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We report on fabrication of organic-inorganic perovskite thin films using a hybrid method consisting of pulsed laser deposition (PLD) of lead iodide and spin-coating of methylammonium iodide. Smooth and highly crystalline CH3NH3PbI3 thin films have been fabricated on silicon and glass coated substrates with fluorine doped tin oxide using this PLD-based hybrid method. Planar perovskite solar cells with an inverted structure have been successfully fabricated using the perovskite films. Because of its versatility, the PLD-based hybrid fabrication method not only provides an easy and precise control of the thickness of the perovskite thin films, but also offers a straightforward platform for studying the potential feasibility in using other metal halides and organic salts for formation of the organic-inorganic perovskite structure. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). [http://dx.doi.org/10.1063/1.4939621]

I. INTRODUCTION

Organic-inorganic perovskite solar cells (PSCs) have recently emerged as one of the most promising alternatives to silicon based solar cells due to their high efficiency, relatively low cost, and flexibility in materials growth and architecture.1–8 Many breakthroughs have been made since PSCs were first unveiled in 2009,1 and a power conversion efficiency (PCE) as high as 20.3% has been reported.8

The superior performance of PSCs is based on the unique characteristics of the organic-inorganic perovskite, namely, its relatively high absorption coefficient,2 tunable bandgap,9–11 low binding energy of photo-generated electron-hole pairs,12 high charge-carrier mobilities, and long charge carrier diffusion lengths.13,14 These factors are of great benefit to the simple planar heterojunction architecture and can lead to low-cost manufacturing with robust device performance.15

The high efficiency of PSCs is generally associated with specific synthesis procedures, where controlling the morphology and the grain size of perovskite materials in the device is of utmost importance.7,8,16,17 Various fabrication methods of the perovskite thin films have been reported to date.18–21

The synthesis methods can be categorized into the one-step method (e.g. one-step precursor deposition18 and dual-source vapor deposition6) and the two-step method (e.g. the sequential deposition method19 and vapor-assisted solution process20). Compared to the one-step method, the two-step deposition is known to provide better control of the composition, the thickness, and the morphology of the organic-inorganic perovskite films, thus resulting in higher performance PSCs.8,22,23 In particular, low-temperature all solution-based processes have attracted considerable attention due to their ease of synthesis and low-cost. However, the low solubility of metal halide precursors in organic solvents has been identified as a limiting factor for possible further improvement.24–26 Thermal evaporation
methods have been reported as successful in overcoming this issue and synthesizing high quality perovskite thin films.\textsuperscript{6,27} Atomic layer deposition (ALD) has also been introduced for growth of halide compounds which are subsequently converted to perovskite thin films by dipping them into a methylammonium iodide (MAI) solution.\textsuperscript{28} The typical substrate temperatures of the thermal evaporation method\textsuperscript{6} and the ALD method\textsuperscript{28} are 325 °C and 150 °C, respectively. Based on these methods, the organic-inorganic perovskite thin films with high purity and crystallinity have been synthesized, they have been used in high-performance devices.\textsuperscript{29}

Here, we used pulsed laser deposition (PLD) to fabricate organic-inorganic perovskite thin films, where the substrate temperature is held at room temperature. PLD is a versatile method for fabricating high-quality films of a variety of materials. The main advantages of PLD include its operational simplicity and its non-equilibrium nature which allows stoichiometric mass transfer of materials from the target to the substrate.\textsuperscript{30} In PLD, only a few parameters such as the laser energy density, the pulse repetition rate, the substrate temperature, and the deposition pressure need to be adjusted.\textsuperscript{30} It is straightforward to apply PLD to the fabrication of multi-layered or composition-spread films by sequential ablation of multiple targets.\textsuperscript{31} There have been only a few reports of the use of PLD for deposition of metal halides.\textsuperscript{32} Very recently, Bansode et al.\textsuperscript{33} prepared perovskite films and solar cells by an off-axis PLD method. In this work, we take advantage of the flexibility of PLD to explore a hybrid method for the fabrication of organic-inorganic perovskites thin films. We show that a PLD-based approach can provide good control of the morphology and the thickness of the perovskite films at room temperature.

II. EXPERIMENTAL SETUP

The fabrication procedure of organic-inorganic perovskite thin films based on our PLD-based hybrid two-step process is schematically shown in Fig. 1. It starts with PLD of PbI\textsubscript{2} at room temperature (Step 1) followed by spin coating of MAI with a subsequent annealing (Step 2). Both Si and glass substrates coated with fluorine doped tin oxide (FTO) are used.

To prepare a PLD target, PbI\textsubscript{2} powders were ground in isopropanol (IPA), baked at 100 °C, pressed as a pellet, and then sintered at 120 °C under a nitrogen atmosphere for 8 hours. Fig. 1(a) shows the finished yellow PbI\textsubscript{2} target used in our work. We optimized the laser energy, the repetition rate, and the distance between the substrate and the target to fabricate a smooth PbI\textsubscript{2} film with a relatively low deposition rate. During the PLD of the PbI\textsubscript{2} target, the distance between the substrate and the target was kept at 5.0 cm and a pulsed excimer laser (KrF; λ = 248 nm) was used with an energy density of 0.25 J/cm\textsuperscript{2} and a repetition rate of 2 Hz. PbI\textsubscript{2} films were deposited on the substrates in vacuum (≈3.0 × 10\textsuperscript{-6} Torr) at room temperature with the deposition rate of ≈0.33 nm/pulse. Step 2 (Fig. 1(c) and 1(d)) consisted of spin-coating of MAI and a subsequent thermal annealing process. Here, we use a conventional spin coating method for the MAI deposition following a procedure described in literature.\textsuperscript{5} After optimizing the concentration (MAI in isopropanol), the spin speed, and the drying temperature, a 150 μl MAI solution (40 mg/ml) was spin-coated onto a dried PbI\textsubscript{2} film at 1000 rpm, and the film was then dried at 120 °C for 1 hour to form the CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} as shown in Fig. 1(e).

FIG. 1. The schematic representation of the organic-inorganic perovskite thin film formation via pulsed laser deposition. (a) The PbI\textsubscript{2} target used in this work; (b) PbI\textsubscript{2} thin film is deposited on Si or FTO coated glass substrates by the PLD method in a vacuum chamber; (c) The 2-propanol-based CH\textsubscript{3}NH\textsubscript{3}I solution is spin-coated onto the PbI\textsubscript{2} thin film; (d) The film is heated at 120 °C for 1 hour to form CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3}; (e) The dark CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} film after annealing.
III. RESULTS AND DISCUSSION

Fig. 2(a) shows the X-ray diffraction (XRD) patterns of a PbI₂ film (after PLD) and a MAPbI₃ film (after Step 2) on Si substrates. Polycrystalline and highly oriented nature of the PbI₂ films is evident in Fig. 2(a) (top), where (00l) peaks of PbI₂ are seen, confirming that the (00l) orientated hexagonal lattice of the PbI₂ crystal [space group: P-3m1(164)] has been generated by the PLD method.

For the perovskite phase formed after Step 2, the main XRD peaks of the film indicate that the tetragonal CH₃NH₃PbI₃ film is predominantly (110) oriented (Fig. 2(a) (bottom)). A small XRD peak indicated by an asterisk corresponds to the (001) peak of PbI₂, which is possibly due to the decomposition of CH₃NH₃PbI₃ in air or due to residual unreacted PbI₂.

FIG. 2. X-ray diffraction patterns, AFM and SEM images of PbI₂ and CH₃NH₃PbI₃ layers. (a) XRD patterns of PbI₂/Si (top), CH₃NH₃PbI₃/Si (bottom); (b) AFM image of PLD PbI₂ film on Si; (c) AFM image of CH₃NH₃PbI₃ on Si; (d) and (e) Cross-sectional and top view SEM images of MAPbI₃ fabricated on Si via PLD method.
We performed atomic force microscopy (AFM) to examine the morphology of our films. A 5 \( \mu \text{m} \times 5 \mu \text{m} \) AFM image of a PbI\(_2\) film prior to spin-coating of a MAI layer is shown in Fig. 2(b). The root mean square (RMS) roughness is 7.74 nm, indicating that relatively smooth PbI\(_2\) thin films can be prepared by PLD at room temperature. The surface morphology of a completed CH\(_3\)NH\(_3\)PbI\(_3\) film (\( \approx 220 \) nm) was found to show significantly larger RMS roughness of 89 nm (Fig. 2(c)). This enhanced roughness is due to the volume expansion when the perovskite phase is formed during the intercalation of MAI into the PbI\(_2\) layer.\(^{35}\) This in-situ growth process of organic-inorganic perovskite crystal also leads to a substantial increase in the grain size as shown in Fig. 2(c).

We further characterized the morphology of our perovskite films by scanning electron microscopy (SEM) (Fig. 2(d), 2(e)). The cross-sectional SEM image of CH\(_3\)NH\(_3\)PbI\(_3\) on Si in Fig. 2(d) shows a smooth and a uniform film (220 nm) indicating highly crystalline nature of the organic-inorganic perovskite film. The top-view SEM image shown in Fig. 2(e) indicates complete coverage by the film on the Si substrate surface. The typical grain size ranges from \( \approx 800 \) nm to \( \approx 1,500 \) nm. Obtaining large grains is very important for the fabrication of high performance devices because large grains can reduce bulk defects and increase the mobility of charge carriers.\(^{36}\)

The perovskite films were also fabricated on FTO coated glasses using the same method. Following a procedure described in literature,\(^{37}\) a 50 nm poly(3,4-ethylenedioxythiophene):poly(styrenesulphonate) (PEDOT:PSS) layer was first spin-coated onto FTO coated glasses as the hole transport layer in the device. Following the hybrid PLD process illustrated in Fig. 1, the perovskite phase was formed on the FTO-glass/PEDOT:PSS.

The XRD pattern of a MAPbI\(_3\) film (300 nm) fabricated by the PLD-based hybrid method on a FTO coated glass substrate is shown in Fig. 3(a) (top). To perform side-by-side comparison of films made by our hybrid method vs. the conventional method, a CH\(_3\)NH\(_3\)PbI\(_3\) thin film (295 nm) has also been prepared via the standard spin coating of PbI\(_2\) from a dimethylformamide (DMF) solution.\(^{37}\) The XRD pattern of the latter film is shown in Fig. 3(a) (bottom). The comparison shows that the film made by the PLD-based hybrid method is preferentially (110) oriented, whereas the film made by the conventional spin-coating method shows a relatively weak intensity of (110) peaks. Haruyama et al.\(^{38}\) reported flat terminations on the (110) and the (001) surfaces are important for the PSC performance.

![X-ray diffraction patterns](image)

**FIG. 3.** X-ray diffraction patterns of (a) CH\(_3\)NH\(_3\)PbI\(_3\) films made by the PLD hybrid method (top) and by standard spin-coating-only method (bottom); (b) Perovskite film thickness as a function of the thickness of the PLD PbI\(_2\) film.
Here, the strongly (110) preferred orientation of CH$_3$NH$_3$PbI$_3$ made by the hybrid method is attributed to the high quality of the PbI$_2$ thin film deposited by PLD.

In perovskite thin-film solar cells, a CH$_3$NH$_3$PbI$_3$ thin film is used as an absorbing layer. Therefore, the thickness of the CH$_3$NH$_3$PbI$_3$ layer is an important device design parameter. To demonstrate precise control of the thickness of the CH$_3$NH$_3$PbI$_3$ thin film using the PLD-based hybrid method, we deposited PbI$_2$ films with different thicknesses and compared them to the thicknesses and the composition of the final CH$_3$NH$_3$PbI$_3$ films. When the thickness of the starting PbI$_2$ thin films is in the range of 80 - 280 nm, the thickness of the final CH$_3$NH$_3$PbI$_3$ thin films is found to be in the range of 185 - 580 nm, as determined by profilometry. Interestingly, in all the films synthesized here, the average ratio between the thickness of the MAPbI$_3$ film and the thickness of the starting PbI$_2$...
layer was consistently found to be around 2 (Fig. 3(b)). This agrees well with a recent report\textsuperscript{35} and suggests that the excess amount of MAI evaporates during the annealing process. Thus, the PLD of PbI\textsubscript{2} precursor allows the fabrication of organic-inorganic perovskite films with a precisely tailored thickness. In addition, we found that we always see a minor XRD peak at 12.6°((001) peak of PbI\textsubscript{2}) when the thickness of PbI\textsubscript{2} is around 240 nm (and the final MAPbI\textsubscript{3} is 490 nm).\textsuperscript{40} The intensity of this peak increases with increasing thickness of PbI\textsubscript{2} in Step 1. This is due to the fact that there is not enough MAI solution to convert all the PbI\textsubscript{2} into the perovskite under our current recipe (Step 2). We expect that a further optimized MAI spin-coating step may help achieve a complete conversion.

We have fabricated complete cell structures using MAPbI\textsubscript{3} films made with our PLD-based hybrid method and also, for comparison, using MAPbI\textsubscript{3} films deposited by the conventional spin coating method. In such structures, after the synthesis of a MAPbI\textsubscript{3} thin film on PEDOT:PSS coated FTO glasses, an electron transport layer of phenyl-C-butyric acid methyl ester (PCBM) was spin-coated on the surface of MAPbI\textsubscript{3}, and then a contact electrode of Al was thermally evaporated on the surface of PCBM\textsuperscript{37} completing an inverted planar FTO/PEDOT:PSS/MAPbI\textsubscript{3}/PCBM/Al device structure. A schematic architecture of the device is illustrated in Fig. 4(a). The photovoltaic performance was measured at illumination (AM 1.5G, 100 mA/cm\textsuperscript{2}). The J-V curves are shown in Fig. 4(b). PCEs of 1.12% and 1.03% were obtained for two cells made by the PLD method with a MAPbI\textsubscript{3} layer of 300 nm and 330 nm, respectively. On the other hand, a relatively high PCE (5.45%) was achieved in a cell fabricated through the conventional spin coating method with a 300 nm MAPbI\textsubscript{3}.

We show the cross-sectional views and the top-view SEM images of MAPbI\textsubscript{3} thin films in the two types of cells (one with PLD-based MAPbI\textsubscript{3}, and another with standard spin-coating MAPbI\textsubscript{3}). Both films in top-view images (Fig. 4(c), 4(e)) display closely-packed grains with full coverage on the surface of PEDOT:PSS, and there is little difference in the crystallite shape and size between the two. The cross-sectional SEM images (Fig. 4(d), 4(f)) also show that both films are similar in texture and relatively smooth. Based on the XRD and SEM results, we therefore conclude that MAPbI\textsubscript{3} thin films fabricated by the PLD method are similar in phase purity and crystallinity compared to those fabricated by the standard spin-coating method, despite the difference in the PCE of the devices. From the J-V curves (Fig. 4(b)), we found that cells made with PLD have similar V\textsubscript{oc} and the fill factor as the spin-coating cells. This is suggestive of the fact that the films are uniform and pin-hole free,\textsuperscript{36–39} and this is consistent with the SEM images. The low PCE is likely due to a dramatically low J\textsubscript{sc}: a possible reason is that the PEDOT:PSS layer may have deteriorated in the vacuum chamber during the PLD process, reducing the conductivity and resulting in a low J\textsubscript{sc} and a low V\textsubscript{oc}. We believe that by further optimizing device parameters and developing materials, achieving higher efficiency values is possible for the PLD-based hybrid deposition process.

**IV. CONCLUSION**

In summary, we have demonstrated a novel hybrid fabrication process that combines PLD of PbI\textsubscript{2} with subsequent spin coating of MAI to prepare continuous, crystalline, uniform, and compact lead iodide perovskite films with a large grain size. We have demonstrated the versatility of the PLD-based hybrid process in synthesizing CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} thin films with well-controlled thicknesses. A device based on the PLD process showed a PCE of 1.12%. The hybrid technique described in this work provides a new route for low-temperature fabrication of organic-inorganic perovskite thin films for PSCs with rapid crystallization and good film-thickness control.

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7 J. H. Heo, S. H. Im, J. H. Noh, T. N. Mandal, and S. I. Seok, Nano Letters 13, 1764 (2013).


40 See supplementary material at http://dx.doi.org/10.1063/1.4939621 for XRD patterns of the CH3NH3PbI3 films with varying thickness on FTO coated glasses in FIG S2.