Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

One-step deposition by slot-die coating of mixed lead halide perovskite for photovoltaic applications

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ARTICLE INFO

ABSTRACT

Recent advances in the performance and stability of lead halide perovskite solar cells announce a promising future for this technology. As the understanding of lab scale device fabrication progresses technology developments in the area of up-scaling are required to demonstrate their viability on an industrial and pre-commercial scale. These developments include replacing slow spin coated deposition techniques with continuous roll to roll compatible slot-die methods. In this work we demonstrate the suitability of a one-step slot-die coating method for the deposition of lead halide perovskite layers, in particular for infiltration into a mesoporous titania scaffold. Appropriate crystallisation dynamics of the perovskite are achieved by careful control of the substrate temperature in combination with a post-processed rapid air knife application. We show that devices fully processed in air using this method deliver a photovoltaic conversion efficiency up to 9.2%, this is comparable to those manufactured using a spin coating process.

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1. Introduction

There are a number of photovoltaic technologies such as organic, dye sensitised, perovskite and quantum dot solar cells which aim to capitalise on the lower manufacturing cost achievable through solution processing combined with low embedded energy costs [1–3]. Since 2012, perovskite solar cells have emerged as the most efficient of the solution processed PV technologies [4,5] with more recent advances demonstrating devices with efficiencies over 20% [6]. Progress on the lifetime of perovskite based devices, up to 1000 h under full AM 1.5 simulated sunlight in ambient air [7–9], suggests that perovskite solar cells are a promising technology for the transition to industrial scale manufacture.

In addition to improvements in materials, to increase efficiency and lifetime, methods of deposition must also evolve in order to progress the technology from the laboratory into production. For fundamental studies at laboratory scale, spin coating is often favoured as a convenient method to deposit solution processed solar cells [4,10,11]. However, spin coating is limited in commercial production by the high percentage of material wastage, necessity for batch processing and constrained substrate size.

Techniques compatible with roll to roll deposition such as slot-die coating [12,13] flexographic printing [14] blade coating [15]

and K-bar [16] deposition have been used for solar cell production and have the added advantage that there is typically less materials wastage than spin coating because of the direct deposition of material onto the substrate. This direct deposition has a disadvantage that the dynamic drying of the solvent, which is associated with spin coating [17] does not occur and so all solvent removal must be achieved during subsequent heating steps. When crystallising perovskite from a precursor solution of lead chloride and methyl ammonium iodide in a single step process this excess solvent affects the crystallisation dynamics and if not controlled can lead to vertical crystal growth which causes a rough perovskite layer with poor surface coverage and therefore low photocurrent.

Single step deposition of perovskite by scaleable techniques such as spray coating [18] doctor blading [19–22] and slot-die coating [12] have been shown to give good coverage when deposited onto a PEDOT: PSS layer in an inverted p-n type architecture but when deposited onto a metal oxide layer the crystallisation dynamics are unfavourable and poor coverage of the perovskite is achieved, limiting photocurrent [12].

In terms of long-term stability, it has been reported that planar cells with inverted device architecture and water-based PEDOT: PSS as the HTM onto the ITO substrate, can easily degrade [23] due to the hygroscopic and acidic nature of PEDOT, ease of diffusion of PSS into other layers and instability of the ITO/organic interface [24,25]. Planar cells with conventional architecture have not shown satisfying lifetime so far [26,27] with only limited studies

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demonstrating higher long-term stability when using a combined halide perovskite [28], a water-free PEDOT: PSS [29] or a vacuum-assisted thermal annealing process to completely remove organic chloride by-products [30].

It is thus more advantageous to use an architecture based on a metal oxide scaffold, since this has been shown to exhibit improved stability, up to 1000 h both in the dark [31] and under full illumination [8,32] compared to planar counterparts (inverted or not) [24].

In order to improve the surface coverage of perovskite deposited onto a mesoporous titania scaffold, a two-step process can be employed [32] where first lead iodide is deposited from solution and this is converted into perovskite by immersion into methyl ammonium iodide [15]. This has enabled the perovskite to be deposited by slot-die coating of PbI_2 supported by air quenching [33] however in order to convert the lead iodide into perovskite a second coating step must be employed which adds to the complexity of the processing. Of the roll to roll compatible processes, slot-die coating is favoured since it can produce patterned layers eliminating the need for complex removal steps associated with un-patterned deposition [15]. By using an airknife to control the temperature gradient, combined with a preheated substrate, the crystallisation dynamics can be controlled and this work demonstrates for the first time a single step deposition by slot-die coating of perovskite onto a mesoporous titania scaffold.

2. Materials and methods

2.1. Slot-die coating trials (temperature and air-knife setup)

Plain soda glass (100 mm × 150 mm) substrates were cleaned with Hellmanex and then sequentially rinsed with de-ionized water, acetone, isopropanol and ethanol before being oxygen plasma treated. A 40 wt% solution of methylammonium iodide (MAI) and $PbCl_2$ (3:1 molar ratio) in DMF was prepared in a nitrogen atmosphere. The solution was then transferred to a class 10,000 clean room maintained at an average relative humidity below 50%. The solution was pumped into the slot-die coating head, kept at 40 °C to avoid issues due to PbI_2 crystallisation. To test the influence of substrate temperature on coating condition this was varied between 20 °C (no external heating source), and 65 °C or 90 °C achieved by preheating the substrate for 30 min in an oven prior to application of the material. The distance between meniscus waveguide and glass substrate was set at 50 μm, the pumping rate at 91 μL/min and the coater belt speed at 4.2 mm/sec. When necessary, a cold air knife impinging on the coated layer, with air pressure of 0.5 bar, was placed at a distance of 200 mm horizontally from the coating head and at a height of 250 mm from the sample. Coated precursors were annealed via two runs in a 2.6 m long convection belt oven (Thieme) at 110 °C at a belt speed of 3.3 mm/sec. Layer features have been investigated through optical microscopy and stylus profilometry measurements. The print head in operation and the subsequent layers produced are shown in Fig. 1..

2.2. Device fabrication

Patterned FTO glass substrates were cleaned and plasma treated as described in Section 2.1. A compact titania layer (50 nm) was deposited via spray pyrolysis at 300 °C from a solution of 1:10 titanium diisopropoxide bis(acetylacetonate) and isopropanol, substrates underwent a sintering step at 550 °C for 30 min. For spin coated devices a TiO_2 paste (DSL18NRT) diluted in ethanol (2:7 in weight) was spun over the samples at 5000 rpm, heated at 150 °C for 15 min and sintered at 550 °C for 60 min in order to give
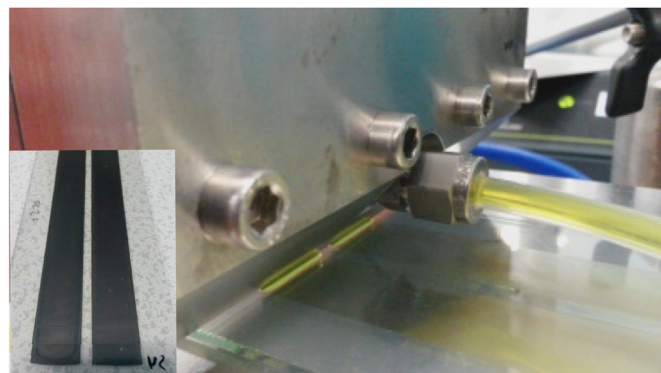

Fig. 1. Photograph of the print head in operation. Inset, perovskite layers post deposition and annealing.

a 300 nm mesoporous layer. Perovskite precursor solution (see Section 2.1) was deposited at 2000 rpm, then the substrates were heated for 90 min at 100 °C. For slot-die coated devices a TiO_2 paste diluted in ethanol (1:1 in weight) was bar coated over the 100 mm × 150 mm substrate, then it was heated at 150 °C for 15 min and sintered at 550 °C for 60 min. Bar coating was used to deposit the mesoporous TiO_2 layer as limitations related to spin coating sample size did not allow large enough substrates to enable a slot-die coating run, see Fig. 1. This different approach led to an increased mesoporous TiO_2 layer, approximately 350 nm for spin coating and 600 nm for bar-coating. The precursor solution was pumped into the slot-die coating head and subsequently deposited over the bar-coated mesoporous layer held at a predetermined temperature (20 °C, 65 °C and 90 °C) and subjected to a single pass under the cold air knife. The sample was then transferred to the belt oven, set at 110 °C, for two passes according to the parameters noted in Section 2.1. The temperature profile of the belt oven can be seen in figure S1 (supplementary). In order to compare performances between cells differentiated only by the mesoporous titania thickness and perovskite layer processing method, slot-die coated samples were scored and reduced in active area to ensure the same device configuration and post processing of subsequent layers (HTM and Au). For the hole transport layer, a 10 wt% solution containing 2,2,7,7-tetrakis-(N,N-di-p-methoxyphenyl-amine) − 9,9-spirobifuorene (Spiro-OMeTAD), doped with 4-tert-Butylpyridine and lithium bis-tri-fluoromethanesulfonimide and oxidised through the addition of vanadium oxide (V_2O_5) [11], was spin coated over the perovskite layer in a nitrogen atmosphere at 2000 rpm. In case of spin coated devices, an additional step was necessary to scrape off the perovskite in order to allow the deposition of the front contact. This step was not necessary in case of slot-die coated devices because this technique produces patterned coatings. Gold contacts were thermally evaporated to complete the device stack.

2.3. Film characterisation

The device nano-structure was characterised using a Carl Zeiss Crossbeam 540 FIBSEM completed with Oxford 50 mm² SDD EDS detector, via the preparation of electron transparent lamellar of approximately 100 nm in thickness. X-ray diffraction spectra of spin and slot-die coated cell stack (just before the Spiro-OMeTAD deposition) were collected on a D8 Discover (Bruker) x-ray diffractometer with a Cu $K\alpha$ source ($\lambda = 1.5418$ Å). The step time was 0.2 s and the step increment was 0.01°.

2.4. Device characterization

I-V testing was carried out using an Oriel solar simulator with a