

Contents lists available at ScienceDirect

### Solar Energy Materials & Solar Cells



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

# Amazing stable open-circuit voltage in perovskite solar cells using AgAl alloy electrode



Ziyao Jiang<sup>a</sup>, Xiaohong Chen<sup>a,\*</sup>, Xuanhuai Lin<sup>a</sup>, Xiangkun Jia<sup>a</sup>, Jinfeng Wang<sup>a</sup>, Likun Pan<sup>a</sup>, Sumei Huang<sup>a</sup>, Furong Zhu<sup>b</sup>, Zhuo Sun<sup>a</sup>

<sup>a</sup> Engineering Research Center for Nanophotonics and Advanced Instrument, Ministry of Education, and Department of Physics, East China Normal University, Shanghai 200062, China

<sup>b</sup> Department of Physics, Institute of Advanced Materials, and Institute of Research and Continuing Education (Shenzhen), Hong Kong Baptist University, 224 Waterloo Road, Kowloon Tong, Hong Kong

### ARTICLE INFO

Article history: Received 5 August 2015 Received in revised form 2 November 2015 Accepted 15 November 2015

Keywords: Perovskite solar cells AgAl alloy AlO<sub>X</sub> Stability Electrode

### ABSTRACT

The progresses made in emerging perovskite solar cells, a promising alternative photovoltaic technology to the conventional solar cells, have quickly set the power conversion efficiency (PCE) record of 20%. Apart from the high PCE, the stability of perovskite solar cells is another important issue for them to be commercially viable. To investigate the impact of electrodes on the stability of the perovskite solar cells. cells with a structure of ITO/PEDOT:PSS/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/PCBM/Cathode, having different cathode contacts of Al, Ag and AgAl alloy, were fabricated. The cells with an AgAl alloy cathode reached a PCE of 11.76%, which is slightly higher than that (11.45%) of the structurally identical cells with Ag contact, much higher than that for the ones with Al electrode (7.95%). The stable open-circuit voltage ( $V_{OC}$ ) of cells having an AgAl contact was demonstrated, with almost no change in the  $V_{OC}$  after 360 h aging under a relative humidity of 10% in air. However, there is an obvious drop in the  $V_{\rm OC}$  of the structurally identical perovskite cells with Ag cathode, e.g., an 85% decrease from its initial  $V_{OC}$  value for cells aged under the same condition. The enhancement in the PCE of cells with AgAl cathode is attributed to the formation of AlO<sub>x</sub>, which can improve built-in potential in the cell and allow an effective electron extraction at the PCBM/ AgAl cathode interface. An interfacial AlO<sub>X</sub> interlayer could be formed at the interface between PCBM and AgAl contact during thermal evaporation and aging. The presence of the interfacial  $AIO_X$  interlayer helps to prevent the diffusion of the Ag atoms into the active layer, to improve the adhesion of the metal contact on PCBM and also to avoid moisture encroachment.

© 2015 Elsevier B.V. All rights reserved.

### 1. Introduction

The emerging perovskite solar cells have evoked widespread scientific and industrial interests because of its promising advantages of low-cost and high efficiency. Since the report of a power conversion efficiency (PCE) of 3.5% for ammonium lead iodide (CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>) based dye sensitization solar cells (DSSCs) by Miyasaka et al. [1] in 2009, significant progresses in perovskite solar cells have been made with PCE of 20.1% reported in 2015 [2]. With the encouraged progresses made in PCE, some other issues such as repeatability and stability become more prominent and urgent. Repeatability is related to morphology, crystalline size and compaction of perovskite films which are sensitive to the surface properties of bottom layer and process conditions including

http://dx.doi.org/10.1016/j.solmat.2015.11.026 0927-0248/© 2015 Elsevier B.V. All rights reserved. deposition methods, solvent selection and annealing condition. The single-step spin-coating method with N,N-Dimethylformamide (DMF) solvent leads to low surface coverage of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> film [3,4], resulting in poor performance and inferior repeatability. The uniform and pinhole-free CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> films can be formed by thermally evaporating Lead (II) iodide (PbI<sub>2</sub>) and/or methylammoniumiodide (CH<sub>3</sub>NH<sub>3</sub>I), which greatly increases the performance of perovskite solar cells [5,6]. In addition, two-step spincoating methods with porous structure or the planar structure are also widely used to improve the morphology of perovskite films [7]. Furthermore, solution engineering [8–10], gas-assisted spinning [11], chloride introduction [12,13] and solvents/additives used [14,15] have been demonstrated effective for improving PCE and repeatability of cells. Meanwhile, CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> itself is sensitive to water and ultraviolet (UV) light, easily decomposed into "PbI<sub>2</sub>" and "I<sub>2</sub>" under exposing moisture and UV light [16], due to interaction between water molecules and the highly hygroscopic

<sup>\*</sup> Corresponding author. Tel.: +86 21 62233676. E-mail address: xhchen@phy.ecnu.edu.cn (X. Chen).

methylammoniumcations [17]. Recently structure engineering of the perovskite component  $(FA)_{1-x}(MA)_xPbI_{3-y}Br_y$  shows an improved stability due to the hydrophobicity of  $(FA)_{1-x}$   $(MA)_x$ cations [18]. The introduction of the hydrophobic materials and interface layer into perovskite solar cells indicate significantly enhanced stability compared to the case using hydrophilic hole transporting materials such as 2,2',7,7'-tetrakis (N,N-di-p-methoxy-phenylamine)-9,9'-spirobifluorene (Spiro-OMeTAD), Lithiumbis(trifluoromethanesulfonyl)imide (Li-TFSI), Poly(3,4-ethylenedioxythiophene):polystyrene sulfonic acid (PEDOT:PSS) [19–21]. Although many other materials including carbon materials, and interface engineering have been developed to improve the ability of water-proof of solar cells [22–24], but there are few report on the influence of metal electrodes.

Al, Ag and Au films have high optical reflectivity and excellent electrical conductivity, which have been widely used as metal electrodes in perovskite solar cells. Between them, Ag is a more ideal electrode material than Au due to its high cost, and is superior to Al due its unstable interfacial contact, caused by the iodine ions induced corrosion in Al. The AgAl alloys are also expected to be an ideal electrode material for perovskite solar cells because they have been successfully applied to solar thermal applications [25] and light emitting diodes (LED) [26]. AgAl alloy electrode compared to Ag shows more thermal stability because Al atoms are firstly diffused out of AgAl alloy and oxidized into AlO<sub>X</sub>, which act as an armor layer and can inhibit Ag atom diffusion and agglomeration. The formation of AlO<sub>X</sub> interlayer can also improve the adhesion between AgAl and the active layer for desired Ohmic contact at the electrode/transporting interface. In Si solar cells and DSSCs [27–29], Al<sub>2</sub>O<sub>3</sub> has been successfully applied to passive the surface of semiconductor and suppress exciton recombination. In this work, the performance of perovskite solar cells with different metal cathodes of Al. Ag and AgAl allov was investigated. It is found that the formation  $AlO_X$  helps to prevent the diffusion of Ag atoms and to avoid the possible damage to the underlying PCBM layer during thermal evaporation. The presence of a thin  $AIO_X$ layer in the AgAl electrode also impedes the moisture encroachment, therefore improving the contact stability.

### 2. Experimental details

Perovskite solar cells with structure ITO/PEDOT:PSS/ CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/PCBM/Cathode, were fabricated using different cathodes of Al, Ag, and AgAl alloy, respectively. The weight ratio (wt%) of Al to Ag in the AgAl alloy is 3 wt%, purchased from Trillion Metals Co., Ltd (Beijing, China). PbI<sub>2</sub> (99.9%) was purchased from Aladdin Reagents. CH<sub>3</sub>NH<sub>3</sub>I was purchased from 1-Material-Organic Nano Electronic (1-Material Inc.). PEDOT:PSS (CLEVIOS P VP Al 4083) was purchased from Heraeus. All solvents and reagents were used as received. The precursor solutions with 40 wt% were prepared as ref [8], and stirred at 40 °C overnight. The precursor solutions were filtered by a 0.45 µm membrane filter prior to the spin-coating.

The pre-patterned indium tin oxide (ITO)/glass substrates with a sheet resistance of 10  $\Omega$ /sq were cleaned by ultra-sonication sequentially in detergent, de-ionized water, acetone and isopropanol for 20 min. After being dried in the oven, ITO glass substrates were treated with ultraviolet ozone for 15 min. PEDOT: PSS solutions were spin-coated at 4000 rpm for 1 min to form 40 nm thick film, followed by annealing at 140 °C for 10 min. The CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> film was spin-coated on the surface of the PEDOT:PSS buffer layer by a consecutive two-step spin-coating process at 2000 rpm and 4000 rpm for 20 s and 60 s, respectively. During the second spin-coating step, toluene drop-casting was employed to replace DMSO solvent. The substrates were dried on a hot plate at 100 °C for 10 min. After being cooled down, the [6,6]-phenyl-C61butyric acid methyl ester (PCBM) solution (10 mg/ml in chlorobenzene) was spin-coated at 1200 rpm to form 40 nm thickness film on top of the perovskite layer. Finally, the metal cathode around 100 nm was deposited on the PCBM by thermal evaporation under the base pressure of  $6 \times 10^{-4}$  Pa.

The current density-voltage (I-V) characteristics were measured using a Keithley model 2440 source meter and a Newport solar simulator system with AM1.5G and 100 mW/cm<sup>2</sup> illumination. The incident photon to current conversion efficiency (IPCE) over the wavelength from 300 to 800 nm was measured using a Newport Optical Power Meter 2936-R. All devices were tested under the ambient atmosphere condition. The surface morphologies of samples were characterized by field-emission scanning electron microscopy (FESEM, Hitachi S-4800). The reflection and absorption spectra of the samples were measured using a UV-vis spectrophotometer (Hitachi U-3900). The work function values of Ag (4.8 eV) and AgAl (4.7 eV) contacts in the cells were measured using the Test Instrument of Surface Work Function (Sunmonde Electric Light Source Technology (Shanghai) Co. Ltd). Cyclic voltammetry (CV) were measured using Autolab PGSTAT 302N electrochemical workstation.

#### 3. Results and discussion

## 3.1. Performance of perovskite solar cells with different metal cathode

The summary of the cell parameters measured for cells with different cathodes of Al, AgAl and Ag, averaged from the respective 24 devices, is listed in Table 1. Fig. 1(a-b) show the *I*-V and IPCE curves of the typical device of each metal electrode. Cells with AgAl cathode have average PCE of 11.16%, which is a little higher than the average PCE (10.47%) of cells with Ag cathode. The PCEs of the best devices with AgAl, Ag and Al cathodes are 11.76%, 11.45% and 7.95%, respectively. But PCE of cells with Al could quickly decay to nearly 4% within 30 min, where mainly because of the recession of fill factor and photocurrent. The improved PCEs of cells with AgAl and Ag cathodes are attributed to larger fill factor (FF) and photocurrent compared to cells with Al cathode. The larger IPCE value curves of cells with AgAl and Ag cathode compared to Al cathode qualitatively demonstrate this photocurrent enhancement, as shown in Fig. 1(b). Integrated  $J_{SC}$  values from IPCE spectra of Ag, AgAl and Al are 16.70 mA/cm<sup>2</sup>, 17.61 mA/cm<sup>2</sup> and 13.18 mA/cm<sup>2</sup> respectively, which are somewhat lower than the  $J_{SC}$ values from the *I–V* curve. This is probably attributed to the defects of cells.

The absorption spectra of  $CH_3NH_3PbI_3$  active layers of cells with three different metal cathodes are derived from Fig. 1(c), as shown in Fig. 1(d). Fig. 1(c) shows the absorption spectra of full structure cells and its inset shows the absorption spectra of only metal films, which is derived by 100% subtracting the reflection spectra of the metal films. The lower absorption of  $CH_3NH_3PbI_3$  layer of cell with Al cathode is ascribed to low reflectivity of Al film compared to Ag and AgAl films. The absorption spectra of  $CH_3NH_3PbI_3$  films with

Table 1

The summary of the cell parameters measured for cells with different cathodes of Al, AgAl and Ag, averaged from the respective 24 devices.

Electrode	$V_{\rm OC}\left({\rm V} ight)$	J <sub>SC</sub> (mA/cm <sup>2</sup> )	FF (%)	η (%)
Al AgAl Ag	$\begin{array}{c} 0.83 \pm 0.02 \\ 0.84 \pm 0.02 \\ 0.84 \pm 0.02 \end{array}$	$\begin{array}{c} 15.33 \pm 1.04 \\ 18.73 \pm 1.05 \\ 17.89 \pm 1.16 \end{array}$	$\begin{array}{c} 58.32 \pm 3.36 \\ 70.93 \pm 1.43 \\ 69.72 \pm 2.58 \end{array}$	$\begin{array}{c} 7.42 \pm 0.53 \\ 11.16 \pm 0.60 \\ 10.47 \pm 0.98 \end{array}$



**Fig. 1.** The optical and electrical characteristics of perovskite cells with different metal cathodes of Al, Ag and Al. (a) *J*-*V* characteristics, (b) IPCE spectra, (c) absorption spectra of perovskite solar cells and metal films (inset), (d) relative absorption spectra of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> active layers derived by subtracting absorption spectra of metal films from perovskite solar cells.

AgAl and Ag cathodes are crossed in the wavelength region between 550 nm and 600 nm. The weight ratio of Al to Ag in the AgAl electrode used in this work is about 3 wt%, the reflectivity of AgAl film is 1–2% lower than that of Ag film, therefore, the actual reflectivity at the PCBM/AgAl and PCBM/Ag in the cells is very comparable. The observed change in the absorption of perovskite cells made with AgAl and Ag contacts, as shown in Fig. 1, is mainly due to the fluctuation in the effective thickness of the active layer in different cells. As the perovskite layer was formed by two subsequent coating and the crystallization processes, it is possible that the thickness of the active layer in different cells may not be identical although the same film process was used, resulting in a slight variation in the film absorption. The slight deviation in absorption over the wavelength of 600 nm seen in the cells with AgAl and Ag contacts is likely due to the derivation in the active layer thickness rather than caused by the slight change in the reflectivity at the PCBM/AgAl and PCBM/Ag interfaces. The obviously increased IPCE values of cells with AgAl electrode compared to Ag electrode over 600 nm wavelength is possibly attributed to the formation of AlO<sub>x</sub>, which is consistent with the previous report that inserted ultrathin Al<sub>2</sub>O<sub>3</sub> layer can result in high IPCE values in the long wavelength [30].

Al is an active element. Al atoms in AgAl alloy can be easily oxidized into  $AlO_X$  during the thermal evaporation, due to the residual oxygen molecule in the vacuum chamber. Jiangjian Shi et al. [30] reported that insertion of an ultrathin  $Al_2O_3$  layer between the electrode and perovskite active layer helps to enhance IPCE of the cells over the long wavelength range, due to an increase in the built-in potential leading to an efficient electron extraction. Hence, the increase in the built-in potential due to the formation of  $AlO_X$  at the PCBM/AgAl interface also is expected, which is beneficial for electron extraction. However, the desired high built-in potential across the active region can be disturbed by the possible of diffusion of Ag at the PCBM/Ag interface, leading to the generation of the interfacial defect traps and thus causing



**Fig. 2.** The dark *J*–*V* curves of cells with different cathodes of Al, Ag and AgAl. The dotted curve labeled Al\* was plotted based on the results of the cell with Al electrode measured again after 30 min.

carrier recombination [31,32]. Therefore, the higher photocurrent and FF observed in the cells with AgAl cathode, compared to that of the cells having Ag cathode, are associated with the presence of an AlO<sub>X</sub> interlayer at the PCBM/cathode interface. The existence of the AlO<sub>X</sub> interlayer would prevent the diffusion of Ag atoms and also improve contact quality at the PCBM/AgAl interface, suppressing the formation of defect state in PCBM for efficient electron extraction. The dark *J–V* characteristic curves of cells with Al, Ag and AgAl electrodes are shown in Fig. 2. The cells with AgAl electrode shows obviously lower reversed saturation current and higher rectification ratio compared to cells of Ag electrode. The superior diode characteristics for AgAl electrode indicate that Ag atoms diffusion can be inhibited during thermal evaporation due to the formation of AlO<sub>X</sub>. The 0.3 V bias voltage of dark *J*-V curves is possibly attributed to the accumulation of space charges at interface due to mobile ions in perovskite solar cells [33]. No bias voltage was observed for cells with Al electrode. Compared to the original J-V curve, the dark J-V curve characteristic of cells with Al was quickly deteriorated after 30 min later. The cells with Al electrode are less stable resulting in an observable difference in J-V characteristics measured for cells with different contacts. However, the mechanism determining the bias voltage needs further investigation. The high density of interface charge due to trapping of charge carriers, inferior contact properties and ion migrations has been speculated to form the phenomenon of *I*-V hysteresis [33–36]. Liang et al. reported that the thinner PCBM layer compared to thicker PCBM layer in perovskite solar cells can result in significant hysteresis, which is attributed to higher density of interface charge [33]. The cyclically scanning J-V characteristics measured AM1.5G illumination as shown in Fig. 3, and that measured in the dark for different cells were analyzed. The cells with AgAl electrode had an obvious lower reverse saturation leaking current and higher rectification ratio compared to that of the cells made with an Ag contact. The more severe *I*–*V* hysteresis behavior was observed in the cells with Ag electrode compared to AgAl electrode. This suggests that the perovskite/AgAl interface is more favorable than perovskite/Ag as the contact for efficient electron collection in the cells, implying a decrease in the possible interfacial charge recombination that would otherwise occur in cells with Ag electrode. For cells based on Al electrode with 40 nm thick PCBM layer, the *I–V* curves show a little hysteresis and quickly produce apparent hysteresis after 30 min later, further indicating the unstable performance of cells with Al electrode (Fig. 3).

### 3.2. Stability of AgAl alloy, Ag and Al electrodes

Al films have good reflectivity and conductivity, which have been successfully used in organic solar cells (OSCs) and organic light-emitting diodes [37–39]. Perovskite solar cells with Al contact have been widely reported [40–42]. However, Al is not an ideal metal electrode in perovskite solar cells because Al can be easily corroded by iodine ions. The optical microscope images measured for different cathode surfaces of Al and AgAl in perovskite solar cells are shown in Fig. 4. Many corrosion holes can be observed in Al electrode. However, except for some dust points, there are no observable holes in the images taken for cells with AgAl electrode, suggesting that AgAl alloy electrode has an excellent corrosion resistance. Considering that Al electrodes are successfully applied in organic electronics, we suggest that the formed corrosion holes of Al electrode are related to  $CH_3NH_3PbI_3$  films.

CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/Al, PbI<sub>2</sub>/Al, CH<sub>3</sub>NH<sub>3</sub>I/Al and PCBM/Al dual layer samples were prepared to examine the possible interfacial interaction between aluminum and the underlying CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> material. The severe corrosion in Al layer due to the reaction between Al and CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> can be observed when an Al film deposited on the surfaces of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>, PbI<sub>2</sub> and CH<sub>3</sub>NH<sub>3</sub>I films, as shown in supplement Fig. S1. The I<sup>-</sup> ions are considered as one of main culprits to corrode Al film. This is because CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> films can be easily decomposed into HI under exposing moisture and high temperature [16,43], which can strongly corrode Al. A completing Al electrode could not even be formed onto the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/PCBM film when we shortened the evaporated distance to 15 cm from 25 cm, because CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> film received too much heat and could be decomposed more intensely. Furthermore, the cells with Ag electrode evaporated at distance of 15 cm are always shortcircuited and never attained efficient PCE because Ag atoms are easily diffused into the active layer when receiving too much heat [44]. However, cells with AgAl electrode evaporated at this



**Fig. 3.** The *J*–*V* characteristics, cyclically scanning five times from -0.3 V to 1.0 V using cyclic voltammetry, measured for (a) cells with 40 nm thick PCBM layer, and (b) cells with 20 nm thick PCBM layer. The inset in Fig. 3(a) is the *J*–*V* characteristic of the same cell measured again after waiting for 30 min.



Fig. 4. The optical microscope images measured for the surfaces of different cathodes Al (a) and AgAl (b) electrodes in the perovskite cells, with 200 times magnification. The inset image (a) is the corresponding image with 1000 times magnification.



Fig. 5. Normalization parameters of V<sub>OC</sub>, J<sub>SC</sub>, FF and PCE of the perovskite cells with different cathodes of Ag, AgAl and Al as with a function of the aging time. The cell parameters were averaged from 12 devices.

distance of 15 cm can easily obtain high PCE under different evaporated rate. Although AgAl alloy has a little lower boiling temperature compared to Ag, it is still concluded that Ag atom diffusion can be inhibited in AgAl alloy film due to the  $AlO_x$  formation during thermal evaporation. The successful cells with Al and Ag electrodes required larger distance between the heat source and the substrate to prevent the substrate from becoming high temperature. The addition of buffer layer such as Bphen, BCP and C<sub>60</sub> inserted before evaporated Al and Ag electrode is also beneficial to inhibiting Ag diffusion and protecting Al electrode [41,42]. Therefore, AgAl alloy as electrode increases the heat tolerance to fabricate perovskite solar cells, which is helpful to simplify cell process and reduce cost of devices.

## 3.3. Stable open-circuit voltage of perovskite solar cells with AgAl alloy electrode

Fig. 5 shows the decay performance of cells with aging time. Devices without encapsulation were stored in the drying cabinet with a relativized humidity of 10% under ambient atmosphere. Cells with AgAl electrode still retained 90% of the initial PCE values after aging 48 h, while PCEs of cells with Ag and Al cathode were dropped to 50% and 20% of the initial PCE values, respectively. The  $V_{\rm OC}$  of cells with AgAl electrode shows amazing stability and even has a little increase during aging 360 h. In the meantime, the  $V_{OC}$ of cells with Ag electrode was gradually decreased to 85% of the initial V<sub>OC</sub> values. The FF values of cells with Al and Ag electrodes were quickly decreased to 70% of the initial FF values and cells with AgAl electrode still retained more than 90% of initial FF values after aging 24 h. The degradation pathways of cells usually include chemical degradation of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> active materials, interfacial materials, electrodes and their interfaces. The  $J_{SC}$  and  $V_{OC}$  of cells with Ag and AgAl electrodes show relative stability within aging



**Fig. 6.** Schematic energy level diagrams of cells with PCBM/Ag and PCBM/AgAl.  $W_D$  represents the width of the depleted region in PCBM,  $\phi_B$  represents the interfacial energy barrier between the PCBM and electrode.

100 h, indicating that the PCBM/Ag (AgAl) interfaces are not apparently decayed. However, the FF values of cells with Ag and Al electrodes are quickly decreased after aging 24 h, which is possibly related to degradation of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> film due to the invasion of moisture.

The maximum achievable  $V_{OC}$  of organic solar cells is determined by the offset between the quasi-Fermi levels of the photoinduced hole ( $E_{F,h}$ ) in the donor and the photoinduced electrons ( $E_{F,e}$ ) in the acceptor. The  $V_{OC}$  is reduced when a Schottky contact is formed on the either side at the interface between the active layer and electrode. The  $V_{OC}$  varies linearly with the work function difference of the electrodes, which can be adjusted by the buffer



Fig. 7. The dark J-V characteristics measured for (a) as-fabricated devices and (b) the cells after 3 days continuous aging. Device structure: ITO/PCBM/electrode.



Fig. 8. SEM images measured for the different surfaces of Ag (a) and AgAl (b) electrodes of the cells.

layer and electrodes [45–47]. Besides the contact interfaces between electron/hole selective layers and active layer, the contact interfaces between electron/hole selective layers and electrodes can also influence the  $V_{OC}$  of organic solar cells [48]. Considering the same buffer layer of PEDOT:PSS and the electron transporting layer of PCBM, the  $V_{OC}$  variance of cells with aging time is primarily ascribed to the contact variance between PCBM/electrode. The work functions of Ag and AgAl measured with Test Instrument of Surface Work Function are 4.8 eV and 4.7 eV, respectively. The energy level structure diagrams of cells are shown in Fig. 6. The diffusion of Ag atoms during thermal evaporation and aging can deteriorate contact quality at the interface of PCBM/Ag [31,32]. The trap states of PCBM formed by diffused Ag atoms can increase recombination of carriers and decrease built-in potential, which results in the low FF value and photocurrent. The  $AlO_X$  at the interface of PCBM/AgAl can be formed during thermal evaporation and aging time. The formation of  $AlO_X$  acted as a diffusion barrier can inhibit the Ag atom diffusion and decrease contact barrier at the PCBM/AgAl interface. The low  $\Phi_{
m B}$  value can promote electron extraction from PCBM layer to AgAl electrode [49]. Therefore, the more dense  $AlO_X$  formation with aging time can achieve superior contact properties at the PCBM/AgAl interface, which helps to retain  $V_{\Omega C}$  stability.

To clearly demonstrate advantages of AgAl alloy electrode with aging time, electron-only devices with different metal cathodes were fabricated. The dark J-V curves of device with AgAl electrode is similar to that of device with Ag electrode at the initial stage, as shown in Fig. 7(a). However, only device with AgAl electrode can retain stable J-V characteristics after aging 3 days, as illustrated in Fig. 7(b). This indicates that AgAl alloy is a better metal electrode to keep stability of contact interface.

Observed from SEM images as shown in Fig. 8, the AgAl film on the cells showed a different crystalline morphology compared to Ag films on the cells, and the crystalline morphologies can be varied with different substrates due to the variance of physical constraint [7]. The Ag and AgAl films on silicon substrates shows the larger size crystalline grain and more apparent distinction from the two morphologies, as shown in supporting Fig. S2. Modified growth kinetics of Ag due to Al alloyed is confirmed. The formation of  $AlO_X$  at the surface plays a role of a passivation layer, which can suppress the migration of Ag atoms. The Al atom distribution is inhomogeneous across AgAl films and rich AlO<sub>x</sub> can be formed at the surface and at the interface of AgAl/PCBM [50]. AlO<sub>X</sub> at the interface behaves as an adhesion layer, which can act as a diffusion barrier. The enhanced adhesion of AgAl film compared to Ag on glass substrate by the test of adhesive tape (not shown) further demonstrates the existence of  $AlO_X$  at the interface. Niu et al. reported better stability of devices by inserting Al<sub>2</sub>O<sub>3</sub> layer between perovskite and hole transporting layers due to blocking moisture of  $Al_2O_3$  [16]. Therefore, formation of  $AlO_x$  in AgAl electrode is expected to improve the capability of blocking moisture.

This postulation is further demonstrated by the test of moisture invasion of samples with AgAl and Ag cathodes, respectively. The samples deposited with AgAl and Ag films were exposed to saturated water vapor pressure at room temperature, as shown in supporting Fig. S3. The CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> films of samples deposited with Ag electrode compared to AgAl electrode are more quickly varied from dark brown to yellow under the interaction of moisture, indicating that CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> film is in part decomposed into CH<sub>3</sub>NH<sub>3</sub>I and PbI<sub>2</sub> [16]. This suggests that AgAl films have superior capability of blocking moisture.

In addition, the stability of cells was further tested according to the International Summit on OSC Stability (ISOS) protocols [51,52],



Fig.9. Normalization parameters of V<sub>OC</sub>, J<sub>SC</sub>, FF and PCE of cells with different cathodes of Ag, AgAl and Al as a function of the aging time, measured under the ISOS-L-3 aging condition.



**Fig. 10.** Normalization parameters of V<sub>OC</sub>, J<sub>SC</sub>, FF and PCE of cells with different cathodes of Ag, AgAl and Al as with a function of the aging time, measured under the ISOS-D-3-like aging condition.

specially employing the ISOS-D-3 and ISOS-L-3, for the purpose of establishing the comparable and standard perovskite solar cells stability test processes. The aging condition of ISOS-D-3 is 85% relative humidity and 65 °C in the dark. Referring to the article [46], here cells were tested using aging conditions closing to ISOS-D-3 with somewhat lower temperature of 50 °C. The ISOS-L-3 is 50% relative humidity and 65 °C under the 0.7 sun illumination. With the special accelerated aging tests, the aging curves were shown in Figs. 9 and 10 responding to ISOS-L-3 and quasi ISOS-D-3. Similarity, cells with AgAl electrode showed better stability of  $V_{OC}$  and slower decay of PCE compared to cells with Ag under both aging conditions. Therefore, the evolutionary trends of cells for AgAl and Ag electrodes under ISOS-L-3 and quasi ISOS-D-3 aging tests are roughly consistent with the trend of cells aged with relativize humidity of 10% under ambient atmosphere. The  $J_{sc}$ and  $V_{\rm oc}$  under on-off illumination cycles for cells with Ag and AgAl electrodes are shown in supporting Fig. S4. Obviously, the  $V_{\rm oc}$  of cells with AgAl shows better stability than that of cells with Ag electrode. These aging results suggest that perovskite solar cells with AgAl alloy electrode always show superior stability, especially for open-circuit voltage.

### 4. Conclusions

In summary, the performance of perovskite solar cells with different cathode contacts of AgAl alloy, Ag and Al electrodes were analyzed. The cells with AgAl electrode show slightly higher PCE value and much improved stability compared to that of the cells having Ag and Al electrodes. The  $V_{OC}$  of cells with AgAl electrode shows amazing stability and even has a little increase after 360 h aging in air. The AlO<sub>X</sub> formed during thermal evaporation can inhibit Ag atom diffusion and increase built-in potential across the active region in the cell, improving the electron extraction at the PCBM/AgAl interface. Formation of AlO<sub>X</sub> interlayer also passivates AgAl films and makes AgAl film compaction which inhibits moisture intrusion and improves cell stability. The use of the AgAl alloy cathode, compared to Ag electrode, can greatly improve heat tolerance during cell fabrication, providing a wider process window for fabricating high performance perovskite cells.

### Acknowledgments

This work was supported by National Natural Science Foundation of China (Grant nos. 61275038, 61275037 and 11274119) and Hong Kong Baptist University Strategic Development Fund (SDF13-0531-A02).

### Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.solmat.2015.11. 026.

### References

- A. Kojima, K. Teshima, Y. Shirai, T. Miyasaka, Organometal halide perovskites as visible-light sensitizers for photovoltaic cells, J. Am. Chem. Soc. 131 (2009) 6050–6051.
- [2] W.S. Yang, J.H. Noh, N.J. Jeon, Y.C. Kim, S. Ryu, J. Seo, S.I. Seok, Highperformance photovoltaic perovskite layers fabricated through intramolecular exchange, Science 348 (2015) 1234–1237.

- [3] J.Y. Jeng, Y.F. Chiang, M.H. Lee, S.R. Peng, T.F. Guo, P. Chen, T.C. Wen, CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> perovskite/fullerene planar-heterojunction hybrid solar cells, Adv. Mater. 25 (2013) 3727–3732.
- [4] Q. Chen, H. Zhou, Z. Hong, S. Luo, H.-S. Duan, H.-H. Wang, Y. Liu, G. Li, Y. Yang, Planar heterojunction perovskite solar cells via vapor-assisted solution process, J. Am. Chem. Soc. 136 (2013) 622–625.
- [5] M. Liu, M.B. Johnston, H.J. Snaith, Efficient planar heterojunction perovskite solar cells by vapour deposition, Nature 501 (2013) 395–398.
- [6] C.W. Chen, H.W. Kang, S.Y. Hsiao, P.F. Yang, K.M. Chiang, H.W. Lin, Efficient and uniform planar-type perovskite solar cells by simple sequential vacuum deposition, Adv. Mater. 26 (2014) 6647–6652.
- [7] T. Salim, S. Sun, Y. Abe, A. Krishna, A.C. Grimsdale, Y.M. Lam, Perovskite-based solar cells: impact of morphology and device architecture on device performance, J. Mater. Chem. A 3 (2015) 8943–8969.
- [8] N.J. Jeon, J.H. Noh, Y.C. Kim, W.S. Yang, S. Ryu, S.I. Seok, Solvent engineering for high-performance inorganic–organic hybrid perovskite solar cells, Nat. Mater. 13 (2014) 897–903.
- [9] H.-B. Kim, H. Choi, J. Jeong, S. Kim, B. Walker, S. Song, J.Y. Kim, Mixed solvents for the optimization of morphology in solution-processed, inverted-type perovskite/fullerene hybrid solar cells, Nanoscale 6 (2014) 6679–6683.
- [10] Y. Wu, A. Islam, X. Yang, C. Qin, J. Liu, K. Zhang, W. Peng, L. Han, Retarding the crystallization of Pbl<sub>2</sub> for highly reproducible planar-structured perovskite solar cells via sequential deposition, Energy Environ. Sci. 7 (2014) 2934–2938.
- [11] F. Huang, Y. Dkhissi, W. Huang, M. Xiao, I. Benesperi, S. Rubanov, Y. Zhu, X. Lin, L. Jiang, Y. Zhou, Gas-assisted preparation of lead iodide perovskite films consisting of a monolayer of single crystalline grains for high efficiency planar solar cells, Nano Energy 10 (2014) 10–18.
- [12] G.E. Eperon, S.D. Stranks, C. Menelaou, M.B. Johnston, L.M. Herz, H.J. Snaith, Formamidinium lead trihalide: a broadly tunable perovskite for efficient planar heterojunction solar cells, Energy Environ. Sci. 7 (2014) 982–988.
- [13] J. Ball, M. Lee, A. Hey, H. Snaith, Low-temperature processed mesosuperstructured to thin-film perovskite solar cells, Energy Environ. Sci. 509 (2013) 4146–4149.
- [14] P.W. Liang, C.Y. Liao, C.C. Chueh, F. Zuo, S.T. Williams, X.K. Xin, J. Lin, A.K.Y. Jen, Additive enhanced crystallization of solution-processed perovskite for highly efficient planar-heterojunction solar cells, Adv. Mater. 26 (2014) 3748–3754.
- [15] C. Zuo, L. Ding, An 80.11% FF record achieved for perovskite solar cells by using the NH<sub>4</sub>Cl additive, Nanoscale 6 (2014) 9935–9938.
- [16] G. Niu, W. Li, F. Meng, L. Wang, H. Dong, Y. Qiu, Study on the stability of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> films and the effect of post-modification by aluminum oxide in all-solid-state hybrid solar cells, J. Mater. Chem. A 2 (2014) 705–710.
- [17] S.N. Habisreutinger, T. Leijtens, G.E. Eperon, S.D. Stranks, R.J. Nicholas, H.J. Snaith, Carbon nanotube/polymer composites as a highly stable hole collection layer in perovskite solar cells, Nano Lett. 14 (2014) 5561–5568.
- [18] N.J. Jeon, J.H. Noh, W.S. Yang, Y.C. Kim, S. Ryu, J. Seo, S.I. Seok, Compositional engineering of perovskite materials for high-performance solar cells, Nature 517 (2015) 476–480.
- [19] Y.S. Kwon, J. Lim, H.-J. Yun, Y.-H. Kim, T. Park, A diketopyrrolopyrrolecontaining hole transporting conjugated polymer for use in efficient stable organic–inorganic hybrid solar cells based on a perovskite, Energy Environ. Sci. 7 (2014) 1454–1460.
- [20] L. Zheng, Y.-H. Chung, Y. Ma, L. Zhang, L. Xiao, Z. Chen, S. Wang, B. Qu, Q. Gong, A hydrophobic hole transporting oligothiophene for planar perovskite solar cells with improved stability, Chem. Commun. 50 (2014) 11196–11199.
- [21] S.-I. Na, G. Wang, S.-S. Kim, T.-W. Kim, S.-H. Oh, B.-K. Yu, T. Lee, D.-Y. Kim, Evolution of nanomorphology and anisotropic conductivity in solventmodified PEDOT:PSS films for polymeric anodes of polymer solar cells, J. Mater. Chem. 19 (2009) 9045–9053.
- [22] A. Sacco, F. Bella, S. De La Pierre, M. Castellino, S. Bianco, R. Bongiovanni, C. F. Pirri, Electrodes/electrolyte interfaces in the presence of a surface-modified photopolymer electrolyte: application in dye-sensitized solar cells, Chem-PhysChem 16 (2015) 960–969.
- [23] F. Bella, G. Griffini, M. Gerosa, S. Turri, R. Bongiovanni, Performance and stability improvements for dye-sensitized solar cells in the presence of luminescent coatings, J. Power Sources 283 (2015) 195–203.
- [24] Z. Wei, X. Zheng, H. Chen, X. Long, Z. Wang, S. Yang, A multifunctional C+epoxy/Ag-paint cathode enables efficient and stable operation of perovskite solar cells in watery environments, J. Mater. Chem. A 3 (2015) 16430–16434.
- [25] J. Gao, C. Tu, L. Liang, H. Zhang, F. Zhuge, L. Wu, H. Cao, K. Yu, Silver nanoparticles with an armor layer embedded in the alumina matrix to form nanocermet thin films with sound thermal stability, ACS Appl. Mater. Interfaces 6 (2014) 11550–11557.
- [26] J.-Y. Kim, S.-I. Na, G.-Y. Ha, M.-K. Kwon, I.-K. Park, J.-H. Lim, S.-J. Park, M.-H. Kim, D. Choi, K. Min, Thermally stable and highly reflective AgAl alloy for enhancing light extraction efficiency in GaN light-emitting diodes, Appl. Phys. Lett. 88 (2006) 043507.
- [27] J. Schmidt, A. Merkle, R. Brendel, B. Hoex, M. Van de Sanden, W. Kessels, Surface passivation of high-efficiency silicon solar cells by atomic-layerdeposited Al<sub>2</sub>O<sub>3</sub>, Prog. Photovolt.: Res. Appl. 16 (2008) 461–466.
- [28] F. Fabregat-Santiago, J. García-Cañadas, E. Palomares, J.N. Clifford, S.A. Haque, J. R. Durrant, G. Garcia-Belmonte, J. Bisquert, The origin of slow electron recombination processes in dye-sensitized solar cells with alumina barrier coatings, J. Appl. Phys. 96 (2004) 6903–6907.

- [29] E. Palomares, J.N. Clifford, S.A. Haque, T. Lutz, J.R. Durrant, Slow charge recombination in dye-sensitised solar cells (DSSC) using Al<sub>2</sub>O<sub>3</sub> coated nanoporous TiO<sub>2</sub> films, Chem. Commun. (14) (2002) 1464–1465.
- [30] S. Jiang-Jian, D. Wan, X. Yu-Zhuan, L. Chun-Hui, L. Song-Tao, Z. Li-Feng, D. Juan, L. Yan-Hong, L. Dong-Mei, M. Qing-Bo, Enhanced performance in perovskite organic lead iodide heterojunction solar cells with metal-insulator-semiconductor back contact, Chin. Phys. Lett. 30 (2013) 128402.
- [31] N. Wang, J. Yu, Y. Zang, J. Huang, Y. Jiang, Effect of buffer layers on the performance of organic photovoltaic cells based on copper phthalocyanine and C<sub>60</sub>, Sol. Energy Mater. Sol. Cells 94 (2010) 263–266.
- [32] S.R. Forrest, The limits to organic photovoltaic cell efficiency, MRS Bull. 30 (2005) 28–32.
- [33] H. Zhang, C. Liang, Y. Zhao, M. Sun, H. Liu, J. Liang, D. Li, F. Zhang, Z. He, Dynamic interface charge governing the current-voltage hysteresis in perovskite solar cells, Phys. Chem. Chem. Phys. 17 (2015) 9613–9618.
- [34] H.J. Snaith, A. Abate, J.M. Ball, G.E. Eperon, T. Leijtens, N.K. Noel, S.D. Stranks, J. T.-W. Wang, K. Wojciechowski, W. Zhang, Anomalous hysteresis in perovskite solar cells, J. Phys. Chem. Lett. 5 (2014) 1511–1515.
- [35] Y. Zhao, C. Liang, H. Zhang, D. Li, D. Tian, G. Li, X. Jing, W. Zhang, W. Xiao, Q. Liu, Anomalously large interface charge in polarity-switchable photovoltaic devices: an indication of mobile ions in organic-inorganic halide perovskites, Energy Environ. Sci. 8 (2015) 1256–1260.
- [36] Y. Shao, Z. Xiao, C. Bi, Y. Yuan, J. Huang, Origin and elimination of photocurrent hysteresis by fullerene passivation in CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> planar heterojunction solar cells, Nat. Commun. 5 (2014) 5784.
- [37] H. Spanggaard, F.C. Krebs, A brief history of the development of organic and polymeric photovoltaics, Sol. Energy Mater. Sol. Cells 83 (2004) 125–146.
- [38] D. Chirvase, J. Parisi, J.C. Hummelen, V. Dyakonov, Influence of nanomorphology on the photovoltaic action of polymer–fullerene composites, Nanotechnology 15 (2004) 1317.
- [39] W. Ma, C. Yang, X. Gong, K. Lee, A.J. Heeger, Thermally stable, efficient polymer solar cells with nanoscale control of the interpenetrating network morphology, Adv. Funct. Mater. 15 (2005) 1617–1622.
- [40] J. You, Z. Hong, Y.M. Yang, Q. Chen, M. Cai, T.-B. Song, C.-C. Chen, S. Lu, Y. Liu, H. Zhou, Low-temperature solution-processed perovskite solar cells with high efficiency and flexibility, ACS Nano 8 (2014) 1674–1680.
- [41] K.-C. Wang, J.-Y. Jeng, P.-S. Shen, Y.-C. Chang, E.W.-G. Diau, C.-H. Tsai, T.-Y. Chao, H.-C. Hsu, P.-Y. Lin, P. Chen, p-type mesoscopic nickel oxide/organometallic perovskite heterojunction solar cells, Sci. Rep. 4 (2014).

- [42] X. Liu, H. Yu, L. Yan, Q. Dong, Q. Wan, Y. Zhou, B. Song, Y. Li, Triple cathode buffer layers composed of PCBM, C<sub>60</sub>, and LiF for high-performance planar perovskite solar cells, ACS Appl. Mater. Interfaces 7 (2015) 6230–6237.
- [43] C.C. Stoumpos, C.D. Malliakas, M.G. Kanatzidis, Semiconducting tin and lead iodide perovskites with organic cations: phase transitions, high mobilities, and near-infrared photoluminescent properties, Inorg. Chem. 52 (2013) 9019–9038.
- [44] W. Julia, Impact of contact evolution on the shelf life of organic solar cells, J. Mater. Chem. 19 (2009) 7638–7642.
- [45] M.C. Scharber, D. Mühlbacher, M. Koppe, P. Denk, C. Waldauf, A.J. Heeger, C.J. Brabec, Design rules for donors in bulk-heterojunction solar cells—towards 10% energy-conversion efficiency, Adv. Mater. 18 (2006) 789–794.
- [46] C.J. Brabec, A. Cravino, D. Meissner, N.S. Sariciftci, T. Fromherz, M.T. Rispens, L. Sanchez, J.C. Hummelen, Origin of the open circuit voltage of plastic solar cells, Adv. Funct. Mater. 11 (2001) 374–380.
- [47] K. Vandewal, K. Tvingstedt, A. Gadisa, O. Inganäs, J.V. Manca, On the origin of the open-circuit voltage of polymer-fullerene solar cells, Nat. Mater. 8 (2009) 904–909.
- [48] G. Yu, J. Gao, J.C. Hummelen, F. Wudl, A.J. Heeger, Polymer photovoltaic cells: enhanced efficiencies via a network of internal donor–acceptor heterojunctions, Science 270 (1995) 1789–1790 AAAS-Weekly Paper Edition.
- [49] S. Narioka, H. Ishii, D. Yoshimura, M. Sei, Y. Ouchi, K. Seki, S. Hasegawa, T. Miyazaki, Y. Harima, K. Yamashita, The electronic structure and energy level alignment of porphyrin/metal interfaces studied by ultraviolet photoelectron spectroscopy, Appl. Phys. Lett. 67 (1995) 1899–1901.
- [50] K. Sugawara, M. Kawamura, Y. Abe, K. Sasaki, Comparison of the agglomeration behavior of Ag (Al) films and Ag (Au) films, Microelectron. Eng. 84 (2007) 2476–2480.
- [51] M.O. Reese, S.A. Gevorgyan, M. Jørgensen, E. Bundgaard, S.R. Kurtz, D.S. Ginley, D.C. Olson, M.T. Lloyd, P. Morvillo, E.A. Katz, Consensus stability testing protocols for organic photovoltaic materials and devices, Sol. Energy Mater. Sol. Cells 95 (2011) 1253–1267.
- [52] D. Angmo, S.A. Gevorgyan, T.T. Larsen-Olsen, R.R. Søndergaard, M. Hösel, M. Jørgensen, R. Gupta, G.U. Kulkarni, F.C. Krebs, Scalability and stability of very thin, roll-to-roll processed, large area, indium-tin-oxide free polymer solar cell modules, Org. Electron. 14 (2013) 984–994.