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Improved electron injection from silver electrode for all solution-processed polymer light-emitting diodes with Cs_2CO_3:conjugated polyelectrolyte blended interfacial layer

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ABSTRACT

This study demonstrates the incorporation of a Cs_2CO_3:conjugated polyelectrolyte blended interfacial layer between the emissive layer and a silver (Ag) cathode, for realizing all-solution processed polymer light-emitting diodes. For a device with poly(9,9-dioctylfluorene-co-benzothiadiazole) (F8BT) as the emissive layer, this approach improves the maximum luminance of approximately 80,000 cd/m^2 and maximum current efficiency of 10.6 cd/A. It is clarified that the interfacial layer prevents Ag nanoparticles from penetrating into the emissive layer, resulting in yellow–green emission from F8BT. We also demonstrate the possibility of all-solution processed polymer light-emitting diodes utilizing solution-processed Cs_2CO_3:conjugated polyelectrolyte interfacial layer and Ag nano-ink.

1. Introduction

Organic semiconductors have attracted considerable attention owing to their simple and low-cost processing, and potential for electronic and optoelectronic applications. In particular, they have demonstrated the possibility of application in electronic and optoelectronic devices fabricated by solution processing for large-area and flexible devices. Polymer light-emitting devices utilizing conjugated polymers [1,2] have attracted considerable interest because of their advantages in large-area device fabrication. Fluorene-type polymers specifically have emerged as an important class of conducting polymers due to their efficient emission, relative high mobility, and high stability [2–4].

In order to produce organic devices at low cost and in large quantity, shortening the process becomes necessary. In many cases, the cathode electrode of organic optoelectronic devices is vacuum-deposited thorough a metal mask. Metal nanoparticles are also expected to be applied as electrodes in all-solution processed organic devices. Low curing temperature of the nanoparticle ink used is important in plastics electronic applications. In particular, silver (Ag) nano-ink is promising for low-temperature solution-processed electrodes in organic light emitting diodes (OLEDs) [5]. Therefore, it is important to develop more effective electron interfacial materials to enhance electron injection for devices with Ag cathodes. Cs_2CO_3 has been shown to be a very efficient electron-injection material in OLEDs [6,7]. Cs_2CO_3 has a high solubility in polar solvents such as water and alcohol, and is almost completely insoluble in most other organic solvents such as toluene and xylene. Conjugated polyelectrolytes, which are conjugated polymers with pendant groups bearing ionic functionalities and with high solubility in polar solvents, are also promising interfacial layer materials in organic optoelectronic devices [8–12].

We report here that a solution-processed Cs_2CO_3:conjugated polyelectrolyte blended interfacial layer plays a significant role in increasing the injection of electrons from an Ag cathode. We also demonstrate the possibility of

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all-solution processed OLEDs utilizing a solution-processed interfacial layer and Ag nano-ink.

2. Experimental procedure

A fluorene-type block copolymer, poly(9,9-dioctylfluorene-co-benzothiadiazole) (F8BT), supplied by Sumitomo Chemical Co., Ltd. with an electron withdrawing group, was used as the emissive layer in the present work. A conjugated polymer, poly(9,9-dioctylfluorene-co-N-(4-butylphenyl)-diphenylamine) (TFB, ADS259BE) and a conjugated polyelectrolyte, poly[(9,9-di(3,3′-N,N′-trimethylammonium) propylfluorenyl-2,7-diyl)-alt-co-(9,9-dioctylfluorenyl-2,7-diyl)] diiodide salt (PFN, ADS180BE) both purchased from American Dye Source Inc. were used as the interlayer and interfacial layer, respectively, without further purification. A glass substrate was degreased with solvents and cleaned in a UV ozone chamber. First, a 40-nm-thick poly (ethylenedioxythiophene):poly(styrenesulfonicacid) (PEDOT: PSS) hole-injection layer was spin-coated on an indium tin oxide (ITO)-coated glass substrate and baked. Next, TFB as the hole transport and electron blocking layer and F8BT as an emissive layer were fabricated by spin-coating [13]. The typical thicknesses of the TFB and F8BT layers were 10 and 50 nm, respectively. Using 2-ethoxyethanol as the main solvent, Cs_2CO_3, PFN and Cs_2CO_3:PFN were formed as interfacial layers by spin-coating on the F8BT layer. An ultrathin Cs_2CO_3 interfacial layer was spin-coated from a 0.5 mg/ml 2-ethoxyethanol solution. The Cs_2CO_3:PFN layer was obtained using Cs_2CO_3:PFN solutions in a 2:1 weight ratio. The typical thicknesses of PFN and Cs_2CO_3:PFN layers were 5 and 10 nm, respectively. Surface morphologies of the interfacial layers on the F8BT films were examined using atomic force microscopy (AFM; JEOL, JSPM-5200). The cathode consisting of Ag or CsF (3 nm)/Al(10 nm)/Ag was deposited in vacuum at a chamber base pressure of about 10^{-4} Pa. The active area of the devices with the evaporated cathode was 4 or 0.3 mm^2.

The patterned OLEDs were fabricated using the conventional photolithography process. The positive-tone photoresist (ZWD-6200 series) suitable for EL-panel processing to make insulators was purchased from Zeon Co., Ltd. The ZWD-6200 series is an alkaline developable and can be formed into a round pattern profile at the corner of the bank by baking after the insulating bank has been formed on the ITO-coated glass substrate. All layers were fabricated by spin-coating. As the formation temperature is 150 °C, the Ag electrode fabricated by the Ag nano-ink (Harima Chemicals, NPS-JL, silver nanoparticle dispersion in tetradecane) can be formed by solution processing on the interfacial layer. A 1-μm-thick Ag cathode was fabricated by spin-coating. The active area of the devices with the solution-processed Ag is a 2 mm circle. The device structure and molecular structures are illustrated in Fig. 1.

The current density–voltage–luminance (J–V–L) characteristics were obtained using a digital multimeter (Keithley 2000), a regulated DC power supply (Kenwood PW36-1.5AD), and a luminance meter (Minolta LS-100). Transient electroluminescence (EL) was measured by applying square-wave voltage pulses generated by an HP8114A source (Agilent). The optical pulse was observed using a photomultiplier tube detector (Hamamatsu Photonics). The obtained EL response and voltage were simultaneously digitized by a LeCroy 104MXi oscilloscope. Impedance spectroscopy measurements were carried out using a Solatron 1260 impedance analyzer with a 1296 dielectric interface. The typical AC oscillation amplitude was 100 mV. The energy levels of the highest occupied molecular orbitals (HOMOs) of the polyfluorene derivatives were measured by a photoelectron spectrometer (Riken Keiki, AC-2). The bandgap energy was simply estimated from the edge of the absorption spectrum.

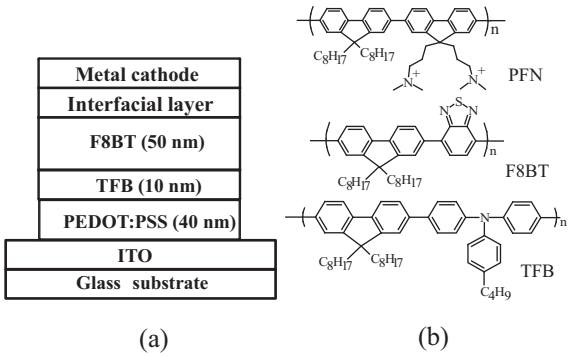

Fig. 1. (a) Device structure and (b) molecular structures of the materials used in this study.

3. Results and discussion

A solution-processed electron transport interfacial layer, which reduced the damage of the emissive layer during the Ag fabrication process, is one of the key factors to realize all-solution processed devices. The low work function metal cathode is easily oxidized by air. It is well-known that a Cs_2CO_3-buffered Al cathode improves the efficiency of electron injection from the cathode and depends on the thickness of the Cs_2CO_3 interfacial layer. A strong chemical reduction occurs between Cs_2CO_3 and the vacuum-deposited Al cathode [7]. Owing to the insulating properties of Cs_2CO_3, its thickness is required to be maintained in the several nanometer range so as not to increase driving voltage. Several previous studies have also used Cs_2CO_3-doped organic low-molecules as a thick electron transport layer for improving the electron injection ability and device performance [14,15]. Ultrathin layers of conjugated polyelectrolytes also lead to improved electron injection [12].

The lowest unoccupied molecular orbital (LUMO) level and HOMO level of F8BT are −3.3 and −5.9 eV, respectively. The work function of Ag is −4.3 eV. Thus, these energy levels suggest that solution-processed ultrathin Cs_2CO_3, PFN and Cs_2CO_3:PFN were inserted individually as an interfacial layer between the emissive layer and Ag cathode to improve electron injection from the cathode. We observed the difference in thin film morphologies in the topographic images of the interfacial layers on F8BT