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Improved longtime stability of highly efficient polymer solar cells by accurately self-formed metal oxide interlayer at metal electrode

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ABSTRACT

Al as a cheap and air-stable metal material has been widely applied to polymer solar cells (PSCs) as an efficient electrode. However, there are few care whether Al is a right electrode in PSCs for longtime stability. The inverted PSCs with the structure of ITO/ZnO/PTB7-Th:$PC_{71}BM$/MoO_3/Metal electrode were fabricated and the performance and stability of inverted PSCs with Al and AgAl electrodes were investigated. PSCs with AgAl electrode got the highest PCE value of 9.3% without aging. While the PCE of PSCs with Al electrode can be gradually improved and reach the highest value of 7.8% after aging for 36 h, which is attributed to the formation of AlO_x interlayer at the interface of MoO_3/Al. PSCs with AgAl electrode still retained 69% of the initial PCE value and got 6.6% of PCE aging for 796 days, showing amazing stability. However, PSCs with Al electrode was dropped to 3.7% of PCE aging for 796 days due to the continuously increased thickness of AlO_x interlayer, which can greatly increase the series resistance of cells. PSCs with AgAl electrode can be further improved and reach 10.2% of PCE using AZO (Al doped ZnO) instead of ZnO and show better UV-light resistance. The enhanced stability of PSCs with AgAl electrode is attributed to the dense and limited thick AlO_x interlayer self-formed at the MoO_3/AgAl interface due to the low content of Al. Our results demonstrated that Ag alloy electrode such as AgAl is a good strategy to accurately control the thickness of the metal oxidation interlayer, which can overcome the disadvantage of Al electrode and greatly improve the longtime stability of devices.

1. Introduction

Polymer solar cells (PSCs) has experienced a progressive development in recent ten years, the power conversion efficiency (PCE) of single junction PSCs has increased over 10% (Jia et al., 2016; Liu et al., 2015; Zhao et al., 2016, 2017). The great progress in low band gap polymer with deep highest occupied molecular orbital (HOMO) energy level contributes to improve open circuit voltage (V_{OC}) and the short circuit photocurrent (J_{SC}) of PSCs (An et al., 2013; Liao et al., 2013). Other efficient approaches, such as optimizing the film nanoscale morphology (Huang et al., 2016; Lim et al., 2017; Thambidurai et al., 2014), inserting functional modification layer (Chen et al., 2008; Wang et al., 2016) or introducing solvent additives (Kyaw et al., 2014) or co-solvent (Zhang et al., 2017), were also employed to improve the excitons dissociation (Zhang et al., 2016), reduce charge recombination (Li et al., 2014) or increase the light absorption (Shi et al., 2017; Yu et al., 2014). Additionally, instead of the regular configuration, PSCs with an inverted structure are usually preferred for efficient operation and better air stability by avoiding using of the low-work-function metal cathode and the corrosive and hygroscopic poly(3,4-ethylenedioxylenethiophene):poly(styrenesulphonic acid) (PEDOT:PSS) as a hole transport layer, both of which are detrimental to device stability (He et al., 2012; Liu et al., 2013). Alternatively, transition metal oxides (TMOs) such as MoO_3 (Cheng et al., 2015), NiO_x (Cheng et al., 2017; Jiang et al., 2015) have widely been used as a hole-transport layer (HTL) to improve the efficiency and stability of PSCs due to its tunable work-function and air stability. Therefore, the less air-sensitive high work function metal anode and metal oxides as carrier transport layer used in the inverted PSCs could apparently inhibit electrode oxidation and prolong cell lifetime (Kyaw et al., 2008; Sun et al., 2011). However, the PCE and stability need further be improved for the viable commercialization of PSCs.

For inverted cells, while a high work function metal is used for the top anode, anode interlayer materials with high work functions are needed to form good Ohmic contacts for enlarging the built-in potential of devices, which is beneficial to reduce the series resistance and increase the carrier extraction (Chen et al., 2012). It is also known that V_{OC} is related to the built-in potential (Luo et al., 2009; Tao et al.,

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2008), and work function of the positive contact (Brabec, 2004). The previous reports indicated that the oxidation of silver electrode can increase the built-in field at the interface of metal electrode and help to improve hole transport and collection abilities, which can enhance V_{OC} and PCE of cells (Kim et al., 2009). The existence of metal oxide favoring the charge transport was also verified in OELD (Zhang and Wallace, 2008). Furthermore, Berredjem and Morsli et al. demonstrated that the presence of a thin Al_2O_3 layer at the C60/Al interface can greatly increase the shunt resistance and thus improve the open-circuit voltage (Berredjem et al., 2008; Morsli et al., 2008). The AlO_x formation at the interface between photoactive layer and Al electrode is effective to improve PCE of cells due to the enhanced built-in potential (Kim et al., 2012; Zhang et al., 2009). However, the series resistance of cells can be obviously increased for too thick metal oxidation layer, which result in the quick deterioration of cells due to its insulation property (Shi et al., 2013; Singh et al., 2006). Although Al as an efficient electrode for PSCs has been widely applied, there are few care whether Al is a right electrode in PSCs for longtime stability.

In this paper, we compared the performance and air stability of PSCs with Al and AgAl electrodes. PSCs with Al electrode can be limited for longtime application because the thickness of AlO_x self-formed at the MoO_3/Al interface can be continuously increased with aging time. The accurately formed thickness of AlO_x interlayer is important to realize the longtime stability of PSCs and AgAl electrode instead of Al can meet this function. However, the formation of AlO_x process for AgAl electrode can also greatly affect the stability of PSCs. In the meantime, using AZO instead of ZnO as an electron transport layer (ETL) can reach 10.2% of PCE for PSCs.

2. Experimental details

PSCs, with an inverted structure of ITO/ETL/PTB7-Th:$PC_{71}BM$/MoO_3/Anode, were fabricated. The pre-patterned indium tin oxide (ITO)/Glass substrates (10 Ω/□) were cleaned sequentially with detergent, de-ionized water, acetone and isopropyl alcohol in an ultrasonic bath for 20 min each, and then blow-dried by pure nitrogen gas. After being heat dried in an oven, ITO/Glass substrates were treated with ultraviolet ozone for 15 min. The sol-gel ZnO nanoparticles were synthesized following the procedures described in the previous publications (Lu et al., 2015; Shao et al., 2013). The typical synthesis, a stoichiometric amount of tetramethyl-ammonium hydroxide dissolved in ethanol (0.5 M) was gradually dropped into 0.1 M zinc acetate dihydrate dissolved in dimethyl sulfoxide (DMSO), followed by stirring for an hour at room temperature. After being washed with hexane and ethanol (2:1) mixing solvents, ZnO nanoparticles were dispersed in ethanol. The AZO nanoparticles were synthesized with a modified method according to the published literatures (Alam and Cameron, 2001; Stubhan et al., 2013). In details, Zinc acetate ($Zn(CH_3CO_2)_2{\cdot}2H_2O$ and aluminum nitrate ($Al(NO_3)_3{\cdot}9H_2O$ were mixed together and dissolved in ethanol. The solution was stirred at 80 °C for 3 h to get a clear solution. The fabrication progress of AZO thin film is the same as that of ZnO layer. Then sol-gel ZnO solutions were spin coated at 4000 rpm for 50 s onto ITO to form 20 nm films, followed by annealing at 150 °C for 30 min in air. PTB7-Th (99%) was purchased from 1-Material INC. and $PC_{71}BM$ (99.5%) was purchased from Solenne BV. An 80 nm thick active layer was deposited on ZnO surface using a blend solution containing PTB7-Th:$PC_{71}BM$ (7 mg/mL:10.5 mg/mL) dissolved in chlorobenzene/1,8-diiodooctane (97:3, v/v) at 1000 rpm for 15 s in argon-filled glove box. A 7 nm thick MoO_3 interlayer and a 100 nm thick Al or AgAl film were then deposited by thermal evaporation at the rate of 0.3 Å/s and 5 or 10 Å/s respectively on the PTB7-Th:$PC_{71}BM$ active layer with base pressure of 3×10^{-4} Pa. A mask with an aperture area of 0.09 cm^2 was used for the current density-voltage (*J-V*) characteristic measurement to avoid the edge effect. The PSCs without encapsulation were stored in a 10% RH chamber in air.

The *J-V* characteristics of PSCs were measured by a Keithley 2440 Sourcemeter together with a Newport solar simulator with an AM1.5G illumination of 100 mW/cm^2 calibrated with a standard silicon reference cell. The incident photon to current conversion efficiency (IPCE) of PSCs was measured over the wavelength range from 300 nm to 800 nm using a Newport Optical Power Meter 2936-R and was recorded using TracQ Basic software. The dark *J-V* characteristics of the cells were measured using an electrochemical workstation (AUTOLAB PGSTAT302N). The absorption spectra of cells with Al electrode were measured using a UV/Vis spectrophotometer (Hitachi U-3900). X-ray photoelectron spectroscopy (XPS) measurements were carried out using an Imageing Photoelectron Spectrometer (Axis Ultra, Kratos Analytical Ltd.) with a monochromatic Al Ka X-ray source. The UV-light illumination was conducted over the wavelength of 365 nm under two 18 W U-type lamp tubes.

3. Results and discussion

3.1. Performance of Al-based inverted PSCs

To investigate the performance variance of Al electrode based PSCs during the aging process, we fabricated a set of inverted PSCs with the structure of ITO/ZnO/PTB7-Th:$PC_{71}BM$/MoO_3/Al. Fig. 1a shows the *J-V* characteristics of Al based cells with different aging time. The average parameters and the standard deviations counting eight devices aging for different time are summarized in Table 1. The V_{OC} and FF of the original PSCs were only 0.695 V and 42.1% respectively, which results in the low PCE of 4.8%. The performance of PSCs were obviously increased aging for 16 h in RH 10% at ambient atmosphere condition and got 0.774 V of V_{OC}, 59.5% of FF and 7.3% of PCE respectively. The highest PCE of PSCs was obtained after aging for 36 h, and V_{OC} and FF values of cells were further increased to 0.784 V and 63.0% respectively, which got the highest PCE of 7.8%. The gradually increased V_{OC} and FF of PSCs are attributed to the gradual formation of AlO_x at the interface of Al/MoO_3 due to the oxygen invasion (Berredjem et al., 2008; Morsli et al., 2008), which helps to reduce the contact potential and carrier recombination. The obviously reduced reversed dark current and R_S, and the increased R_{SH} of cells after aging for 16 h and 36 h compared to the original cells further support this conclusion (Kim et al., 2005; Luo et al., 2009), as shown in Fig. 1b and Table 1.

However, as shown in Fig. 1d, the gradually self-formed AlO_x interlayer at the Al/MoO_3 interface can reduce the reflectivity of Al electrode, which would decrease the absorption of the photoactive layer because of the limited thickness of the photoactive layer. The slightly reduced photocurrent and IPCE values of cells aging for 16 h and 36 h compared to the original cells is consistent with this trend, as shown in Fig. 1c and Table 1. Fortunately, the enhanced V_{OC} and FF can easily offset the reduced photocurrent, indicating that the optimal thickness of AlO_x at the interface of Al/MoO_3 can be gradually formed after cells are exposed to air with the right time, which can get superior performance of PSCs. However, the AlO_x thickness can easily further increase with increasing time of cells exposed to air because accurately controlling thickness of AlO_x film at the Al film surface is impossible due to the easy oxidization of Al metal. The too thick AlO_x film can greatly increase the series resistance of cells due to the insulation property of AlO_x, which would accelerate the deterioration of Al electrode based PSCs. Therefore, the optimal and easily controlling AlO_x interlayer at the Al/MoO_3 interface is important to improve the PCE and stability of PSCs.

3.2. Effect of AgAl alloy electrode on the performance of PSCs

To suppress the continuous growth of AlO_x interlayer at the Al electrode surface, the AgAl alloy (3 wt% Al) was introduced as metal electrode of PSCs (Jia et al., 2016; Jiang et al., 2016). Fig. 2 shows the X-ray photoelectron spectroscopy (XPS) spectra of AgAl alloy film. The main element characteristic peaks of Ag 3d5/2, 3d3/2 and O1s are