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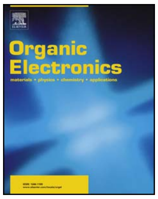

Inorganic perovskite light emitting diodes with ZnO as the electron transport layer by direct atomic layer deposition

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ABSTRACT

Inorganic n-type metal oxide materials, i.e., ZnO have been developed and employed as interface layers for energy level matching and electron transport in order to achieve high performance perovskites based optoelectronic devices. In this work, we successfully apply atomic layer deposition (ALD) technique to deposit ZnO directly on top of $CsPbBr_3$ to serve as the electron transport layer. A regular perovskite light emitting diode (PeLED) in a configuration of glass/ITO/PEDOT:PSS/$CsPbBr_3$/ZnO/Ag was fabricated. In the $CsPbBr_3$ emitting layer, polyethyleneimine ethoxylated (PEIE) dissolved in an anti-solvent chlorobenzene (CB) was introduced to assist the nucleation and crystal growth of perovskite films, as well as providing surface reactive sites for ALD deposition of ZnO layer particularly. The ALD deposition temperature on the growth, crystallinity and morphology of ZnO and subsequent device performance was investigated. We obtained PeLEDs of the best performance with the best current and external quantum efficiency (EQE) of 0.49 cd/A and 0.14%, respectively, which is as 14 folds high as an inorganic $CsPbBr_3$ device using F8 as the electron transport layer reported previously.

1. Introduction

Perovskites materials exhibit high photoluminescence quantum yield (PLQY), wavelength tunable emission, high color purity and ambipolar charge transport characteristic, thus are promising materials for light-emitting diodes (LEDs) [1–4]. Amongst of perovskites, inorganic perovskites have drawn tremendous attention due to their high thermal stability and excellent optoelectronic properties compared with organic-cation perovskites, such as higher PLQE, smaller exciton binding energy (35 meV), and larger electron mobility (1000 cm^2/V.s) [5]. Up to now, great progress has been achieved in solution processable inorganic perovskite light emitting diodes (PeLEDs) [5–11]. Ling et al. and Li et al. reported green emitting $CsPbBr_3$-based PeLEDs with the EQEs of 4.3% and 6.8% respectively by introducing organic additives PEO [11] and PEO-PVP [10] into the emitting layer. In addition to employing the organic additive PEO, Wu et al. fabricated an all inorganic PeLED device through post-treatment of the $CsPbBr_3$ layer with an anti-solvent of chloroform, which displayed a brightness of 51890 cd/m^2 and an EQE of 4.76% [9].

The selection of charge transport layers for energy level matching and charge transport is critical in constructing high performance perovskites based optoelectronic devices. In inorganic PeLEDs, both organic and inorganic materials were used as the transport layers. For example, PEDOT:PSS was widely used as the hole transport layer [5,7–9]; while organic materials, such as B3PYMPM [8], TPBi [6,9], F8 [5] and inorganic metal oxides, i.e. ZnO, were employed as the electron transport layers [12].

ZnO has been used as the n-type transport layers in not only inorganic PeLEDs [12], but also in organic-inorganic hybrid PeLEDs in an inverted device architecture, where a radio-frequency (RF) magnetron sputtered dense ZnO thin film served as the electron transport layer [13]. Credgington et al. produced the first PeLED using ZnO instead of organic electron transport layer [14] through directly depositing ZnO film onto green-emitting methylammonium lead tribromide ($CH_3NH_3PbBr_3$) perovskites using atomic layer deposition (ALD) technique. Compared with organic n-type transport layers, the application of ZnO as electron transport layer brings quite a few advantages, such as, tunable electron injection level via doping, high electron mobility, good hole blocking effect, and enhanced device stability, etc. [14,15].

By far, various methods for the fabrication of metal oxide transport layers have been investigated, i.e. solution processing [16–18], spray pyrolysis [19], RF sputtering [13] and ALD [14,15,20,21]. Amongst of them, ALD technique presents outstanding capabilities, such as accurate and precise thickness control at atomic level, low deposition

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temperature, excellent film conformality, uniformity and reproducibility over large area surfaces [15,22], which meets the requirements of preparing uniform and pin-hole free metal oxide layers at low process temperature for perovskites based devices [15]. Low-temperature processed (≤100 °C) ALD ZnO films have been used as functional layers in perovskite solar cells, with the device performance superior to those using solution processed ZnO nanoparticles films [15].

Despite the advantages of ALD technique, only a few studies have been devoted to incorporating ALD processed films into PeLEDs so far, only Credgington et al. produced green PeLEDs by a direct deposition of ALD ZnO onto $CH_3NH_3PbBr_3$ perovskite [14]. The challenges of directly depositing metal oxides onto perovskites lie in: 1) thermal instability of perovskite at higher temperatures; 2) instability of perovskite under humid condition [23,24]. Thus, novel non-hydrolytic surface chemistry has to be developed to synthesize metal oxide layers directly on perovskites without damage [25].

In this work, for the first time, we introduced ALD deposited ZnO electron transport layer directly onto inorganic perovskites and fabricated green emitting PeLEDs in a device configuration of ITO/PEDOT:PSS/Perovskite/ZnO/Ag Polyethyleneimine ethoxylated (PEIE) was introduced into chlorobenzene (CB) solvent to assist the nucleation and crystal growth of perovskites films, thus to govern the film morphology and obtain perovskite films of high optoelectronic quality [26–28]. The hydroxyl, amino, and imino groups in PEIE served as physical adsorption or chemical reaction sites for ZnO precursor-diethylzinc (DEZ) [29], to achieve a better ALD deposition quality. The extremely high reactivity of DEZ absorbed or chemically linked on PEIE will immediately react with water vapour in the later ALD deposition cycles, which also functioned as a protection layer to prevent the water vapour from attacking the perovskite film. A reduced work function of ZnO was induced due to the modification of PEIE [30]. In addition, variable temperature for the ALD deposition process was tuned and optimized, which determines the carrier concentration and mobility of ZnO [29].

2. Experimental section

2.1. Materials

Patterned ITO-coated glass substrates with a sheet resistance of 15 ohm sq^{-1} were purchased from Shenzhen Hua Yu Joint Technology Co. Ltd. PEDOT:PSS aqueous solution (Heraeus-Clevios P VP AI 4083) was purchased from Xi'an Polymer Light Technology Co. Cesium bromide (CsBr, 99.999%) was purchased from Aldrich. Lead bromide ($PbBr_2$, 99.999%) was purchased from Alfa Aesar. All of the reagents were used without further purification. DEZ was purchased from MNT® Micro and Nanotech Co. Ltd.

2.2. Atomic layer deposition of ZnO

Compact ZnO layer was prepared by ALD which was carried out by Atomic Layer Deposition System (MNT Micro 100) using typical procedures [29]. The precursors used in ALD ZnO were $ZnEt_2$ and H_2O. The deposition temperature was kept at 60 °C, 65 °C, 70 °C and 75 °C, respectively. The process pressure was 0.4 Torr with high-purity N_2 (flow rate 20 sccm) as the carrier and purging gas. When the purge, pump line and heater reached the set temperature, the equipment started to run as designed program. The ALD program was as follows: 30ms pulse of $ZnEt_2$, 13s purge for 15 half cycles at first, and then 30ms pulse of $ZnEt_2$, 13s purge, 20 ms pulse of H_2O, 20s purge for every full cycle. The ALD growth was observed with deposition rate of 0.07nm/cycle, ZnO layer was deposited with 150 cycles (about 10 nm).

2.3. Light emitting diodes fabrication

ITO-coated substrates were cleaned stepwise in detergent, water, acetone, and ethanol under ultrasonication for 20 min each. The substrates were dried and subsequently pretreated by UV ozone for 20 min. PEDOT:PSS layer (56 nm) was spin-coated on an ITO surface (at 500 rpm for 10 s, 4500 rpm for 40s and 6000 rpm for 10s) and then annealed at 140 °C for 20 min in air to remove water. $CsPbBr_3$ layer (68 nm) was deposited on the PEDOT:PSS coated ITO substrates by using a one-step spin-coating method [29]. Firstly, the $CsPbBr_3$ precursor (10 wt% CsBr and $PbBr_2$ 2:1 molar ratio in dimethylsulfoxide) solution were spin-coated onto the PEDOT:PSS-coated ITO/glass substrates at 2000 rpm for 60 s and then annealed on a hot plate at 70 °C for 30 min under inert conditions in a glove box to achieve a better coverage. The solution was filtrated before used. Secondly, PEIE solution of different concentrations in chlorobenzene was pipetted onto the perovskite layer at a time delay of 45s after spin-coating started. Thereafter, ZnO electron transport layer was deposited by ALD technique. Finally, the devices were transferred into a vacuum chamber for Ag deposition. Ag (150 nm) layer was deposited by thermal evaporation using a shadow mask to pattern the electrodes under high vacuum ($< 10^{-6}$ Torr). The device active area was 5 mm^2. After completing the process of fabrication, the devices were tested outside without encapsulation.

2.4. Film characterization

A Field Emission Scanning Electron Microscope (SEM) (JSM-7800F, Oxford Instruments) combined with an energy dispersive spectrometer (EDX) was used to acquire SEM images and analysis elements composition. The instrument uses an electron beam accelerated at 3 KV. Absorption spectra and Photoluminescence (PL) spectra were recorded with a Shimadzu UV-1750 UV–Vis spectrophotometer and a Hitachi F4600 fluorescence spectrophotometer, respectively. Time-resolved photoluminescence (TRPL) experiments were performed using Transient State Fluorescence Spectrometer (FLS980-STM) by exciting the samples deposited on quartz substrate at 380 nm with a laser light source (Quantel Laser Q-Smart 850). The X-ray diffraction (XRD) patterns were recorded by a SmartLab Automated Multipurpose X-ray Diffractometer equipped with a Cu-Kα ($\lambda = 1.5405$ Å) radiation source. Scans were taken with 8 mm wide source and detector slits, and X-ray generator setting at 40 kV and 30 mA. The work function (HOMO values) of the samples was measured by an Ionization Energy Measurement System (Model IPS-4, Nanjing SunnyTech Ltd., China). The Raman measurements were conducted in air at room temperature (RT) on a Laser confocal microscopic Raman spectrometer (WITEC Alpha 300 M^+). The excitation source was a diode laser with the output at 488 nm.

2.5. Device characterization

J-V characteristics of the PeLEDs were taken using a Keithley 2400 source meter in combination with a Photo Research PR745 spectroradiometer. A Lambertian was assumed in the calculation of EQE [31]. The measurement was performed at RT.

3. Results and discussion

$CsPbBr_3$ LEDs consisting of glass/ITO/PEDOT:PSS/$CsPbBr_3$/ZnO/Ag (Fig. 1 (a)) were fabricated, where $CsPbBr_3$ is the emitting layer. Apart from cathode layer of Ag, which was deposited in vacuum, all layers were solution processed vis spin coating. The corresponding band diagram with energy levels is shown in Fig. 1 (b). ZnO and PEDOT:PSS were used as electron injection and hole injection layers, respectively. Solution with CsBr/$PbBr_2$ at an optimized ratio 2:1 was made in DMSO solvent [5], as CsBr-rich solution could decrease the probability of halogen vacancies and reduce the nonradiative defect densities in the film [5]. Light emitting layer $CsPbBr_3$ is spun on top of PEDOT:PSS and during the process, different concentrations of PEIE in the solvent CB