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Molybdenum oxide anode buffer layers for solution processed, blue phosphorescent small molecule organic light emitting diodes

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ABSTRACT

In this work we present solution processed organic light emitting diodes (OLEDs) comprising small molecule, blue phosphorescent emitter layers from bis(4,6-difluorophenylpyridinato-N,C2)picolinatoiridium doped 4,4′,4″-tris(carbazol-9-yl)-triphenylamine and molybdenum trioxide (MoO_3) anode buffer layers. The latter were applied from a molybdenium(V)ethoxide precursor solution that was thermally converted to MoO_3 at moderate temperatures. The high work function MoO_3 facilitated hole injection into the emission layer. The MoO_3 layer properties were investigated by means of energy-dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy, ultraviolet photoelectron spectroscopy and Kelvin probe force microscopy. MoO_3 buffer layers performed superior to the commonly used poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) and enabled an enhanced OLED device efficiency.

1. Introduction

Roll-to-roll solution processing of organic semiconductors is widely considered as the key to low-cost electronic devices such as solar cells, transistors and organic light emitting diodes (OLEDs). While solution processed solar cells commonly rely on conjugated polymers, OLEDs from low-molecular weight materials (small molecule OLEDs, SMOLEDs) perform superior to OLEDs based on conjugated polymers, since small molecules can be purified more efficiently e.g. by gradient vacuum sublimation and hence enable stable and efficient devices [1]. Polymers can contain intrinsic defects from synthesis that lead to defects or traps, non-radiative recombination and thus a faster efficiency decline of OLEDs. Today, SMOLEDs are commonly fabricated by vacuum deposition. The respective light emitting layers are designed according to the host–guest concept: Charges are injected from the electrodes through buffer layers into the host and subsequently form excitons on the highly luminescent guest dye molecules [2]. In order to yield higher conversion efficiencies, phosphorescent dyes such as tris(phenylpyridine)iridium ($Ir(ppy)_3$, green emission) are used as guest molecules in the emission layers [3]. For future applications, blue emitting OLEDs are of utmost importance as they enable the fabrication of white emitting devices and hence open pathways to general lighting. A well investigated blue phosphorescent emitter is iridium(III)bis[(4,6-fluorophenyl)-pyridinato-N,C2′]picolinate (FIrpic). Suitable hosts for FIrpic are e.g. a blend of

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poly(N-vinylcarbazole) (PVK) and 1,3-bis[(4-tert-butylphenyl)-1,3,4-oxadiazolyl]phenylene (OXD-7) [6,7] or 4,4′,4″-tris(carbazol-9-yl)-triphenylamine (TCTA) [4,5] that both exhibit a higher triplet band-gap than FIrpic. With sophisticated vacuum deposited multi-layer device architectures comprising TCTA:FIrpic emission layers, efficiencies of up to 60 lm/W have been achieved [4]. To inject holes into the deep highest occupied molecular orbital (HOMO) of TCTA ($E_{HOMO} \approx 5.7$ eV [8,9]) or other suitable host materials, hole injection layers with a comparable or deeper hole transport energy level are mandatory. The commonly used conductive polymer blend poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) exhibits a work-function of $\Phi_a \approx 5.2$ eV [10,11] and hence is not an optimum hole injection layer in particular for blue OLEDs. Transition metal oxides such as molybdenum trioxide (MoO_3) [12,13], tungsten trioxide (WO_3) [14,15] or vanadium pentoxide (V_2O_5) [16,17] with higher work functions appear much more suitable for hole injection. Consequently, layers from thermally evaporated transition metal oxides have been used for hole injection into wide band-gap emitters in SMOLEDs that were fabricated in vacuum [18]. On the other hand, the need for stable and solution processable charge carrier transport layers in organic solar cells gave rise to a comprehensive development of precursor processes for transition metal oxide layers. Today, solution processed charge carrier transport layers from MoO_3 [19,20], WO_3 [21,22] and V_2O_5 [23,24] have been examined in organic solar cells while their benefits for OLEDs remain widely uninvestigated.

In this work we combine the concept of solution processing with the advantages of low-molecular weight materials and transition metal oxides. We investigate polymer-free, solution processed SMOLEDs comprising TCTA:FIrpic emission layers and MoO_3 hole injection layers that were fabricated from a molybdenium(V)ethoxide ($Mo(OEt)_5$, Fig. 1a) precursor solution. This MoO_3 layer appears as an ideal candidate for hole injection into blue emitting molecules due to its high work function.

2. Experimental

According to the device architecture depicted in Fig. 1b, all OLEDs were fabricated on indium tin oxide (ITO) coated glass substrates ($R_\square \approx 13\ \Omega/\square$) that had been structured in hydrochloric acid. The substrates were cleaned with acetone and isopropanol for 15 min in an ultrasonic bath. Afterwards the substrates were exposed to an oxygen plasma for 2 min in order to remove organic residues and to polarize the ITO surface for better $Mo(OEt)_5$ precursor and, for reference, PEDOT:PSS adhesion.

The MoO_3 layer was fabricated from an 1:120 ethanol diluted, ready-to-use $Mo(OEt)_5$ precursor solution (abcr GmbH & Co. KG). The solution was spincast at 4000 rpm for 30 s on the rotating substrate and subsequently annealed for 10 min at 150 °C under ambient conditions. The comparably low conversion temperature ensures process compatibility with future roll-to-roll fabrication on polymer foils. Then the samples were moved to a glovebox with nitrogen atmosphere and kept there for the remaining fabrication and characterization process. 7 nm MoO_3 reference layers were evaporated in high vacuum (10^{-6} mbar). PEDOT:PSS (VPAi 4083, Heraeus) reference layers were spincast at 4000 rpm for 30 s from a 1:1 water diluted dispersion. Afterwards the substrates were annealed for 10 min in a vacuum oven at 120 °C.

TCTA and FIripc were separately dissolved in tetrahydrofuran (THF, 10 mg/ml and 1 mg/ml) and then mixed 9:1 by weight. The 40 nm TCTA:FIrpic emission layer was spincast at 1000 rpm for 20 s. The 1,3,5-tris(1-phenyl-1H-benzimidazol-2-yl)benzene (TPBi)/LiF/Al (20 nm/0.7 nm/200 nm) counter electrode was thermally evaporated in high vacuum (10^{-6} mbar).

The OLED current density–voltage (J–V) characteristics were recorded with a source measure unit (Keithley 238) at room temperature in nitrogen atmosphere. The device luminance in forward direction was calculated from the emission spectrum. The spectrometer had been calibrated with a secondary standard calibration halogen lamp (Philips FEL-1000W). Current efficiencies (cd/A) and power efficiencies (lm/W) were calculated from the electrical and optical properties assuming Lambertian light distribution.

Kelvin probe force microscopy (KPFM) measurements were carried out on a multi-mode atomic force microscope (AFM) head (Veeco Instruments) under ambient conditions and a scanning probe microscopy (SPM) Control System (Nanonis GmbH). Conductive silicon cantilevers (PPP-FMR, 75 kHz, Nanosensors) were used as sensors.

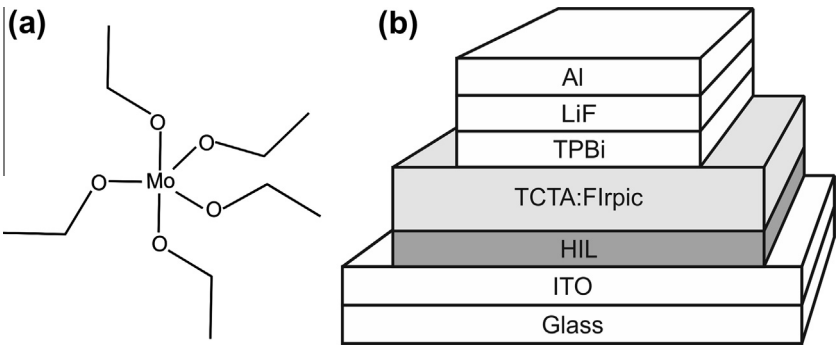

Fig. 1. (a) Chemical structure of the $Mo(OEt)_5$ precursor. (b) Device layer stack of the solution processed OLED comprising MoO_3 or PEDOT:PSS as hole injection layer (HIL).