



공학박사학위논문

대면적 폐로브스카이트 태양전지를 위한 코팅 및 전극 디자인 설계

Design of Coating and Electrode for Large-area Perovskite Solar Cells

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서울대학교 대학원

기계항공공학부

한 민 성

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Abstract

Perovskite solar cells have been actively researched, demonstrating a high conversion efficiency of more than 25% in a short amount of time. Perovskite solar cells have so far primarily been produced in small-area configurations, and a largearea process is needed to speed up commercialization. As a result, two different types of research on the large-area process were carried out. First, a large-area perovskite thin film was created through bar coating using a gas with thermal energy. A high crystalline perovskite thin film with large grains and no voids or pinholes could be produced using 75 °C nitrogen gas, which provided sufficient energy to evaporate solvents and proceed with proper crystallization, when gas blowing under three temperature conditions (25 °C, 75 °C, and 125 °C) was conducted. Accordingly, the solar cell created with the 75 °C gas demonstrated the highest performance among the conditions; the PCE was 20.85% for small-area solar cells, and 15.4% for solar modules with an area of 5x5 cm². Second, a conductive and light-weight flexible electrode substrate was created by adding a metal mesh to the commercially available ITO electrode flexible substrate. A 50 µm thick PEN substrate is used to photolithograph a 100 nm Au mesh that is then completely covered by a 160 nm thick ITO layer that was deposited using sputtering. This led to the formation of an electrode with a transmittance of 76.7% and a sheet resistance of 12.98 ohm/sq, as well as the fabrication of a thin, flexible, transparent electrode with a large surface area of 100 cm². Additionally, it was discovered that the flexible transparent electrode with the metal mesh conductivity

changes depending on how many paths lead from a given point. As a result, we were able to fabricate the perovskite light absorption layer and the flexible electrode substrate, two crucial elements of perovskite solar cells on a large area. This research will hopefully help perovskite solar cells become widely commercialized in the future.

Keyword : perovskite solar cell, large-area process, bar coating, hot gas blowing, metal mesh, flexible electrode substrate

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Chapter 1. Introduction

1.1. Study Background

The field of photovoltaics has been actively researching perovskite solar cells. Perovskite solar cells have the advantage of being simple to manufacture compared to silicon solar cells, which need to use high-quality crystalline silicon; the perovskite acts as a light absorption layer and can be made using a solution process. The perovskite also has material characteristics, such as shallow trap density, high dielectric constant, and high charge mobility, that make it suitable for use in solar cells.

Until now, primarily using the spin coating process, it has been possible to fabricate perovskite thin films in small-area sizes that can be handled in the lab. The fabrication of large-area perovskite solar cells using techniques like bar coating, slot die, and vacuum deposition has been researched in order to advance the field of perovskite solar cells. The perovskite layer can easily be used to fabricate solar cells or solar modules over a large area in a continuous process because it is made using a solution-based process. Among them, the bar coating method spreads the perovskite solution over a large area with a consistent film coating.

The advantages of bendability and elasticity of various electronic devices, such as wearable technology, folding displays, or smart phones, have increased the significance of flexible electrode substrates recently. This has also been applied to the field of perovskite solar cells.

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1.2. Purpose of Research

In a brief period of less than 20 years, perovskite solar cells have attained high power conversion efficiencies of more than 25%, but only for solar cell devices made with a small area of less than 1 cm². The spin coating method, which has typically been used to create perovskite films, can only be relied upon to ensure uniformity over a small area. Perovskite films should be produced in large areas in order to compete with silicon solar cells, which have a power conversion efficiency of about 25% even in an area of 100 cm² or more. The power conversion efficiency of large-area perovskite solar cells or modules with an area of more than 1 cm² created using various large-area processes like blade coating, slot-die coating, and inkjet printing, however, has not yet exceeded 20%. Two research facets were taken into account, which are detailed below, in order to improve the performance of perovskite solar cells.

The correct solvent removal step must be carried out in order to fabricate a perovskite thin film from the perovskite precursor solution. In the spin coating method, the solvent is eliminated by the centrifugal force produced by rotating the substrate, and the perovskite crystallization is induced; however, in the bar coating method, there is no such solvent removal step. At this point, the solvent can be induced to evaporate from the perovskite precursor solution coated on the substrate by blowing gas through an air knife with a thin slit width. Additionally, a more volatile solvent than the one typically used in the spin coating method, such as DMF or GBL, must be used to facilitate easy evaporation

Flexible transparent electrode substrates based on good electrode properties are necessary to fabricate a high-performance perovskite flexible solar cell. The majority of flexible electrodes currently on the market are ITO-based. ITO, a conductive oxide, must be treated at high temperatures in order to have a high conductivity of the electrode, however, this treatment will damage flexible substrates made of polymers because of their low glass transition temperature. Due to the low manufacturing temperature requirements, the conductive oxide has poor electrode properties. An electrode structure made of metal or one that incorporates metal can be used as a substitute to make up for the low conductivity that results from this.

These benefits of perovskite solar cells must be emphasized in order to successfully commercialize them as they cannot be obtained from traditional silicon solar cells. The solution processing and bending properties of the perovskite solar cells are currently their two main strengths. Roll-to-roll (R2R) manufacturing is a popular continuous process for producing perovskite solar cells quickly and easily over a large surface area. Research for the large-area process of perovskite layer coating and the technique of flexible transparent electrode substrates should be carried out concurrently for effective fabrication of perovskite solar cells by the R2R.

Chapter 2. Large-area Bar-coated Perovskite Solar Cells with Hot Gas Blowing-Assisted Crystallinity Management

This chapter has been collaborated with Dr. Junseop Byeon, Department of Mechanical Engineering, Seoul National University.

2.1. Introduction

Due to their exceptional optoelectronic properties, lead halide perovskite materials are frequently used in a wide range of devices, including detectors, LEDs, and flexible electronics.¹⁻⁴ Expectations that perovskite solar cells (PSCs) will replace traditional thin film photovoltaics have quickly increased, especially in the field of photovoltaics, given their certified power conversion efficiency (PCE) exceeding over 25% in less than two decades.^{5,6} However, given a significant PCE gap compared to those of cutting-edge devices on the lab scale, these results are regrettably still far from the perovskite solar modules' required commercialization performances.⁷ To commoditize PSCs in the real market, scalable coating techniques are needed to guarantee uniform coverage, reproducibility, and high crystallinity of perovskite films. Since the traditional spin coating method is restricted to producing films over a large area, many scalable coating techniques, including bar/blade, slot-die, and vapor phase deposition methods, have been investigated in an effort to fabricate high-quality large area films.⁸⁻¹⁴ The barcoating method, which uses an air knife, is thought to be the easy and cost-effective scalable coating method because it can be printed in ambient air and doesn't waste much of the precursor solution.¹⁵ Large-area perovskite solar modules made by bar coating have done very well, showing that mass production is possible.^{16,17}

When coating a large area of perovskite film with a precursor solution, the choice of solvent is very important to make sure the film is evenly covered, since the solvent's drying rate has a big effect on how crystals form and grow.^{18–20} Unlike the spin-coating method, which uses an anti-solvent method to quickly remove the solvent, the blade and bar coating methods don't use the anti-solvent method. This

makes it hard to remove the solvent quickly and makes it harder to evaporate the solvent selectively.^{20,21} Even though blowing air and heating a substrate can help solvent evaporate, commonly used polar solvents like N, Nthe Dimethylformamide (DMF), y-butyrolactone (GBL), and Dimethyl sulfoxide (DMSO) have a high boiling point and low volatility at room temperature, which makes it hard to quickly and selectively evaporate the solvents.^{17,22} Because a slow solvent evaporation can cause very large islands with poor surface coverage, like crystallites, it is important to use a solvent that evaporates quickly.^{17,18,22} Among the many possible solvents, 2-methoxyethanol (2ME) has been found to be a good substitute for preventing late evaporation in meniscus coatings. Compared to the polar solvents that have been used up until now, 2ME has a low boiling point, a high volatility, a low donor level, and a high wetting ability with substrates.^{22,23} For these reasons, 2ME is seen as a good solvent for a scalable meniscus coating that can play a big part in bringing the commercialization of PSCs closer. Several studies have shown that you can make perovskite solar modules using a scalable bar coating method and 2ME as a solvent. Huang et al. got a PCE of 15.86% in a MAPbI3-based flexible perovskite solar mini-module with an active area of 42.9 cm^{2,24} Seok et al. also show an effective FAPbI3-based perovskite solar module with a certified PCE of 17.53% and an aperture area of 31 cm².¹⁷

Perovskite crystallinity is thought to be as important as the right solvent for a scalable coating for making perovskite solar devices that work well. Aside from methods that involve changing materials, such as replacing cations/anions and/or adding additives, many researchers have tried to come up with technical ways to improve the crystallinity of perovskite by changing a process, such as by annealing at a high temperature for a short time, annealing in a solvent, and the hot-casting

method.^{25–27} In particular, the hot casting method has been used a lot to try to make perovskite films with large grains and high crystallinity.²⁷⁻²⁹ The hot casting method takes advantage of how quickly the solvent evaporates by preheating the precursor solution or the substrate to a certain high temperature, which makes a film with a low defect density.^{27,29} The method can also be used to make a twodimensional (2D) perovskite layer because it helps a 2D crystal plane have a preferred orientation.^{30,31} But in scalable coating methods, the hot casting method is usually used when the perovskite film was made using a precursor solution made from a solvent with a high boiling point.^{13,27,29,32} This means that the hot casting method is rarely used to make perovskite films based on a volatile solvent using a scalable coating method. This is because the method makes it hard to control how fast the solvent evaporates, which leads to an incomplete perovskite film. It would be hard to find the best temperature to get a hot casting effect because volatile solvents like 2ME and acetonitrile (ACN) have a low boiling point and a high vapor pressure at room temperature, which is the opposite of solvents like DMF and GBL.^{22,33–35} So, we need to find a way to make a technology that works like hot casting by using a solvent with a low boiling point that can be used in large-scale coating processes.

Here, we came up with a new way to make perovskite more crystalline, cover it evenly, and improve the performance of perovskite solar cells by using a hot gas blowing (HGB) method during the bar coating procedure. The temperature of the blowing gas is an important part of controlling how quickly the solvent dries and how the grains grow when the solvent is the volatile 2ME. In this case, the rate of 2ME evaporation after blade coating is controlled by blowing N₂ gas at a certain temperature, which changes the shape of the perovskite film. Spatial photoluminescence (PL) mapping showed that the temperature of the gas being blown has a big effect on how long photo-generated carriers last. The electronic band alignment and the Pb/I ratio were studied to learn more about how the change in the work function (WF) of perovskite films caused by the formation of defects during the coating method helped by hot gas blowing. We made 2ME-based perovskite solar cells that have a PCE of 20.85% under hot-gas-blowing conditions at 75°C (denoted as HGB75). We made a 5 cm² x 5 cm² perovskite solar module with a PCE of 15.4% to see if it was possible to make perovskite photovoltaics that could be commercial. Our method is the first way to use hot casting without preheating a substrate and improve the quality of a perovskite solar module in a coating that can be used on a large scale.

2.2. Results and Discussion

We show that bar coating with the hot gas blowing (HGB) system can improve the crystallinity of perovskite and make it easier to make a conformal thin film, which can be used in a coating technique that can be scaled up. The main idea behind this system is to use an air knife with a certain temperature of N_2 gas. The system not only improves crystallinity caused by hot casting, but it also stops side effects that can happen when the highly volatile 2ME solvent and hot casting are used together. Figure 2.1a shows how blowing hot gas helps the bar coating process. In the system, the 2ME-based perovskite precursor spread out as the bar moved on the substrate and kept the same distance from it. Figure 2.1b shows what happens when N_2 gas at a certain temperature flows over a bar-coated 2ME-based precursor on the substrate. This evaporates some of the solvent and leaves the perovskite intermediate phase. (In the system, the 2ME-based precursor spread out as the rod moved while keeping the same distance from the substrate.)

Then, the substrate is annealed to make sure that all of the solvent is gone and to make the grains grow. To make sure that perovskite solar cells work well, the quality of the perovskite film and the fact that there are no pinholes in the film are very important. Measurements with a scanning electron microscope (SEM) were done to confirm the shape of the perovskite film made with this system. Figures 2.1c–e show SEM images of perovskite films made using the hot gas blowing system with blowing gas temperatures of 25 °C, 75 °C, and 125 °C, respectively (HGB25, HGB75, and HGB125). Keep in mind that the hot blowing gas at 25 °C is the same as coating a bar with an air knife and normal air. Formamidinium (FA)-

based perovskite crystals made with HGB25 and HGB75 have a good morphology and cover the glass substrate completely. However, perovskite films made with HGB125 have voids and pinholes that make them cover the glass substrate unevenly. Since the boiling point of 2ME is around 125 °C and 2ME evaporates easily at 125 °C, the poor coverage may be due to how quickly the solvent evaporates compared to how quickly mass transfers for grain growth.^{23,36} To see how the temperature of the blowing gas affected the size of the perovskite grains, we used ImageJ software to figure out the grain size from SEM images and made a statistical histogram based on the temperature of the blowing gas. Figure 2.1f shows that the average grain size of the HGB25 perovskite film is 537.7 nm. But the grain size of perovskite films made with the hot gas blowing method increased by a lot, reaching 841.5 nm and 932.7 nm, respectively (see Figures 2.1g and 2.1h). These results show that the energy from the temperature of the gas blowing was used not only to make the solvent evaporate, but also to help the grain grow. The effect of hot gas blowing was seen in a perovskite film made by the hot casting method.^{27,29} As shown in Figure 2.2, the advantages of this system are similar to those of hot casting because it stops the fast evaporation of the solvent from causing a non-uniform morphology.



Figure 2.1. Hot gas-blowing assisted bar coated perovskite films. a. Schematic pictures of hot gas blowing for bar-coated large area perovskite films: first, the solution layer gets thinner as the bar moves through. Second, when gas is blown, an intermediate phase is made. Last, annealing is used to make a layer of perovskite. b. The way 2-methoxyethanol evaporates to make an intermediate layer through hot gas blowing. c–e. SEM images of hot gas blowing perovskite film surface morphologies that change with temperature. The images have scale bars that are 500 nm. f-h. Histogram of the size of perovskite grains and their average values at 25, 75, and 125 °C(HGB25, HGB75, and HGB125, respectively).



Figure 2.2. Photographs of change of perovskite precursor solution on different temperatures of hot plate up to 60 sec. The solution at room temperature, 25 °C (upper line), stays the same. However, the solution at 75 °C or 125 °C changes quickly to a non-homogeneous state. (in 20 to 30 seconds).

We used classical nucleation theory to figure out how the temperature of the blowing gas affected the size of the grains, which is shown by equations (1), (2), and (3).^{37,38} A thermodynamic model says that the nuclei, which have enough energy to be stable in solution, can keep growing in a controlled way.

$$\Delta G_T = \Delta G_V + \Delta G_S \tag{1}$$

$$\Delta G_V = \frac{4}{3} \pi r^3 \Delta g_V \tag{2}$$
$$\Delta G_S = 4 \pi r^2 \gamma \tag{3}$$

Where, ΔG_V is the change of the volume energy and ΔG_S is a change of the surface energy. Δg_V , γ , and r indicate the change of the bulk-Gibbs energy per volume, the surface tension per unit area and the particle radius in the solution, respectively. So, the change in the total Gibbs energy must have a critical point for stability, and the radius of the nuclei corresponding to the critical point of the total Gibbs energy can be thought of as a critical radius beyond which the nuclei don't dissolve in the solution, as shown in Figure 2.3a. So, nuclei with a radius larger than the critical radius (r_c) can be stable in the solution, while nuclei with a radius smaller than the critical radius are likely to dissolve back into the solution on their own. So, r_c can be thought of as the minimum radius at which the phase can be kept and growth can keep happening. Based on statistical thermodynamics, the energy distribution of the nucleus can be described as a Boltzmann distribution. As the temperature of the system goes up, the probability density of nuclei with energy above the critical Gibbs energy goes up.^{38,39}

$$\rho \sim \exp(-\frac{\Delta G_c}{K_T}) \tag{4}$$

During the bar coating process, blowing 25°C gas would not be able to move enough energy to overcome the critical Gibbs free energy in the wet film. So, nucleation of the perovskites doesn't happen very often, as shown in Figure 2.3b, because many of the embryos don't have enough energy and fall apart in the solution. On the other hand, when perovskite is heated to 75 °C and annealed, perovskite nuclei that are bigger than the critical radius grow right away from perovskite seeds if enough energy is given during the annealing process. In Figure 2.3c, the seeds that form in the wet film help the solute move through the film and the grain grow. In previous studies of a self-seeding growth method, the same effects were seen.^{40,41} At 125 °C, the high temperature and excess energy of the blowing gas cause the solvent to evaporate very quickly. This slows down the mass transport of the solute in the wet film. This makes pinholes and voids, as we've talked about before and as shown in Figure 2.1e.



Figure 2.3. a) A schematic drawing of a nucleation free energy diagram showing the critical radius of the nucleus and the critical gibbs energy barrier. b) A diagram of the process of crystallization in HGB25. The nucleus must overcome the Gibbs energy barrier to keep growing (Region 1). c) A diagram of the process of crystallization in HGB125. In HGB75 and HGB125, crystallization started on its own because the size of the nucleus was bigger than the critical radius (Region 2)

Atomic force microscopy was used to get a topography image to learn more about how the morphology of the perovskite film changed in response to the temperature of the blowing gas (AFM). Figures 2.4a-c show typical AFM pictures of the perovskite film made with the HGB25, HGB75, and HGB125 conditions. The grain size of the perovskite film in each condition is pretty close to what the results from the SEM images show. Figures 2.4d-f show that we also checked how rough the surface of each perovskite film was. The surface roughness of the films made in the HGB25 and HGB75 conditions, which both have uniform coverage, is 23.31 nm and 21.23 nm, respectively. Figure 2.1e shows that the surface roughness of the perovskite film in the HGB125 condition was higher (32.09 nm), possibly because voids and pinholes formed. Table 2.1 gives detailed information about the roughness of a film. Using conductive AFM (c-AFM), as shown in Figure 2.5, we also looked at how the surface's electronic transport properties changed depending on the temperature of the blowing gas. Figure 2.4a shows the morphology mapping and current spectra of controlled perovskite films. The c-AFM image of HGB25 and HGB75 film showed even distributions of current intensity, but some areas had low current intensity due to the roughness of the surface. In HGB125, on the other hand, all of the monitored areas were not the same because the perovskite crystals were very rough. The bottom photocurrent spectra showed flat and clear spectra. We found that the shape of a perovskite film's space plays a big part in how well it conducts electricity. Surface roughness and voids can make it hard for charges to move to the layer that moves charges. This causes high J-V hysteresis and poor performance.⁴²⁻⁴⁴ Based on this result, we can estimate that each perovskite solar cell with a different HGB condition would have a different J-V curve.



Figure 2.4. Characteristics of perovskite films. a-c. Topography images of the surfaces of perovskite HGB25, HGB75, and HGB125. Root mean square (RMS) roughness values are shown in the figures. The scale bar in the figures is 1 μ m. d-f. Their roughness graph for different gas-blowing temperatures. g-i. Photoluminescence mapping on perovskite surfaces with different gas blowing temperatures (HGB25, HGB75, and HGB125, respectively). The scale bar in the figures is 4 μ m.

Sample	Rq ^{a)} (nm)	Ra ^{b)} (nm)	$Rz^{c)}(nm)$
HGB25	23.31	18.78	157.91
HGB75	21.23	16.77	130.25
HGB125	32.08	25.80	190.08

Table 2.1. RMS roughness data of perovskite surfaces of different gas blowing temperatures. ^{a)} Root mean square roughness; ^{b)} Roughness average; ^{c)} Average maximum height of the profile.



Figure 2.5. C-AFM images of the perovskite films of different gas blowing temperatures. Perovskite's current distribution is strongly affected by how rough the surface is. So, the overall current intensities of HGB25 and HGB75 c-AFM are the same, but the surface current intensity of HGB125 is not coherent. The difference in surface roughness height is big, and so is the difference in surface current, according to the c-AFM measurement.

We used fluorescence lifetime imaging microscopy to learn more about how carriers move on a microscopic scale. Fluorescence lifetime imaging microscopy (FLIM) is a special way to see how long photo-generated charge carriers stay in a film.⁴⁵ Through the measurement, the location of the perovskite and the uniformity of the carrier lifetime across the entire film can be found. Figures 2.4g-i show how the lifetimes of photogenerated charge carriers change with the temperature of the gas. Blue and dark green show places where the charge carriers have short lifetimes, while light green and red show places where the charge carriers have long lifetimes. Figure 2.4h shows that the FLIM results show that the photoluminescence (PL) lifetimes of the perovskite film in the HGB75 condition were uniform and long, giving it a light green color. In the HGB25 and HGB125 cases, on the other hand, dark green areas show a shorter lifetime and take up most of the image. Figure 2.4i shows that, for the HGB125 condition, there are dark spots in some parts of the image, which means that voids and pinholes are forming. The SEM and AFM images in Figure 2.1c-e and Figure 2.4a-c, respectively, show the same things. When radiation recombination is the main process and there aren't many defects in the film, the V_{OC} in the device can be increased, which brings the carrier lifetimes longer.^{46,47} From what we've seen before, we know that blowing hot gas can not only make the grains bigger in materials with high crystallinity, but it can also make the carriers last longer.

To figure out how the process temperature affects the optical properties of perovskite films, the UV-Vis absorption and PL spectra were measured. As shown in Figure 2.6a, the band gap calculated from the optical absorption edges of all films doesn't change much, no matter what the temperature of the process is. But as the process temperature goes up, the signal of absorption from 300 nm to 500 nm goes down. As has been shown in other papers, the change can be seen as a decrease in intensity caused by the formation of voids and pinholes.^{48,49} In Figure 2.6b, the steady-state PL intensities of films made at different process temperatures are shown. In comparison to the other conditions, the perovskite film from the HGB75 condition has the strongest PL emission. Figure 2.7 shows that the thicknesses of the perovskite films are similar. This means that the perovskite film with the highest crystallinity in the HGB75 condition has the fewest non-radiative recombination centers, where radiation can be scavenged most efficiently. Deeplevel defects can be caused by defects on the surface of the perovskite or at the grain boundary. When this happens, non-radiative recombination losses happen, which lowers the PL intensity.^{47,50} The reason the PL intensity is higher in HGB75 than in HGB25 is because the crystallinity is better and there are fewer grain boundaries. The PL intensity is lower in HGB125 because voids and pinholes are forming. Figure 2.6c shows the charge carrier lifetimes of perovskite films made under different conditions. The carrier lifetimes of the perovskite films made in the HGB25, HGB75, and HGB125 conditions are estimated to be 294, 312 and 264 ns, respectively. The improved carrier lifetimes in the HGB75 condition are closely tied to the previous PL results. This is also in line with the increased α -phase signal in Figure 2.8's X-ray diffraction (XRD) results. In relation to this, we calculated the full width at half maximum (FWHM) of the perovskite peaks. The (110) diffraction

peak got stronger as the gas temperature went up, and its FWHM went from 0.157° (HGB25) to 0.095° (HGB75) to 0.097° (HGB125) to very similar values with 0.097. This result shows that the quality of the perovskite crystal depends on the temperature of the gas used to blow it and the size of the grains after they are blown. The information is listed in the table below in the Figure 2.8. Both steady-state and time-resolved PL measurements confirm that the perovskite film from the HGB75 condition effectively blocked non-radiative recombination paths with relatively few deep-level defects, which led to a longer carrier lifetime.



Figure 2.6. Investigation of the gas blowing temperature dependent perovskite films a. UV-vis absorbance of perovskite films of different gas blowing temperatures. (HGB25, HGB75, and HGB125) b. Steady-state photoluminescence and c. Time-resolved photoluminescence of perovskite films of different gasblowing temperatures. d. Space charge limit current (SCLC) measurement of perovskites using ETL-based structures; FTO/SnO₂/perovskite/C₆₀/BCP/Ag. e. Ultraviolet photoelectron spectroscopy (UPS) measurement shows valance band maximum and cut-off binding energy of perovskite films of different gas-blowing temperatures. f. Band alignments of perovskite films derived from UPS data.



Figure 2.7. Cross-sectional SEM images of perovskite layers of different gasblowing temperatures (HGB25, HGB75, and HGB125, respectively) on the glass substrate. All of the perovskite layers are about 400 nm thick and have good crystallinity in a vertical direction, no matter what the conditions are. Perovskite grains are closely packed in HGB25, but they are small. In HGB75, large perovskite grains are densely formed. In HGB125, big grains form, but there are also voids.



Figure 2.8. XRD graph of different gas blowing temperature and their full-width at half maximum (FWHM) data. Without any sign of PbI2 or the delta phase of the perovskite, the alpha phase of the perovskite is confirmed in all situations. The alpha phase of the perovskite was used to figure out the FWHM data.

Space charge limited current (SCLC) measurements were also done to find out how the temperature of the blowing gas changed the number of electron traps in the perovskite film.^{51,52} Electron-only types of devices were prepared with the structure of FTO/SnO₂/perovskite/C₆₀/BCP/Au. Figure 2.6d shows that there is an ohmic region where the bias voltage is proportional to the current density voltage. The trap-filled limit voltage (VTFL) can be used to prove that the voltage in the ohmic region and the voltage in the trap-filled region meet in the middle. Perovskite films made in HGB25, HGB75, and HGB125 conditions have VTFL values of 0.35, 0.29, and 0.35 V, respectively. The following equation can be used to figure out the number of traps (Nt):^{51,52}

$$V_{\rm TFL} = \frac{eN_{\rm t}d^2}{2\varepsilon\varepsilon_0} \tag{5}$$

Here, e, d, ε , and ε_0 are the elementary charge, the thickness, the vacuum permittivity, and the relative dielectric constant of the perovskite films, respectively. Perovskite is considered to have a relative dielectric value of around 46.9.⁵³ Figure 2.7 shows a cross-sectional SEM image, which can be used to calculate that the thickness of the perovskite film is about 400nm. The calculated N_t values of the perovskite film in the HGB25, HGB75 and HGB125 cases are 1.21×10^{16} cm⁻³, 9.45×10^{15} cm⁻³ and 1.12×10^{15} cm⁻³, respectively. (see Figure 2.6d, inset table) This result shows that the perovskite film from the HGB75 condition has a significant decrease in the number of traps. This is in good agreement with previous FLIM and PL results.

Ultraviolet photoelectron spectroscopy (UPS) measurements were done to find out
how the temperature of the blowing gas changed the electronic structure of the perovskite film. Figure 2.6e and Table 2.2 show the maximum binding energy of the valance band and the cut-off binding energy of perovskite films with different temperatures of gas blowing. Figure 2.6e shows that the difference in energy between the valence band and the Fermi level in a film under the HGB25 condition is 1.46 eV and the Fermi level is 3.93 eV. On the other hand, the difference in energy between the valence band and the Fermi level in the HGB75 and HGB125 perovskite films is 1.39 eV, which is less than the value for the HGB25. At 4.03 eV and 4.02 eV, the EF energy alignment is the same for both the HGB75 and HGB125 films. Despite having the same bandgap, these results show that the ntype properties of the HGB25 film are stronger than those of the HGB75 and HGB125 films. Figure 2.6f is a schematic drawing of how UPS measurements show the energy alignment of perovskite films made at different temperatures. We proved that the type of perovskite film changed depending on the temperature of the gas being blown over it. The type of defect, called the self-doping effect, decides how the type of perovskite thin film changes.^{54,55} When there are many ntype defects in a thin film, the film has n-type properties. On the other hand, a perovskite thin film has p-type properties if it has many p-type defects. The amount of lead (Pb) and iodine (I) in the perovskite film can be changed to change the types of flaws in the film.^{54,56} Studies have shown that perovskite films with more Pb or less Pb have n-type properties and those with less Pb have p-type properties. This is because the energy of the defects depends on the atomic ratio of Pb to I.^{57,58} Table 2.3 shows how the atomic ratio of the iodide elements to Pb is compared to the temperature of the blowing gas to figure out how WF is changing. The I to Pb ratio of the HGB25 perovskite film is 2.76, while the I to Pb ratios of the HGB75

and HGB125 perovskite films are 2.84 and 2.86, respectively. The ratio of I/Pb goes up as the process temperature goes up, which suggests that process temperature is a key factor in the overall composition of the perovskite. We also found that a high blowing gas temperature makes it easier to make a perovskite film that is similar to an intrinsic semiconductor and has a full perovskite composition, compared to making a perovskite film with gas at room temperature. This happens because blowing gas at a high temperature gives the perovskite film a low concentration of defects and makes it easier for the solvent to evaporate quickly, making an effect similar to that of hot casting.^{27,29}

Conditions	HGB25	HGB75	HGB125
Cut-off (eV)	17.29	17.18	17.19
Work Function (eV)	3.93	4.04	4.03
Valence Band Maximum (eV)	5.39	5.43	5.42

Table 2.2. Cut-off energy and work function calculated from UPS data of perovskite films of different gas-blowing temperatures. The cutoff energy and valance band maximum were figured out by fitting curves to the He photon source (21.22 eV). From those values, work function is derived.

Quantification								
HGB25	BE [eV]	FWHM [eV]	RSF	Atomic conc. [%]	Error [%]	Mass conc. [%]	Error [%]	I/Pb ratio
Br 3d	71.09	0.00	1.06	0.3	0.10	0.4	0.14	
O 1s	531.59	0.00	0.78	3.4	0.40	0.9	0.11	
N 1s	399.99	0.00	0.48	16.5	0.49	3.9	0.12	
Pb 4f7	137.89	0.00	4.76	9.1	0.15	31.8	0.21	I/Pb
I 3d5	618.59	0.00	6.21	25.2	0.37	53.8	0.25	2.70110
C 1s	284.49	0.00	0.28	45.4	0.77	9.2	0.24	
HGB75	BE [eV]	FWHM [eV]	RSF	Atomic conc. [%]	Error [%]	Mass conc. [%]	Error [%]	
Br 3d	71.29	0.00	1.06	0.2	0.09	0.3	0.11	
O 1s	530.39	0.00	0.78	2.9	0.40	0.7	0.10	
N 1s	399.99	0.00	0.48	19.4	0.55	4.0	0.12	
Pb 4f7	137.89	0.00	4.76	10.5	0.18	32.3	0.20	I/Pb
I 3d5	618.59	0.00	6.21	29.8	0.48	56.1	0.24	2.83097
C 1s	284.39	0.00	0.28	37.1	0.92	6.6	0.23	
HGB125	BE [eV]	FWHM [eV]	RSF	Atomic conc. [%]	Error [%]	Mass conc. [%]	Error [%]	
Br 3d	71.29	0.00	1.06	0.3	0.11	0.3	0.13	
O 1s	530.49	0.00	0.78	4.2	0.43	1.0	0.11	
N 1s	399.99	0.00	0.48	19.2	0.51	4.1	0.11	
Pb 4f7	137.89	0.00	4.76	10.2	0.17	31.9	0.20	I/Pb 2 86040
I 3d5	618.59	0.00	6.21	29.0	0.45	55.9	0.24	2.00049
C 1s	284.49	0.00	0.28	37.1	0.88	6.8	0.23	

Table 2.3. The amount of each element can be seen in the XPS data of perovskite layers of HGB25, HGB75, and HGB125 (C, N, O, Pb, I, and Br). The data could be used to figure out the ratio of I to Pb, which is linked to the formation of p-type defects.

The performance of perovskite solar cells is measured depending on the temperature of the blowing gas. The structure of PSCs can be summarized as FTO/SnO₂/Cs-doped $(FA_xMA_y)Pb(I_zBr_{1-z})/Spiro-OMeTAD/Au$ as illustrated in Figure 2.9a. Figure 2.9b shows the J-V curves of the PSCs with the best performance from both backward and forward scans. Table 2.5 has more information about these curves. More than 30 PCE samples were listed and put in the right order. For the HGB25, HGB75, and HGB125 PSCs, the highest PCE at a reverse scan is 19.70%, 20.85%, and 19.20%, respectively (see Table 2.4). While the J-V hysteresis in the PSCs for HGB25 and HGB75 is smaller (HI 3.55% for HGB25 and HI 3.27% for HGB75), it is clear in the PSC for HGB125 (HI 5.38% by HGB125). This could be because the perovskite film of HGB125 is very rough and has a lot of holes in it. This level of roughness and the number of voids make it easier for charge to build up and ions to move at the interface, which makes the J-V hysteresis worse. Figure 2.9c shows statistical histograms of the J-V characteristics of the PSCs made under each condition. The average PCEs of the PSCs for the HGB25, HGB75, and HGB125 conditions were 18.51%, 19.32%, and 18.14%, respectively. The PSCs from the HGB75 condition had the highest PCE because their open-circuit voltage (Voc), shot-circuit current density (Jsc), and fill factor (FF) were all higher than those from the HGB25 and HGB125 conditions. Figure 2.10 shows the photovoltaic parameters of Voc, Jsc, and FF for the HGB25, HGB75, and HGB125 samples based on the data from 30 cells for each case. These results are the same as what PL mappings and SCLC have shown in the past. Figure 2.9d shows that the stabilized power output (SPO) of the PSCs at different temperatures follows the same pattern as the PCE measured from a J-V scan. PSCs from the HGB75 condition had a PCE difference from the measured J-V scan of only 0.01% at a maximum power point voltage of 0.89 V. Also, we looked at the long-term photostability of an encapsulated HGB75 optimized condition sample under 1 Sun (RT, 100m Wcm-2) without a cooling system and a UV cut filter. This showed that the device has reliable photostable perovskite solar cells that keep about 93% of their initial PCE after 300 hours. (see Figure 2.11) The dark current density-voltages of PSCs with different process temperatures were scanned to figure out how good the diode was. On semi-logarithmic plots, the dark current density-voltage curve can be used to find the dark saturation current. A perovskite solar cell's quality is closely linked to its dark saturation current (J_0) . When J_0 goes up, it means that the diode isn't working well and that more charge carriers are recombining.^{59,60} Figure 2.9e shows that the PSC for the HGB75 condition has a low dark saturation level, which is a good sign for a diode with a high open-circuit voltage. Also, electrochemical impedance spectroscopy (EIS) was used to find out how the perovskite solar cells that were made at different temperatures worked. Figures 2.9f and 2.9g show Nyquist plots with an equivalent circuit for the fitting resistance and recombination resistance, which were calculated from the Nyquist plots.⁶¹ The PSCs from the HGB75 condition have a higher recombination resistance than those from the HGB25 condition. This means that the PSCs from the HGB75 condition were able to stop recombination losses. In particular, the PSCs made by HGB125 have the lowest recombination resistance. This is because the many voids and pinholes in this case can get in the way of efficient charge transfers. The results of the EIS show that the HGB75 condition with the lowest recombination losses of PSCs causes an increase in Voc and FF. We got external quantum efficiency (EQE) spectra with wavelengths between 300 and 900 nm to find out how well photons from the outside are turned into electrons. (see Figure

2.9h). From the external quantum efficiency (EQE) values of the HGB25, HGB75, and HGB125 cases, the integrated J_{SC} of PSCs is calculated to be 22.4, 23.2, and 23.1 mA/cm-2, which is the same as the measured J_{SC} value and the integrated value of PSCs under 1 sun illumination. (See Table 2.5 and Figure 2.10). Compared to the HGB25 and HGB125 PSCs, the HGB75 PSCs had higher integrated current densities. This showed that they were good at extracting charge because their film quality was better and they had low shunt paths with even coverage, as we talked about in the discussion of our previous results.



Figure 2.9. Schematic and characteristics of bar coated perovskite solar cells. a. Scheme of structure of a perovskite solar cell. b. *J-V* measurements of perovskite solar cells fabricated by using different gas-blowing temperatures; from left to right, HGB25, HGB75, and HGB125, respectively. c. Power conversion efficiency (PCE) statistics perovskite solar cells and d. Maximum power point tracking (MPPT) and stable power output (SPO) measurements of perovskite solar cells with different gas-blowing temperatures. e. Dark current measurements of perovskite solar cells and f. Electrochemical impedance spectroscopy (EIS) of perovskite solar cells of different gas blowing temperatures Nyquist plots (inset figure shows an equivalent circuit for the calculation) g. Recombination resistance was calculated from the Nyquist plots. h. External quantum efficiency (EQE) and their calculated current density (*Jsc*) of perovskite solar cells of different gas blowing temperatures.

Sample	V _{OC} [V]	J _{SC} [mA/cm ²]	FF [%]	PCE [%]	
HGB25	1 13	23.13	75.28	19 70	
(Reverse)	1.15	25.15	15.20	19.70	
HGB25	1 1 1	22.20	70.66	18 35	
(Forward)	1.11	23.39	70.00	10.35	
HGB75	1 1 4	24.02	76 16	20.85	
(Reverse)	1.14	24.02	70.10	20.83	
HGB75	1 12	24.02	72.12	10.53	
(Forward)	1.15	24.02	12,12	19.55	
HGB125	1.07	22.95	74.02	10.20	
(Reverse)	1.07	23.83	74.92	19.20	
HGB125	1.00	23.83	68.29	17.24	
(Forward)	1.00				

Table 2.4. Characteristic of perovskite solar cells of different blowing gas temperatures including reverse and forward scans of *J-V* measurements.



Figure 2.10. Statistical data of perovskite solar cells of HGB25, HGB75, and HGB

125; (left) Voc, (middle) Jsc, and (right) FF.



Figure 2.11. Long-term photostability measurement of the HGB75 sample. The device was encapsulated and the measurement was conducted under 1 sun illumination at room temperature. The HGB75 device maintained about 93% of its original power after 300 hours.

UCP25	V _{oc}	J _{SC}	Fill Factor	PCE
HOD25	[V]	[mA/cm ²]	[%]	[%]
1	1.12	22.34	72.94	18.30
2	1.10	21.39	75.53	17.76
3	1.08	23.09	72.85	18.23
4	1.10	21.68	76.11	18.23
5	1.12	22.44	74.32	18.67
6	1.12	23.60	73.64	19.53
7	1.08	23.17	74.59	18.74
8	1.12	21.79	75.65	18.44
9	1.13	23.56	72.63	19.28
10	1.10	21.65	75.07	17.92
11	1.12	22.11	73.40	18.21
12	1.11	22.22	75.15	18.56
13	1.11	22.56	73.23	18.41
14	1.11	22.25	74.21	18.27
15	1.13	23.21	73.39	19.21
16	1.11	22.29	74.61	18.43
17	1.12	22.44	75.85	19.02
18	1.11	22.74	75.54	19.03
19	1.09	22.96	74.91	18.67
20	1.11	22.11	75.08	18.36
21	1.11	22.66	74.28	18.67
22	1.11	21.58	76.20	18.22
23	1.10	22.56	75.06	18.71
24	1.11	22.45	74.65	18.53
25	1.10	21.75	74.00	17.67
26	1.10	21.75	74.00	17.67
27	1.11	21.57	76.28	18.19
28	1.13	23.13	75.28	19.70
29	1.10	21.79	74.06	17.75
30	1.12	22.37	75.92	18.96
Average.	1.11	22.37	74.61	18.51

UCP75	V _{oc}	J _{SC}	Fill Factor	PCE
IIOD75	[V]	[mA/cm ²]	[%]	[%]
1	1.12	24.51	71.00	19.52
2	1.10	23.43	72.65	18.72
3	1.10	22.34	75.88	18.69
4	1.13	23.63	75.37	20.04
5	1.10	22.43	74.73	18.48
6	1.12	23.09	76.78	19.92
7	1.12	23.12	74.25	19.25
8	1.10	23.01	71.90	18.27
9	1.10	23.11	73.29	18.69
10	1.10	22.30	75.39	18.55
11	1.13	24.02	72.12	19.53
12	1.10	23.22	72.11	18.47
13	1.10	22.31	75.23	18.46
14	1.14	23.92	73.59	20.01
15	1.13	24.11	72.57	19.74
16	1.14	23.78	75.08	20.31
17	1.14	23.98	73.64	20.08
18	1.11	22.92	71.71	18.21
19	1.13	24.14	74.22	20.28
20	1.11	22.81	75.06	19.05
21	1.12	22.09	74.56	18.41
22	1.13	24.14	74.45	20.36
23	1.11	22.25	75.94	18.72
24	1.11	23.30	75.61	19.61
25	1.13	24.02	75.56	20.54
26	1.13	23.72	75.39	20.22
27	1.14	23.74	74.25	20.03
28	1.12	22.24	72.85	18.15
29	1.14	24.02	76.16	20.85
30	1.12	22.50	73.37	18.42
Average.	1.12	23.27	74.16	19.32

HGB125		J_{SC} [mA/cm ²]	Fill Factor	PCE
1	1.06	23.06	74.28	18.16
2	1.10	22.78	69.82	17.51
3	1.10	23.35	72.93	18.67
4	1.10	23.63	71.62	18.54
5	1.06	22.73	74.44	17.92
6	1.08	23.55	74.46	18.88
7	1.06	22.86	74.31	17.93
8	1.10	23.30	73.61	18.83
9	1.10	22.48	74.67	18.40
10	1.07	23.85	74.92	19.20
11	1.06	23.27	72.62	17.90
12	1.10	22.37	69.65	17.12
13	1.08	23.46	75.15	19.04
14	1.10	22.50	74.69	18.48
15	1.11	22.70	72.55	18.28
16	1.09	23.48	71.36	18.31
17	1.10	22.80	69.75	17.56
18	1.09	22.42	71.65	17.51
19	1.10	22.73	71.94	17.92
20	1.09	22.82	71.22	17.73
21	1.11	24.07	67.57	18.03
22	1.11	24.05	68.30	18.20
23	1.09	22.69	70.56	17.49
24	1.09	22.69	71.37	17.71
25	1.10	22.37	70.81	17.49
26	1.11	22.50	72.66	18.13
27	1.07	24.02	71.95	18.57
28	1.11	24.25	69.98	18.85
29	1.11	22.51	72.72	18.19
30	1.07	23.07	71.26	17.59
Average.	1.09	23.08	72.09	18.14

Table 2.5. Characteristic of perovskite solar cells of different blowing gas temperatures (HGB25, HGB75, and HGB125) about reverse and forward scans of *J-V* measurements, including parameters; *Voc, Jsc, FF,* and *PCE*. An average values are calculated at the bottom.

By making perovskite modules using the bar coating method, we were able to test how well the hot gas blowing method works with upscaling methods. To see if a uniform coating over a large area is possible, the HGB75 condition is used to make a perovskite film that covers almost 400 cm² of a glass substrate. Figure 2.12a and Figure 2.13 show that the perovskite film has a clean surface. After making sure that the perovskite films are all the same, Also, an ellipsometry analysis is done to figure out how the thickness of the perovskite film is distributed. The same coating method is used to make the perovskite layer on a 100 cm² Si wafer (see Figure 2.14). The thickness is distributed uniformly, and the average thickness of the perovskite layer is 391.06 nm, which is similar to the value found in the SEM cross-section image in Figure 2.8. Perovskite solar modules are made with an aperture area of 18 cm^2 (Figure 2.12c) The modulation is done with three laser etching processes (P1, P2, and P3), and the best modules had a geometric fill factor (GFF) of 93.45%. (see Figure 2.12b and Figure 2.15). The large size module with eight sub-cells had high aperture efficiencies of 13.78% (Figure 2.12d shows that for each sub-cell with an area of 2.25 cm², $V_{OC} = 1.04$ V, $J_{SC} = 19.92$ mA/cm², and FF = 0.613%). With $V_{OC} = 8.75$ V, $J_{SC} = 2.48$ mA/cm², and FF = 0.711, the bestperforming module has a power conversion efficiency of 15.43%, and the perovskite module has kept its good performance from MPPT measurements (see Figure 2.12e and Figure 2.12f). As a result, it is clear that our hot gas blowing method for making perovskite solar cells can be used consistently even in largescale production.



Figure 2.12. Images of laser patterned perovskite module and characteristics. a. A 400 cm² substrate with a perovskite film on it, made by hot gas blowing and bar coating. b. SEM pictures of the line widths of laser-cut P1, P2, and P3 patterns. The GFF factor is about 93.45%. c. Photo of the perovskite module with laser-cut designs d. J-V curves for each cell in a perovskite module that is linked in series. By connecting 8 cells, a module was made, and the measurement was shown by increasing the number of cells that were connected. e. The best performing perovskite module has J-V traits. Area in use is 18 cm². f. At a maximum voltage, the steady-state current of the laser-patterned module was measured.



Figure 2.13. Detailed photos of the bar coated perovskite film on an area of 400 cm². The substrate is a square with sides that are about 20 cm long (left), and the perovskite film has a glassy surface. (right)



Figure 2.14. The thickness of bar coated perovskite layer via ellipsometry. Photograph of bar-coated perovskite layer on Si substrate (left) and measured thickness (right). The average thickness of total 25 points is 391.06 nm.



Figure 2.15. Configuration of perovskite solar modules with modulation by laser etching process (P1, P2, and P3). P1 shorts the FTO electrode, P2 engraves from the ETL to the HTL to connect sub-cells with the Au electrode, and P3 shorts the Au electrode.

2.3. Conclusion

In short, we came up with a way to coat a large area of a bar using a hot gas blowing technique that lets us control the size of the grains in high-crystalline perovskite solar cells. In a large-area process, getting a highly crystalline perovskite film depends on how the solvent is chosen, how fast it evaporates, and how the grains grow. Developed HGB method at an appropriate blowing temperature affected both the high volatile 2ME solvent based perovskite precursor evaporation control and the grain growth mechanism, which could make an ideal situation for perovskite crystallization. Compared to HGB25 and HGB125, HGB75 made a perovskite layer that was void-free, flat, and had large grains. This made the optical and electrical properties like carrier lifetime and trap density better. The HGB75 perovskite solar cell had the highest PCE, at 20.85%, of all the gasblowing temperature conditions. The HGB75 perovskite solar modules with a size of 25 cm² had a PCE of 15.4% and a high photostability over 300 h. This means that they could be made on a large scale and in a stable way.

2.4. Experimental Methods

Materials: Substrates (FTO/Glass and Bare Glass) were purchased from AMG tech. Tin(IV) oxide (SnO₂) colloidal dispersion (15% in H₂O) and Pb-related materials (PbI₂ and PbCl₂) were purchased from Alfa Aesar. CsI was purchased from TCI chemical. Ammonium halides (FAI, PEABr) were purchased from Greatcell Solar Ltd., 2,2',7,7'-Tetrakis(N, N-di-p-methoxyphenylamino)-9,9'-spirobifluorene (Spiro-OMeTAD) was purchased from Lumtec. Au pellets for top electrode were purchased from iTASCO. All other materials were purchased from Sigma Aldrich.

Solar Cell Fabrication: FTO glass was cleaned by sonication for 15 mins with acetone, 2-propanol, and DI water. SnO₂ solution for device fabrication was made by mixing the SnO₂ colloidal solution and DI water in a volume ratio 1:4. The SnO₂ solution was spin coated on the FTO glass with 4000 rpm for 30 sec, and annealed at 150 °C for 30 min. Perovskite precursor solution was made to a concentration of 1.5 M by mixing following materials in 2-methoxyethanol (2ME); 461 mg of PbI₂, 13.9 mg of PbCl₂, 206.4 mg of FAI, 7.2 mg of CsI, 1.3 mg of PEABr, and 100 μ L of 1-Methyl-2-pyrrolidinone (NMP) in 0.8 mL of 2ME. The substrate was loaded on a bar coating equipment, and 100 μ L of the precursor solution was dropped on the substrate and filled a gap between the substrate and the bar. The perovskite layer was fabricated by the bar moving at a speed of 40 mm/s, followed by blown by an air knife with nitrogen gas with a pressure of 20 psi followed at the same speed, and annealed at 150 °C for 10 min and 100 °C for 10 min. The gaps between the substrate and the bar and between the substrate and the air knife are 100 μ m and 500 μ m, respectively. Spiro-OMeTAD solution was

prepared by dissolving 90 mg of the Spiro-OMeTAD in 1 mL of chlorobenzene (CB) with addition of 39.5 μ L of tBP, 23 μ L of Li-TFSI solution (520 mg of Li-TFSI in 1 mL of acetonitrile), and 10 μ L of FK209 Co(III)-TFSI solution (375 mg of the Co-TFSI in 1 mL of acetonitrile). The Spiro-OMeTAD solution was spin coated on the perovskite layer with 3000 rpm for 30 sec. Finally, a 50 nm thickness of Au electrode was fabricated by thermal evaporation.

Large area Solar Module Fabrication: Modulation for large area solar device was conducted via picosecond laser scriber (wavelength of the laser is 532 nm). Three laser scribing (P1, P2, and P3) were performed; P1 was for separation of the FTO electrode, P2 was for interconnection of top and bottom electrodes, and P3 was for separation of the Au electrode. The other procedures for fabrication of each layer were the same as for solar cell fabrication.

Characterization: SEM images of top view and cross-section view of perovskite layers were obtained from Field Emission Scanning Electron Microscope (Merlin Compact; ZEISS) with 2 kV working voltage. AFM, C-AFM images and roughness data of perovskite layers were obtained from atomic force microscopy (NX10; Park systems). Steady-state photoluminescence was conducted via steadystate and lifetime spectro fluorometers (Fluoromax-4; Horiba). Time-resolved photoluminescence and PL mapping were conducted by time-resolved fluorescence confocal microscope (Microtime-200; PicoQuant) Absorbance of perovskite layers was measured via by using UV-Vis-NIR Spectrometer (Cary 5000; Agilent). XPS and UPS analysis was conducted by Electron Spectroscopy for Chemical Analysis (AXIS SUPRA; Kratos) SCLC and EIS measurements were performed by using electrochemical workstation (AUT302N; Metrohm Autolab). J-V measurement and maximum power point tracking (MPPT) of perovskite solar cells were conducted via a sourcemeter (Keithley2400; Tektronix). EQE data of perovskite solar cells were measured from quantum efficiency measurement solution (IQE200B-E; Newport). XRD data of perovskite layers were obtained from a X-ray diffractometer (D8 advance, Bruker) in a rage of 2 theta of 5 degree to 80 degree. FT-IR measurements were conducted via a fourier transform Infrared spectrometer (TENSOR27; Bruker).

Chapter 3. Metal Mesh Incorporation and its Pattern Designing for Large-area and Lightweight Flexible Electrode Substrates

This chapter has been collaborated with Unsoo Kim, Department of Mechanical Engineering, Seoul National University.

3.1. Introduction

Perovskite solar cells have a remarkable certified efficiency of over 25%, making them one of the most promising new solar technologies.⁶² Flexible perovskite solar cells are recommended for realizing PSC's full potential because of their low temperature processability, compatibility with roll-to-roll (R2R) manufacturing, and thinness of the total layers constituting the device. ^{63,64} These features are not guaranteed simultaneously by other photovoltaic technologies. Power conversion efficiency (PCE) of flexible perovskite solar power has been increased to 22.54 percent thanks to advancements in charge transporting layers, defect passivation methods, and large-area coating technologies.^{65,66,67,68} It is also important to ensure that flexible perovskite solar cells can be shaped to fit curved surfaces, integrated into wearable and foldable electronics, or used as a portable power source in stationary structures like buildings or vehicles.^{69,70} However, there are few PCE and flexible perovskite solar cell and module investigations due to the usage of metal oxide-based transparent conducting electrodes that have inadequate mechanical stability.

One common method for increasing the adaptability of flexible perovskite solar cells is to replace the metal oxides in the electrodes with more malleable alternatives including graphene, carbon nanotubes, conducting polymers, and metal nanowires.^{71,72} However, the performance of perovskite solar cells based on these materials is inferior to that of transparent conductive electrodes made of metal oxides, such as indium-tin-oxide (ITO) or fluorine-doped tin oxide (FTO), and these materials are still expensive and difficult to make in large areas. Given that the majority of high-performance perovskite solar cells are based on metal oxide-

based electrodes, it would be preferable to develop metal oxide-based highflammability transparent conductive electrodes with excellent optoelectronic properties rather than switching out metal oxide materials for different substitutes. In fact, it is challenging for flexible electrode substrates based on metal oxide to show better performance than electrodes on rigid substrates. Polymer-based flexible substrates are easily destroyed in a high-temperature environment due to their low glass transition temperature of the polymer, while metal oxides can have high conductivity through the sintering process at high temperatures. Moreover, when the larger the device is constructed, the greater the charge transfer distance, increasing the power loss caused by the high resistance, which is evident when using an electrode with low conductivity. To improve the performance of solar cell devices, it is crucial to develop large-area electrode substrates with good electrode properties.

Here, by incorporating a metal mesh into the ITO metal oxide-based structure, flexible electrode substrates that are both conductive and lightweight were created. A 50 µm PEN substrate was used to fabricate an Au mesh with a thickness of 100 nm via photolithography, and an ITO layer of 160 nm was fully covered via sputtering process on the structure to create transparent flexible electrode substrates that are both conductive. In comparison to commercial flexible electrodes, the mesh/ITO electrode (MIE) exhibits good electrode properties with a transmittance of 76.7% and a sheet resistance of 12.98 ohm/sq. This method allowed for the uniform fabrication of a large-area flexible electrode substrate over a 100 cm² surface. Additionally, a metal mesh design associated with the number of paths from a point was introduced to a method for boosting the conductivity of the MIE without lowering any of the electrode's transmittance. This work exhibits the

outcomes of producing transparent, flexible, large-area electrodes that are stable for commercial use.

3.2. Results and Discussion

According to Figure 3.1a, a large-area flexible transparent substrate with a structure of an ITO electrode substrate and an Au metal mesh has been designed. The fabrication of an Au mesh and an ITO layer on a polyethylene naphthalate (PEN) substrate that has a 50 μ m thickness is done in stages. A photolithography procedure is used to build the 100 nm nm thick Au mesh, and a sputtering process is used to create the 100 nm thick ITO on top of it with full coverage. As a result, it is possible to create the flexible transparent electrode shown in Figure 3.1b, which has a large area of 100 cm². The pattern of the Au mesh is square-shaped, with a 200 μ m pitch and a width of 3 μ m. The optical microscope (OM), which is represented inset in Figure 3.1b, can be used to verify the metal mesh.

We prepared two types of commercially available ITO/PEN flexible electrode substrates for comparison; one commercial electrode (CE1) is a 125 µm thick electrode that exhibits good electrode properties (transmittance and sheet resistance), and the other commercial electrode (CE2) is a 50 µm thick electrode that exhibits poor electrode properties but is lightweight. We evaluated the transmittance of the flexible electrode substrates for wavelengths between 400 and 800 nm to verify the performance of the electrode substrates. Figuring 3.2a Between 400 and 800 nm, the average transmittance of electrodes is 79.2% (CE1), 82.6% (CE2), and 75.7% (CE3) (MIE). Also, the sheet resistance of the flexible electrodes is measured, with values of 13.0 ohm/sq (CE1), 39.8 ohm/sq (CE2), and 10.9 ohm/sq (MIE). By incorporation of the metal mesh for the transparent electrode, the MIE exhibits high conductivity (i.e., low sheet resistance) but lowered transmittance because the metal itself has a very high conductivity, yet it barely transmits light. We prepared two types of commercially available ITO/PEN flexible electrode substrates for comparison; one commercial electrode (CE1) is a 125 μ m thick electrode that exhibits good electrode properties (transmittance and sheet resistance), and the other commercial electrode (CE2) is a 50 μ m thick electrode that exhibits poor electrode properties but is lightweight. We evaluated the transmittance of the flexible electrode substrates for wavelengths between 400 and 800 nm to verify the performance of the electrode substrates. Figuring 3.2a Between 400 and 800 nm, the average transmittance of electrodes is 79.2% (CE1), 82.6% (CE2), and 75.7% (CE3) (MIE). Also, the sheet resistance of the flexible electrodes is measured, with values of 13.0 ohm/sq (CE1), 39.8 ohm/sq (CE2), and 10.9 ohm/sq (MIE). By incorporation of the metal mesh for the transparent electrode, the MIE exhibits high conductivity (i.e., low sheet resistance) but lowered transmittance because the metal itself has a very high conductivity, yet it barely transmits light. For example, an Au film with 100 nm thickness shows resistivity about 2.9 u Ω cm⁷³ and transmittance near 0%⁷⁴.

To evaluate the capability of the electrode substrates for photovoltaic devices, perovskite solar cells are fabricated with the electrode substrates. The structure of the perovskite cells is solar n-i-p normal structure: Electrode/SnO2/Perovskite/Spiro-OMeTAD/Au. Figure 3.2b displays the J-V curves as a function of solar cell performance. The CE1, CE2, and MIE have power conversion efficiencies (PCE) of 16.2%, 15.2%, and 16.0%, respectively. Despite having a lower transmittance than either the CE1 or the CE2, the MIE has a greater PCE than the CE2 and a reasonable PCE when compared to the CE1. The outcome shows that the MIE created in this work can be used as a flexible electrode substrate for perovskite solar cells with no problems.

5 5



Figure 3.1. Fabrication of the MIE (the mesh/ITO flexible electrode). On the flexible PEN substrate, Au mesh is produced using photolithography, and ITO is produced using sputtering. b. A photograph of a large-area MIE with a 100 cm² total area and an optical microscope image as an inset image that demonstrates the Au mesh's 200 μ m pitch and 3 μ m width.



Figure 3.2. Electrode characteristics and solar cell efficiency evaluation of the MIE. a. Transmittance graph for three different types of flexible electrode substrates from wavelengths of 300 nm to 800 nm. Average transmittance and sheet resistance from 400 to 800 nm wavelengths are displayed in the inset table. b. J-V measurements of perovskite solar cells made on three distinct flexible electrode substrates are represented by the colors black, red, and blue for CE1, CE2, and MIE, respectively. The parameters for the J-V measurement are displayed in the inset table.

Several experiments were carried out to adjust the thickness of the ITO layer and the spacing of the mesh pattern in order to optimize the structure of the Au mesh and ITO electrode. A portion of the mesh structure that is filled with a pattern and another part that is empty both have different densities, which causes a step difference depending on the mesh's height. The homogeneous fabrication of perovskite solar cells on the flexible electrodes may be a challenge if the surface is too rough by the severe step. The step difference can be reduced compared to when a metal mesh only exists because the ITO layer is coated over the entire surface by a sputtering technique. We used a focused ion beam (FIB) to examine three different ITO layer thicknesses—120 nm, 160 nm, and 200 nm—sputtered on the 100 nm Au mesh in order to look at step coverage of the ITO layer (Figure 3.3). ITO with a thickness of 160 nm exhibits good step coverage, in contrast to ITO with a thickness of 120 nm, which exhibits poor step coverage.



Figure 3.3. Cross-section of the mesh/ITO structure by Focused Ion Beam (FIB). ITO layers with three distinct thicknesses were created on 100 nm Au mesh. ITO with a thickness of 160 nm exhibits the least offset and good step coverage. ITO that is either thin (120 nm) or thick (200 nm) exhibits poor step coverage, which causes a significant offset.

There is a need to raise the MIE's transmittance since, despite the MIE's strong performance with the perovskite solar cell, it performs somewhat worse than the CE1 due to its lower transmittance. We tried to raise the MIE's transmittance in the direction of raising the mesh pattern's pitch from 200 to 300 μ m since the addition of the metal mesh is what causes the electrode substrate's transmittance to decrease. When the transmittance and conductivity of the MIE with 300 μ m pitch are measured, the transmittance and sheet resistance are, respectively, 76.7% and 12.98 ohm/sq. This means that, in comparison to the MIE with 200 μ m, the transmittance is higher and the conductivity is lower. (Figure 3.4a) This time, we fabricated further perovskite solar cells with a p-i-n inversion structure using the CE1, MIE with 200 or 300 μ m to assess the capabilities of the changed electrode structure. Perovskite solar cells with the inverted structure were fabricated: Electrode/PTAA/Perovskite/C₆₀/BCP/Cu. PCEs of the perovskite solar cells were of 17.3% (MIE with 300 μ m pitch), 16.9% (MIE with 200 μ m pitch), and 17.5% (CE1), respectively, as shown in Figure 3.4b.

Notably, the MIE enabled the production of perovskite solar cells with both normal and inverse configurations. There are several different kinds of electrodes for flexible substrates, including conductive polymers, carbon nanotubes, and nanowires. Nevertheless, the manufacture of solar cells is constrained when such electrodes are utilized because they can only be used with normal or inverted structures. From a commercial point of view, it is very likely that the ITO-based electrode will be used. Finally, after all of this time, the MIE has been designed and fabricated to the following specifications: PEN with 50 μ m thickness, Au mesh with 3 μ m width, 300 μ m pitch, and 100 nm thickness, and ITO with 160 nm thickness.



Figure 3.4. Mesh pattern design to increase pitch from 200 μ m (MIE200) to 300 μ m (MIE300). a. The table shows the average transmittance from 400 to 800 nm wavelength and sheet resistance of the MIE200 and the MIE300. b. J-V measurement of perovskite solar cells fabricated on the three different flexible electrode substrates; CE1, MIE200 and MIE300 are expressed in black, red, and blue, respectively. The inset table shows parameters related to the J-V measurement.

To check whether the electrode characteristics are uniform from the viewpoint of a large area, we divided the flexible transparent electrode with an area of 100 cm² into 16 equal parts (that is, each part is a square piece with a side length of 2.5 cm) and measured the respective conductivity and sheet resistance values. (Figure 3.5a) Both characteristics of the MIE showed high uniformity with respect to the corresponding area; the average value and its standard deviation of the transmittance is 76.18% and 0.19%, respectively, and the average value and its standard deviation of the sheet resistance is 12.74 ohm/sq and 0.34 ohm/sq, respectively. (Figure 3.5b and 3.5c)

Next, the weights of the flexible electrode substrates are measured, which is an important property when considering mobility of flexible substrate-based devices. As shown in Figure 3.6, the weights of the CE1, CE2, and MIE with an area of 100 cm² is 1.742g, 0.685g, and 0.690g, respectively. It is noted that the weight of the flexible electrode substrate depends on the thickness of the flexible substrate, because the thickness of the flexible substrate is much larger than the thickness of the electrode layer. For the MIE, the density of ITO, Au, and PEN is 7.14 g/cm3, 19.32 g/cm3, and 1.36 g/cm3, respectively.^{75–77} However, the thickness of ITO or Au mesh in the MIE is about 100 nm, which is 50 times less than the thickness of the PEN. This comparison is also consistent when considering the weight of perovskite solar cells or solar modules, since the layers in the perovskite solar devices are relatively much thin. For the normal structure of the perovskite solar cell, the expected weight of each layer is summarized in Table 3.1. As can be seen, even when a perovskite solar cell with an area of 100 cm² is fabricated, the total weight of the layers excluding the electrode substrate does not exceed 0.1 g. It means that reducing the thickness of the electrode substrate is effective in reducing
the weight of the solar cell. A reduction in weight of perovskite solar cells has also the advantage of increasing power-to-weight ratio.

Meanwhile, reducing the thickness of the flexible substrate may cause deterioration of the stability of the flexible electrode substrate. Conducting oxides such as ITO or FTO need sintering process at high temperature (over 300 °C) to have high conductivity. High temperature processes are not problem for rigid substrates such as glass substrates commonly used, whereas polymer-based flexible substrates cannot withstand high temperatures. Because a polymer has a low glass transition temperature, it is easily deformed in a high temperature environment. To solve this problem, many researches have been studied to fabricate the ITO film on polymer substrates at low temperatures. Nevertheless, the flexible substrates are still bent by a residual stress caused by the sputtering process of ITO, and strain by the residual stress becomes more severe in case of thin substrates. As shown in Figure 3.6, the CE2 may be bent by the residual stress from ITO sputtering process, making it difficult to reliably fabricate perovskite solar cells. Inserting a metal mesh into the electrode substrate is a good alternative to solve this problem, which gives high conductivity while minimizing the residual stress from the sputtering process.



Figure 3.5. Uniformity check results of the large-area MIE. a. A photograph of the large-area MIE, which is divided into 16 small electrode substrates in total. b. Transmittance and c. sheet resistance distribution of the 16 MIEs. Average values of transmittance and sheet resistance are 76.18% and 12.74 ohm/sq, respectively.



Figure 3.6. Weight of 3 different flexible transparent electrode substrates (CE1, CE2, and MIE) with an area of 100 cm². The CE1 (left) is 1.742 g, the CE2 (middle) is 0.685 g, and the MIE (right) is 0.690 g.

Materials	density [g/cm³]	thickness [nm]	weight [g]
TiO ₂	4.23	30	0.001
SnO ₂	6.95	30	0.002
MAPbl ₃	4.16	500	0.021
PEDOT:PSS	1.18	20	< 0.001
Spiro-OMeTAD	1.06	20	< 0.001
Au	19.3	100	0.019
Total weight of all layers			< 0.1

Table 3.1. Estimated weight of each layer according to the density and thickness of the layer constituting the perovskite solar cell. The total weight of all layers is less than 0.1g.

We've looked into the design of metal mesh patterns in more detail. D. Atkinson and F. J. van Steenwijk discussed how mesh patterns affect the resistance of infinite mesh lattices.⁷⁸; They figured out how much effective resistance becomes when a current of 1 A goes through a certain point in an infinite lattice mesh where the resistance of each line is 1 ohm. Considering both Ohm's law and Kirchhoff's law, if the point where the current of 1 A is applied is called the origin (0,0), the following equation can be used to find the effective resistance of the arbitrarily chosen point (n,p):

$$R_{np} = \frac{1}{2\pi} \int_0^{\pi} \frac{d\beta}{\sinh|\alpha|} \left[1 - e^{-|n\alpha|} \cos p\beta \right]$$
(6)

Here, α and β have a relation like below

$$\cos\alpha + \cos\beta = 2 \tag{7}$$

When the effective resistance at the nearest point (i.e. (0,1), (1,0), etc.) is calculated using the equation, the result is 1/2 ohm. Also, if the design of the mesh is different from the square pattern, the effective resistance at the closest point will be different. For example, the effective resistance value of a honeycomb pattern is 2/3. Also, the effective resistance value for the triangle pattern is 1/3. So, it means that the actual resistance value can change depending on how the mesh pattern is designed, especially how many paths it has coming out of a single point.

To confirm that this trend is still valid for the Au mesh and ITO structure for the MIE, three additional patterns were designed to compare with the original square

pattern. As shown in Figure 3.7a and 3.7b, the maximum number of paths it extends from a point is three, four, six, and eight, respectively. For accurate comparison, pitches of each pattern were adjusted so that the transmittance of the mesh pattern was the same. With 4 different MIEs, transmittance and sheet resistance were measured. As shown in Figure 3.7c, there is little difference in transmittance, but the sheet resistance decreased as the number of paths increased. The MIE with 3 paths shows the highest sheet resistance 14.34 ohm/sq, whereas the MIE with 8 paths shows the lowest sheet resistance 13.14 ohm/sq. It is meaningful that the characteristics of the electrodes can be improved only by the pattern designing of the metal mesh.



Figure 3.7. Design of mesh patterns with controlling the number of paths for the MIE. a. Calculated shadowing ratio for each metal mesh pattern to make the transmittance of all patterns the same. b. Optical microscope (OM) images of the MIEs for 4, 3, 6, and (max) 8 paths. Scale bar is 300 μ m. c. Transmittance graph of 3 types of flexible electrode substrates from 300 nm to 800 nm. The inset table shows the average transmittance from 400 to 800 nm wavelength and sheet resistance.

3.3. Conclusion

We incorporated the metal mesh into ITO-based flexible electrode to produce flexible electrode substrates without any high temperature processes. The Au mesh for flexible substrate electrodes greatly improves the conductivity of the electrode and the perovskite solar cells fabricated on the mesh/ITO electrode (MIE) showed good performance compared to commercial flexible electrode substrates. With the Au mesh/ITO structure with the specifications of 100 nm thickness, 3 µm width, and 300 µm pitch for the Au mesh, the MIE showed a transmittance of 76.7% and a sheet resistance of 12.98 ohm/sq was formed, and a light, flexible, transparent electrode weighing about 0.7 g was made over a large area of 100 cm². For further improvement of the electrode, it was shown that the number of paths from a point in the metal mesh changed the conductivity of the electrode substrates. Without any loss on transmittance, the MIE with 3 paths has the highest sheet resistance at 14.34 ohm/sq, while the MIE with 8 paths has the lowest sheet resistance at 13.14 ohm/sq. Based on these results, it will be easier to make flexible electrode substrates with better electrode properties that cover a large area in the future.

3.4. Experimental Methods

Materials: Commercial ITO substrates were purchased from Peccell Co. (CE1; ITO/PEN 125 μ m) and Ziotec (CE2; ITO/PEN 50 μ m). Bare PEN films with 50 μ m thickness were purchased from TEKRA. Tin(IV) oxide (SnO₂) colloidal dispersion (15% in H₂O) and PbI₂ were purchased from Alfa Aesar. Ammonium halides (MAI, FAI, MABr) were purchased from Greatcell Solar Ltd., 2,2',7,7'-Tetrakis(N, N-di-p-methoxyphenylamino)-9,9'-spirobifluorene (Spiro-OMeTAD) was purchased from Lumtec. C₆₀ and BCP were purchased from OSM. ITO sputtering targets, Au pellets, Cu pellets for top or bottom electrodes and 6-inch Si wafers were purchased from TASCO. All other materials were purchased from Sigma Aldrich. PI tapes was purchased from Coretech.

Mesh/ITO Electrode Fabrication: Bare PEN film was cleaned by sonication for 15 mins with 2-propanol, ethanol, and DI water. To proceed the photolithography process on the PEN film for the metal mesh, the PEN film was attached on a 6-inch Si wafer by using PI tapes. Then, the Au mesh was fabricated on the surface of the PEN substrate via photolithography. The Au mesh was made according to the pattern designed on the photomask with 100 nm thickness and 3 μ m width. After that, an ITO layer with 160 nm thickness was fully covered by deposition on the PEN/Au mesh sample.

Solar Cell Fabrication: Flexible electrode substrates (CE1, CE2, and MIE) were cleaned by sonication for 15 mins with 2-propanol, ethanol, and DI water. For n-i-p structure cells, SnO₂ solution for device fabrication was made by mixing the SnO₂

colloidal solution and DI water in a volume ratio 1:4. The SnO₂ solution was spin coated on the FTO glass with 4000 rpm for 30 sec, and annealed at 130 $^{\circ}$ C for 30 min. Perovskite precursor solution was made by mixing following materials in 0.6 mL DMF; 461 mg of PbI₂, 159 mg of MAI, and 75 μ L of dimethyl sulfoxide (DMSO). The precursor solution was spin coated on the substrate with 4000 rpm for 20 sec, 0.4 mL of diethyl ether was dropped at 8 sec passed. Then the film was annealed at 100 °C for 10 min. Spiro-OMeTAD solution was prepared by dissolving 90 mg of the Spiro-OMeTAD in 1 mL of chlorobenzene (CB) with addition of 39.5 µL of tBP, 23 µL of Li-TFSI solution (520 mg of Bis(trifluoromethane)sulfonimide lithium salt in 1 mL of acetonitrile), and 10 µL of FK209 Co(III)-TFSI solution (375 mg of the Tris(2-(1H-pyrazol-1-yl)-4-tertbutylpyridine)-cobalt(III)tris(bis(trifluoromethylsulfonyl)imide)) in 1 mL of acetonitrile). The Spiro-OMeTAD solution was spin coated on the perovskite layer with 2000 rpm for 30 sec. Finally, a 50 nm thickness of Au electrode was fabricated by thermal evaporation.

For p-i-n structure cells, poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA) solution was made by dissolving 2 mg of PTAA in 1 mL of CB. The PTAA solution was spin coated on the electrode substrate with 6000 rpm for 30 sec, and annealed at 100 $^{\circ}$ C for 10 min. Perovskite precursor solution was made by mixing following materials in 0.6 mL DMF; 461 mg of PbI₂, 79.5 mg of MAI, 68.8 mg of FAI, and 11.2 mg of MABr, and 75 µL of DMSO. The perovskite precursor solution was spin coated on the substrate with 4000 rpm for 20 sec, 0.4 mL of diethyl ether was dropped at 8 sec passed, and annealed at 130 $^{\circ}$ C for 20 min. After that, C₆₀, BCP, and Cu layers were fabricated by thermal evaporation with thickness 20 nm, 6 nm,

and 50 nm, respectively.

Characterization: SEM images of top view of electrodes were obtained from Field Emission Scanning Electron Microscope (Merlin Compact; ZEISS) with 2 kV working voltage. Cross-section image of electrodes was obtained via conducting Focused Ion Beam (Crossbeam 550; ZEISS). Sheet resistance was measured by using Semiauto 4-Point Probe System (CMT-SR 1000N; AIT). Transmittance of flexible electrode substrates was measured by using UV-Vis-NIR Spectrometer (Cary 5000; Agilent). J-V measurements of perovskite solar cells were conducted via a sourcemeter (Keithley2400; Tektronix).

Chapter 4. Conclusion

In this dissertation, large-area processes for the perovskite film as a light absorbing layer and the metal mesh/ITO structure as a flexible electrode were performed.

First, we applied hot gas blowing for bar-coating of the perovskite film. The gas blowing with thermal energy not only induces solvent evaporation, but also increases the nucleation rate of the perovskite, resulting in fabrication of high-quality of perovskite films. When the gases at three temperatures of 25 °C, 75 °C, and 125 °C were compared, a crystalline perovskite film without voids or pinholes was fabricated at 75 °C. The best PCE of solar cells was 20.85% and the best one of solar modules was 15.4% with an area of 5x5 cm².

Secondly, we introduced the metal mesh into ITO-based flexible electrode to produce flexible electrode substrates. Incorporation of the Au mesh into flexible substrate electrodes greatly improves the conductivity of the electrode even without any high temperature processes, and good device efficiency can be obtained even compared to commercial flexible electrode substrates. With the Au mesh/ITO structure, an electrode having a transmittance of 76.7% and a sheet resistance of 12.98 ohm/sq was formed, and an light-weight flexible transparent electrode about 0.7 g in a large area of 100 cm^2 was fabricated.

As the final outcome, two different components for perovskite solar cells, the perovskite layer and the flexible electrode, were developed from the perspective of large-area processing. These two types of technologies can be applied for the roll-to-roll (R2R) process of perovskite solar cells. First, the flexible electrode substrate with good conductivity and bending stability will maintain good performance even when rolled in or rolled up during the R2R process. Next, the hot gas blowing

(HGB) will effectively dry the perovskite solution on the substrate moving on the rollers and induce crystallization of the perovskite. In the future, these large-area technologies will contribute to the commercialization of perovskite solar cells.

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Abstract

페로브스카이트 태양전지는 최근 활발한 연구로 단기간에 25% 높은 변환 효율을 갖게 되었다. 현재까지는 주로 소면적 이상의 페로브스카이트 태양전지를 제조하여 높은 성능을 확인했으며, 상용화를 실현시키기 위해서는 페로브스카이트의 대면적화 공정이 필요하다. 이에 본 논문에서는 바코팅을 통한 대면적 페로브스카이트 박막 제조에 있어 열에너지를 가진 가스를 활용하였다. 세 가지 온도 조건(25 ℃, 75 ℃, 125 ℃)의 가스 블로잉을 진행했을 때, 75 ℃의 질소 가스로 적절한 에너지를 주었을 때 보이드나 핀홀 없이 큰 결정립의 페로브스카이트 박막을 제조할 수 있었다. 이에 따라 75 ℃ 가스로 제작한 태양전지가 조건들 중 가장 높은 성능을 보여주었으며, 소자의 경우 20.85%, 5x5 cm² 모듈의 경우 15.4%의 효율을 구혀하였다. 또한, 기존 상용화된 ITO 전극 유연기판에 금속 메쉬를 도입하여 고전도성의 전극 및 경량화된 유연전극기판을 제작하였다. 50 µm 두께의 PEN 기판에 100 nm의 Au 메쉬를 포토리소그래피로 제작하고 그 위에 스퍼터링을 통해 ITO를 160nm 전면 증착한다. 그 결과로 투과도 76.7% 및 12.98 ohm/sg 의 면저항을 갖는 전극을 형성하고, 100 cm² 의 대면적에서 1g 이하의 무게를 갖는 초경량 유연투명전극을 제작하였다. 추가로 금속 메쉬 패턴의 설계를 통해 한 지점으로부터의 경로의 수가 메쉬가 포함된 유연투명전극의 전도도에 주는 영향을 확인하였다. 결과적으로 태양전지에 중요한 구성요소인 광흡수층과 전극 기관의 대면적화를 성공하였으며, 향후 대면적화를 통한 페로브스카이트 태양전지 상용화에 기여할 수 있는 연구가 될 것이다.

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주요어 : 페로브스카이트 태양전지, 대면적 제작 공정, 바코팅, 고온 가스 블로잉, 금속 메쉬, 유연전극기판

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