Chemical Physics Letters 661 (2016) 131–135

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Research paper

High-coverage organic-inorganic perovskite film fabricated by double spin coating for improved solar power conversion and amplified spontaneous emission

Toshinori Matsushima [a,b,*], Munetomo Inoue [a], Takashi Fujihara [c], Shinobu Terakawa [a], Chuanjiang Qin [a,b], Atula S. D. Sandanayaka [a,b], Chihaya Adachi [a,b,d,*]

[a] *Center for Organic Photonics and Electronics Research (OPERA), Kyushu University, 744 Motooka, Nishi, Fukuoka 819-0395, Japan*
[b] *JST, ERATO, Adachi Molecular Exciton Engineering Project, Kyushu University, 744 Motooka, Nishi, Fukuoka 819-0395, Japan*
[c] *Innovative Organic Device R&D Laboratory, Institute of Systems, Information Technologies and Nanotechnologies (ISIT), Fukuoka Industry-Academia Symphonicity (FiaS) 2-110, 4-1 Kyudaishinmachi, Nishi, Fukuoka 819-0388, Japan*
[d] *International Institute for Carbon Neutral Energy Research (WPI-I2CNER), Kyushu University, 744 Motooka, Nishi, Fukuoka 819-0395, Japan*

ARTICLE INFO

Article history:
Received 12 July 2016
In final form 25 August 2016
Available online 26 August 2016

Keywords:
Organic-inorganic perovskite
Solar cell
Amplified spontaneous emission
Double spin coating
Substrate coverage

ABSTRACT

We demonstrate that double spin coating, where a perovskite film is covered with another perovskite film, can increase substrate coverage from 81% to 97% along with an increase of film thickness from 151 ± 17 to 246 ± 18 nm. The increased substrate coverage by double coating improves the solar power conversion efficiency from 7.1 ± 0.6 to 10.3 ± 1.0%, an approximate 1.5-fold increase. Additionally, a double-coated film of higher substrate coverage exhibits amplified spontaneous emission (ASE) while a single-coated film of lower substrate coverage does not exhibit ASE. Double coating is an attractive method for increasing substrate coverage and improving solar power conversion and ASE.

1. Introduction

Solar cells containing organic-inorganic perovskite light absorbers have attracted considerable attention. They can provide cost-effective, high-efficiency solar power conversion. This results from their excellent light harvesting ability [1–5], weak exciton binding energies [1–3,6], long carrier diffusion lengths [7–9], high carrier mobilities [10–12], and few serious defect states [13–16]. They are also solution processable [4–16]. Perovskite solar cells were first reported in 2009 [4]. Since then, optimized perovskite film fabrication conditions and solar cell structures have significantly increased efficiencies [5,17,18]. The highest certified efficiency is currently in excess of 20% [19–21].

Agglomeration of perovskites often occurs upon heating solution-processed films, because of crystallization and dewetting [22–31]. Agglomeration forms pinholes and gaps between grains, and incomplete coverage of substrates by the perovskite. This incomplete substrate coverage can reduce solar power conversion efficiencies because of low-resistance shunting paths and lost absorption of light passing through pinholes and gaps. Uniform perovskite films with full coverage have been formed by spin coating under optimized conditions [22]. Perovskite films with high coverage have been obtained by vapor deposition [23], vapor-assisted two-step reaction [24], compositional control [25], interdiffusion [26], solvent annealing [27], solvent-induced fast crystallization [28], hot uniaxial pressing [29], hot isostatic pressing [30], and solvent bathing [31].

In the current study, we show that double spin coating is an alternative method for increasing substrate coverage. Substrate coverage by perovskite films fabricated by single spin coating is low, because of numerous gaps formed between perovskite grains. Substrate coverage can be significantly increased by covering the initial film with another film, by a second spin coating procedure. The double spin coating method increases the substrate coverage, and improves electron and hole diffusion. This combination improves the solar power conversion efficiency from 7.1 ± 0.6 to 10.3 ± 1.0%, an approximate 1.5-fold increase. This results from reduced low-resistance shunting paths, improved light absorption, and enhanced electron and hole diffusion. Amplified spontaneous emission (ASE) is exhibited by the high-coverage double-coated

---

* Corresponding authors at: Center for Organic Photonics and Electronics Research (OPERA), Kyushu University, 744 Motooka, Nishi, Fukuoka 819-0395, Japan.

E-mail addresses: tmatusim@opera.kyushu-u.ac.jp (T. Matsushima), adachi@cstf.kyushu-u.ac.jp (C. Adachi).

http://dx.doi.org/10.1016/j.cplett.2016.08.067

film. The low-coverage single-coated film exhibits no ASE. The observed ASE results from reduced light propagation loss by the high coverage.

2. Experimental

A 25-nm-thick film of poly(3,4-ethylenedioxythiophene)polystyrene sulfonate (PEDOT:PSS) was spin-coated on a clean substrate. A yellow precursor film was spin-coated from a solution containing $PbCl_2$ and CH_3NH_3I in *N*,*N*-dimethylformamide (DMF), and the coated substrate was then heated on a hot plate at 60 °C for 30 min, and subsequently at 100 °C for 90 min. This resulted in the conversion to a brown perovskite of chemical formula of $CH_3NH_3PbI_{3-x}Cl_x$ (see single spin coating scheme, Fig. 1a). This initial perovskite film was immediately transferred to the sample stage of our spin coating system. An additional perovskite film was then prepared on the initial perovskite film in the same manner as described earlier, except that the precursor solution was directly dropped on the hot, spinning initial perovskite film (see double spin coating scheme, Fig. 1a). The surface morphologies, thicknesses, absorption spectra, and structural properties of the single- and double-coated perovskite films were investigated by scanning electron microscopy (SEM) (JCM-5700, JOEM), surface profilometry (DektakXT, Bruker), absorption spectrophotometry (Lambda 950, Perkin Elmer), and X-ray diffraction (XRD) using the $2\theta/\theta$ technique [$\lambda = 1.54$ Å (Cu Kα)] (Ultima IV, Rigaku), respectively. (See the Supplementary Information for more details of the perovskite film fabrication conditions, carrier diffusion length and ASE measurements, and solar cell fabrication and evaluation.)

3. Results and discussion

Double spin coating leads to higher substrate coverage. Substrate coverage by the single-coated film is low, because of numerous gaps formed between grains, as shown in Fig. 1b. The substrate coverage was quantified using Adobe Photoshop, to calculate the fraction of dark areas in SEM images. Calculated substrate coverages are 81% and 97% for the single- and double-coated films, respectively. Although coverage increases by 16% during the second coating, a 3% gap area remains in the double-coated film. The perovskite fabrication conditions require optimizing to achieve 100% coverage.

The improved substrate coverage is attributed to the covering of gaps formed in the initial film. The thicknesses of the single- and double-coated films are 151 ± 17 and 246 ± 18 nm, respectively, as determined by subtracting the thickness of the PEDOT:PSS film (25 nm) from the sum of the thicknesses of the PEDOT:PSS and perovskite films. The volumes (V) of the single- and double-coated films in the solar cell active area (4 mm^2) can be calculated using the equation:

$$V = C \times d \times A \tag{1}$$

where C is the substrate coverage, d is the thickness, and A is the film area. The V values of the single- and double-coated films are 4.9×10^{-7} and 9.5×10^{-7} cm^3, respectively. The difference in perovskite V values is nearly double, indicating that the initial perovskite film is not significantly dissolved by the precursor solution during the second coating.

A precursor solution was dropped on a perovskite film at room temperature, which was not spinning. This substrate was then subjected to spinning for the second coating procedure. The resulting double-coated film had similar morphologies and film thicknesses to those of the single-coated film. This is because of dissolution of the underlying perovskite film in the dropped solution, during the second coating. Dropping the precursor solution onto a hot, spinning perovskite film is therefore an important requirement of the second coating. With this condition, DMF quickly evaporates from the sample, minimizing perovskite dissolution.

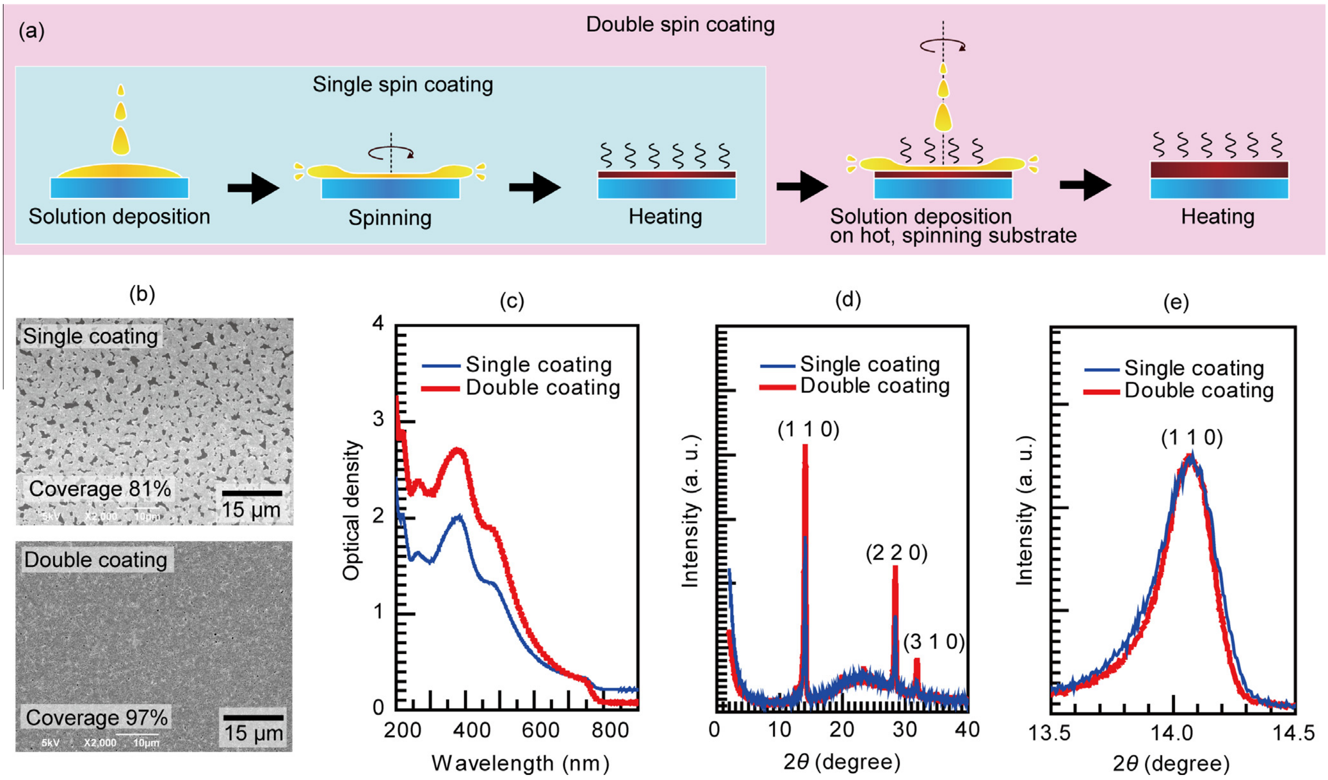

Fig. 1. (a) Schematic illustrations of the single and double spin coating processes. (b) SEM images, (c) absorption spectra, and (d) XRD patterns of single- and double-coated perovskite films. (e) Magnified, normalized XRD patterns from (d).