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Ethoxylated polyethylenimine as an efficient electron injection layer for conventional and inverted polymer light emitting diodes

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ABSTRACT

We report inverted light emitting devices using ethoxylated polyethylenimine (PEIE) as a single electron injection layer for indium tin oxide cathode, which possess comparable efficiency to those using ZnO/PEIE double electron injection layers. Implementation of a PEIE layer between light emitting polymer layer and aluminum has been shown to significantly enhance device efficiency as well. Improvement of device efficiency can be attributed to increased electron injection due to the reduced work function of PEIE modified cathode as well as the hole blocking effect of PEIE layer. Furthermore, PEIE serves as an efficient electron injector for a range of light emitting polymers with wide distribution of energy levels.

1. Introduction

Polymer light emitting diodes have been actively studied for applications of flat-panel displays and solid-state lighting due to their unique advantages of flexibility, self-emitting, low-cost and large area processing [1]. The typical configuration of conventional devices is indium tin oxide (ITO)/hole injection layer/light emitting polymer (LEP)/metal, where commonly adopted hole injection layer is poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT: PSS). Efficient injection of electrons and holes from the electrodes into LEPs is required to achieve high efficiency. To facilitate electron injection, low work-function (WF) metals such as calcium and barium are generally used [2], which on the other hand cause devices very sensitive to ambient moisture and oxygen. Various materials such as alkaline/alkaline earth metal fluorides [3], poly(ethylene glycol) [4] or polyelectrolytes [5] have been incorporated into devices for efficient electron injection from high WF metals such as aluminum. Among them, poly(ethylene glycol) and polyelectrolytes can be deposited onto LEP layer from alcohol or aqueous solution, representing a facile approach toward fully solution-processed light emitting devices. Alternatively, inverted devices with the structure of ITO/metal oxide/LEP/metal oxide/metal, which utilize air-stable low WF metal oxides such as ZnO and TiO_2 as electron injection layers and high WF metal oxides such as MoO_3 as hole injection layers, exhibit improved environmental stability [6]. In such devices, ITO serves as the cathode as the work function difference is important for the polarity of the devices [7]. The conduction band minimum of TiO_2 and ZnO lies at

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ca. −4 eV below the vacuum level and thus enables electron injection into a few LEPs with the deep-lying Lowest Unoccupied Molecular Orbital (LUMO) level such as poly(9,9-dioctylfluorene-co-benzothiadiazole) (F8BT), achieving reasonable device efficiency. But there is significant energy barrier for electron injection from such metal oxides into the vast majority of LEPs having LUMO energy in the range of 2–3 eV [8]. To address this problem, manifold electron injection materials including dipolar self-assembled (SAM) materials [9], polyelectrolytes [10] and metal salts such as cesium carbonate [11] and barium hydroxide [12] have been placed between the metal oxide and LEP layer. Highly efficient inverted light emitting devices using a thick F8BT layer in combination with a Cs_2CO_3 or $Ba(OH)_2$ interlayer were reported by Lu et al. [12]. The superior efficiency of the $Ba(OH)_2$ device compared to the Cs_2CO_3 device was attributed to higher luminescence quantum yield of F8BT film, more effective hole-blocking capability and less disturbance of bulk hole-transport in F8BT. ZnO and TiO_2 layers are typically prepared by thermal-conversion of metal salt ‘‘sol’’ at ca. 300–450 °C, which is time-consuming, increases the cost and cannot be used for plastic substrates. Further efforts are directed to reduce the annealing temperature and simplify device fabrication process. For example, ZnO [13] and SnO_2 [14] nano-particles are used as electron-injection layers, significantly reducing the heat treatment temperature.

Parallel studies indicate the WF of ITO can be adjusted to a large extent via molecular absorption method. For example, chemical absorption of acid or base on ITO surface dramatically affects its WF and the chemical composition of ITO surface prior to the treatment plays an important role in determining the WF shift as well [15]; Expose of tetrakis(dimethylamino)ethylene (TDAE) was reported to significantly diminish the WF of ITO from 4.6 to 3.7 eV, which was attributed to the formation of interfacial dipole due to charge transfer from TDAE to ITO [16]; Incorporation of a water-soluble polyelectrolyte layer reduced the WF of ITO by ca. 0.4 eV as measured by Kelvin probe [17]; Zhong et al. [18] described the synthesis of amino-functionalized polyfluorenes and application of such polymers as ITO surface modifiers, which shifted the WF of ITO by ca. −0.44 eV and enabled efficient electron injection into LEPs. Organic electron injectors are more compatible with the adjoining organic layer than inorganic counterparts, leading to the formation of the integral contact [10]. Zhou et al. [19] reported that aliphatic amine-containing polymers such as ethoxylated polyethylenimine (PEIE) can significantly reduce the WF of manifold substrates such as metals, metal oxides, conducting polymers and graphene, which allowed flexible device structure designs and improved properties of various organic electronic devices. In particular, incorporation of a PEIE layer between 4,7-diphenyl-1,10-phenanthroline electron transport layer and Al led to high-efficiency light emitting devices. Despite the fact that PEIE as a surface modifier possesses many tempting properties such as a wide range of adaptability, durability and robustness, polymer light emitting devices using PEIE electron-injection layer, in particular inverted devices with PEIE modified ITO as the electron injection contact, remain largely unexplored. In this manuscript, we report incorporation of PEIE layer at either the ITO/LEP or LEP/Al interface can significantly enhance the luminance efficiency of inverted and conventional polymer light emitting devices. Comparison of the current density–voltage characteristics of electron-only devices with or without a PEIE layer indicates that addition of a PEIE layer greatly increases electron injection. We also examine inverted light emitting devices employing various LEPs and find out that PEIE works as an efficient electron injector for a range of LEPs with wide distribution of energy levels.

2. Experimental section

Materials: 80% ethoxylated polyethylenimine (PEIE, Mw = 70,000 g mol^{-1}), zinc acetate dihydrate ($Zn(OAc)_2\cdot 2H_2O$) and PEDOT: PSS (Clevios P VP AI4083) were purchased from Sigma–Aldrich and Heraeus Clevios GmbH, respectively and were used as received.

Preparation of ZnO layer: 100 mg $Zn(OAc)_2.2H_2O$ was dissolved in 1 mL 2-methoxyethanol at 80 °C and 56 μL ethanolamine as stabilizer was added into $Zn(OAc)_2$ solution. The mixture was then heated and stirred at 60 °C for 12 h. The solution was spin-coated onto UV–ozone treated ITO substrates and the resultant film was annealed at 300 °C for 1 h under ambient conditions, giving a 30 nm ZnO layer.

Fabrication of inverted light emitting devices: PEIE was diluted using 2-methoxyethanol by a factor of 50 and the solution was then spin-coated onto either bare or ZnO-covered ITO substrates. Part of PEIE layers were spin-rinsed with 2-methoxyethanol for 2–3 times. A 100 nm poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV), poly[9,9-dioctylfluorene-co-(bis-thienylene)benzothiadiazole (PF-TBT) or a fluorene–amine copolymer (PF-A) layer was deposited from the respective chlorobenzene solution. The MEH-PPV, PF-TBT and PF-A samples were annealed on a hotplate at 60, 180 and 180 °C for 10 min, respectively. 10 nm MoO_3 and 100 nm aluminum were evaporated as the hole-injection layer and anode for bipolar devices. The CsF (1 nm)/Al (100 nm) cathode was deposited on top of a 300 nm MEH-PPV layer for electron-only devices.

Fabrication of conventional light emitting devices: A 50 nm PEDOT: PSS layer was prepared by spin-coating its aqueous solution, which was subsequently tempted at 170 °C for 10 min under ambient conditions to remove the moisture. A 100 nm MEH-PPV layer, followed by a PEIE layer, was deposited onto PEDOT: PSS layer. The samples were annealed at 60 °C for 10 min. A CsF electron injection layer with nominal thickness of 1 nm was deposited onto MEH-PPV layer. Conventional devices were completed by thermal-deposition of 100 nm Al. Electron-only devices, where PEDOT: PSS layer in the above bipolar devices was replaced by a 30 nm ZnO layer to block hole injection, were prepared. With the exception of the deposition of PEDOT: PSS layer, all processes were carried out in a dry nitrogen atmosphere.

Characterization: The thickness of ZnO, PEDOT: PSS, PEIE and LEP layers was determined by a Dektak 6M stylus