cation, and X-site with halide is one of effective methods to reduce trap density (Fig. 1-7(e and f)) [55]. In FA_{0.83}MA_{0.17}Pb(I_{0.83}Br_{0.17})_3 perovskites, incorporation of Cs reduces the density and depth of trap states, and charge recombination rates confirmed by thermally stimulated current (TSC) and time-resolved microwave conductivity (TRMC) measurement, respectively (Fig. 1-8(a)).[56] On the other hand, Rb incorporation increase the charge carrier mobility of perovskite films mitigating current-voltage hysteresis. Adding both Cs and Rb in perovskites, trap density and mobility are simultaneously improved resulting in better photovoltaic performance compared to the only Cs or Rb incorporated films. Adding KI in the perovskite precursors also improves the optoelectronic properties of films by passivating the interfaces and grain boundaries (Fig. 1-8(b)).[57] Excess I⁻ ions in precursor from addition of KI can fill any halide vacancies which are the pathways of non-radiative recombination. K⁺ ions selectively depletes Br⁻ in the perovskite crystal structure by forming potassium halide species. As a result, both photoluminescence quantum efficiency (PLQE) of films and photovoltaic performance of solar cells (especially for the $V_{OC}$) are notably enhanced. Incorporation of NaF in the triple perovskite precursor results in longer carrier lifetime in time-resolved PL and reduced trap density leading to the best PCE of 21.9% and outstanding device stability in various condition.[58] The fluorine ions segregating on interfaces form hydrogen bonds with organic cation of perovskites and increase ionic charge of Pb, thereby passivating both cation and anion vacancies.

Passivation of defects on surface and grain boundary by post treatment on the perovskite films has also been investigated. Phenyl-C61-butyric acid methyl ester (PCBM), an electron transport material, deposited on the perovskite film can mitigate trap
density of states.[59] The trap level of Pb-I antisite initially located at deep states shifts to near the bandedge with the introduction of PCBM from the DFT calculation.[60] Various Lewis bases including thiophene, pyridine, ICID, or methoxy group have been applied onto the perovskite to passivate the under-coordinated Pb ions.[61-63] By donation of electron density to the Pb from Lewis bases forming a coordinate or covalent bond, the net positive charge of Pb atom can effectively be neutralized.
Fig. 1-7. (Color) (a) The contact angle of water and morphology of MAPbI$_3$ films by SEM on various substrate. (b) Different grain size of MAPbI$_3$ films depending on substrate (PEDOT:PSS and c-OTPD) with varying the annealing time at 105°C. (c-f) Trap density of states estimated from frequency dependent capacitance analysis. (c) MAPbI$_3$ films grown on PEDOT:PSS and c-OTPD substrate. From Ref. [50]. (d) MAPbI$_3$ single crystal and thin film. From Ref. [51]. (e) FAPbI$_3$ films with (blue square) and without (red circle) Cs doping. From Ref. [55]. (f) (Cs$_{0.05}$FA$_{0.54}$MA$_{0.41}$)Pb(I$_{0.98}$Br$_{0.02}$)$_3$ films with (pink circle) and without (sky-blue circle) NaF additive. From Ref. [58].
Fig. 1-8. (Color) (a) Schematics of the perovskite unit cell incorporated with Cs/Rb and the effect of Cs/Rb incorporation on the trap density and charge mobility (left). Photovoltaic parameters of the perovskite solar cells with different cation composition (right). From Ref. [56] (b) Schematics showing halide vacancy management by potassium iodide (left). J-V curves of perovskite solar cell with and without addition of potassium iodide (right). Inset shows stabilized power output. From Ref. [57].
1.5. References


[9] Long, M.; Zhang, T.; Chai, Y.; Ng, C.-F.; Mark, T. C. W.; Xu, J.; Yan, K. Nonstoichiometric Acid-Base Reaction as Reliable Synthetic Route to Highly Stable CH$_3$NH$_3$PbI$_3$ Perovskite Film. *Nat. Commun.*, 2016, 7, 13503.


Chapter 2.
Evaluating the Optoelectronic Quality of Hybrid Perovskites by Conductive AFM with Noise Spectroscopy

2.1. Introduction

In pursuit of developing high-efficient devices utterly utilizing renewable energy sources, various researches have been carried out.[1-5] Especially, organic-inorganic hybrid perovskite solar cells exhibit enormous improvement of their performances in a few years after they were applied to solid state devices, and ~20% of a certified solar-to-energy conversion efficiency was attained.[6,7] This outstanding performance stems from the properties of the perovskites such as a high absorption coefficient, a superior carrier mobility, a low exciton binding energy, a bipolar transport, and a long carrier diffusion length.[8-11] Furthermore, the merits of cost-efficient and low-temperature solution processibility enable perovskite solar cells to be a viable candidate for the commercialization among the next generation solar cells.

To achieve a high photovoltaic efficiency, the complete coverage of the perovskite layer is necessary to absorb a larger portion of incident lights and reduce unwanted shunting paths. A lot of synthetic routes have been reported to produce the full coverage of perovskite films, such as two-step deposition, vapor-assisted deposition, solvent annealing, and second solvent engineering.[12-17] Among them, second solvent engineering is a
straightforward and low-cost method to deposit high quality films. In this approach, the secondary solvents like chlorobenzene or toluene are dripped during the spin-coating process. As such solvents hardly dissolve the solutes of perovskite precursor solution, the uniform nucleation of perovskite crystallites can occur instantly upon dripping of the solvent, and thereby the full-coverage films are readily obtained.[16] Along with the importance of a coverage, reducing the defects which act as traps and scattering centers is another critical issue to enhance a photoconversion efficiency.[18-23] Enlarging the grain size to lessen grain boundaries with the enhanced crystallinity of perovskites has been also considerably studied.[17,24-26]

Apart from the synthesis of well-structured morphology for photovoltaic applications, analyses to effectively figure out the quality of perovskites are crucial. Specifically, observing the nanostructures and electronic properties simultaneously is quite profitable, because it can suggest guidelines to improve the photovoltaic performances by directly matching the morphology and property.[27] Topography and photocurrent maps are obtained at the same time through conductive atomic force microscopy (cAFM), and the optoelectronic properties can be investigated on the micro- or even nanoscale.[28-30] For instance, by locating the conductive-probe tip on different positions, both photocurrent characteristics in specific area, like grain interiors or grain boundaries, and inhomogeneities of photocurrent in each grain can be examined. On the other hand, measurement and analysis of electrical noises can be also extensively utilized to study the reliability and defects of electronic devices like solar cells, field effect transistors, and light emitting diodes.[31-35] For example, noise spectroscopy can be used to evaluate the magnitude of the 1/f noise which can directly affect the quality of an electronic device.[34] Combined with a high-spatial-resolution electronic measurement method by cAFM, noise
spectroscopy can be an effective tool to characterize localized noise sources (or defects) in electronic channels.[35] However, despite its useful outcomes with a simple method, noise spectroscopy has not been widely used in the field of perovskite solar cells yet.

Herein, perovskites were deposited by toluene dripping on non-stoichiometric precursors. The synthesized perovskites appeared to have a larger average grain size and a higher crystallinity compared with those from stoichiometric solutions. Moreover, planar perovskite solar cells from non-stoichiometric precursors exhibited improved photovoltaic properties. To scrutinize the performance enhancement, main factors affecting the photocurrent were analyzed in detail via topography and photocurrent mappings through cAFM. Also, the reduction of intragrain defects for the perovskites from non-stoichiometric precursors was confirmed by noise spectroscopy.
2.2. Experimental Section

Device fabrication

Fluorine-doped tin oxide (FTO, TEC 8: Pilkington) glasses were cleaned in an ultrasonic bath by ethanol and deionized water, followed by O₂-plasma treatments for 3 min. To deposit a TiO₂ blocking layer of 50-nm thickness, 150 mM and 300 mM titanium diisopropoxide bis(acetylacetonate) in 1-butanol (75.0 wt. % in isopropanol) were sequentially spin-coated at 2500 rpm for 20 s, and annealed at 500°C for 30 min. The substrates were further treated with 40 mM titanium-chloride aqueous solutions at 70°C for 30 min, followed by annealing at 500°C for 30 min. For perovskites, precursor solutions were prepared with different PbI₂/CH₃NH₃I (PbI₂/MAI) molar ratios of 1:1 and 2:3 in n,n-dimethylformamide (DMF), and the nominal concentration of PbI₂ was fixed to 1.2 M. The solutions were spin-coated at 5000 rpm for 20 s, and 200 µL of toluene was dripped during the spin coating. Then, the films were annealed at 120°C for 50 min. To deposit hole transport layers, precursor solutions were prepared by mixing spiro-OMeTAD in chlorobenzene with tert-butylpyridine and lithium bis(trifluoromethylsulfonyl)imide salt in acetonitrile. The solutions were spin-coated at 4000 rpm for 40 s, and the samples were kept overnight in air for the oxidation. Finally, 150 nm of Au electrodes were deposited by a thermal evaporation.

Characterization

The morphology of the perovskite films was observed using a field-emission scanning electron microscope (FE-SEM, Merlin-Compact: Carl Zeiss), and the crystal structure was analyzed by x-ray diffraction (XRD, D8 Advance: Bruker). The absorbance was recorded by a UV-Vis spectrophotometer (Lambda 20: Perkin-Elmer). The
photoluminescence (PL) spectra were obtained using a spectrofluorometer (Photon Technology International, Inc.) at an excitation wavelength of 520 nm. The photocurrent-voltage (J-V) curves of the perovskite solar cells were obtained using a solar cell measurement system (K3000: McScience) under a solar simulator (Xenon lamp), with a reverse scan rate of 300 mV/s and an active area of 0.09 cm². The incident photon-to-current conversion efficiency (IPCE) spectra were measured using an IPCE measurement system (K3100: McScience). The topography and photocurrent mapping data were obtained utilizing cAFM (XE-70: Park System). A solid metal probe based on Pt (25Pt300B: Park System, spring constant of ~18 N/m with a diameter of ~10 nm) was used as a conductive AFM probe. To obtain reliable mapping data, the pixel sizes of cAFM images were set to be larger than the diameter of the probe tip. Using an AFM contact mode, the probe was directly contacted on the surface of a perovskite film to form a heterojunction solar cell structure of Pt-probe/perovskite/TiO₂/FTO, as described in Fig. 2(a). In the contact mode operation, the contact force between the AFM probe and the film surface was maintained as ~2 μN by a contact force feedback loop in the XE-70 AFM system. Using a power-adjustable light source (LS-F100HS: Seokwang Optical), a white light of ~80 mW/cm² was illuminated on the perovskite film to generate the photocurrents. Then, the photocurrents through the Pt probe were amplified by a low-noise preamplifier (SR570: Stanford Research Systems), and the amplified signals could be recorded along with the position of the AFM probe by the data acquisition system. By scanning the perovskite film surface with the Pt probe measuring the photocurrent, we could obtain the photocurrent map showing the distribution of local photocurrents on the perovskite film. For the scanning, the typical scan speed of the AFM was ~1 μm/s. In addition, when the AFM probe was at a specific location on the perovskite film, the power spectral densities
of the photocurrent through the probe could be measured via a fast Fourier transform (FFT) network analyzer (SR770: Stanford Research Systems) for noise analyses.
2.3. Results and Discussion

Perovskite films comprised of large grains and dense structures can be achieved via a precursor-composition control combined with the solvent engineering. Toluene dripping during spin coating is known to immediately induce uniform nucleation over the whole surface of substrates, due to the low solubility of precursor components in toluene, enabling dense and pinhole-free film morphology.[16] We have further investigated the effect of precursor composition (i.e., PbI$_2$/MAI ratio) employing the toluene dripping, and MAI-rich (non-stoichiometric) precursor resulted in the increase of grain size while maintaining the dense morphology (Fig. 2-1(a)).

Figure 2-1(b) exhibits the perovskite films obtained by using either stoichiometric or non-stoichiometric precursors with toluene dripping. In both of the perovskite films, perfect coverages were observed with relatively larger grain sizes for perovskites from the non-stoichiometric precursors. To examine the effect of stoichiometry thoroughly, the distributions of grain sizes were extracted from the SEM images. As a result, the average grain size (~1.5 µm) of the perovskite film obtained from the MAI-rich solution increased by a factor of three, compared to the film obtained from the stoichiometric solution (~530 nm), as shown in Fig. 2-1(c). The effect of grain enlargement was also ascertained from the red shift of the optical bandgap, estimated from the $\alpha^2$ vs. $h\nu$ plots of the films (Fig. 2-1(d)).[36] Moreover, less PbI$_2$ with a higher crystallinity was confirmed for the perovskites from non-stoichiometric precursors in the x-ray diffraction data Fig. 2-1(e). Blue-shifted PL peak for the perovskite film using a non-stoichiometric precursor was also observed (Fig. 2-2). With radiative recombination correlated to the PL data, peak shift to shorter wavelength suggests reduced trap states (band tails) in the high-quality perovskite.
In the case of non-stoichiometric precursors which have excess MAI, it was reported that the perovskite grains toward <001> direction are observed at the intermediate stage of annealing which are not found for the perovskites from stoichiometric precursors.[38,39] With further annealing, grains having <001> orientation disappeared, and the perovskite films were more oriented toward <110> direction. From the diffraction results, the crystal growth mechanism can be suggested as follows: at the initial stage of annealing, in the case of non-stoichiometric precursor solution, both <110> and <001>-oriented grains are nucleated simultaneously owing to the presence of excess MAI which may retard the crystallization kinetics, enabling the formation of less stable <001>-oriented grains. On the other hand, <110>-oriented grains are dominantly nucleated for the stoichiometric precursor case. Additional annealing leads to the grain growth of films, and grains toward <110> direction grow at the expense of the <001>-oriented grains in the perovskites from non-stoichiometric precursors for further coalescence than those from stoichiometric precursors, presumably due to the orientation-dependent interfacial energies of the perovskite material.[40]

Large grain perovskite films with a dense morphology can be produced by using non-stoichiometric precursors. Based on these high quality films, planar perovskite solar cells were fabricated using TiO₂ and spiro-OMeTAD as selective contacts. An enhanced photovoltaic performance of the solar cell based on the perovskite film produced using the non-stoichiometric precursor was clearly confirmed with the efficiency of 14.3% (Fig. 2-1(f) and Table 2-1), which was mainly due to the suppressed recombination by better crystallinity and reduced PbI₂ impurities. It is interesting that the thicknesses of the perovskite films were constant to ~370 nm regardless of the MAI amount (Figs. 2-1(f) and
2-3). The J-V curves with different scan rates exhibited almost similar shapes, and some photocurrent hysteresis (which is a general problem for the perovskite solar cells, especially in a planar structure using TiO$_2$ and spiro-OMeTAD as selective contacts) was observed (Fig. 2-4).[41]

Spectral responses were compared through IPCE which appeared almost identical for both solar cells (Fig. 2-5), with slightly higher integrated current for the non-stoichiometric precursor case. When the ratio of PbI$_2$/MAI further increased to 1:2, an incomplete perovskite coverage with many pinholes, causing shunting paths, resulted in poor cell performance (Fig. 2-6). The device from the 100°C-annealed perovskites (stoichiometric solutions) resulted in the lower photovoltaic efficiency (Figs. 2-7 and 2-8) owing to the extended grain boundary regions and inferior crystallinity compared with 120°C-annealed perovskites.
Fig. 2-1. (Color) Comparison of the perovskite films based on the stoichiometric or non-stoichiometric precursors. (a) Schematic for the effect of toluene dripping with different precursors. (b) SEM images of the perovskite films and (c) grain size distribution extracted from SEM. (d) UV-Vis absorption spectra. The inset shows a plot of $\alpha^2$ vs. $h\nu$ near the band edge. (e) X-ray diffraction patterns and (f) photocurrent-voltage ($J-V$) curves of the perovskite solar cells. The red dashed line represents the highest efficient cell, and the cross-sectional SEM image is shown for the perovskite solar cell from non-stoichiometric precursor.
Fig. 2-2. (Color) Photoluminescence (PL) spectra of the perovskite films based on the stoichiometric or non-stoichiometric precursors of PbI$_2$:MAI (deposited on the glass substrates).
Table 2-1. Photovoltaic parameters of the perovskite solar cells based on the stoichiometric or non-stoichiometric precursors. The data in the parentheses are from the highest efficient device by more than 9 cells in each condition.

<table>
<thead>
<tr>
<th>PbI₂:MAI</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>$V_{oc}$ (V)</th>
<th>$FF$</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>20.7 ± 0.9</td>
<td>0.88 ± 0.05</td>
<td>0.66 ± 0.03</td>
<td>12.1 ± 0.9</td>
</tr>
<tr>
<td></td>
<td>(20.0)</td>
<td>(0.94)</td>
<td>(0.70)</td>
<td>(13.2)</td>
</tr>
<tr>
<td>2:3</td>
<td>21.2 ± 0.3</td>
<td>0.90 ± 0.01</td>
<td>0.72 ± 0.02</td>
<td>13.7 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>(21.1)</td>
<td>(0.92)</td>
<td>(0.74)</td>
<td>(14.3)</td>
</tr>
</tbody>
</table>
Fig. 2-3. (Color) Cross-sectional SEM images of the perovskite solar cells from the 1:1 or 1:2 molar ratio of PbI$_2$:MAI precursor solutions.
Fig. 2-4. (Color) Photocurrent-voltage curves of the perovskite solar cells based on the non-stoichiometric precursor: (a) various scan rates, and (b) reverse and forward directions at 1000 mV/s.
Fig. 2-5. (Color) Incident photon-to-current conversion efficiency (IPCE) of the perovskite solar cells from the 1:1 or 2:3 molar ratio of PbI$_2$:MAI precursor. The abnormal increase of IPCE below ~450 nm arises from the instrumental factors.
Fig. 2-6. Perovskite films deposited from the 1:2 ratio of PbI$_2$:MAI precursor. (a) SEM image of the perovskite film. (b) Photocurrent-voltage curve of the perovskite solar cell.
Fig. 2-7. Perovskite films deposited from the 1:1 ratio of PbI₂:MAI precursor and annealed at 100°C for 20 min. (a) SEM image of the perovskite film. (b) Grain size distribution extracted from SEM.
Fig. 2-8.  (a) Photocurrent-voltage curve of the perovskite solar cell annealed at 100°C for 20 min for stoichiometric precursor solution. (b) X-ray diffraction of perovskite films with different annealing conditions. Annealing at a higher temperature for an improved grain size with enhanced crystallinity is correlated to the improved photovoltaic efficiency in spite of the presence of PbI$_2$ phase.
To investigate the microscopic origin of the performance enhancement, $c$AFM analyses were carried out. The perovskite samples were prepared with electron-selective contacts ($\text{TiO}_2$) as an underneath layer to maintain the morphology and quality of perovskite films used in $c$AFM measurement to be the same with those of solar cells, and topography and photocurrent maps were simultaneously obtained using the $c$AFM system. Figure 2-9(a) shows the schematic of the AFM measurement setup and the energy level diagram of the solar cell structure.[42] Details of the photocurrent mapping method are described in the characterization section. Photocurrent-voltage ($I$-$V$) curves were measured at grain interior regions, as shown in Fig. 2-9(b). Here, enhanced short-circuit current and open-circuit voltage were observed for the perovskite film produced using the non-stoichiometric precursors.
Fig. 2-9. (Color) (a) Schematic illustration of conductive AFM setup and energy level diagram. (b) Photocurrent-voltage (I-V) curves obtained using a conductive AFM at a grain interior.
In the topography images (Fig. 2-10(a)), the differences in grain sizes were confirmed again. The overall photocurrent level was larger for the 2:3 ratio than that for the 1:1 case, and more than twofold increase in the average photocurrent was observed, as shown in Fig. 2-10(b). For the in-depth study of the optoelectronic performance, the variation in the AFM-photocurrent data is reasonably categorized by three factors: (i) difference between grains and grain boundaries, (ii) the degree of nonuniformity inside grains, and (iii) grain to grain variation. We have sequentially validated these factors in order to figure out the main underlying mechanisms of the performance enhancement.

Firstly, when the topography and photocurrent signals were compared by overlapping the line profiles (Fig. 2-10(c)), there was not any evidence showing that the grain boundaries produce lower or higher photocurrents compared to the grain interior. Grain boundaries have been generally considered as a recombination center. Thus, it can be expected that photocurrents at the grain boundaries in cAFM images are lower than those at the grain interiors due to the higher density of defects. However, several researches have also addressed that band bending around grain boundaries, due to the interstitials and vacancies resulting divergence of polarity between grain boundary and grain interior, can favorably separate photogenerated carriers.[28,43,44] The effects of grain boundaries on the photocurrents act differently depending on each grain structure, composition, device structures, etc.[29,45] Also, current hysteresis at grain boundaries owing to the ion migration can affect the photocurrent in cAFM.[45] Such diverse causes can vary the photocurrent behavior at grain boundaries, and we have not found any consistent relationship between grain boundary and photocurrent in the synthesized perovskites. To rationally investigate the photocurrent at grain boundaries, further studies are needed.
Fig. 2-10. (Color) (a) Topography and (b) photocurrent maps at a short-circuit condition for the perovskite films based on the stoichiometric or non-stoichiometric precursors. (c) Heights and photocurrents are indicated along the white line. The pink dashed lines are for some representative positions of several selected grain boundaries.
Secondly, all the photocurrent data in the scanned area are plotted against the height of the topography map, and any correlation is not observed (Fig. 2-11(b)). Thus, the inhomogeneous distribution of the photocurrents cannot be attributed to the height effects (e.g., thickness inhomogeneities in grains). Finally, we statistically analyzed photocurrent as a function of grain size (Fig. 2-11(a)). The average value and standard deviation of photocurrents from all the grains were extracted by overlapping the topography and photocurrent maps. As a result, a linear relationship between photocurrent and grain size was confirmed in each perovskite film, indicating that the grain size works as the main factor for the photocurrent variation.
Fig. 2-11. (Color) Photocurrent dependence on (a) the grain size and (b) height of the perovskite films at a short-circuit condition.
The analysis of electrical noises is a powerful tool to evaluate the quality of electronic materials by a non-destructive manner.[31-35] The inset of Fig. 2-12 shows the time-domain measurement results of random-fluctuating photocurrents obtained for the 2:3 and 1:1 samples, while the AFM probe was at an average-sized grain interior in each sample. Note that the power spectral density (PSD) analysis is a powerful tool to characterize a random fluctuation of a value. Thus, the noise can be quantified by the PSD spectra \( S(f) \) in the frequency domain:

\[
S(f) = \lim_{T \to \infty} \left( \frac{1}{2T} \left| \int_{-T}^{T} X(t) e^{-\frac{2\pi i ft}{T}} dt \right|^2 \right)
\]

where \( X(t) \) is a fluctuating quantity of photocurrent against a zero mean value. It was reported that the noise \( S(f) \) spectra in many electronic materials can be described by Hooge’s relation[46-48]:

\[
S(f) = A \frac{I^2}{f}
\]

where \( A \) represents a noise amplitude, and the current-normalized PSD \( S/I^2 \) should be a useful parameter representing a level of the electrical noise in an electronic material.

The current-normalized noise PSD spectra for each perovskite film clearly exhibited the \( 1/f \) behavior (Fig. 2-12). Such \( 1/f \) noises in a perovskite film may originate mainly from the trapping and detrapping of charge carriers by multiple inhomogeneous defects with different trapping-time constants in the film.[34,35,49-52] (A single defect with a specific trapping-time constant generates a Lorentzian-shaped noise spectra.[48]) It was reported that defects in a perovskite film provide electronic states which can trap or release charge carriers in the film.[34] The random trapping and detrapping of the carriers
with characteristic lifetime will generate the fluctuation of the total number of mobile carriers in the film, resulting in the electrical noises. In this perspective, the measured noise PSD was the summation of noises generated by defects in a perovskite film. Therefore, the magnitude of \(1/f\) noise will presumably have a positive correlation with the density of defects, as previously reported in various semiconductor materials.[34,35,48]

Thus, the reduced magnitude of the \(1/f\) noise in the 2:3 sample reveals that the use of non-stoichiometric precursor not only enhances the grain growth but also diminishes the density of defects in grain interiors (i.e., improved crystallinity), as confirmed by SEM, optical absorption, diffraction, photocurrent in cAFM, and PL spectra, which in turn increases the photoconversion efficiency. The presence of PbI\(_2\) can also be one of the reasons increasing the magnitude of noise PSD for the perovskites using stoichiometric precursor. Since PbI\(_2\) is almost insulating, the grains containing PbI\(_2\) phase should exhibit negligible photocurrent in cAFM.[53,54] To reduce the effect of PbI\(_2\), we carefully chose the grains in photocurrent maps to have an average current value of average-sized grains for the noise spectroscopy. These statistical analyses indicate a strong relationship between the crystalline quality inside grain interiors (bulk effects) and photoconversion responses, rather than grain-boundary effects. Although various causes such as grains, interfaces, or device structures may affect the solar cell results as aforementioned, this novel research provides a clear message on the great importance of the crystallinity for the photoelectronic responses.
Fig. 2-12. (Color) Current-normalized power spectral densities ($S/I^2$) quantifying the noise magnitude of the perovskite films based on the stoichiometric or non-stoichiometric precursors at grain interiors. Average values (blue dots) from different grains with standard deviations are plotted. The dashed fitting lines exhibit the $1/f$ noise behavior, with the inset for the photocurrents as a function of time.
2.4. Conclusions

In this work, the quality of perovskite films, deposited using a second solvent dripping method, was improved by controlling the composition of precursor solutions. The perovskite films using MAI-rich solutions had a higher crystallinity and ~3 times larger grain sizes compared to that from stoichiometric solutions. The resulting perovskite films were adopted to the solar cells, and the cells exhibited enhanced photovoltaic parameters with the efficiency of 14.3%. Topography and photocurrent maps were compared to analyze the origin of the efficiency improvement. Grain boundaries or inhomogeneities of film thicknesses did not affect the disparity in photocurrents, but the grain size was found to be one of the main factors varying the photocurrents with a linear dependence. Moreover, we carried out noise analyses using a conductive probe at a grain interior. As a result, the lower degree of a noise level was observed for perovskites from the non-stoichiometric precursors indicating that less defective films were synthesized compared to those from stoichiometric precursors. From these consequences, we confirmed that the crystalline quality of grain interiors significantly influences the optoelectronic performance rather. Our approach with cAFM and noise spectroscopy can be a useful guideline for evaluating and quantifying a crystalline quality, eventually leading toward a high photovoltaic efficiency.
2.5. References


[39] Yu, H; Wang, F.; Xie, F.; Li, W.; Chen, J.; Zhao, N. The Role of Chlorine in the


Chapter 3.
Microstructural Evolution of Hybrid Perovskites Promoted by Chlorine and its Impact on the Performance of Solar Cell

3.1. Introduction

An organic-inorganic hybrid perovskite solar cell has emerged as a most promising photovoltaic among next-generation solar cells owing to their proper optical/electronic properties resulting in the photovoltaic efficiency over 23%, with low loss of open-circuit voltage and low-temperature processability reducing the production cost.[1-6] Particularly, the role of Cl in the perovskite solar cells has drawn tremendous attention in light of its intriguing and effective impacts on improving the device performance. The most common method of incorporating Cl into CH$_3$NH$_3$PbI$_3$ (MAPbI$_3$) is adding Cl-containing precursors such as PbCl$_2$ or MACl for the spin-coating process. However, the vast majority of Cl in the as-spun films is dissipated from the films during thermal annealing through sublimation and/or decomposition:[7-9] Cl which manages to remain in the final films is mainly observed at grain boundaries, and in the vicinity of the perovskite/TiO$_2$ interface in the case of n-i-p solar cells with TiO$_2$.[10-13] The maximum amount of Cl that can be incorporated into MAPbI$_3$ via conventional spin-coating process has been reported to be limited to < 4 at. % (chlorine vs. iodine) due to the substantial


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differences in ionic radii.[14] Despite the small amount present in the perovskite films, incorporation of Cl has been shown to significantly improve the performance of perovskite solar cells.[15]

Two major known benefits of the Cl incorporation are in improving the optoelectronic properties and microstructures of MAPbI$_3$. Cl has been demonstrated to passivate defects in surfaces, grain boundaries, and interfaces, therefore, suppressing parasitic nonradiative recombination.[16-20] For example, theoretical studies have shown that Cl present at the perovskite/TiO$_2$ interface reduces deep-level defects by substituting Pb-I antisites with Pb-Cl antisites which have higher formation energy with shallower level.[19] In terms of the microstructural modification, Cl significantly influences the formation process of perovskite films. Changes in the chemistry of Pb-halide ionic complexes and colloids with PbCl$_2$ or MACl precursor has been shown to enable high coverage of perovskite films.[21-22] Additionally, intermediate phases containing Cl, which eventually transform into MAPbI$_3$ upon thermal annealing, slow down the reaction kinetics contributing to the enhanced coverage.[7,23,24] After thermal annealing, large lateral grain size exceeding ~1 μm is frequently accompanied with high <110>-preferred orientation in MAPbI$_3$(Cl) films regardless of the Cl source.[25-29] Although it has been well known that Cl develops large grains in the perovskite films, a mechanistic study revealing the detailed roles of Cl in the film growth kinetics and the correlation between enhanced grain size, crystallinity and concentration of Cl in the film still lacks.

Herein, we demonstrate the mechanisms of large grain growth in MAPbI$_3$(Cl) films synthesized with excess-MACl containing precursors. Apparent correlation between the changes in preferred orientation, distribution of grain size, and the amount of
remaining Cl in the films is observed elucidating the effect of Cl on the formation processes. At the initial stage of annealing with Cl in the films, <110>- and <001>-oriented grains grow faster than other grains. Extended annealing time causes dissipation of Cl, and <001> grains become unstable while <110> grains continuously grow. As a result, grains much larger than—by an order of magnitude—those from stoichiometric precursors are obtained with an average grain size exceeding 2 μm and highly <110>-preferred orientation. Due to the improved texture and diminished deep trap density, the fill factor of solar cells reached over 80%. We expect that these findings will provide further guidance on how to control the morphology and grain orientation of perovskite films with Cl.
3.2. Experimental Section

Device Fabrication

Unless stated otherwise, all chemicals were purchased from Sigma-Aldrich. Fluorine-doped tin oxide (FTO, TEC 8: Pilkington) glasses were ultrasonically cleaned in acetone, ethanol, and deionized water, followed by UV-ozone treatments for 15 min. For TiO$_2$ blocking layer, 0.25 M titanium isopropoxide and 0.44 M acetic acid (DAEJUNG) in ethanol was spin-coated at 3000 rpm for 30s, and annealed at 500°C for 30 min. The substrates were dipped in 40 mM TiCl$_4$ aqueous solutions at 70°C for 30 min, followed by annealing at 500°C for 30 min. The precursor solutions for the perovskites were prepared with 1.4 M of equimolar PbI$_2$ (TCI) and CH$_3$NH$_3$I (Greatcell Solar) in $N,N$-dimethylformamide (DMF), and 0.2, 0.4, or 0.6 molar ratio of CH$_3$NH$_3$Cl relative to CH$_3$NH$_3$I was introduced as an additive. The solutions were deposited onto the substrates by spin coating at 5000 rpm for 20 s, and 300 µL of chlorobenzene was dripped at 5 s into the spinning process. Then, the films were annealed at 120°C for 10 min. The hole transporting layers were deposited by spin-coating at 3000 rpm for 45 s using the precursor solutions prepared by mixing 72.3 mg/ml spiro-OMeTAD (Lumtec) in chlorobenzene with 28.8 µL of 4-tert-butylypyridine, a 17.5 µL of lithium bis(trifluoromethylsulfonyl)imide (Li-TFSI) solution (520 mg/ml in acetonitrile), and a 21.9 µL of Co(II)-TFSI (Lumtec) solution (300 mg/ml in acetonitrile). Finally, 150 nm-thick Au electrodes were deposited by thermal evaporation.

Characterization

The crystal structure and texture of perovskite films were analyzed by x-ray diffraction (XRD) in $\theta$-$2\theta$ scan mode (D8 Advance: Bruker) and rocking curve mode.
(X’Pert Pro MRD: PANalytical). For chemical analysis of the perovskite films, wavelength-dispersive x-ray fluorescence (WDXRF, XRF-1800: Shimadzu) using Rh Ka as x-ray source (20.216 keV) with analyzing single crystals of LiF (200) and Ge (111) was carried out. The morphologies of the perovskite films were observed using a field-emission scanning electron microscope (FE-SEM, Merlin-Compact: Carl Zeiss). The absorptance was measured by a UV-Vis spectrophotometer (V-770: JASCO). Steady-state and time-resolved photoluminescence spectra (LabRAM HV Evolution: Horiba, FluoTime 300: Picoquant) were obtained with excitation wavelength of 532 and 398 nm, respectively. The films were prepared on glass substrates with the incident light direction on the perovskite surface. The photocurrent-voltage (J-V) characteristics of the solar cells were obtained using a solar simulator (K3000: McScience, AM 1.5G, 100 mW/cm²), with an active area of 0.09 cm² and 100-mV/s voltage scan rate. The external quantum efficiency (EQE) spectra of the solar cells were measured by an incident photon-to-current conversion efficiency (IPCE) measurement system (K3100: McScience). Impedance analysis in dark condition was carried out using a potentiostat (Zive SP1: WonATech CO., Ltd.) to obtain frequency dependent capacitances with 10-mV amplitude of ac signal at zero applied bias and frequency ranging from 0.01 to 10⁵ Hz.
3.3. Results and Discussion

The perovskite films are spin-coated with the antisolvent dripping method to ensure uniform coverage.[2,30] In the case of perovskite with stoichiometric precursor, intensities of all of the perovskite peaks are enhanced with annealing, and minor PbI\(_2\) peak appears at 12.7° after annealing for 180 s indicating partial thermal decomposition of the perovskite, as shown in the log-scale diffraction patterns of Fig. 3-1(a). With the 40-mol.-% MACl additive, peaks from MAPbCl\(_3\) at 15.5° and 31.4°, and from intermediate phase related to the excessive Cl at around 12.0° and 16.0° are observed.[7,24,31,32] The intensities of these peaks increase with annealing for 60 s, weaken at 180 s, and eventually disappear after 600 s. As far as peaks from MAPbI\(_3\) are concerned, the as-deposited perovskite with MACl-containing precursor exhibits almost identical patterns with the perovskite from the stoichiometric precursor, except slightly higher <110>-preferred orientation with intermediate phases (Fig. 3-2). After annealing for 600 s, however, the degree of preferred orientation is significantly altered compared to the non-annealed films. As shown in Fig. 3-1(b), integrated intensity of (220) peak of the 600-s annealed perovskite using MACl-containing precursor enhances by 50 times compared to the as-deposited film, while intensity enhancement by annealing is much weaker for the perovskite with stoichiometric precursor (only ~5 times increase). Especially, the intensity mainly rises during the first 30 s of annealing. In addition, the integrated intensity of (211) peak based on the stoichiometric precursor increases during annealing with similar tendency to (220) peak, while it gradually reduces and eventually disappears in the perovskite with the MACl precursor. This intensity weakening by annealing occurs in other MAPbI\(_3\) peaks in a similar manner except <110> and <001> peaks. The intensity of (004) peak, which is
hardly observed from the stoichiometric-precursor-based perovskite, increases during the first 60 s of annealing in the perovskite with MACl-containing precursor. However, further annealing beyond 180 s reduces the (004) peak intensity while (110) peak intensity intensifies.

It has been reported that excess MACl in the as-spun state of a perovskite film dissipates during annealing by sublimation or via decomposition into CH$_3$NH$_2$ and HCl.[7,8] While Pb $L\beta_1$ peak intensity remains nearly constant with annealing (Fig. 3-3), the intensity of Cl $Ka$ gradually decreases and becomes below the noise level after 600 s, as confirmed by the XRF spectra vs. annealing time in Fig. 3-1(c). It is noted that the large reduction of Cl after 180 s is accompanied by the weakening of XRD intensities of the intermediate phase and MAPbCl$_3$ phase (see Fig. 3-1(a)), which suggests that the main source of Cl signal is the intermediate phase or MAPbCl$_3$. Also, there are correlations between the integrated intensity of MAPbI$_3$ in XRD ((220) and (004) peaks) and the remaining amount of Cl. With the reduction of Cl, growth of (220) peak intensity is slowed down, and the (004) peak becomes negligible after 600 s.
Fig. 3-1. (Color) Grain orientations and remaining Cl with different annealing times at 120°C. (a) X-ray diffraction, (b) relative integrated intensities of (220), (004), and (211) peaks, and (c) XRF spectra of Cl from the perovskite films. Precursor compositions are PbI$_2$:MAI:MACl = 1:1:0.4 (40 mol. % MACl) or PbI$_2$:MAI:MACl = 1:1:0 (0 mol. % MACl).
Fig. 3-2. X-ray diffraction of perovskite films without annealing. Perovskites based on the MACl-containing precursor (40 mol. % MACl) and stoichiometric precursor (0 mol. % MACl).
Fig. 3-3. (Color) XRF spectra of Pb with different annealing times at 120°C. Perovskite films with MACl-containing precursor (40 mol. % MACl) and stoichiometric precursor (0 mol. % MACl).
The effects of annealing on the grain growth are significantly different depending on the precursor composition, as shown in SEM (Figs. 3-4(a) and (b)). For the as-deposited films, both perovskites exhibit similar grain sizes of ~50 nm (Fig. 3-5). In the case of perovskite from the stoichiometric precursor, an average grain size of ~300 nm is achieved after 180-s annealing (Figs. 3-4(c) and 3-5). The lateral grain size less than film thickness (~450 nm) may result from the Zenner pinning induced by PbI₂ located at the grain boundary, formed after 180 s of annealing from the thermal decomposition of perovskite. However, the PbI₂ cannot be observed in the SEM images of perovskite until annealing for 600 s, presumably due to its small size. When annealing was prolonged up to 30 min, preferential formation of PbI₂ particles at the grain boundaries is clearly observed: PbI₂ particles appear as bright dots in the SEM image owing to the insulating nature (Fig. 3-6).

The grain growth rate of perovskite based on the MACl-containing precursor is significantly enhanced compared to the stoichiometric case (Fig. 3-4(d)). During the first 30 s of annealing, average grain size increases from 50 nm to 700 nm. When we compare the average grain size with the integrated intensity in Fig. 3-1(b), increase in the grain size for 60 s accompanies the intensified (220) and (004) peaks while other randomly oriented peaks such as (211) diminish. Therefore, the augmentation of the average grain size can be mainly attributed to the growth of <110> and <001> grains. The faster growth kinetics of <110> and <001> grains in the presence of Cl may be explained by a recent computational study which showed that Cl at the MAPbI₃/TiO₂ interface reinforces the binding of (110) and (001) planes of MAPbI₃ with TiO₂.[33] During annealing from 60 to 180 s, Cl is largely dissipated as evident from XRF in Fig. 3-1(c) with further increase in (220) and reduction of (004) peak in XRD. However, grain growth rate is still faster.
than the stoichiometric-precursor perovskite, and eventually slows down after 180 s annealing (Fig. 3-5). After annealing for 600 s, the final average grain size reaches ~2 μm which is much improved compared to the perovskite with stoichiometric precursor.

Combing XRD, XRF, and SEM data, microstructural evolution of the perovskite from MACl-containing precursor is schematically illustrated in Fig. 3-7. A high density of nuclei is formed by the antisolvent dripping. During the first 30 s of annealing, the growth rates of <110>- and <001>-oriented grains are faster than other orientations. During the continued annealing for 60 s, <110> and <001> grains continue to grow until they are in contact with each other. Further annealing leads to the reduction of Cl content in the film, and <110> grains further grow over the 2-μm grain size at the expense of neighboring random and <001> grains.
Fig. 3-4. Grain size analyses. Evolution of grains in the perovskite films (by SEM) for (a) stoichiometric precursor (0 mol. % MACl) and (b) MACl-containing precursor (40 mol. % MACl) with different annealing times. (c,d) Distributions of grain sizes for the perovskites with fitting lines. Grain sizes without annealing are plotted in Fig. 3-5.
Fig. 3-5  Grain sizes of perovskite films with different annealing times.  (a) Distributions of grain sizes without annealing and (b) average grain sizes of the perovskites based on the MACI-containing precursor (40 mol. % MACI) and stoichiometric precursor (0 mol. % MACI).
Fig. 3-6  Formation of PbI$_2$ in the perovskite films.  X-ray diffraction and SEM image of a perovskite with a stoichiometric precursor annealed at 120°C for 30 min. PbI$_2$ particles (bright region due to insulating nature) are formed at the grain boundaries.
Fig. 3-7  (Color) Schematic diagram for the microstructural evolution of perovskite films with MACl-containing precursor.
Evolution of structural and chemical properties of the perovskite from the 20-mol.-% MACl-containing precursor is presented in Fig. 3-8. The evolution of the grain-size distribution and orientation is qualitatively similar to the case of 40-mol.-% MACl, with a relatively faster evolution. MAPbCl$_3$ and intermediate phase are observed up to 60-s annealing and disappear after 180 s from XRD. The intensities of (220) and (004) peaks of MAPbI$_3$ significantly increase during the first 30 s of annealing accompanied by the rapid grain growth as can be seen from the SEM images. On the other hand, the intensity of (004) peak decreases after 60 s, and finally disappears after 180 s. XRF spectra exhibits reduced intensity of Cl Kα with the prolonged annealing and negligible signal after 180-s annealing, which is consistent with the dissipation of Cl-related phase from XRD. In addition, disappearance of (004) peak with complete loss of Cl in the film is analogous to the case of 40-mol.-% MACl. These results reveal that rapid texturing of <110>- and <001>-oriented grains in the presence of Cl followed by the growth of <110>-oriented grains, at the expense of <001>-oriented grains once Cl is dissipated.
Fig. 3-8 Evolution of structural and chemical properties of perovskite films (20-mol.-% MACl) with annealing time. (a) Grain growth (by SEM), (b) grain-size distribution with fitting lines, (c) x-ray diffraction, and (d,e) XRF spectra of Pb and Cl, respectively, for the perovskite films with different annealing time at 120°C.
The larger amount of MACl in the precursor has induced larger grain size, as shown in Fig. 3-9(a) after 600-s annealing. While light absorption characteristics do not change much by the MACl content (Fig. 3-9(b)), the <110>-peak intensity is the highest with the addition of 40% MACl to the precursor solutions (Fig. 3-9(c)). From ω scans of perovskite (110) plane, both the intensity and full-width at half maximum (FWHM) improve with the increasing MACl content (Figs. 3-9(d) and (e)), again confirming the enhanced <110> texture of the perovskite films. In addition, steady-state and time-resolved PL spectra of the perovskite from differing amount of Cl in the precursor solutions are compared in Fig. 3-10. With the addition of MACl, the emission peaks of perovskites shift to shorter wavelength suggesting the reduced trap states (band tails). Time-resolved PL spectra are fitted to a bi-exponential decay curve, and the extracted fast ($\tau_1$) and slow ($\tau_2$) decay components are listed in Fig. 3-10. The lifetimes improve with the increasing MACl contents in the precursor supporting the suppression of defect-mediated nonradiative recombination. The enhanced PL characteristics can be attributed to the reduced grain boundaries and enhanced <110> texture of perovskite films.[16] While 60-mol.-% MACl makes grain sizes over 3 µm, the coverage of a perovskite film is only ~90%, and therefore these results are not included here.
Fig. 3-9  (Color) Effects of MACl concentration on the morphology, light absorption, and texture of the perovskite films.  (a) Grain sizes by SEM and (b) absorptance spectra.  X-ray diffraction with (c) $\theta$ - 2$\theta$ scan, (d) $\omega$ scan for the (110)-plane rocking, and (e) FWHM of rocking curves from (d).  All the films are annealed at 120°C for 600 s.
Fig. 3-10 (Color) Photoluminescence (PL) properties of the perovskite films. (a) Steady-state PL spectra. Purple arrow indicates blue shift of emission peaks with increasing MACl contents in the precursors. (b) Time-resolved PL spectra with bi-exponential decay fitting (solid lines). Fast ($\tau_1$) and slow ($\tau_2$) components are listed in the inset.
Figure 3-11(a) exhibits $J$-$V$ characteristics of the perovskite solar cells (with the detailed photovoltaic parameters in Table 3-1). Addition of 20-mol.-% MACl largely improves the short-circuit current ($J_{sc}$) and fill factor ($FF$), and the best photovoltaic efficiency of $\eta = 17.7\%$ with a $FF$ of 81% is achieved. In the case of 40-mol.-% MACl, $V_{oc}$ and $FF$ decrease while $J_{sc}$ is similar to those of the 20-mol.-% MACl. Series and shunt resistances are extracted by fitting the light $J$-$V$ curves to the ideal one-diode model (Fig. 3-12).[34,35] Series resistance from the 20-mol.-% MACl cell is much better (0.5 Ω·cm$^2$) than that of the stoichiometric-precursor-based cell (1.7 Ω·cm$^2$). A cross-sectional SEM image exhibits that horizontal grain boundaries are hardly observed from the 20-mol.-% MACl solar cell, and the shunt resistance is the highest which we attribute to the large grains without pin-holes (Fig. 3-13).[36,37] More MACl induces incomplete perovskite coverage, thereby reducing the shunt resistance. In addition to the enhanced photovoltaic efficiency, $J$-$V$ hysteresis is improved by incorporating MACl, presumably due to the suppressed defects and ion migration in the synthesized perovskites with the electron/hole transport layers (Table 3-1).[38,39] Furthermore, stabilized power outputs for the cells based on MACl-containing precursors exhibit similar values to their average efficiency of reverse and forward scans in the $J$-$V$ curve with relatively stable output during the measurement, while the solar cell from the stoichiometric precursor shows poor stability (Fig. 3-14). EQE of the perovskite solar cells based on various concentrations of MACl clearly show different spectral responses (Fig. 3-11(b)), and the integrated current of each spectra matches well to the observed $J_{sc}$. EQE of solar cells with 20-mol.-% MACl is higher compared to that of the stoichiometric perovskite cell for the entire wavelength range. It is noted that annealing time shorter than 10 min yield poorer efficiency probably due to the smaller grain size and presence of the intermediate phase which may prevent
carrier transport (Fig. 3-15). With the larger amount of MACl, the solar cells become more stable in air due to the reduced grain boundary, which is suggested to be the main degradation routes to react with H₂O and O₂ (Fig. 3-16).[40,41] The efficiencies of solar cells based on the MACl-containing precursors maintain over 90% of their initial values after 20 days exhibiting stable device performance.

To quantify the trap density in the perovskite solar cells, impedance spectroscopy measurements are carried out. By analyzing the frequency dependent capacitances $[C(\omega) = \text{Real} \{i\omega Z(\omega)^{-1}\}]$, trap levels with respect to the valence-band maximum and trap density can be extracted.[42] As shown in Fig. 3-11(c), the capacitance plot exhibits similar high frequency plateau irrespective of the MACl contents and different rising level in the frequency region dependent on the amount of MACl. The rate of capture and emission of charge carriers by trap states depends on the level of the trap states with respect to the band edge, and charging/discharging of these trap states contributes to measured capacitance. Only shallow traps, which have been shown to reside in the bulk of perovskite,[43,44] respond to high-frequency modulation, and deep traps at interfaces or grain boundaries can be responsible at relatively low frequency resulting in the capacitance rise. Figure 3-11(d) compares distributions of the trap density of state extracted using the derivative of the capacitance with respect to the frequency:

$$N_t = -\frac{V_{bi} dC}{qW d\omega k_B T} \frac{\omega}{\omega}$$

(1)

where $V_{bi}$ is the built-in potential, $q$ is the elementary charge, $W$ is the depletion width, $\omega$ is the angular frequency, $k_B$ is the Boltzmann constant, and $T$ is temperature.[42,45] The built-in potentials are obtained from the Mott-Schottky plots (Fig. 3-17), and
perovskites are assumed to be fully depleted and hence are considered as an intrinsic layer. \[46\] The applied angular frequency is related to a trap level with respect to the valence-band maximum \((E_\omega)\):

\[
E_\omega = k_B T \ln \left( \frac{\omega_0}{\omega} \right)
\]  

(2)

where \(\omega_0\) is an attempt-to-escape frequency, and assumed to be \(\sim 10^{11} \text{ s}^{-1}\).\[46,47\]

The integrated defect densities of MACl-containing cells (20 mol. %: \(1.83 \times 10^{18} \text{ cm}^{-3}\), 40 mol. %: \(1.75 \times 10^{18} \text{ cm}^{-3}\)) reduce by \(\sim 10\%\) compared to that of a stoichiometric-precursor-based perovskite cell \((2.08 \times 10^{18} \text{ cm}^{-3})\). These defect reduction can be attributed to the improved grain boundaries and interfaces where deep-level defects like Pb-I antisites are segregated in the perovskite film,\[48,49\] and eventually results in the enhanced photovoltaic performances.
Fig. 3-11 (Color) Solar-cell performance and trap-density characterization.  (a) $J-V$ curves at both reverse and forward voltage scans. The blue dashed line represents the highest efficient cell. (b) Incident photon-to-current conversion efficiency (IPCE). (c) Frequency dependent capacitances ($C(\omega) = \text{Real} \left[ \left\{ i\omega Z(\omega) \right\}^{-1} \right]$) obtained from the impedance analysis. (d) Trap density of states as a function of trap level with respect to the valance-band maximum, from Eqs. (1) and (2). The dashed lines denote Gaussian fitting for the calculation of traps per volume ($n_t$). All the perovskite films are annealed at 120°C for 600 s.
<table>
<thead>
<tr>
<th>Sample</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>$FF$</th>
<th>$\eta$ (%)</th>
<th>$HI$ ($1 - \eta_{FOR}/\eta_{REV}$)</th>
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<tr>
<td>0 mol. % MACl (REV)</td>
<td>20.3 ± 1.1 (21.4)</td>
<td>0.98 ± 0.03 (1.03)</td>
<td>0.69 ± 0.05 (0.76)</td>
<td>13.8 ± 2.1 (16.7)</td>
<td>0.21</td>
</tr>
<tr>
<td>0 mol. % MACl (FOR)</td>
<td>20.4 ± 1.1 (21.3)</td>
<td>0.88 ± 0.06 (0.92)</td>
<td>0.60 ± 0.09 (0.66)</td>
<td>10.9 ± 2.6 (13.0)</td>
<td></td>
</tr>
<tr>
<td>20 mol. % MACl (REV)</td>
<td>21.3 ± 0.5 (21.3)</td>
<td>1.01 ± 0.02 (1.02)</td>
<td>0.77 ± 0.04 (0.81)</td>
<td>16.6 ± 1.0 (17.7)</td>
<td>0.05</td>
</tr>
<tr>
<td>20 mol. % MACl (FOR)</td>
<td>21.3 ± 0.5 (20.9)</td>
<td>0.97 ± 0.04 (1.01)</td>
<td>0.76 ± 0.04 (0.81)</td>
<td>15.7 ± 1.4 (17.1)</td>
<td></td>
</tr>
<tr>
<td>40 mol. % MACl (REV)</td>
<td>21.4 ± 0.6 (21.5)</td>
<td>0.96 ± 0.02 (1.01)</td>
<td>0.72 ± 0.04 (0.79)</td>
<td>14.9 ± 1.1 (17.1)</td>
<td>0.03</td>
</tr>
<tr>
<td>40 mol. % MACl (FOR)</td>
<td>21.6 ± 0.5 (21.8)</td>
<td>0.92 ± 0.03 (0.99)</td>
<td>0.72 ± 0.04 (0.79)</td>
<td>14.4 ± 1.2 (17.0)</td>
<td></td>
</tr>
</tbody>
</table>

Table 3-1. Photovoltaic parameters of the solar cells (more than 11 cells). Perovskites based on the various ratios of MACl to MAPbI$_3$ in precursors. The data in the parentheses are from the highest efficient devices. $HI$, $\eta_{REV}$, and $\eta_{FOR}$, are the hysteresis index, average photovoltaic efficiencies at reverse and forward scans, respectively.
Fig. 3-12  Series resistance ($R_{series}$) and shunt resistance ($R_{shunt}$) of the solar cells. The results are obtained by fitting the $J$-$V$ curves with an ideal one-diode model.
Fig. 3-13. Cross-section images of perovskite cells (SEM).
Fig. 3-14. Stabilized power outputs of the perovskite solar cells. The power conversion efficiencies were measured with applied bias voltage at the maximum power point for each device (0-mol.% MACl: 0.70 V, 20-mol.% MACl: 0.82 V, and 40-mol.% MACl: 0.80 V).
Fig. 3-15. Solar cell performance with different annealing times at 120°C. $J–V$ curves at both reverse and forward voltage scans with tables of the average photovoltaic parameters from more than 3 cells.
Fig. 3-16. Stability test of the perovskite solar cells in air. The devices without encapsulation were stored in ambient air under dark condition (25°C and relative humidity < 20%). The power conversion efficiencies were extracted from the $J-V$ curves with reverse scans.
Fig. 3-17. Mott-Schottky plots of perovskite solar cells with various MACl concentration. The built-in potentials were extracted from the dashed fitting lines. The measurements were carried out under dark condition with 10-mV amplitude at 5 kHz.
3.4. Conclusions

In this work, it is shown that inclusion of Cl in the precursor solutions leads to large grain size. At the initial stage of annealing when a large amount of Cl remained, <110>- and <001>-oriented grains grew faster than others. With further annealing which reduced the Cl content, <110> grains were further coarsened at the expense of intermediate phase and other perovskite grains. Grain size over 2 \( \mu \)m, almost an order of magnitude larger than the case of stoichiometric precursor, was achieved. In addition, texturing of the perovskite films was enhanced with the increased MACl, as evident from the narrowing of rocking curves. Applications of the perovskites with the optimized concentration of MACl in the precursor solutions to the light absorber improved resistance of the devices resulting in a fill factor over 80%. Deep trap density was reduced from \( 2.08 \times 10^{18} \text{ cm}^{-3} \) (no Cl) to \( 1.83 \times 10^{18} \text{ cm}^{-3} \) (with Cl). Our study elucidates correlation between commonly reported <110>-preferred orientation and large grain sizes with Cl in the films, which will further help with better microstructural design of the perovskites.
3.5. References


138, 5028–5035.


[37] Kim, D. U.; Hangarter, C. M.; Debnath, R.; Ha, J. Y.; Beauchamp, C. R.; Widstrom,


[48] Shan, W.; Saidi, W. A. Segregation of Native Defects to the Grain Boundaries in

Chapter 4.

Aminosilane-Modified CuGaO$_2$ Nanoparticles Incorporated with CuSCN as a Hole-Transport Layer for Efficient and Stable Perovskite Solar Cells

4.1. Introduction

The record power conversion efficiency (PCE) of a perovskite solar cell has now surpassed those of other single-junction thin film solar cells such as CdTe and Cu(In,Ga)Se$_2$, approaching closer to the Shockley-Queisser theoretical limit owing to its superior physical properties.[1-6] However, one of the remaining challenges for commercializing the perovskite solar cells is relatively poor long-term stability.[7-10] Perovskite films tend to degrade into a hydrate form in humid atmosphere, and decompose into PbI$_2$ in the presence of oxygen under illumination via the reaction with superoxide.[11-13] Many strategies have been proposed to mitigate the intrinsic degradation of perovskite films, and they include augmentation of grain size and alloying of cations with Cs or Rb and anions with Br.[14-17] Another approach involves encapsulation of the devices that prevents O$_2$ and H$_2$O in the atmosphere from interacting with the perovskite films. However, thermal stress, which is one of main factors affecting stability, is still an issue even for well-encapsulated devices. Not only does thermal stress degrade perovskite films, but it can also damage 2,2’,7,7’-tetrakis- (N,N-di-4-methoxyphenylamino)-9,9’-spirobifluorene (spiro-OMeTAD), one of the most common hole-transport layers (HTLs) used in high performing perovskite solar cells.[18-21] To improve the electrical conductivity of spiro-OMeTAD, it is common to incorporate dopant additives such as lithium.
bis(trifluoromethanesulfonyl)imide (Li-TFSI) and 4-tert-butylpyridine (TBP) to spiro-OMeTAD. When a doped spiro-OMeTAD layer is subjected to a temperature above 85°C, pin-holes begin to form in the film, leading to the deterioration of device performance.[19-21] As a remedy, polymer-modified spiro-OMeTAD has recently been introduced and demonstrated some success in improving the long-term thermal stability.[22] Still, the use of costly organic hole-transport materials is ultimately not desirable for the commercialization.[23-25]

Intrinsic thermal instability of organic charge-transport layers leads to serious research efforts on the inorganic HTLs.[26-34] Among the potential candidates as an inorganic HTL, CuSCN is an attractive choice because it is cheap and solution-processible with solvents such as diethyl sulfide and dipropyl sulfide.[24,25,30,34] Although the thermal stability of a CuSCN layer itself is excellent, it is known to react with the underlying perovskite to form PbI\(_2\) and CuI impurities when the layers are subjected to a temperature above 85°C.[34] In order to reduce the interfacial reaction between CuSCN HTL and a perovskite layer, Snaith et al. have inserted a mesoporous layer of Al\(_2\)O\(_3\) nanoparticles before the CuSCN deposition and have demonstrated improved thermal stability of the devices.[34] However, insulating Al\(_2\)O\(_3\) can impede hole extraction to HTL from the perovskite, giving rise to the reduction of the photovoltaic performance. It is then expected that a thin layer of conductive metal oxide in place of the Al\(_2\)O\(_3\) will improve thermal stability without sacrificing PCE. One of the promising candidates for the conductive metal oxide layer is CuGaO\(_2\) because it has a high mobility (~0.1 cm\(^2\) V\(^{-1}\) s\(^{-1}\)) and favorable valence-band maximum (~5.3 eV vs. vacuum level) to form a junction with perovskite.[35] Deposition of CuGaO\(_2\) thin films by vacuum process such as sputter or pulsed laser deposition (PLD) at a temperature below 500°C results in Cu\(_2\)O or CuGa\(_2\)O\(_4\).
impurities.[36,37] On the other hand, spin-coating a suspension of pre-synthesized CuGaO$_2$ nanoparticles in a solvent is a facile method to deposit phase-pure thin films. However, preparing a uniform CuGaO$_2$ film with a full coverage by solution-process is difficult due to the agglomeration of CuGaO$_2$ nanoparticles in suspension.

Herein, CuGaO$_2$ nanoparticles are used for the HTL with CuSCN in $n$-$i$-$p$ structured cells to enhance both PCE and thermal stability. The surface of CuGaO$_2$ nanoparticles is modified by (3-aminopropyl)triethoxysilane (APTES) to reduce the agglomeration of nanoparticles, resulting in a substantial improvement in the uniformity of nanoparticle films. Compared to the HTL consisting of only CuSCN or CuGaO$_2$, a CuGaO$_2$/CuSCN HTL stack exhibits more efficient carrier extraction. Also, trap density of the solar cell using CuGaO$_2$ with CuSCN is reduced by ~40% compared to the reference with only CuSCN, leading to the enhanced PCE. Moreover, an excellent thermal stability of the perovskite solar cells is demonstrated: ~80% of the initial PCE retention after 400 h under 85°C/85% relative humidity (RH) condition (encapsulated).
4.2. Experimental Section

Synthesis of CuGaO$_2$ Nanoparticles and APTES Treatment

7 g of P123 (Sigma-Aldrich) was dissolved in 140 ml of DI water by stirring for 4 h at room temperature (RT). Then 2 mmol of Cu(NO$_3$)$_2$·2.5H$_2$O (Alfa Aesar) and Ga(NO$_3$)$_3$·xH$_2$O (Alfa Aesar), 4 ml of ethylene glycol (Alfa Aesar), and 4.5 ml of 1 M KOH aqueous solution (Daejung) were added sequentially during vigorous stirring. After the solution was stirred for 1 h, the precursor was transferred to 200 ml Teflon-lined stainless-steel autoclave. The sealed autoclave was placed in a preheated oven at 220°C for 4 h, then cooled under water flow. The synthesized particles were centrifuged and washed with diluted ammonia solution (5 wt. %), diluted nitric acid (5 wt. %), and DI water for 2 times, respectively. Then, the particles were additionally washed with ethyl alcohol for 3 times and isopropyl alcohol (IPA) for 5 times. For surface modification, 1 vol. % of (3-aminopropyl)triethoxysilane (APTES, Sigma-Aldrich) was added to the CuGaO$_2$ suspension in IPA (10 mg ml$^{-1}$), and stirred for 3 h at 30°C. After the reaction, the suspension was ultrasonically treated for 2 min, and washed with IPA for 3 times to remove any physically adsorbed APTES.

Device Fabrication

ITO glasses were ultrasonically cleaned in acetone, ethanol, and deionized water, followed by a UV-ozone treatment for 15 min. For SnO$_2$ electron-transport layer, 15 wt. % SnO$_2$ aqueous solution (Alfa Aesar) was diluted in DI water with the volume ratio of 1:4. The solution was spin-coated at 3000 rpm for 30 s, and annealed at 120°C for 30 min. The 1.3 M precursor solution for the Cs$_{0.05}$(FA$_{0.83}$MA$_{0.17}$)$_{0.95}$Pb(I$_{0.83}$Br$_{0.17}$)$_3$ perovskite was
prepared by dissolving cesium iodide (CsI, TCI Chemicals), formamidinium iodide (FAI, Greatcell Solar), methylammonium bromide (MABr, Greatcell Solar), lead iodide (PbI₂, TCI Chemicals), and lead bromide (PbBr₂, TCI Chemicals) in a mixture of N,N-dimethylformamide (DMF, Sigma-Aldrich) and dimethyl sulfoxide (DMSO, Sigma-Aldrich) with the volume ratio of 4:1. The solution was deposited onto the substrate by spin-coating at 5000 rpm for 20 s, and 300 µL of chlorobenzene was dripped at 17 s during the spinning process. Then, the film was annealed at 100°C for 45 min. For the CuGaO₂ hole-transport layers, CuGaO₂ suspension in IPA (20 mg ml⁻¹) was used for spin-coating at 3000 rpm for 30 s. The spin-coating was conducted for 2 times, then the film was annealed at 100°C for 5 min. To deposit CuSCN film (for both CuSCN-only and CuGaO₂/CuSCN), CuSCN solution in diethyl sulfide (24 mg ml⁻¹) was used for spin-coating at 3000 rpm for 30 s, and annealed at 50°C for 10 min. Finally, 150-nm-thick Au electrodes were deposited by thermal evaporation. For the stability test, devices were encapsulated using cover glass with UV curable epoxy resin in a glovebox.

Characterization

The crystal structure and grain size of CuGaO₂ nanoparticles were analyzed by x-ray diffraction (XRD, D8 Advance: Bruker). Fourier transform infrared spectroscopy (FTIR, TENSOR27: Bruker) was carried out to observe vibrational modes of chemical bonding in CuGaO₂ nanoparticles. The morphologies of the films were observed using a field-emission scanning electron microscope (FE-SEM, Merlin-Compact: Carl Zeiss). The surface topography of the film was obtained by atomic force microscopy (NX-10: Park Systems). The absorbance was obtained by a UV-Vis spectrophotometer (V-770: JASCO). Steady-state and time-resolved photoluminescence spectra were observed in the films.
prepared on glass substrates with excitation wavelength of 532 and 405 nm (LabRAM HV Evolution: Horiba, FluoTime 300: Picoquant), respectively. The photocurrent-voltage (J-V) curves of the solar cells were measured using a solar cell measurement system (K3000: McScience, AM 1.5G, 100 mW cm$^{-2}$), with an active area of 0.09 cm$^2$ and 100-mV s$^{-1}$ voltage scan rate. The external quantum efficiency (EQE) spectra were obtained by an incident photon-to-current conversion efficiency (IPCE) measurement system (K3100: McScience). Frequency dependent capacitances were obtained by impedance analysis in dark condition using a potentiostat (Zive SP1: WonATech CO., Ltd.) with 50-mV amplitude of ac signal at zero applied bias and frequency ranging from 0.01 to $10^5$ Hz.
4.3. Results and Discussion

In order to prepare the metal-oxide HTL with a high coverage, controlling the nanoparticle size is important. We have used P123 as a surfactant in the hydrothermal synthesis to reduce the CuGaO$_2$ particle size below 100 nm. X-ray diffraction from the synthesized CuGaO$_2$ nanoparticles exhibits peaks corresponding to CuGaO$_2$ without impurity phases, confirming high purity of the CuGaO$_2$ nanoparticles (Fig. 4-1(a)). The grain size is $\sim$5 nm along the <001> direction and $\sim$35 nm for the <110> direction, as calculated by the Scherrer equation suggesting plate-shaped nanoparticles. To enhance the dispersion property of the nanoparticles in a solvent, APTES treatment is conducted (details in the Experimental Section). During the APTES treatment, hydroxyl groups on the nanoparticle surface are replaced by the silane groups of APTES, and the amine groups are exposed causing repulsive force between the nanoparticles, therefore enhancing their dispersion. The comparison of FTIR spectra from CuGaO$_2$ nanoparticles before and after the APTES treatment reveals that Cu-O-Si vibration peak (980 cm$^{-1}$) appears after the APTES treatment with the disappearance of -OH groups (1337 and 1387 cm$^{-1}$) (Fig. 4-1(b)).[31,38-40] This confirms that APTES becomes chemically adsorbed on the CuGaO$_2$ nanoparticles via the silane group. It is noted that the vibrational modes of P123 surfactant used in the hydrothermal process are not observed confirming the complete removal of P123 after the washing step.

Even after storage for 24 h without stirring under ambient air, CuGaO$_2$ nanoparticles in isopropyl alcohol (IPA) maintain their dispersion with APTES treatment (inset of Fig. 4-1(b)). CuGaO$_2$ film is deposited on the perovskite by spin-coating (Fig. 4-1(c)). Without the APTES treatment, a low-coverage CuGaO$_2$ film is resulted exposing
some areas of the underlying perovskite film (yellow circle). On the other hand, a full coverage film is obtained with the APTES-treated CuGaO$_2$ nanoparticles. Although the APTES treatment enhances the dispersion of nanoparticles in suspension, careful adjustment of the treatment time is necessary so that the formation of multilayer APTES can be avoided: otherwise, electrical conductivity can decrease. The optimal treatment time is determined by in-plane conductivity measurements (Fig. 4-2).
Fig. 4-1. (Color) The effect of APTES treatment on the CuGaO$_2$-nanoparticle nanostructures. (a) X-ray diffraction of CuGaO$_2$ nanoparticles, and extracted grain size by Scherrer equation. (b) FTIR of CuGaO$_2$ nanoparticles. The inset shows optical images of nanoparticle suspension after 24-h storage with and w/o APTES treatment. (c) Coverage of CuGaO$_2$ films on the perovskite by SEM. A yellow circle indicates exposed perovskite.
Fig. 4-2. (Color) Optimization of APTES-treatment time. (a) $J-V$ curves of perovskite solar cells using CuGaO$_2$ as HTL with different treatment times. (b) In-plane conductivity of CuGaO$_2$ thin films measured by four-point probe. The thicknesses of films are 300 nm.
Solar cells comprised of SnO\textsubscript{2} as an electron-transport layer, triple-cation perovskite [Cs\textsubscript{0.05}(FA\textsubscript{0.83}MA\textsubscript{0.17})\textsubscript{0.95}Pb(I\textsubscript{0.83}Br\textsubscript{0.17})\textsubscript{3}] as a light absorber, and either CuSCN or CuGaO\textsubscript{2} with CuSCN (CuGaO\textsubscript{2}/CuSCN) as HTLs are fabricated (Fig. 4-3(a)). The CuGaO\textsubscript{2}/CuSCN HTL is prepared by spin-coating CuGaO\textsubscript{2} suspension, followed by spin-coating CuSCN solution. As shown in Fig. 4-4, the surface topography varies significantly depending on the types of HTLs. The root-mean-squared (RMS) roughness of the perovskite is 17.8 nm, and it is reduced to 7.4 nm after the deposition of CuSCN. For the CuGaO\textsubscript{2}-only HTL on perovskite, the RMS roughness exhibits the highest value of 40.9 nm, and it is reduced to 31.4 nm for the CuGaO\textsubscript{2}/CuSCN device, indicating that the CuSCN solution can infiltrate into a porous CuGaO\textsubscript{2} film reducing pin-holes and roughnesses. The in-plane conductivity of the CuGaO\textsubscript{2} film is not improved by the infiltrated CuSCN because the conductivity of the bare CuSCN is lower by more than an order of magnitude compared to the CuGaO\textsubscript{2} film (Fig. 4-5). The average performance of solar cells with CuGaO\textsubscript{2}/CuSCN HTL improves compared to the CuSCN-only HTL (Figs. 4-3(b-f)). Photocurrent-voltage (J-V) curves of the best-performing cells are shown in Fig. 4-3(g) (improved PCE of 16.7% from 15.4%). Shown in the inset of Fig. 4-3(g) is a cross-sectional SEM image of the solar cell with the CuGaO\textsubscript{2}/CuSCN HTL which suggests a uniform layer of CuGaO\textsubscript{2} infiltrated with CuSCN, instead of distinct bilayers of separate CuGaO\textsubscript{2} and CuSCN. It is noted that PCE of a solar cell with CuGaO\textsubscript{2}-only HTL is poor due to a limited contact area between perovskite and CuGaO\textsubscript{2} nanoparticles, causing potential shunting path from pin-holes in the CuGaO\textsubscript{2} layer (Fig. 4-2).[41]
Fig. 4-3. Device performance without and with nanoparticles for the HTL. (a) Morphologies of perovskite, perovskite/CuSCN, and perovskite/CuGaO$_2$/CuSCN by SEM. (b) $J_{sc}$, (c) $V_{oc}$, (d) $FF$, (e) $\eta$, and (f) $HI = 1 - \eta_{FOR} / \eta_{REV}$ of solar cells with different hole-transport layers. (g) $J$-$V$ curves of champion cells with solar cell geometry (without Au) by SEM.
Fig. 4-4. (Color) Surface roughness. Topographies of perovskite and each HTLs on the perovskite obtained from AFM.
In-plane conductivity of HTLs measured by four-point probe. The thicknesses of films are 300 nm for CuGaO$_2$, 310 nm for CuGaO$_2$/CuSCN, and 160 nm for CuSCN.
To better understand the reasons of the performance enhancement with the CuGaO$_2$/CuSCN HTL, photoluminescence (PL) analysis is carried out. For steady-state PL measurements, the excitation light is incident on the HTL side to probe the perovskite/HTL interface better. The PL intensity of the perovskite is substantially quenched with the presence of a HTL. However, the degree of the quench is larger for the CuGaO$_2$/CuSCN compared to the CuSCN-only one (Fig. 4-6(a)). It is noted that the PL peak position of the perovskite is close to the estimated optical bandgap (1.63 eV), i.e., very small Stokes shift, suggesting the high quality of perovskite film,[42] and the blue-shifted PL after the deposition of HTL suggests that additional defects are not generated at the perovskite/HTL interface.

The efficacy of carrier extraction across the perovskite/HTL is examined by time-resolved PL spectra (Fig. 4-6(b)). Unlike the steady-state PL measurements, the excitation light is incident on the glass side to simulate the illumination condition identical to the solar-cell operation. The PL lifetimes are approximately 291, 17 and 10 ns, respectively, for glass/perovskite, glass/perovskite/CuSCN and glass/perovskite/CuGaO$_2$/CuSCN.[43] The reduced PL lifetime can be attributed to the efficient hole extraction from the perovskite to the HTL. When only CuGaO$_2$ is used for the HTL, carrier extraction is less efficient compared to the CuGaO$_2$/CuSCN owing to the insufficient contact area between the perovskite and the CuGaO$_2$ (Fig. 4-7). This result suggests that CuSCN infiltrates into the CuGaO$_2$ nanoparticle film assisting the hole transfer from the perovskite layer. More efficient charge extraction between the perovskite and CuGaO$_2$/CuSCN HTL can be also inferred by the improved external quantum efficiency (EQE) response over the nearly entire wavelength range in which the
solar cells respond (Fig. 4-6(c)). Additionally, the plot for the ratio of $\text{EQE}_{\text{CuGaO}_2/\text{CuSCN}}$ to $\text{EQE}_{\text{CuSCN}}$ shows better EQE response at longer wavelength with the CuGaO$_2$/CuSCN device, indicating improved hole carrier collection (Fig. 4-6(d)).
Fig. 4-6. (Color) Carrier extraction properties. (a) Steady-state PL spectra (excitation wavelength = 532 nm) and plots of \((a\eta)^2\) vs. \(\eta\) for the estimation of optical bandgap \(E_g\) of perovskite before/after the deposition of HTL. (b) Time-resolved PL spectra with solid fitting lines (excitation wavelength = 405 nm). (c) External quantum efficiencies (EQEs) of the solar cells. (d) The ratio of \(\text{EQE}_{\text{CuGaO}_2/\text{CuSCN}}\) to \(\text{EQE}_{\text{CuSCN}}\) as a function of wavelength.
Fig. 4-7. (Color) Carrier extraction properties. Time-resolved PL spectra (excitation wavelength = 405 nm). The measurement geometry is schematically illustrated.
Capacitance measurements of solar cells using two different HTLs exhibit a similar high frequency plateau but different response in a low frequency range (Fig. 4-8(a)). The high frequency value can be attributed to the geometric/depletion capacitances, while the disparity in the low frequency range can be ascribed to the difference in the trap density at the perovskite and/or interfaces.[44-46] The trap density can be estimated using the derivative of the capacitance with respect to the frequency, and the corresponding trap level with respect to the bandedge is related to the applied angular frequency.[44-46] The resultant distributions of trap density exhibit lower integrated trap density (by a Gaussian fitting) for the CuGaO$_2$/CuSCN device compared to the CuSCN-only device (Fig. 4-8(b)). Therefore, it is deduced that wetting by CuSCN through the CuGaO$_2$ nanoparticles may suppress or passivate surface/interface trap states.

The stability of a perovskite solar cell is evaluated under 85°C/85% RH environment (Fig. 4-8(c)). A much improved thermal stability is confirmed with the CuGaO$_2$/CuSCN HTL: almost 80% of the initial PCE retention after 400 h. To investigate the effect of CuGaO$_2$ layer on the degradation between perovskite and CuSCN, perovskite films with each HTL (encapsulated by using poly(methyl methacrylate) (PMMA)) before and after storage at 85°C for 100 h are analyzed by XRD (Fig. 4-9). We have compared the integrated-intensity ratios of a pristine sample to a sample after storage at 85°C for 100 h for the perovskite and PbI$_2$ peaks. The decomposition of perovskite and the formation of PbI$_2$ are accelerated with the CuSCN compared to the bare perovskite film. The interfacial reaction between perovskite and CuSCN may aggravate the device stability at high temperature.[34] The degradation is mitigated by using CuGaO$_2$ with CuSCN, which can be ascribed to the reduced contact area between perovskite and CuSCN. It
represents that metal-oxide nanoparticles with CuSCN can be an effective strategy to improve the thermal stability of perovskite solar cell.
Fig. 4-8. (Color) Trap density analysis and stability of the devices. (a) Frequency dependent capacitances. (b) Trap density of states as a function of trap level with respect to the bandedge. The dashed lines denote Gaussian fitting for the trap density per volume ($n_t$). (c) Stability test of solar cells in 85°C/85% relative humidity (RH) condition with encapsulation.
Fig. 4-9. Degradation of perovskites with HTLs at 85°C. X-ray diffraction of perovskite, perovskite/CuSCN, and perovskite/CuGaO$_2$/CuSCN for (a) pristine samples and (b) after 100-h storage at 85°C. All of the films are encapsulated with poly(methyl methacrylate) (PMMA) by spin-coating (30 mg/ml) in chlorobenzene at 2000 rpm for 60 s. (c) Integrated-intensity ratios between pristine and after 100-h storage for the PbI$_2$ (001) and perovskite (001) peaks in XRD.
4.4. Conclusions

We have fabricated perovskite solar cells with inorganic HTL consisting of CuGaO₂ nanoparticle film and CuSCN to improve the thermal stability of devices. First, the dispersion of CuGaO₂ nanoparticles in the suspension is enhanced by the surface modification of nanoparticles with aminosilane groups by APTES. After treatment, the resultant CuGaO₂ suspension is effectively spin-coated yielding films with better coverage and uniformity. The HTL with a dual-inorganic layer CuGaO₂/CuSCN shows more efficient carrier extraction from the underlying perovskite. This leads to the improved EQE response, and therefore, a higher short-circuit current from the CuGaO₂/CuSCN solar cell. The trap density is also reduced by ~40% by the CuGaO₂/CuSCN compared to the CuSCN-only case. Consequently, the average PCE for the CuGaO₂/CuSCN solar cells is larger than the CuSCN-only solar cells. The encapsulated CuGaO₂/CuSCN solar cell maintains ~80% of its initial PCE for 400 h under 85°C/85% RH condition. Our study presents an effective strategy that can both improve performance and thermal stability of perovskite solar cells.
4.5. References


[27] Nazari, P.; Ansari, F.; Nejand, B. A.; Ahmadi, V.; Payandeh, M.; Salavati-Niasari, M. Physicochemical Interface Engineering of CuI/Cu as Advanced Potential Hole-Transporting Materials/Metal Contact Couples in Hysteresis-Free Ultralow-Cost and


Appendix:
List of Publications and Presentations

A.1. Publications (International)


[2] "Uniform Cs₂SnI₆ Thin Films for Lead-Free and Stable Perovskite Optoelectronics via Hybrid Deposition Approaches"

[3] "From Nanostructural Evolution to Dynamic Interplay of Constituents: Perspectives for Perovskite Solar Cells"


[6] "Methylammonium-Chloride Post-Treatment on Perovskite Surface and its Correlation to Photovoltaic Performance in the Aspect of Electronic Traps"


[13] "Solvent and Intermediate Phase as Boosters for the Perovskite Transformation and
Solar Cell Performance”

[14] "Bandgap Grading and Al_{0.3}Ga_{0.7}As Heterojunction Emitter for Highly Efficient GaAs-Based Solar Cells"

[15] "Organic-Acid Texturing of Transparent Electrodes Toward Broadband Light Trapping in Thin-Film Solar Cells"

[16] "The Construction of Tandem Dye-Sensitized Solar Cells from Chemically-Derived Nanoporous Photoelectrodes"
Hongsik Choi, Taehyun Hwang, Sangheon Lee, Seunghoon Nam, Joonhyeon Kang, Byungho Lee, and Byungwoo Park*

[17] "Facile Conversion Synthesis of Densely-Formed Branched ZnO-Nanowire Arrays for Quantum-Dot-Sensitized Solar Cells"

[18] "Nanoroughness Control of Al-Doped ZnO for High Efficiency Si Thin-Film Solar Cells"

[19] "Electronic Effect in Methanol Dehydrogenation on Pt Surfaces: Potential Control during Methanol Electrooxidation"
Joonhyeon Kang, Seunghoon Nam, Yuhong Oh, Hongsik Choi, Sungun Wi, Byungho


[21] "The Role of ZnO-Coating-Layer Thickness on the Recombination in CdS Quantum-Dot-Sensitized Solar Cells"

[22] "The Effect of TiO₂-Coating Layer on the Performance in Nanoporous ZnO-Based Dye-Sensitized Solar Cells"

[23] "An Effective Oxidation Approach for Luminescence Enhancement in CdS Quantum Dots by H₂O₂"
## A.2. Presentations (International and Domestic)

Taehyun Hwang, **Byungho Lee**, Sangheon Lee, Jinhyun Kim, Bumjin Gil, Alan Jiwan Yun, and Byungwoo Park

[2] "Imidazole as a Cation-Dopant for Stable and Efficient Perovskite Solar Cells"
Jinhyun Kim, Taehyun Hwang, **Byungho Lee**, Sangheon Lee, Bumjin Gil, Kimin Park, and Byungwoo Park

Jinhyun Kim, Taehyun Hwang, Sangheon Lee, **Byungho Lee**, Jaewon Kim, and Byungwoo Park

Jinhyun Kim, Taehyun Hwang, Sangheon Lee, **Byungho Lee**, Jaewon Kim, and Byungwoo Park

[5] "Investigation of Chlorine-Mediated Microstructural Evolution of CH$_3$NH$_3$PbI$_3$(Cl) for Enabling High Performance Solar Cell"
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[10] "Mixture of Nanoporous Spheres and Nanoparticles for High-Efficiency ZnO-Based Dye-Sensitized Solar Cells"
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"Organic-Acid Texturing of Transparent Electrodes Toward Broadband Light Trapping in Thin-Film Solar Cells"
Byungwoo Park, Woojin Lee, Taehyun Hwang, Sangheon Lee, Seung-Yoon Lee, Joonhyeon Kang, Byungho Lee, Jinhyun Kim, and Taeho Moon

춘계금속재료학회, Changwon, Korea, April 22-24, 2015.
국문 초록

태양전지는 태양 빛을 전기 에너지로 직접 변환하는 에너지 하베스팅 소자로 친환경 대체에너지원으로서 가장 유망한 후보 중에 하나다. 다양한 태양전지 광흡수체로 쓰이는 소재 중에서 유・무기 하이브리드 페로브스카이트는 엑시톤 결합 에너지, 전하 이동도, 전하 확산 거리, 흡광계수 등의 물리적 특성이 우수하다. 이로 인해 2012년 최초 전고체 (all solid-state) 소자로 적용된 이래로 여타의 태양전지에 비해 광전변환효율이 가장 급격히 향상되고 있다. 이와 더불어, 태양전지의 대부분을 저비용의 용액 공정으로 제작할 수 있어 상용화에 이르게 되었다.

페로브스카이트 태양전지의 상용화를 앞당기기 위한 주된 연구 이슈는 에너지 생산단가를 낮추기 위해 태양전지의 광전변환효율을 향상시키고 빛, 열, 수분, 산소 등의 다양한 외부 환경에서 소자의 장기 안정성을 확보하는 것이다. 본 학위 논문에서는 태양전지의 효율 향상을 목적으로 페로브스카이트 박막의 결정립 크기가 광전변환 성능에 미치는 영향에 대해 연구하였다. 또한, 염소 (Cl)가 첨가된 전구체를 사용한 페로브스카이트의 조대 결정립 성장 과정에 대해 자세히 밝혔다. 이와 더불어, 소자의 장기 열 안정성 향상을 위한 무기 정공 전달층 개발에 대해 논의하였다.

1장에서는 광전변환 소자의 기본적인 작동 원리와 페로브스카이트 격자 및 태양전지의 구조에 대해 간략히 소개한다. 또한, 고품질의 균일한 페로브스카이트 박막 형성을 위한 핵심 요소들을 핵생성부터 결정립 성장까지의 박막 형성 과정에 대한 메커니즘과 함께 논의한다. 더불어 태양전지의 광전 성능 향상을 위한 다양한 전략들을 트랩 준위 농도의 감소에 초점을 맞춰서 리뷰한다.

2장에서는 페로브스카이트 박막의 결정립 크기와 광전변환 성능의 상관계에 대해서 조사한다. 아이오딘화메틸암모늄납 (CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3}) 페로브스카이트를 아
이오딘화메틸암모늄 이 과량 첨가된 비화학량론적 전구체에 이차 용매 낙하 방법을 통해 합성한 결과, 박막의 결정성과 결정립 크기가 화학량론적 전구체를 사용한 경우에 비해 증가하였다. 또한 이를 이용한 태양전지의 성능이 향상되었고 최고 14.3%의 효율을 나타내었다. 이러한 페로브스카이트 박막을 전도성 원자현미경 및 노이즈 분광법을 이용하여 효과적으로 분석하였다. 나노스케일에서의 광전류 차이를 토폴그래피 (topography)와 광전류 지도를 비교하여 세계적으로 분석한 결과 결정립 크기와 광전류 사이에 선형적 비례관계가 나타나는 것을 밝혔다. 또한, 전도성 탐침을 이용한 노이즈 분석을 통해 결정립계의 효과를 평가하고 특정 결정립 내에서의 결함 농도를 평가할 수 있었고, 과량의 이오딘화메틸암모늄이 첨가된 전구체를 사용한 페로브스카이트에서 결함이 줄어든 것을 확인하였다.

3장에서는 염화메틸암모늄을 과량 첨가한 전구체를 사용하여 이오딘화메틸암모늄 납 페로브스카이트를 합성하는 경우 나타나는 박막과 태양전지 효율의 변화에 대해 조사한다. 페로브스카이트 박막에 있어서 화학량론적 전구체를 사용한 경우에 비해 염화메틸암모늄을 첨가한 경우 결정립 크기가 약 10배 증가하였고 〈110〉 방향으로의 배향성이 향상되었다. 염소를 첨가하는 경우 나타나는 조대 결정립 성장의 종합적인 메커니즘을 열처리 과정에서의 결정립 방향과 결정립 크기의 분포 및 박막 내의 전류 염소 변화를 연관지어 자세히 설명하였다. 박막 내 염소가 다량 존재하는 열처리 초기에 페로브스카이트 〈110〉과 〈001〉 결정립이 다른 결정립에 비해 빠르게 자라난다. 추가적인 열처리는 박막 내 염소를 고갈시키고 〈001〉 결정립은 축소되고 〈110〉 결정립은 계속적으로 성장하여 조대 결정립을 형성한다. 결정립계의 감소와 〈110〉 텍스쳐 (texture)의 향상으로 페로브스카이트 태양전지의 트랩 농도가 약 10% 감소하였으며 80% 이상의 높은 채우기 비율 (fill factor)을 나타내었다.
마지막으로 4장에서는 산화구리갈륨 나노입자를 페로브스카이트 태양전지의 정공전달층으로 적용하여 광전변환 성능과 장기 열안정성에 미치는 영향에 대해 분석한다. 우선 산화구리갈륨의 아이소프로필알코올에서의 분산도를 향상시키기 위해 나노입자 표면을 아미노실레인기로 처리하였고, 이 현탁액을 스피스코팅하여 균일한 산화구리갈륨 박막을 완성하였다. 그 후, 페로브스카이트 용액을 산화구리갈륨 박막 위에 올려 정공전달층으로 사용하였으며, 이러한 태양전지는 페로브스카이트만을 정공전달층으로 사용한 경우에 비해 향상된 광전변환성능을 나타내었다. 또한, 두 물질을 동시에 정공전달층으로 사용한 태양전지에서의 향상된 정공 추출 성능과 줄어든 트랩 농도를 광발광 수명과 촉진 분석으로부터 확인하였다. 이와 더불어 해당 태양전지는 고온 고습 (85°C/85% 상대습도) 조건에서 400시간 동안 초기 효율의 약 80% 성능을 유지하는 높은 열안정성을 보였다.

주요어: 페로브스카이트 태양전지, 광전변환효율, 아이오딘화메틸암모늄첨가물, 전도성 원자현미경, 노이즈 분광법, 염화메틸암모늄첨가물, 트랩농도, 결정립 크기, 텍스처, 산화구리갈륨, 페로브스카이트, 장기 안정성

학번: 2012-24164
감사의 글

대학원 생활을 시작한지 이제 7 년 반이 지났습니다. 지금까지 살아온 인생의 4 분의 1 을 이곳에서 보내면서 때로는 회의감과 절망감에 휩싸인 적도 있었으나, 그 모든 힘든 과정을 겪어내고 이겨낼 수 있었던 건 주위 사람들의 격려와 응원 덕분임을 잘 알고 있습니다. 지금까지의 시간을 돌아보며 이 지면을 빌어 감사한 마음을 전하고자 합니다.

먼저 학위 과정을 지도해주신 박병우 교수님께 진심으로 감사드립니다. 아무것도 모르던 입학 초기부터 박사 학위를 받게될 지금까지 세심한 부분에도 조언을 아끼지 않으시고 잘하고 있을 때 믿음으로, 부족할 때 결책으로 저를 이끌어 주셔서 연구자로서 역량을 기를 수 있었습니. 앞으로의 인생에 있어서도 지금까지의 가르침을 밑거름 삼아 열심히 정진하며 살아가겠습니다.

학위 과정 중간에 기꺼이 저를 공동 지도해주신 많은 시간을 내어주신 신병하 교수님께도 감사의 말씀을 드립니다. 연구에 관한 다양한 조언들을 통해 한층 발전할 수 있었고, 필요한 사항들이 생길 때마다 아낌없이 도와주시는 모습이 연구자로서 큰 본보기가 되었습니다. 더불어 바쁜 와중에도 제 학위논문을 심사해주시고 많은 조언을 해주신 김장주 교수님, 이태우 교수님, 김진영 교수님, 김상범 교수님께도 감사드립니다. 첫 페로브스카이트 논문을 공동 지도해주신 문태호 교수님께도 감사의 말씀을 드립니다. 제가 많이 부족한 시기에 치부하 이끌어 주시고 항상 제 입장을 배려해주시고 용기와 힘을 주셔서 이렇게 잘 마무리할 수 있었습니다.

학위 기간 동안 많은 시간 함께 동고동락하며 버림목이 되어주셨던 연구실 선후배님들께도 감사의 말씀을 전합니다. 연구실에 많은 관심을 갖고 도움을 주시는 김천중 교수님, 연구실에 처음 입학했을 당시 왕고이셨던 대룡이형, 여쭤본 모든 질문에 답을 주시고 부드럽게 챙겨주셨던 종민이형, 앞으로 메일 받게될 항상 유머가 넘치시셔 같이 있으면 즐거운 유흥이형, 무섭지만 저것저것 꼿꼿이 챙겨주셨던 창우형, 지금도 연구실 멤버들과 함께
연구하고 계신 축구 잘하시는 승훈이형, 연구실에서 처음 실험을 알려주시고 많은 것을 쟁취구했던 홍식이형, 제 첫 논문을 이끌어 주시느라 많이 고생하신 재익이형, 후배들에게 편안한 선배이자 책임감 있는 준희형, 회사에 다니시면서도 열심히 연구실 일에 참여하였던 순수한 준희형, 종종 연구실에 찾아와 후배들 밥사주는 인간미 넘치는 성언이형, 연구도 잘하고 위님도 잘하는 순수한 준희형, 적극적으로 실험을 알려주신 밝은 에너지의 초희누나, 입학 초에 잡간 같이 있었지만 재미있었던 진현이형, 운동 메이트였던 항상 열심히 사는 쉐이더 성준이형, 다정하게 대해주셨던 기민이, 조용하고 차분한 앞으로 연구실을 이끌어주신 나한테만 안 엉겨붙는 손맛이 기가막힌 기민이, 조용하고 차분한 앞으로 연구실을 이끌어주신 헨리형, 독특하게 유머러스하고 진중한 면도 있는 지완이, 많이 고생하고 있는 예의바른 영현이, 연구실 업무로서 이모저모 사소한 것들을 다 쟁취구었던 재욱이형, 한번 시작하면 끝을 보고마는 경환이, 재미있는 니네임을 갖고 있는 친절한 국한이, 운동 같이했던 미국가다가 못지게 돌아온 복기가까지. 힘들고 지칠 때도 멤버들과 함께하여 즐겁게 생활할 수 있었습니다.

옆에서 힘이 되어 주었던 친구들에게도 감사의 인사를 전합니다. 힘들 때 전화하면 바로 만나시 이야기 들어주고 힘을 주었던 태수는 얼른 좋은 사람 만나서 행복해졌으면 좋겠고, 공장 운영하느라 많이 바빠진 기태도 하고자 하는 일들이 술을 잘 풀렸으면 좋겠다. 시험 준비로 바빴던 인습이는 마무리 잘 되어서 목표로 한 일을 잘 이루길 바라고, 언제나 친목 모임을.
주도해준 상율이도 좋은 사람과 순탄히 행복하게 지냈으면 좋겠어. 대학부터 대학원까지 같이 와서 더 의지가 되었던 주현이도 대전에서 힘든 일 없이 잘 지내길 바란다. 근래에는 졸업 준비 때문에 바쁘다는 평계로 자주 연락하거나 만나지 못해서 항상 미안한 마음이 있었지만, 마음 속으로는 항상 다들 행복하게 잘 지내길 기원하고 있었습니 다. 지금까지 졸업주지 못한 만큼 앞으로는 더 즐겁게 교류하고 편지를 보는 친구가 되겠습니다. 이 지면에 다하지 못한 많은 분들에게 감사의 인사를 드립니다.

가장 힘들고 바쁜 시기부터 함께해서 많이 졸업주지 못했는데도 예쁜 목소리로 옆에서 열심히 응원해주고 힘을 되어준 사랑하는 김주희양에게도 깊은 감사를 전합니다. 앞으로 함께할 시간동안 지금까지 보여주었던 마음을 기억하며 보답하겠습니다.

마지막으로 오랜시간 동안 목복히 믿어주시고 응원해주신 부모님께 감사의 말씀을 드립니다. 장남에 거는 기대가 크셨음에도 계속 지체되신 졸업 때문에 남몰래 숙명이를 하셨음에도 불구하고 저의 행복과 마음을 우선 생각해주시고 내색 없이 항상 응원해주시고 힘을 북돋아 주셔서 감사합니다. 연세가 드셔서 많이 편찮으시지만 집에 가면 채일 반겨주시고 졸업주려고 하시는 할머니께서도 항상 감사드려요. 그리고 은퇴한 내동생 병관이와 귀여운 내동생 영준이도 존재만으로 정말 큰 힘이 되어아. 가족은 제 인생에 있어서 가장 큰 의미입니다. 앞으로도 지금처럼 오래오래 행복하게 지내길 마음 깊이 바랍니다. 사랑합니다.

2019년 8월
이병호 드림

서울대학교

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