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Fabrication of CH$_3$NH$_3$SnI$_3$ perovskite solar cells using vacuum process

2016년 2월

서울대학교 대학원
재료공학부
최 민 형
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지도 교수 김 장 주

이 논문을 공학석사 학위논문으로 제출함

2016년 2월

서울대학교 대학원
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Abstract

Fabrication of CH$_3$NH$_3$SnI$_3$ perovskite solar cells using vacuum process

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Recently, hybrid organic-inorganic perovskite solar cells have attracted the great attention because of their remarkably high power conversion efficiency (PCE) combined with simple and low temperature process. But most of the devices reported up to now are Pb-based perovskite (e.g., CH$_3$NH$_3$PbI$_3$) solar cells which have potential risk such as heavy metal pollution, lead poisoning and lead accumulation. Therefore, replacing Pb in the perovskite is one of the most important issues in the field of perovskite solar cells for their commercialization and practical applications in the future. Until now, Sn has been considered the most viable element for replacing Pb in perovskite since Sn is the group 14 elements in periodic table and it is also known that Sn can adopt perovskite structure with CH$_3$NH$_3^+$ and I$^-$.
ions. Based on this knowledge, some papers have reported lead-free Sn-based perovskite solar cells since 2014, however, all reported devices have been fabricated by spin-coating process. In the spin-coating process, electron transporting layer (ETL) under the perovskite is limited to mesoporous TiO$_2$ (mp-TiO$_2$) which causes poor surface morphology of CH$_3$NH$_3$SnI$_3$ perovskite film. Low stability to oxidation and short carrier diffusion lengths have been also pointed out as the critical problems for solution-processed CH$_3$NH$_3$SnI$_3$ perovskite. In this regard, vacuum process can be appropriate method for deposition of lead-free CH$_3$NH$_3$SnI$_3$ perovskite film because vacuum process has several advantages such as clean environment, wide selection of charge transporting layer and high reproducibility. The clean deposition condition in vacuum process is very effective to easily oxidizable CH$_3$NH$_3$SnI$_3$ film and various charge transporting layers can be chosen in consideration of better morphology of perovskite and well-matched energy level alignment.

In this work, various hole transporting layers (HTLs) are introduced and the effect of HTLs on the growth of vacuum-processed CH$_3$NH$_3$SnI$_3$ perovskite film is investigated. As a result, CH$_3$NH$_3$SnI$_3$ film shows the most improved crystallinity on ITO/MoO$_3$/NPB sublayer compared to on ITO and on ITO/MoO$_3$ sublayer. The initial growth of 2 nm-thick SnI$_2$ on each sublayer strongly affects total
growth of CH$_3$NH$_3$SnI$_3$, which is confirmed by X-ray diffraction (XRD) patterns. In addition, the effect of working pressure and thickness on the growth and film qualities of CH$_3$NH$_3$SnI$_3$ perovskite is investigated. Controlling the increase in working pressure by evaporated CH$_3$NH$_3$I, stoichiometric and unifrom CH$_3$NH$_3$SnI$_3$ perovskite film with nearly crystalline morphology is successfully formed at the apparent working pressure of 5×10$^{-5}$ torr. The perovskite film fabricated at this pressure also shows the highest hole mobility due to the increased crystallinity and band gap energy of 1.33 eV. Lastly, optical simulation and fabricating real CH$_3$NH$_3$SnI$_3$ perovskite solar cells are conducted. Although real lead-free device exhibits poor performance due to the lack of optimization, optical simulation results indicate that short-circuit current ($J_{SC}$) of the device can be increased up to ~23 mA/cm$^2$ when thickness of perovskite reaches around 500 nm. If open-circuit voltage ($V_{OC}$) reaches 0.88 V and fill factor (FF) attains ~0.7, the PCE of lead-free perovskite solar cells is expected to be ~14.2 % which is comparable to the Pb-based perovskite solar cells.

**Keywords:** Organic/inorganic hybrid perovskite solar cell, vacuum process, sublayer, CH$_3$NH$_3$SnI$_3$, lead-free perovskite, MoO$_3$, NPB

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Abstract

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Chapter 1
Introduction

1.1 Motivation and outline of thesis

1.1.1 Motivation

Hybrid organic-inorganic perovskite solar cells have attracted the great attention due to their remarkably high power conversion efficiency ($PCE$) combined with simple and low temperature processes [16-20]. Compared to conventional organic solar cells, perovskite solar cells have been rapidly developed since 2009 and the $PCE$ has reached ~20 % recently [4-5]. But most of the devices reported up to now is Pb-based perovskite (e.g., CH$_3$NH$_3$PbI$_3$) solar cells which can have potential side effects on environment and human body such as heavy metal pollution, lead poisoning and lead accumulation, etc. Thus replacing Pb in the perovskite is one of the most critical issues in the field of perovskite solar cells for their commercialization and practical applications in the future. In view of this, Sn is considered the most viable element for replacing Pb because Sn is the group 14 elements with the same ionic valency as Pb and Sn has the ionic radius of 69 pm.
which is similar to that of Pb. In 2014, M. G. Kanatzidis and his coworker first reported lead-free Sn-based perovskite solar cells fabricated by spin-coating process and the device exhibited the efficiency of 5.48 % [7]. However, methylammonium tin iodide (CH$_3$NH$_3$SnI$_3$) perovskite film on mesoporous titanium dioxide (mp-TiO$_2$) used as electron transporting layer (ETL) in the device showed rough surface morphology with many pin-holes in this report. After that, H. J. Snaith and his coworker has also reported CH$_3$NH$_3$SnI$_3$ perovskite solar cells and the $PCE$ has improved up to 6.4 %, however, stability of CH$_3$NH$_3$SnI$_3$ to oxidation and short carrier diffusion lengths were pointed out as the severe problems for solution-processed lead-free perovskite film [8].

Vacuum process can be appropriate way to fabricate efficient lead-free CH$_3$NH$_3$SnI$_3$ perovskite solar cells because vacuum process has several advantages such as clean environment, wide selection of charge transporting layer and high reproducibility [22-24]. The clean deposition condition in vacuum process is very effective to easily oxidizable CH$_3$NH$_3$SnI$_3$ film. In addition, various charge transporting layer, so-called sublayer because it is located under the perovskite layer, can be chosen in consideration of better morphology of perovskite and well-matched alignment of energy level. Furthermore, precise controls of deposition rate and working pressure in the chamber are possible in
vacuum process resulting in uniform and stoichiometric perovskite film with high reproducibility. In this thesis paper, characterization of CH₃NH₃SnI₃ perovskite film fabricated in vacuum process will be conducted through X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), atomic force microscopy (AFM) and optical absorption measurement, etc. The effect of sublayer under the perovskite, working pressure and film thickness on the growth of perovskite in vacuum process will be precisely investigated. Optical simulation and real performance of lead-free perovskite solar cells will be also measured and discussed in the final stage.

1.1.2 Outline of thesis

In chapter 1, the brief introduction of the perovskite materials and operation principles of perovskite solar cells will be described. Short explanation for appearance of Sn-based perovskite solar device and fabricating CH₃NH₃SnI₃ film in vacuum process will be also included in this chapter.

In chapter 2, the effect of hole transporting layers (HTLs) under the perovskite on the growth of CH₃NH₃SnI₃ film will be investigated by using X-ray diffraction (XRD). In addition, experimental details for
depositing perovskite in vacuum process are concretely described and the reason why crystallinity of CH₃NH₃SnI₃ differs depending on each sublayer will be discussed.

**In chapter 3**, composition of CH₃NH₃SnI₃ perovskite film will be controlled by the increase in apparent working pressure resulting from evaporated CH₃NH₃I. The effect of this working pressure on elemental composition and total growth of the CH₃NH₃SnI₃ film will be investigated using several spectroscopes and other measurements. In addition, electrical properties of stoichiometric CH₃NH₃SnI₃ film which shows nearly crystalline morphology will be analyzed.

**In chapter 4**, the influence of film thickness on the properties of CH₃NH₃SnI₃ perovskite film will be investigated. Change of crystallinity in perovskite film with thickness and elemental composition of overall CH₃NH₃SnI₃ film will be analyzed by using XRD and cross-sectional energy-dispersive X-ray spectroscopy (EDS) measurement, respectively.

**In chapter 5**, refractive index of stoichiometric CH₃NH₃SnI₃ film is obtained by ellipsometry and transfer matrix method. Optical simulation of lead-free CH₃NH₃SnI₃ perovskite solar cells will be conducted using these optical constants. In addition, the maximum PCE of lead-free perovskite solar cells will be predicted and fabrication of real lead-free device in vacuum process will be done based on the
optical simulation results.

1.2 Perovskite solar cells

1.2.1 Material properties of perovskite

Perovskite is a type of crystal structure with chemical formula of ABX₃. In perovskite solar cells, organometal halide perovskite is most commonly used as absorber materials where A is CH₃NH₃⁺, B is Pb²⁺ or Sn²⁺, and X is I⁻ although there are a few reported papers that use HC(NH₂)₂⁺ [25-26], Cs⁺ [27-29] and mixed halide [30]. In case of mostly used CH₃NH₃PbI₃, this perovskite has optical band gap of 1.5 eV and shows high absorption coefficient in the visible light range. In addition, several papers have reported that diffusion lengths of electrons and holes are up to 1 micrometer in CH₃NH₃PbI₃, which is probably due to the shallow traps against electronic band edge of perovskite. Furthermore, CH₃NH₃PbI₃, perovskite has other unique properties such as ambipolar charge transport, low exciton binding energy, and easily tunable electronic band gap. These characteristics make it well suited for photovoltaic (PV) devices, light-emitting diodes
(LEDs), and even lasers.

In case of CH$_3$NH$_3$SnI$_3$, this material adopts perovskite structure crystallizing in the pseudocubic space group $P4mm$ in any conditions with lattice parameters of $a = b = 6.240$ Å and $c = 6.281$ Å [21]. Also, [SnI$_6$]$^{4-}$ polyhedra in all perovskite lattice make an infinite 3D lattice structure with Sn–I–Sn connecting angles of $\sim 177.4^\circ$ and $180^\circ$ along the a- and c-axes [6].
Figure. 1.1 The structure of organometal halide perovskite consisting of A cations located at tetragonal edge (thick lines) and corner-sharing BX$_6^{4-}$ octahedron (drawn with thin lines). The bold marks in the parentheses are most widely used components which are CH$_3$NH$_3^+$, Pb$^{2+}$ and I$, respectively.
1.2.2 Operating principles of perovskite solar cells

CH$_3$NH$_3$PbI$_3$ perovskite has a very low exciton binding energy about 20-50 meV which is comparable to the room temperature thermal energies of $k_B T \sim 25$ meV. Recently, several papers have suggested that free carriers are dominantly generated in the CH$_3$NH$_3$PbI$_3$ perovskite at room temperature which is calculated by thermodynamic simulation and optical density [1-2]. Therefore, generation of free carriers is mainly considered in perovskite solar cells.

After the free carriers are generated in perovskite active layer, they diffuse to charge transport layer benefiting from excellent electrical properties of perovskite. L. M. Herz and H. J. Snaith found that both monomolecular and bimolecular charge carrier recombination rates are extremely low with using transient THz spectroscopy [3]. They also have proposed the lower bound limits of charge carrier mobilities in perovskite is $\sim 8$ cm$^2$ V$^{-1}$ s$^{-1}$ which is several orders larger than the value of common conjugated organic molecules. These low recombination rates and large carrier mobility ensure long carrier diffusion length and charge carrier can be effectively extracted from perovskite layer and collected at the electrodes.

1.2.3 Lead-free perovskite solar cells
After Kojima et al. has first reported organic-inorganic lead halide perovskite solar cells, the power conversion efficiency (PCE) of Pb-based perovskite solar cells has been rapidly improved and reached ~20% recently [4-5]. In addition to this prompt advance, low-cost and abundant starting materials, simple processing and its flexibility make Pb-based perovskite solar cells promising alternative to silicon solar cells.

However, one emerging concern is the toxicity of Pb in the perovskite solar cells. It is widely known that Pb causes severe heavy metal pollution to environment and critical lead accumulation to human being. Therefore, one of the most important issues in perovskite solar cells is to replace the Pb by another element which has less toxicity. In this regard, Sn has been nominated as the most viable element for replacing Pb in perovskite since Sn is the group 14 elements in periodic table and it is known that Sn can also adopt perovskite structure with CH$_3$NH$_3^+$ and I$^-$ ions [6]. In 2014, M. G. Kanatzidis and his coworker first reported lead-free perovskite solar cells using mesoporous TiO$_2$ (mp-TiO$_2$) as electron transporting layer (ETL). The device showed notable PCE of ~5.7%, however, solution-processed CH$_3$NH$_3$SnI$_3$ film on mp-TiO$_2$ exhibited poor film coverage with several pinholes [7]. Soon after, H. J. Snaith and his coworker reported another lead-free CH$_3$NH$_3$SnI$_3$
solar cells whose efficiency increased up to \(^{\sim}6.4\) % and argued that Sn\(^{4+}\) generated by oxidation of Sn\(^{2+}\) acts as a p-type dopant and makes CH\(_3\)NH\(_3\)SnI\(_3\) p-type semiconductors, which increases background hole concentration and results in significant carrier recombination [32]. Furthermore, charge carrier diffusion length was found to be \(^{\sim}30\) nm in the solution-processed CH\(_3\)NH\(_3\)SnI\(_3\) perovskite by using transient THz spectroscopy [8]. This poor electrical property might be a factor to limit the performance of lead-free perovskite solar cells. M. G. Kanatzidis group has recently elucidated the solvent effect on crystallization of CH\(_3\)NH\(_3\)SnI\(_3\) film and short-circuit current (\(J_{SC}\)) of lead-free device increased up to \(^{\sim}21\) mA cm\(^{-2}\) with uniform perovskite film on mp-TiO\(_2\) layer by using dimethyl sulfoxide (DMSO) as solvent [9].

1.2.4 Fabrication of CH\(_3\)NH\(_3\)SnI\(_3\) thin film in vacuum process

CH\(_3\)NH\(_3\)PbI\(_3\) (or CH\(_3\)NH\(_3\)SnI\(_3\)) is easily formed by the reaction between CH\(_3\)NH\(_3\)I (Methylammonium Iodide, MAI) and PbI\(_2\) (or SnI\(_2\)). Most of processes for fabricating perovskite thin films are based on spin-coating process because of its ease and simplicity. In this process, the solvent should be resolving both CH\(_3\)NH\(_3\)I and PbI\(_2\) (or SnI\(_2\)). Dimethylformamide (DMF) is widely used as solvent for spin-coating of perovskite, however, transporting layers are generally limited in this process due to the solubility of transporting layer under the perovskite.
Also, reproducibility of device, poor morphology of perovskite film and need for additional annealing process are often regarded as drawback in solution process.

To solve the problem mentioned above, some groups reported the vacuum deposition of perovskite layer for the solar cell [23]. In this process, MAI and the metal iodide (PbI$_2$ or SnI$_2$) are co-evaporated in the vacuum chamber and the composition is controlled by the amount of each source deposited. Vacuum deposition has several advantages such as clean environment, high reproducibility, wide choice of materials and usefulness for mass production [22-24]. There are notable things to fabricate perovskite thin films in vacuum process as follows.

**Unusual behavior of CH$_3$NH$_3$I in the vacuum deposition**

Typical thermal evaporating materials do not cause the increase in working pressure in vacuum chamber because the ejected molecules from the source adsorb on the substrates or the any part of the chamber rather than exist in the gaseous state. When CH$_3$NH$_3$I is evaporated in the vacuum chamber, however, the CH$_3$NH$_3$I source are randomly distributed in the chamber and it behaves as gaseous species causing the increase in the working pressure infiltrating to the ion gauge. This behavior is probably resulting from the low molecular weight of CH$_3$NH$_3$I (157 g/mol), low evaporation temperature (~150°C) and low
stacking properties. Due to these characteristics when the CH$_3$NH$_3$I is only deposited onto the glass substrate, it is difficult to measure the exact thickness since the CH$_3$NH$_3$I is hardly adsorbed on the substrate. It is also considered that evaporated CH$_3$NH$_3$I is rarely stuck to gold (Au) substrate, that is, the quartz crystal microbalances (QCMs) which read the deposition rate of CH$_3$NH$_3$I by detecting the mass of evaporated materials adsorbed on them. In other words, controlling the amount of deposited CH$_3$NH$_3$I by using the only QCM may be inaccurate and unreliable. Therefore, it is reasonable for deposition amount of evaporated CH$_3$NH$_3$I to be controlled not by using QCM but by the increase in working pressure of vacuum chamber.

**Co-evaporation of CH$_3$NH$_3$I and SnI$_2$**

Figure 1.2. shows the schematic description of experimental set-up for co-evaporating CH$_3$NH$_3$I and SnI$_2$ in the vacuum chamber. The triiodide tin perovskite, CH$_3$NH$_3$SnI$_3$, is easily formed with the reaction between the evaporated CH$_3$NH$_3$I and evaporated SnI$_2$. As shown in figure 1.2, the quartz crystal microbalances 1 (QCM) was located on the SnI$_2$ source which reads only the deposition rate of SnI$_2$. The QCM 1 was enclosed by the aluminum foil to exclude the effect of the CH$_3$NH$_3$I, due to its gas-like behavior in the vacuum chamber. In this co-evaporation process, the deposition rate of SnI$_2$ was firstly reached
to the steady state. And then, QCM 2 located at the near the substrate which enables to read the deposition rate of CH$_3$NH$_3$I and also the thickness of the perovskite reads the rate of both SnI$_2$ and CH$_3$NH$_3$I which forms the Sn perovskite on the substrate. The base pressure of the vacuum chamber was about $1 \times 10^{-6}$ torr and this pressure was increased up to $1 \times 10^{-5}$ torr when CH$_3$NH$_3$I starts to be evaporated. Although the deposition rates of the SnI$_2$ and CH$_3$NH$_3$I are maintained constant during the co-deposition, molar ratio of deposited CH$_3$NH$_3$I and SnI$_2$ is controlled by not the rate but the increase in apparent working pressure for the reason described in the prior section. In addition, the ‘working pressure’ in this paper means the pressure detected by ion gauge and indicated on the controller. To be exact, this pressure should be called ‘apparent working pressure’ since ion gauge in vacuum chamber is adjusted to the air gas, however, two terms will be used interchangeably in this paper for convenience sake.
Figure 1.2. The schematic description of co-evaporating CH$_3$NH$_3$I and SnI$_2$ in the vacuum chamber.
Chapter 2

The effect of HTLs on formation and growth of \( \text{CH}_3\text{NH}_3\text{SnI}_3 \) perovskite film

2.1 Introduction

One of the most important issues in perovskite solar cells is to grow perovskite film which is nearly single crystalline. It has been reported that optical and electrical properties such as absorption, carrier diffusion length and surface quality are dramatically improved in single crystal perovskite [31], which is essential for accomplishing high device performance. In order to epitaxially grow single crystalline perovskite film, pre-depositing suitable sublayer under the active layer is significant with regard to lattice structure as well as energy level. A. Amassian and his coworker reported that \( \text{CH}_3\text{NH}_3\text{PbI}_3 \) perovskite film has more dense interface on copper(I) thiocyanate (CuSCN) than on poly(3,4-ethylenedioxythiophene) : poly(styrenesulfonate) (PEDOT : PSS) [10] by using scanning electron spectroscopy (SEM) image. In addition, Alex K. Y. Jen and his coworker suggested that \( \text{CH}_3\text{NH}_3\text{PbI}_3 \) perovskite film has similar morphology on both ITO and PEDOT : PSS layers, and they successfully fabricated hole-transporting layer-free
perovskite solar cell. However, it is still an unresolved question which sublayer results in the best surface morphology of lead-free CH$_3$NH$_3$SnI$_3$ perovskite film and increases the crystallinity. Therefore, the crystallinity of CH$_3$NH$_3$SnI$_3$ perovskite film on the various sublayers will be investigated by using X-ray diffraction (XRD) measurement in this chapter.

### 2.2 Experiments

150 nm-thick ITO coated glass substrates were successfully cleaned with acetone and isopropyl alcohol (IPA) solution. All of the materials except CH$_3$NH$_3$SnI$_3$ perovskite were thermally heated and evaporated at the base pressure of $<1 \times 10^{-6}$ torr in the chamber. When CH$_3$NH$_3$I (Jida Ruibo Optoelectronics Tech.) is thermally evaporated in the chamber, the apparent working pressure was raised up to $1 \times 10^{-5}$ torr which is similar to the previous reports [23,24].

The deposition rate of CH$_3$NH$_3$I was monitored in real time using a crystal thickness sensor (INFICON, 5MHz) with simultaneously checking the working pressure of the chamber by ion gauge. The deposition rate of SnI$_2$ (Alpha Aesar) was kept constant during the co-deposition. The perovskite layer was deposited in vacuum chamber without annealing process and the details about co-deposition process.
for perovskite are deliberately described in chapter 1.2.4. The MoO$_3$ (Sigma Aldrich) and the BCP (Nichem) layers were deposited at a rate of 0.2 Å/s. The NPB (Nichem) and the C$_{60}$ (SES Research) layers were deposited at a rate of 1 Å/s. The BCP (Nichem) and the Al layers were deposited at a rate of 0.5 Å/s and 4 Å/s respectively. The deposition rates were calibrated using a profilometry (KLA-Tencor Alpha-Step IQ) before depositing each material. The active area of each device was 4 mm$^2$ and 72 devices could be fabricated to the max. After finishing all the evaporation, the devices were encapsulated using an epoxy resin with glass cans in an N2 environment. The UV-vis absorption spectra of the films were recorded with a VARIAN Cary 5000 UV-vis spectrophotometer. The current density-voltage (J–V) characteristics were measured under simulated AM 1.5G sunlight of 100 mW/cm$^2$ using Newport (91160A) solar simulator, and recorded using a Keithley 237 source measurement unit at room temperature. The light intensity was calibrated using a standard Si-solar cell (NREL). The scan step of J-V characteristics was 0.02 V with 0.3 seconds of interval time for each step, and the scan direction was from negative to positive voltage. The incident photon to electron conversion efficiency (IPCE) was measured using a 1000 W Xe lamp combined with a monochromator and its intensity was calibrated with a Si photodiode. The IPCE was measured without light bias under the short circuit condition. The
atomic force microscopy (AFM) image was taken by PSIA XE-100 scanning probe microscope in noncontact mode

2.3 Results and discussion

Figure 2.1 shows the XRD pattern of CH$_3$NH$_3$SnI$_3$ perovskite film grown on 150 nm-thick ITO substrate at different working pressures. All CH$_3$NH$_3$SnI$_3$ films deposited on ITO substrate exhibit sharp (110) peak which corresponds to the reported one. But peak intensity of CH$_3$NH$_3$SnI$_3$ film on ITO is somewhat low indicating that perovskite has poor crystallinity on the substrate.

To obtain better crystalline perovskite film, MoO$_3$ (5 nm) and MoO$_3$ (5 nm)/NPB (20 nm) sublayers under the perovskite are deposited on ITO. Both layers are widely used as hole transporting layers (HTLs) in the field of organic solar cells [33-34]. Figure 2.2 (a) shows the XRD pattern and absorbance of CH$_3$NH$_3$SnI$_3$ perovskite films deposited on different sublayers. It seems that CH$_3$NH$_3$SnI$_3$ perovskite is rarely formed on MoO$_3$ sublayer. It should be noted that CH$_3$NH$_3$SnI$_3$ film fabricated on MoO$_3$/NPB layer shows extremely strong and sharp (100) and (200) peaks in XRD pattern, which means that the crystallinity of perovskite film amazingly increases on MoO$_3$/NPB sublayer. In addition, absorption of perovskite film is the highest on the MoO$_3$/NPB
sublayer as shown in figure 2.2 (b), which is consistent with increased crystallinity of CH$_3$NH$_3$SnI$_3$ film. To figure out the reason for different crystallinity of perovskite film on each sublayer, XRD pattern of 50 nm-thick SnI$_2$ film is measured. Interestingly, tendency of XRD pattern for SnI$_2$ film is in accordance with that for CH$_3$NH$_3$SnI$_3$ film depending on sublayers. This indicates that initial growth of 2 nm-thick SnI$_2$ on each sublayer strongly affects the total growth of CH$_3$NH$_3$SnI$_3$ film.
Figure 2.1. The X-ray diffraction (XRD) patterns CH$_3$NH$_3$SnI$_3$ films deposited on 150 nm-thick ITO at different working pressures. Thickness of perovskite films is 46 nm, 52 nm, 66 nm and 70 nm at $1 \times 10^{-5}$ torr, $3 \times 10^{-5}$ torr, $5 \times 10^{-5}$ torr and $9 \times 10^{-5}$ torr, respectively. Reported XRD pattern with peak index is powder XRD. Peak intensities of CH$_3$NH$_3$SnI$_3$ films and SnI$_2$ film are enlarged and reduced by 2.5 times, respectively.
Figure 2.2. (a) The X-ray diffraction (XRD) patterns and (b) absorbance of CH$_3$NH$_3$SnI$_3$ films deposited on ITO (150 nm), ITO (150 nm)/MoO$_3$ (5 nm) and ITO (150 nm)/MoO$_3$ (5 nm)/NPB (20 nm) sublayers. XRD peak intensities of CH$_3$NH$_3$SnI$_3$ films and SnI$_2$ film are enlarged and reduced by 2.5 times, respectively.
Figure 2.3. (a) The X-ray diffraction (XRD) patterns of 50 nm-thick SnI$_2$ films deposited on different sublayers and (b) The X-ray diffraction (XRD) patterns of 50 nm-thick CH$_3$NH$_3$SnI$_3$ films on the various sublayers.
2.4 Conclusion

In this chapter, the effect of sub-HTLs on the formation of CH$_3$NH$_3$SnI$_3$ perovskite is investigated. The XRD results show that CH$_3$NH$_3$SnI$_3$ perovskite is difficult to be formed on ITO (150 nm)/MoO$_3$ (5 nm) layer and has a poor crystallinity on ITO (150 nm) substrate. But crystallinity of perovskite film is extremely improved when deposited on ITO (150 nm)/MoO$_3$ (5 nm)/NPB (20 nm) layer. This increased crystallinity implies better electrical and optical properties of perovskite film and is essential for enhancing device performance. The reason why CH$_3$NH$_3$SnI$_3$ perovskite film has the highest crystallinity on ITO/MoO$_3$/NPB layer is probably related to initial 2 nm-thick crystalline SnI$_2$ film. This interesting result can be applied to vacuum-processed CH$_3$NH$_3$PbI$_3$ perovskite solar cells to obtain better lead perovskite film as well as lead-free perovskite solar cells.
Chapter 3

The effect of working pressure on composition and growth of CH$_3$NH$_3$SnI$_3$ perovskite film

3.1 Introduction

The control of elemental composition of perovskite film is another critical factor to determine growth of perovskite [11]. N. G. Park and his coworker reported that concentration of CH$_3$NH$_3$I solution in two-step spin-coating process strongly affects the crystal growth of CH$_3$NH$_3$PbI$_3$ and hold sway in final cuboid size of the perovskite film [12]. They found that higher CH$_3$NH$_3$I concentration resulted in the smaller cuboid size of perovskite because the growth of seed crystal was easily inhibited by other neighbouring seed crystals at the higher concentration. Also, several reports suggest that composition of perovskite in solution process significantly influences reaction kinetics, absorption, stability and surface morphology of perovskite film which are closely related to the overall device performance [11-14]. Elemental composition of perovskite film can be directly controlled by concentration of initial CH$_3$NH$_3$I (or metal iodide) solution in solution process. In vacuum process, composition of perovskite film can be
more easily and delicately controlled by deposition rate of CH$_3$NH$_3$I and metal iodide. But as described in chapter 1, CH$_3$NH$_3$I has a poor sticking property and this material may be difficult to be adsorbed to crystal thickness sensor causing reliability problem in deposition rate displayed on the controller. Therefore, we controlled the elemental composition of CH$_3$NH$_3$SnI$_3$ film via the increase in apparent working pressure by evaporated CH$_3$NH$_3$I and the detailed explanation can be found in chapter 1.1.4.

3.2 XRD and absorption spectrum

Figure 3.1 (a) shows the XRD patterns of CH$_3$NH$_3$SnI$_3$ perovskite films deposited on ITO (150 nm)/MoO$_3$ (5 nm)/NPB (20 nm) at the different working pressures. It should be noted that (100) and (200) peak intensities become maximum when perovskite is deposited at 5×10$^{-5}$ torr, which means the crystallinity of perovskite film gets most improved at this condition. In addition, XRD patterns of the samples fabricated at 1×10$^{-5}$ torr and 3×10$^{-5}$ torr show (100) peak of SnI$_2$. This means that some amount of SnI$_2$ material is unreacted with CH$_3$NH$_3$I because the amount of evaporated CH$_3$NH$_3$I is insufficient in these working pressures. Therefore, it can be deduced that working pressure of 5×10$^{-5}$ torr is the optimal condition for formation of growth
CH$_3$NH$_3$SnI$_3$ perovskite film whose composition is nearly ideal ratio of CH$_3$NH$_3$I and SnI$_2$. Real
Figure 3.1. (a) XRD patterns and (b) absorbance of CH$_3$NH$_3$SnI$_3$ films deposited on ITO (150 nm)/MoO$_3$ (5 nm)/NPB (20 nm) at different working pressures. Thickness of perovskite films is 46 nm, 52 nm, 66 nm and 70 nm at $1 \times 10^{-5}$ torr, $3 \times 10^{-5}$ torr, $5 \times 10^{-5}$ torr and $9 \times 10^{-5}$ torr, respectively. Peak intensity of SnI$_2$ film is reduced by 2.5 times in
composition of CH$_3$NH$_3$SnI$_3$ perovskite film on ITO/MoO$_3$/NPB will be precisely investigated in chapter 3.4. By using the XRD results, crystalline sizes of all perovskite samples are also calculated from Scherrer equation as shown in Table 3.1. This equation is described as

\[ \tau = \frac{K \lambda}{\beta \cos \theta} \]  

(3.1)

Where $K$ is a dimensionless shape factor which is typically 0.9, $\lambda$ is the wavelength of X-ray, $\beta$ is the full width at half maximum (FWHM) in radians and $\theta$ is the Bragg angle. The calculation result indicates that crystalline size of perovskite is the largest at $5 \times 10^{-5}$ torr. These results can be rationalized by the hypothesis that compositional ratio of CH$_3$NH$_3$I and SnI$_2$ is so close to 1:1 at this pressure that formation and growth of CH$_3$NH$_3$SnI$_3$ perovskite are optimized and with little hindrance by unreacted CH$_3$NH$_3$I or SnI$_2$. Absorbance of CH$_3$NH$_3$SnI$_3$ perovskite films fabricated on ITO (150 nm)/MoO$_3$ (5 nm)/NPB (20 nm) at different pressures is also shown in figure 3.1 (b). Interestingly, absorbance of CH$_3$NH$_3$SnI$_3$ films gets increased as working pressure gets higher in the wavelength range of around 400-800 nm. This increase is in accordance with the increase in thickness of perovskite samples, which is probably because the amount of deposited CH$_3$NH$_3$I increases. The deposited CH$_3$NH$_3$I cannot be detected by XRD due to the small molecular amorphous characteristics of the
material, however, it has a kind of absorption in the visible light rage.
Table 3.1 Crystalline size of CH$_3$NH$_3$SnI$_3$ films deposited on ITO (150 nm)/MoO$_3$ (5 nm)/NPB (20 nm) at different working pressures calculated from Scherrer equation using XRD pattern in figure 3.1 (a).
3.3 Morphology of perovskite film

As discussed in chapter 3.2, crystallinity of CH$_3$NH$_3$SnI$_3$ perovskite films on ITO (150 nm)/MoO$_3$ (5 nm)/NPB (20 nm) varies with working pressures. Figure 3.2 shows the scanning electron microscopy (SEM) image of perovskite films fabricated on ITO/MoO$_3$/NPB layer at different pressures. As working pressure by evaporated CH$_3$NH$_3$I goes up from 1×10$^{-5}$ torr to 5×10$^{-5}$ torr, larger size of particles emerge which is consistent with the tendency of XRD patterns in figure 3.1 (a). In case of sample fabricated at 9×10$^{-5}$ torr, size of particles hardly changes compared to the one at 5×10$^{-5}$ torr. Also, the sample shows very rough surface morphology and there are several pinholes on the films which can cause current leakage and severe short-circuiting of the real device. Figure 3.3 shows atomic force microscopy (AFM) image of the same samples as shown in figure 3.2. Every AFM image takes after the SEM image and it should be noted that root mean square roughness (RMS roughness, Rq) becomes 3 times larger at 9×10$^{-5}$ torr than 5×10$^{-5}$ torr. This poor morphology means growth of compact and uniform perovskite film at the pressure of 9×10$^{-5}$ torr is retarded by excessive CH$_3$NH$_3$I. In other words, CH$_3$NH$_3$SnI$_3$ films grown at 5×10$^{-5}$ torr shows the most compact morphology which is nearly crystalline and this film is expected to exhibit improved structural and electrical
properties.
Figure 3.2. The scanning electron microscopy (SEM) image of CH$_3$NH$_3$SnI$_3$ films on ITO (150 nm)/MoO$_3$ (5 nm)/NPB (20 nm) deposited at different pressures. Thickness of perovskite films is 122 nm, 143 nm, 180 nm and 198 nm at $1 \times 10^{-5}$ torr, $3 \times 10^{-5}$ torr, $5 \times 10^{-5}$ torr and $9 \times 10^{-5}$ torr, respectively.
Figure 3.3. The atomic force microscopy (AFM) image of CH$_3$NH$_3$SnI$_3$ films on ITO (150 nm)/MoO$_3$ (5 nm)/NPB (20 nm) deposited at different pressures. Size of each image is 2 $\mu$m $\times$ 2 $\mu$m. Thickness of perovskite films is 122 nm, 143 nm, 180 nm and 198 nm at $1 \times 10^{-5}$ torr, $3 \times 10^{-5}$ torr, $5 \times 10^{-5}$ torr and $9 \times 10^{-5}$ torr, respectively.
3.4 Elemental composition of perovskite film

Figure 3.4 shows energy-dispersive X-ray spectroscopy (EDS) result of CH$_3$NH$_3$SnI$_3$ perovskite films on ITO (150 nm)/MoO$_3$ (5 nm)/NPB (20 nm) at different working pressures. The most notable thing is that elemental composition of Sn and I is almost close to 1:3 in the sample fabricated at $5 \times 10^{-5}$ torr where nearly crystalline morphology appears as discussed in the previous chapter. This indicates that the apparent working pressure of $5 \times 10^{-5}$ torr is the optimal condition for formation and growth of CH$_3$NH$_3$SnI$_3$ perovskite film where both excess SnI$_2$ and excess CH$_3$NH$_3$I are nearly absent. It is also interesting that portion of iodine steeply increases as the working pressure changes from $5 \times 10^{-5}$ torr of $9 \times 10^{-5}$ torr. The morphology of CH$_3$NH$_3$SnI$_3$ perovskite film becomes rough and many pinholes emerge in the sample as elucidated in the previous chapter. In other words, excessive CH$_3$NH$_3$I generated when depositing perovskite film in the chamber probably inhibits not only the growth of CH$_3$NH$_3$SnI$_3$ perovskite but also its crystallization.
Figure 3.4. Energy-dispersive X-ray spectroscopy (EDS) result of CH₃NH₃SnI₃ films on ITO (150 nm)/MoO₃ (5 nm)/NPB (20 nm) deposited at different pressures. Thickness of perovskite films is 122 nm, 143 nm, 180 nm and 198 nm at 1×10⁻⁵ torr, 3×10⁻⁵ torr, 5×10⁻⁵ torr and 9×10⁻⁵ torr, respectively.
3.5 Eletrical properties of perovskite film

Figure 3.5 (b) shows the electronic band gap of CH$_3$NH$_3$SnI$_3$ perovskite calculated by using Tauc plot the absorption spectrum of figure 3.5 (a). Tauc equation is written as

\[(\alpha h\nu)^2 = A(h\nu - E_g)\] (3.2)

where $\alpha$ is absorption coefficient, $h$ is Planck constant, $\nu$ is the frequency of photon, $A$ is constant and $E_g$ is the band gap energy. Absorption spectrum of the ITO (150 nm)/MoO$_3$ (5 nm)/NPB (20 nm)/CH$_3$NH$_3$SnI$_3$ (180 nm) sample fabricated at $5 \times 10^{-5}$ torr is used for the calculation because CH$_3$NH$_3$SnI$_3$ perovskite is well formed on MoO$_3$/NPB interfacial layer and unreacted CH$_3$NH$_3$I (or SnI$_2$) is absent at working pressure of $5 \times 10^{-5}$ torr as discussed previously. Electronic band gap of CH$_3$NH$_3$SnI$_3$ perovskite is found to be $\sim$1.33 eV by Tauc plot which corresponds to the several reported ones [7]. The band gap energies of CH$_3$NH$_3$SnI$_3$ perovskite previously reported in other papers are summarized in Table 3.2. It becomes more obvious that CH$_3$NH$_3$SnI$_3$ perovskite is successfully formed and grown on MoO$_3$/NPB interfacial layer in vacuum process along with XRD pattern. After identifying the successful formation of perovskite, hole-only devices are fabricated to measure hole mobility of perovskite. The charge carrier mobility can be obtained by Mott–Gurney law in space.
charge limited current (SCLC) region. The equation is described as

\[ J = \frac{9\varepsilon\varepsilon_0\mu_0 V^2}{8d^5} \exp \left( \gamma \sqrt{V/d} \right) \]  

(3.3)

where \( \varepsilon \) is dielectric constant of the material, \( \varepsilon_0 \) is permittivity in vacuum, \( \mu_0 \) is zero field mobility of charge carrier, \( d \) is the distance between the electrodes and \( \gamma \) is the field effect mobility coefficient.

The results are displayed in figure 3.6. Hole mobility for CH\(_3\)NH\(_3\)SnI\(_3\) perovskite fabricated at 5×10\(^{-5}\) torr is remarkably higher than the other samples because improved crystallinity of perovskite film results in the increased charge carrier mobility [31]. It can be predicted that other electrical properties of this perovskite film will be also most improved, which is a great help to enhancing the photovoltaic performance.
Figure 3.5. (a) The absorption spectrum of ITO (150 nm)/MoO$_3$ (5 nm)/NPB (20 nm)/CH$_3$NH$_3$SnI$_3$ (180 nm) sample fabricated at 5×10$^{-5}$ torr and (b) Tauc plot obtained from the absorption spectrum.
<table>
<thead>
<tr>
<th>Years</th>
<th>Paper</th>
<th>Band gap</th>
<th>Method</th>
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**Table 3.2** Reported band gap energy of CH$_3$NH$_3$SnI$_3$ perovskite in other papers.
Figure 3.6. (a) The dark current curve of hole-only devices fabricated at different working pressure and (b) hole mobility calculated by the fitting in space charge limited current (SCLC) region. Thickness of perovskite films is 122 nm, 143 nm and 180 nm at $1 \times 10^{-5}$ torr, $3 \times 10^{-5}$ torr and $5 \times 10^{-5}$ torr, respectively. The structure of hole-only device is ITO (150 nm)/MoO$_3$ (5 nm)/NPB (20 nm)/CH$_3$NH$_3$SnI$_3$/MoO$_3$ (10nm)/Al (100 nm).
3.6 Conclusion

In this chapter, the optimal working pressure where grown CH$_3$NH$_3$SnI$_3$ perovskite has compact and crystalline morphology, stoichiometric composition and the most improved electrical properties is investigated. XRD patterns of CH$_3$NH$_3$SnI$_3$ film on MoO$_3$/NPB layer indicate that the crystallinity of perovskite is dramatically enhanced at $5 \times 10^{-5}$ torr. It is clearly shown by SEM and AFM image that CH$_3$NH$_3$SnI$_3$ film has dense and largely crystalline morphology when fabricated at the apparent working pressure of $5 \times 10^{-5}$ torr. EDS data also stands for stoichiometric perovskite film at this pressure. Electrical characteristics of perovskite is found to be consistent with the reported ones and hole mobility becomes the most improved at $5 \times 10^{-5}$ torr. In summary, the apparent working pressure of $5 \times 10^{-5}$ torr is the best growth condition for CH$_3$NH$_3$SnI$_3$ film on MoO$_3$/NPB interfacial layer.
Chapter 4

Characterization of CH$_3$NH$_3$SnI$_3$ perovskite film with various thickness

4.1 Introduction

To achieve planar lead-free perovskite solar cells, it is essential to deposit a few hundred nanometers of CH$_3$NH$_3$SnI$_3$ perovskite film for enough absorption of the sunlight. In addition, precise control over the thickness of perovskite film is a very important engineering issue to optimizing real devices. T. L. Kelly and his coworker found that the relative amount of unreacted PbI$_2$, light absorption and individual nanocrystalline size of perovskite gradually increases as the perovskite thickness gets larger [15]. They also revealed that device with 330 nm-thick perovskite film shows the most improved $PCE$ of 11.8 %, which results from optimization of the perovskite film thickness in regard to trade-off between light harvesting efficiency and carrier diffusion lengths in CH$_3$NH$_3$PbI$_3$. Therefore, in this chapter, the effect of the CH$_3$NH$_3$SnI$_3$ perovskite thickness on absorption, film structure and overall composition will be investigated.
4.2 XRD and absorption spectrum

Figure 4.1 (a) shows the XRD pattern of CH$_3$NH$_3$SnI$_3$ perovskite film deposited on MoO$_3$ (5 nm)/NPB (20 nm) sublayers at 5×10$^{-5}$ torr with changing thickness of perovskite. Every XRD pattern of perovskite shows strong and sharp peaks of (100) and (200) grains, however, the crystallinity of perovskite changes only slightly with thickness. The variation of XRD peak intensity with thickness is more exactly displayed in figure 4.2. Peak intensities of (100) and (200) perovskite grains are both increased as perovskite gets thicker, however, the increase is not that significant. This means that structure of film and morphology are hardly changing as though perovskite film is more thickly deposited in vacuum process. Also, figure 4.1. (b) indicates that the absorbance of CH$_3$NH$_3$SnI$_3$ perovskite film also increases as perovskite gets thicker, which is essential for absorbing enough light and generating more photocurrent in planar-structured perovskite solar cells.
Figure 4.1. (a) The XRD pattern and (b) absorbance of ITO (150 nm)/MoO$_3$ (5 nm)/NPB (20 nm)/CH$_3$NH$_3$SnI$_3$ sample fabricated at 5×10$^{-5}$ torr with different thickness. The reported XRD pattern with peak index is powder XRD. Peak intensity of SnI$_2$ film is reduced by 2.5
Figure 4.2. The peak intensity change of each oriented grain with thickness. The sample is ITO (150 nm)/MoO$_3$ (5 nm)/NPB (20 nm)/CH$_3$NH$_3$SnI$_3$ fabricated at $5 \times 10^{-5}$ torr. MASnI$_3$ thickness means the thickness of CH$_3$NH$_3$SnI$_3$ perovskite film on ITO/MoO$_3$/NPB layer.
4.3 Cross-sectional SEM and EDS

Figure 4.3 (b) shows the elemental mapping of Sn and I for ITO (150 nm)/MoO$_3$ (5 nm)/NPB (20 nm)/CH$_3$NH$_3$SnI$_3$ (320 nm) sample fabricated at $5 \times 10^{-5}$ torr. It is measured by cross-sectional SEM and EDS. Note that both Sn and I are all uniformly distributed in CH$_3$NH$_3$SnI$_3$ perovskite film and much of Sn also exists in the lower ITO substrate. Cross-sectional SEM image is additionally obtained for reference as shown in figure 4.3 (a). For more quantitative analysis of elements in perovskite film, atomic ratio of Sn and I is measured by using cross-sectional EDS with measuring point changed and the results are exhibited in figure 4.4. The atomic ratio of I to Sn is in the range of 2.85–3.05 and it can be concluded that the elemental compositions are nearly uniform all over the CH$_3$NH$_3$SnI$_3$ perovskite film. It is a merit of vacuum process that controlling and maintaining the deposition rate (or working pressure) are easy. Finally, CH$_3$NH$_3$SnI$_3$ perovskite film deposited by thermal evaporation in vacuum process shows considerably uniform composition as well as enhanced crystallinity by the control of growth condition although thickness of perovskite film increases a lot.
Figure 4.3. (a) Cross-sectional SEM image of ITO (150 nm)/MoO$_3$ (5 nm)/NPB (20 nm)/CH$_3$NH$_3$SnI$_3$ (320 nm) sample fabricated at $5 \times 10^{-5}$ torr, (b) reduced image and elemental mapping for (c) Sn and (d) I.
Figure 4.4. (a) Detecting image for cross-sectional EDS, (b) EDS data for each position and (c) plot of EDS results with the position. The sample is ITO (150 nm)/MoO$_3$ (5 nm)/NPB (20 nm)/CH$_3$NH$_3$SnI$_3$ (320 nm) fabricated at $5\times 10^{-5}$ torr.
4.4 Conclusion

In this chapter, the effect of film thickness on the properties and stoichiometry of CH$_3$NH$_3$SnI$_3$ perovskite is studied. The XRD pattern and absorption spectrum reveal that thicker perovskite layer absorbs more light while its crystallinity changes only slightly with thickness. This result is optimistic to accomplish vacuum-processed CH$_3$NH$_3$SnI$_3$ perovskite solar cells where thickness of perovskite layer is needed to be over a few hundred nanometers for absorbing enough light. In addition, vacuum-processed CH$_3$NH$_3$SnI$_3$ perovskite film exhibits ideal and totally uniform elemental composition owing to the successful control of perovskite film growth in vacuum. The conclusion is that properties of CH$_3$NH$_3$SnI$_3$ film remain the almost same even if thickness of perovskite film gets larger. Based on the results in this chapter, optical simulation and fabrication of real device with thick CH$_3$NH$_3$SnI$_3$ film will be conducted in the next chapter.
Chapter 5

Optical simulation for CH$_3$NH$_3$SnI$_3$ perovskite solar cells and real device performance

5.1 Introduction

Sn-based perovskite solar cell has been first reported in 2014 and the PCE has also improved up to 6.4 % recently [7-8]. But the device efficiency of lead-free perovskite solar cell is still lower than Pb-based one. Therefore, it is needed to predict maximum PCE of lead-free device and analyze the reason why Sn-based perovskite solar cell shows insufficient performance. In this chapter, maximum short-circuit current ($J_{SC}$) of lead-free perovskite device will be calculated by using refractive index of CH$_3$NH$_3$SnI$_3$ perovskite to predict maximum PCE and real CH$_3$NH$_3$SnI$_3$ perovskite solar cells is to be fabricated in vacuum process on the basis of optical simulation results.

5.2 Optical simulation

Figure 5.1 shows the fitting results of absorption spectrum for fused
silica/MoO$_3$ (5 nm)/NPB (20 nm)/CH$_3$NH$_3$SnI$_3$ samples fabricated at different working pressures. Only the sample at $5 \times 10^{-5}$ torr exhibits well-fitted result, which is probably because unreacted CH$_3$NH$_3$I or SnI$_2$ is absent in this sample as discussed in chapter 3.4. By fitting the absorption spectrum, the refractive index $(n, k)$ values can be obtained only for the sample deposited at $5 \times 10^{-5}$ torr and these optical constants are shown in figure 5.2. And then, theoretical short-circuit current ($J_{SC}$) is calculated as a function of CH$_3$NH$_3$SnI$_3$ thickness in the device depicted in figure 5.3 (a) with assumption that all absorbed photons are totally converted to charge carriers and they are extracted. According to the result of figure 5.3 (b), $J_{SC}$ can be increased up to $\sim 23$ mA/cm$^2$ when thickness of perovskite reaches around 500 nm. If open-circuit voltage ($V_{OC}$) reaches 0.88 V which is previously reported value and fill factor ($FF$) attains $\sim 0.7$, the power conversion efficiency ($PCE$) of lead-free perovskite solar cells is expected to be $\sim 14.2 \%$ which is comparable to the one of Pb-based perovskite solar cells. In addition, the incident photon to converted electron ratio (IPCE) spectrum in this device is simulated as a function of perovskite thickness with the same assumption. The simulation result of IPCE spectrum is shown in figure 5.3 (a). It can be confirmed that 100 nm-thick perovskite absorbs enough light in the wavelength range of 350-700 nm and absorption of light in 700-850 nm wavelength is gradually increased as perovskite
thickness changes from 100 nm to 300 nm.
**Figure 5.1.** Fitting of absorption spectrum for fused silica/MoO$_3$ (5 nm)/NPB (20 nm)/CH$_3$NH$_3$SnI$_3$ samples fabricated at different working pressures.
Figure 5.2. Optical constants of CH$_3$NH$_3$SnI$_3$ sample fabricated at $5 \times 10^{-5}$ torr where $n$ and $k$ are the real and imaginary part of refractive index, respectively.
(a) 

![Diagram of device structure](

(b) 

![Graph showing Jsc versus Perovskite thickness](

(c) 

![Graph showing IPCE versus Wavelength](

- ITO
- MoO₃
- NPB
- Perovskite
- C₆₀
- BCP
- Al
- MASnI₃ 50 nm
- MASnI₃ 100 nm
- MASnI₃ 200 nm
- MASnI₃ 300 nm
- MASnI₃ 400 nm
- MASnI₃ 500 nm
Figure 5.3. (a) Device structure used in optical simulation, (b) simulated short-circuit current ($J_{SC}$) and (c) incident photon to converted electron ratio (IPCE) spectrum in the device by using the refractive index of CH$_3$NH$_3$SnI$_3$ perovskite deposited at $5 \times 10^{-5}$ torr.
5.3 Real device performance

Figure 5.4 shows the performance of real device whose structure is described in figure 5.3 (a). Unlike the result of optical simulation, all of the real devices exhibit poor performance. Every CH$_3$NH$_3$SnI$_3$ perovskite solar cell shows $PCE$ of ~0.1 %, which mainly stems from extremely low $J_{SC}$ which is under 5 % of simulated value as well as low $FF$ regardless of perovskite thickness as shown in table 5.1. The reason for this is unclear now, however, it is probably because optimization of device is insufficient in the current state or some electrical defects interrupt the operation of lead-free perovskite solar cells.
Figure 5.4. (a) J-V characteristics and (b) IPCE spectrum of the real lead-free perovskite solar device
<table>
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<tr>
<th>Perovskite thickness (nm)</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>$V_{OC}$ (V)</th>
<th>$FF$</th>
<th>$PCE$ (%)</th>
<th>$J_{SC, \text{int}}$ (mA/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.92</td>
<td>0.56</td>
<td>0.20</td>
<td>0.11</td>
<td>0.49</td>
</tr>
<tr>
<td>100</td>
<td>1.01</td>
<td>0.53</td>
<td>0.25</td>
<td>0.13</td>
<td>0.55</td>
</tr>
<tr>
<td>180</td>
<td>0.41</td>
<td>0.47</td>
<td>0.23</td>
<td>0.05</td>
<td>0.19</td>
</tr>
</tbody>
</table>

**Table 5.1.** Table of device performance with changing CH$_3$NH$_3$SnI$_3$ thickness. $J_{SC, \text{int}}$ is short-circuit current calculated by using IPCE spectrum.
5.4 Discussion and conclusion

In this chapter, refractive index of CH$_3$NH$_3$SnI$_3$ perovskite is obtained from absorption spectrum to conduct optical simulation. We can obtain optical constants ($n$, $k$) of only one sample fabricated at $5\times10^{-5}$ torr since complete and stable perovskite is formed in this condition. Optical simulation result reveals that $J_{SC}$ is able to reach $\sim$23 mA/cm$^2$ and maximum $PCE$ of lead-free perovskite solar cells fabricated in vacuum process is to be over 14 %. To the best of our knowledge, this is first prediction for efficiency limit of lead-free perovskite solar cells calculated by using refractive index. Unfortunately, real device shows poor performance contrary to the simulation result. The reason is ambiguous, however, it is probably due to insufficient optimization of real device, certain electrical defects, or short carrier diffusion length reported. If optimization of CH$_3$NH$_3$SnI$_3$ perovskite solar cells and factors that limit device performance are to be verified, the efficiency of lead-free perovskite solar cells will shortly come close to the Pb-based perovskite solar cells.
Bibliography


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초 록

유기물/무기물 혼합 페로브스카이트 태양전지는 최근 높은 전력변환 효율을 보이며 간단한 저온 공정으로 제작 가능하기 때문에 많은 주목을 받고 있다. 그러나 현재까지 보고된 대부분의 소자는 납을 기반으로 한 페로브스카이트 태양전지에 이 태양전지는 중금속 오염, 납 중독, 납 축적과 같은 심각한 문제를 일으킬 가능성이 있다. 따라서 페로브스카이트 내의 납을 다른 원소로 대체하는 것은 페로브스카이트 태양전지 분야에서 매우 중요한 주제 중의 하나이다. 주석은 주기를 표 상에서 납과 같은 14족에 해당하는 원소이며 CH₃NH₃⁺ 이온, I⁻ 이온과 함께 페로브스카이트 구조를 형성한다고 알려져 있기 때문에 현재까지 주석이 납을 대체할 수 있는 가장 유력한 원소로 생각되어왔다. 이러한 지식을 바탕으로 2014년 이후 납이 없는 주석 기반 페로브스카이트 태양전지를 일부 논문에서 보고하였으나 모든 주석 기반 소자들은 용액 공정으로 제작되었다. 용액 공정에서는 페로브스카이트 아래의 전자 수송 층이 다공성 TiO₂로 제한되어 CH₃NH₃SnI₃ 박막의 표면 특성이 나빠지
는 문제점이 있다. 또한 용액 공정으로 제작된 CH$_3$NH$_3$SnI$_3$ 페로브스카이트 박막은 산화에 대한 안정성이 낮고 전하 확산 거리가 짧다는 것이 문제점으로 보고되었다. 따라서 진공 공정이 CH$_3$NH$_3$SnI$_3$ 페로브스카이트 박막을 증착하는데 효과적인 방법이 될 수 있다. 왜냐하면 진공 공정은 깨끗한 환경, 다양한 전하 수송 층의 선택 가능성, 높은 재현성과 같은 여러 가지 장점을 가지고 있기 때문이다. 진공 공정에서 수분 및 용매가 없는 깨끗한 증착 환경은 산화에 민감한 CH$_3$NH$_3$SnI$_3$ 박막에 매우 효과적이며, 페로브스카이트의 표면 구조와 에너지 준위를 고려하여 가장 적합한 전하 수송 층을 선택할 수 있다.

본 학위 논문에서는 다양한 정공 수송 층을 도입하여, 이 하부의 정공 수송 층이 진공 증착된 CH$_3$NH$_3$SnI$_3$ 페로브스카이트 박막의 성장에 미치는 영향을 조사하였다. 그 결과 ITO, ITO/MoO$_3$와 비교했을 때 ITO/MoO$_3$/NPB 층 위에 증착된 CH$_3$NH$_3$SnI$_3$ 페로브스카이트 박막이 가장 향상된 결정성을 나타내었다. 또한 X선 회절 분석을 통해 초기에 정공 수송 층 위에 증착되는 2 nm의 SnI$_2$가 최종적인 CH$_3$NH$_3$SnI$_3$의 성장 및 결정성에 직접적인 영향을 미친다는 사실을 알 수 있었다. 추가적으로 진공 챔버의 작동 압력과 박막 두께가 CH$_3$NH$_3$SnI$_3$ 페로브스카이트 박막의 성장 및 특성에 미치는
영향이 조사되었다. 전화된 CH$_3$NH$_3$I에 의해 작동 압력을 상승시켜 가며 증착한 결과, 이온 게이지에 표시되는 작동 압력이 $5 \times 10^{-5}$ torr일 때 화학량론적이고 결정질에 가까운 표면을 갖는 CH$_3$NH$_3$SnI$_3$ 페로브스카이트 박막이 성공적으로 형성되었다. 이 압력에서 만들어진 페로브스카이트 박막은 가장 높은 정공 이동도와 함께 1.33 eV의 밴드 갭 에너지를 나타내었다. 또한 페로브스카이트의 두께가 증가하여도 박막의 특성과 균일성에는 큰 영향을 주지 않는 것으로 확인되었다. 그리고 최종적으로 광학 시뮬레이션과 실제 CH$_3$NH$_3$SnI$_3$ 페로브스카이트 태양전지를 제작을 시도하였다. 비록 실제 소자는 완전한 최적화가 되지 않아 좋은 못한 성능을 보였지만, 광학 계산 결과 페로브스카이트의 두께가 약 500 nm에 도달하였을 때 단락 전류 밀도가 최대 23 mA/cm$^2$까지 향상될 수 있음을 확인하였다. 만약 개방 전압과 충진율이 이전에 보고된 수준인 약 0.88 V, 0.7까지 각각 도달한다고 가정하면, 납이 없는 페로브스카이트 태양전자의 효율은 최대 14.2 %까지 향상될 것이며 납을 기반으로 한 페로브스카이트 태양전지에 비금가는 수준의 효율에 도달할 것으로 기대된다.

주요어: 유기물/무기물 혼합 페로브스카이트 태양전지, 진공
공정, 하부층, CH₃NH₃SnI₃, 납이 없는 페로브스카이트, MoO₃, NPB
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