Improved Reproducibility and Intercalation Control of Efficient Planar Inorganic Perovskite Solar Cells by Simple Alternate Vacuum Deposition of PbI₂ and CsI

Md. Shahiduzzaman,*†‡ Kyosuke Yonezawa,† Kohei Yamamoto,‡ Teresa S. Ripolles,§ Makoto Karakawa,†‡± TAKEYUKI KUWABARA,† KOHSHIN TAKAHASHI,† Shuzi Hayase,§ and Tetsuya Taima†§∥

†Institute for Frontier Science Initiative (InFiniti), ‡Graduate School of Natural Science and Technology, and ∥Research Center for Sustainable Energy and Technology, Kanazawa University, Kakuma-machi, 920-1192 Kanazawa, Japan
§Graduate School of Life Science and Systems Engineering, Kyushu Institute of Technology, Kitakyushu, 808-0196 Fukuoka, Japan

ABSTRACT: Vacuum deposition is a simple and controllable approach that aims to form higher-quality perovskite films compared with those formed using solution-based deposition processes. Herein, we demonstrate a novel method to promote the intercalation control of inorganic cesium lead iodide (CsPbI₃) perovskite thin films via alternate vacuum deposition. We also investigated the effect of layer-by-layer deposition of PbI₂/CsI to fabricate efficient planar heterojunction CsPbI₃ thin films and solar cells. This procedure is comparatively simple when compared with commonly used coevaporation techniques; further, precise intercalation control of the CsPbI₃ thin films can be achieved by increasing the number of layers in the layer-by-layer deposition of PbI₂/CsI. The best control and the highest reproducibility were achieved for the deposition of four double layers owing to the precise intercalation control during the deposition of the CsPbI₃ thin film. A power conversion efficiency of 6.79% was obtained via alternate vacuum deposition of two double layers with a short-circuit current density (Jsc) of 12.06 mA/cm², an open-circuit voltage (Voc) of 0.79 V, and a fill factor (FF) of 0.72. Our results suggest a route for inorganic precursors to be used for efficient perovskite solar cells via alternate vacuum deposition.

INTRODUCTION

Hybrid organic–inorganic halide perovskites are an attractive potential candidate for use as energy-efficient light-absorbing materials for thin-film photovoltaic applications owing to their superior properties such as their solution-processability,1 low exciton binding energy,2,3 long free charge carrier diffusion lengths,4 high charge carrier mobilities in conjunction with long lifetimes,5,6 and excellent cost- and energy-efficient light absorption.7,8 Kojima et al. first introduced perovskite solar cells in 2009 with a power conversion efficiency (PCE) of 3.8%.9 Park et al.10 have further improved the PCE to 6.5% in 2011. Park, Grätzel, and colleagues reported that perovskite solar cells with a PCE of 9.7%11 were fabricated by introducing spiro-OMeTAD as a hole-transporting material. This encouraging discovery led to further performance enhancements, resulting in a remarkable efficiency of 22.1% at present.12

Planar heterojunction (PHJ) perovskite solar cells are particularly interesting for future commercialization owing to their simple device structures and their ability to be fabricated at low temperatures on flexible substrates. This is in contrast to the mesostructured perovskite devices, which require high-quality mesoporous scaffold films that are prepared using a high-temperature sintering process (>450 °C); such temperatures are too high for commercial applications.5,14 To avoid using a mesoporous TiO₂ layer, several groups have aimed to increase the efficiency of PHJ perovskite solar cells.5,16

The use of alternative precursors such as cesium halides (CsX) opened up a way to obtain vacuum-deposited perovskite thin films and solar cells while also maintaining a precise control over the deposition rate and thickness. Cesium iodide (CsI) is considered to be a good substitute for organic materials such as CH₃NH₃I [methylammonium iodide (MAI)]. Eperon et al. introduced CsPbI₃-based perovskite solar cells with a PCE of 2.9% that were fabricated, for the first time, via a facile solution process by using a mesosporous scaffold such as TiO₂.17 Meanwhile, Ripolles et al. further increased the PCE of CsPbI₃-based mesoporous TiO₂ perovskite solar cells up to 4.7%; these cells were also fabricated using solution processing.18 In
addition, Sutton et al. improved the PCE of perovskite solar cells based on PHJ CsPbIBr up to 9.8% (fabricated via solution processing).19 However, it is difficult to precisely control the thickness of cesium-based perovskite films while also achieving high-quality films using solution processing. A precise control of the morphology and the crystallization of perovskite thin films is well-correlated to higher perovskite solar cell performances.20,21 A nonuniform perovskite morphology limits device performances owing to electrical shorting and charge dissociation, transport, and recombination effects.22-24

Vacuum deposition offers a promising way of obtaining high-quality films with easy-to-control thicknesses as well as large-area multistack thin films with high reproducibility and utilizing mature industrial fabrication facilities.25 However, the energy requirements associated with vacuum processing are substantial and could undermine the potential advantage that perovskites have regarding their rapid energy payback time.13 Furthermore, Malinkiewicz et al.14 have reported perovskite solar cells with a PCE of 12% that were fabricated by sublimation in an ultrahigh vacuum chamber. Chen et al. developed an all-inorganic perovskite solar cell with a PCE exceeding 11% that was fabricated via the coevaporation of cesium halide and lead halide precursors in ultrahigh vacuum.15

Commonly, vacuum deposition methods involve the sublimation of two kinds of precursors such as an organic halide (e.g., MAI) and a metal halide (e.g., lead iodide, PbI2) in a vacuum chamber. However, the main reason for such techniques not being commonly used may be the gasification behavior of MAI, which has a small molecular weight that causes the molecules to randomly diffuse inside the vacuum chamber; this makes it very difficult to monitor and control the deposition rate using quartz microbalance sensors.14,23 To overcome this issue, many researchers have fabricated highly efficient vacuum-deposited perovskite solar cells via sequential vacuum deposition and chemical vapor deposition methods.16,26-28 There are now some other ways to fabricate perovskite films via vacuum evaporation while precisely controlling the thickness and deposition rate of the material without using a precursor with gas-like properties.15,23 Recently, we reported sequentially vacuum-deposited PHJ CsPbI3 perovskite solar cells with a PCE of 5.71% that were fabricated via solution processing, which increased device performances; (iii) alternate layer-by-layer vacuum deposition and a controlled deposition rate was obtained using alternate layer deposition methods.16,20-26 There are now some other ways to fabricate perovskite films via vacuum evaporation while precisely controlling the thickness and deposition rate of the material without using a precursor with gas-like properties.15,23 Recently, we reported sequentially vacuum-deposited PHJ CsPbI3 perovskite solar cells with a PCE of 5.71% that were fabricated with various annealing times.29 In this way, we developed an efficient approach to fabricate perovskite thin films with precise intercalation, thickness, and deposition rate control, as required for enhancing the performance of perovskite solar cells.

In this study, we replaced MAI with CsI and used an alternating vacuum deposition method (layer-by-layer) to alternately fabricate PbI2 and CsI layers with a precise intercalation control to yield efficient, inorganic PHJ CsPbI3 thin films and solar cells. A precise control over the morphologies of CsPbI3 thin films was achieved. Our findings revealed that the alternate deposition method facilitated precise intercalation control for CsPbI3 perovskite films with enhanced performances that also had a high reproducibility compared with films fabricated via coevaporation, which increased device reproducibility.

**RESULTS AND DISCUSSION**

Figure 1 shows a schematic illustration of the device configuration of solar cells based on CsPbI3.

Figure 2 illustrates a variation of the number of double layers while maintaining the overall thickness of the active layer. The thickness of the individual PbI2 and CsI layers was calculated based on the thickness of the PbI2/CsI layer at a 1:1 molar ratio throughout the stack. A CsI thin film with a uniform thickness and a controlled deposition rate was obtained using alternate layer vacuum evaporation.

The deposition of the two double layers produces three interfaces within the stack (Figure 2b); the thickness of each PbI2 and CsI in this stack is lower than that in a stack containing only one double layer. The device fabricated by evaporating four double layers (Figure 2d) has seven interfaces within the stack, which may result in a higher penetration depth of the CsI molecules into PbI2. We assumed that the greater the number of evaporated double layers in the stack, the higher the solar cell performance would be owing to better intercalation of the resulting CsPbI3 film. The process used to fabricate the CsPbI3 film by annealing at 350 °C for 1 min is schematically illustrated in Figure 2f.

Varying the number of PbI2/CsI double layers while maintaining the overall thickness of the active layer yields the following characteristics: (i) as the number of double layers increases, the intercalation control of the CsPbI3 morphology also increases via the individual manipulation of the PbI2 and CsI depositions; (ii) a perfectly transformed CsPbI3 thin film may enhance the charge dissociation and transport efficiency while preventing recombination, thus yielding higher solar cell performances; (iii) alternate layer-by-layer vacuum deposition offers the potential to minimize the contamination issues that
result from the precursors owing to the shutters of the K-cell when the precursors are evaporated, even at high evaporation temperatures.

The J–V characteristics at a scan speed of 0.01 V/s with a forward scan of the solar cells obtained using the alternate vacuum deposition method were measured under AM 1.5G illumination (shown in Figure 3), and the corresponding forward scan solar cell parameters are listed in Table 1. The positive to negative bias) scans are detailed in Figure S6. A solar forward (from negative to positive bias) and reverse (from reference device had a PCE of 5.81% with a short-circuit illumination (shown in Figure 3), and the corresponding vacuum deposition method were measured under AM 1.5G. The enhancement and efficient charge dissociation as well as superior transport properties with reduced recombination, which leads to the improvement of the J_sc, FF, and PCE of the resulting devices. While a PCE of 6.79% was obtained for the solar cell fabricated with two double layers, a lower PCE of 4.77% was observed for the solar cell prepared using four double layers. We had assumed that increasing the number of double layers during deposition would facilitate a more precise intercalation of CsI into PbI2, leading to a more complete transformation into a CsPbI3 perovskite film. The J–V characteristics of the thin films produced by depositing the CsI/PbI2 double layers are similar to those obtained by depositing the PbI2/CsI double layers (Figure S7).

Incident photon-to-current conversion efficiency (IPCE) curves of the solar cells fabricated using an active layer constructed using the alternate evaporation technique are shown in Figure 4. The enhancement of the PCE of the devices using either the alternate evaporation method or the coevaporation method is consistent with their corresponding IPCE values. The photocurrents determined from the IPCE values were 12.02 and 14.17 mA/cm² for solar cells fabricated with alternate evaporation and coevaporation, respectively. The PHJ CsPbI3-based perovskite solar cells exhibited a spectral response that extends from the visible to the near-infrared wavelength region with absorption peaks at intensities between 60 and 90% at approximately 300 to 750 nm.

To ensure the reproducibility of our results, solar devices were fabricated by the deposition of one double layer (17 devices), two double layers (11 devices), three double layers (8 devices), and four double layers (11 devices), as shown in Figure 5. The best control and the highest reproducibility were obtained for the deposition of four double layers owing to the precise intercalation control during the deposition of the CsPbI3 thin film, leading to an enhanced charge dissociation and transport efficiency and a reduction in recombination events in the solar cells. This highlights that a perfect transformation into CsPbI3 is required in the thin films for the perovskite solar cells to be highly reproducible.

To further investigate the reason for the enhancement of the solar cell performance through varying the number of vacuum-evaporated double layers, we analyzed the surface morphology of the CsPbI3 thin film using scanning electron microscopy (SEM). The morphologies of CsPbI3 thin films fabricated with a different number of double layers are shown in Figure 6a–d. The alternate deposition process plays an important role in the precise intercalation control of the CsPbI3 thin films.

### Table 1. Summary of Performance Characteristics of Fluorine-Tin-Oxide (FTO)/Compact TiO2/CsPbI3/Poly(3-hexylthiophene-2,5-diyl) (P3HT)/Ag Devices

| Layers       | J_sc (mA/cm²) | V_oc (V) | FF  | PCE (%) |
|--------------|---------------|----------|-----|---------|
| one double layer | 11.98         | 0.71     | 0.67| 5.71    |
| two double layers   | 12.06         | 0.79     | 0.72| 6.79    |
| three double layers  | 9.46          | 0.76     | 0.70| 5.01    |
| four double layers   | 11.04         | 0.66     | 0.65| 4.77    |
| coevaporation       | 14.33         | 0.68     | 0.60| 5.81    |

Figure 3. Current density–voltage (J–V) characteristics obtained for the devices with a different number of double layers.

Figure 4. IPCE spectra for one to four double layers and for the coevaporated film.
double layers being either PbI$_2$/CsI or CsI/PbI$_2$ on the SEM images, the as-deposited PbI$_2$/CsI thin into PbI$_2$ and leads to a perfect transformation into a CsPbI$_3$ the number of double layers increases the intercalation of CsI particles is lower on the resulting thin figures. The image in Figure 6a–d reveals that the number of white particles is lower on the resulting thin film, whereas increasing the number of double layers increases the intercalation of CsI into PbI$_2$ and leads to a perfect transformation into a CsPbI$_3$ perovskite film. These observations were verified using atomic force microscopy (AFM), as shown in Figure S3a–d. The SEM images, the as-deposited PbI$_2$/CsI thin film exhibited a small grain size (see Supporting Information, Figure S1a). Figure S1c,d shows the morphologies (as determined by SEM) of a CsI single layer and a coevaporated CsPbI$_3$ thin film produced at 350 °C for 1 min, respectively. The effect of the double layers being either PbI$_2$/CsI or CsI/PbI$_2$ on the resulting CsPbI$_3$ thin-film morphologies was studied. Figure S4 reveals that the as-deposited CsI/PbI$_2$ thin film had a flower-like surface. After annealing, the surface morphology of the resulting thin film produced by CsI/PbI$_2$ evaporation was similar to that obtained by PbI$_2$/CsI evaporation, as determined by SEM (Figure S4b).

The energy-dispersive X-ray (EDX) mapping (Figure S5) was performed to address the existence of white particles on the perovskite films. The color intensity aids to judge the relative amounts of elements distributed on the surface, as shown in Figure S5a,b. The details of the elemental composition of CsPbI$_3$ thin films are shown in Table S1. The SEM-EDX analysis of the CsPbI$_3$ films revealed that it was very difficult to detect white particles on the surface of the CsPbI$_3$ thin films. Therefore, to further study the white particles on the surface of the CsPbI$_3$ thin films, the X-ray diffraction (XRD) method was used. The XRD patterns of the CsPbI$_3$ films fabricated using various numbers of double layers are shown in Figure 7.

Figure 5. PCE of the perovskite solar cells for one to four double layers and for the coevaporated film. Error bars indicate plus or minus one standard deviation from the mean.

Figure 6. SEM images of the CsPbI$_3$ films fabricated using (a) one, (b) two, (c) three, and (d) four double layers.

Diffraction peaks related to two different structures were found; they are marked in the figure. The diffraction peaks of the α-CsPbI$_3$ films were detected at 2θ angles of 14.39° and 20.59°, which were assigned to the (100) and (110) crystal planes, respectively. These peak positions are consistent with a cubic crystalline structure.31,32 The mean crystallite sizes for the α-CsPbI$_3$ crystals formed for one, two, three, and four double layers were 33.4, 33.4, 36.3, and 39.8 nm, respectively, as estimated from the full width at half-maximum of the (100) peak using the Scherrer formula (see Table S2). In addition, the diffraction peaks observed at around 11.91°, 24.12°, and 28.91° correspond to the Cs$_4$PbI$_6$ crystal phase.33 It should be noted that there was no Cs$_4$PbI$_6$ peak at 11.91° in either of the as-deposited CsPbI$_3$-based XRD patterns, which indicates that Cs$_4$PbI$_6$ was not responsible for the intermediate peak. The analysis of the XRD peak positions of the film reveals that both CsPbI$_3$ and Cs$_4$PbI$_6$ phases exist in the resulting thin films. We thus conclude that the presence of white particles on the surface of the CsPbI$_3$ thin films may be attributed to the presence of Cs$_4$PbI$_6$. The resulting XRD parameters are summarized in Table S2. When two double layers were deposited, the resulting film appeared to have a low crystallinity. However, an improved device performance was obtained for a mixture of CsPbI$_3$ and Cs$_4$PbI$_6$ crystal phases. We propose that this may be due to the grain boundary effect that leads to an improvement of the device performance when two double layers were used. It is worth mentioning that the large grain boundaries, which facilitate to an efficient charge separation and collection, result in better solar cell performance.34 Hence, we speculate that the photogenerated carriers are more effectively separated when two double layers were evaporated owing to the large grain boundaries in the CsPbI$_3$ film compared with that in the other alternate evaporation films. The number of white particles decreased as the number
of double layers of PbI2/CsI increased. We controlled the crystal phases by changing the thickness of the alternately deposited films, which resulted in a perfect transformation into CsPbI3. Our findings show that the existence of the white particles is completely dependent on the thickness of the alternately deposited layers.

The evolution of the UV–visible (UV–vis) spectra of the CsPbI3 thin films from the alternately deposited layers with a molar feeding ratio of PbI2/CsI = 1:1 for one to four double layers is shown in Figure 8. The strong absorption peak observed at around 360 nm can be attributed to the Cs4PbI6 phase as evidenced by Nikl et al.31 The observations from the UV–vis data were further verified by the XRD and SEM results. Additionally, the film produced with four double layers showed a clear absorption peak at around 410 nm, corresponding to CsPbI3.31 We propose that the deposition of four double layers leads to a more precise intercalation control in the CsPbI3 thin film because the individual, alternately deposited layers are each thinner. The thin film fabricated with one double layer had PbI2 and CsI layer thicknesses of 113 and 87 nm, respectively. The thin film fabricated with four double layers had PbI2 and CsI layer thicknesses of 28.3 and 21.8 nm, respectively. However, while the thicknesses of the PbI2 and CsI layer decreased, the number of interfaces increased along with the number of deposited double layers, as shown in Figure S2. A larger number of interfaces facilitated a greater reaction penetration depth of the smaller CsI molecules into PbI2, resulting in precise intercalation control of the CsPbI3 thin film. By changing the thickness of the alternately deposited films, we were able to create a very good chemical reaction field that led to a perfectly transformed CsPbI3 thin film. The inset of Figure 7 clearly shows a strong absorption peak at around 410 nm, which corresponds to the CsPbI3 thin film fabricated with four double layers. This observation is in agreement with the results of the XRD analysis, which confirms that a precise intercalation of CsPbI3 thin films could be obtained by changing the thickness of the alternately deposited layers, thus providing a greater reaction diffusion depth of the smaller CsI molecules into PbI2.

■ CONCLUSIONS

The alternate layer deposition method strongly influenced the CsPbI3 thin-film morphologies, thus significantly affecting the resulting solar cell performances. By optimizing the number of double layers (two was optimal), a maximum PCE of 6.79% was achieved for the resulting solar cells. An increased reproducibility of the results was observed when using four double layers owing to the increased intercalation control of the CsPbI3 thin film.

■ EXPERIMENTAL METHODS

FTO-patterned glass substrates were pretreated using oxygen plasma for 20 min prior to use. Compact TiO2 films for use as electron collection layers were deposited via a simple chemical bath deposition method according to the procedure developed by Kuwabara et al.32 The CsPbI3 perovskite layer was formed by the alternate vacuum deposition of PbI2 and CsI layers with thicknesses of 113 and 87 nm, respectively, at a pressure of 4.0 × 10⁻⁴ Pa. Small amounts of PbI2 and CsI powders were placed in the K-cell (diameter size 5 cm and depth 1.2 cm) and tungsten boat, respectively, inside the chamber and carefully heated to allow outgassing. The K-cell temperature was applied at 420 °C, and the growth rates were kept at 0.5 Å/s for PbI2 deposition. In the case of CsI deposition, the tungsten boat with 20 A (electricity runs on 200 V) was placed, and the growth rates were kept at 0.3 Å/s. The thickness and growth rate were monitored with a quartz crystal oscillator. The distances between K-cell, tungsten boat, and sample substrate are 30 and 35 cm, respectively. We repeated the layer-by-layer deposition of PbI2/CsI (while varying the thicknesses of the layers) up to four times to obtain a precise control of the intercalation for the perovskite thin films. The thicknesses of the PbI2 and CsI layers were calculated based on the thickness of the PbI2/CsI layer (molar ratio 1:1). The as-deposited films were annealed at 350 °C for 1 min to obtain 200 nm thick CsPbI3 films. A P3HT solution in chlorobenzene (15 mg/mL) was then spin-coated as a hole-transporting layer on CsPbI3 perovskite thin films. The films were annealed at 150 °C for 5 min on a hot plate in a glovebox. Finally, the films were transferred to a vacuum chamber where 60 nm thick silver electrodes were deposited onto the P3HT layer at 4.0 × 10⁻⁴ Pa. The active device area was 4 mm². The current density versus voltage (J–V) characteristics of the cells were analyzed under simulated AM 1.5G solar illumination using a Keithley 2401 digital source meter. SEM (JEOL JSM-7610F) was used to analyze the surface morphology. The XRD (Rigaku SmartLab) spectra of the prepared films were measured using an X-ray diffractometer with an X-ray tube (Cu Ka radiation with a wavelength of 1.5406 Å).

■ ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00814.

SEM images of CsPbI3 and CsI layers; AFM images of CsPbI3; J–V curves measured with various scan directions; elemental compositions of CsPbI3; and crystalline size calculation of CsPbI3 (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: shahiduzzaman@staff.kanazawa-u.ac.jp (M.S.).
*E-mail: taima@se.kanazawa-u.ac.jp (T.T.).

ORCID

Md. Shahiduzzaman: 0000-0002-3092-7793

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Takayuki Kuwabara: 0000-0001-7442-471X

Notes
The authors declare no competing financial interest.

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