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Letter

Contact printing of the emitting layer for high performance multilayered phosphorescent organic light-emitting diodes

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ABSTRACT

Efficient multilayered organic light-emitting diodes (OLEDs) were fabricated using contact printing. In order to overcome the mixing problem occurring between the organic layers during the solution processes, contact printing was utilized on a small molecule layer. Since this contact printing allows multilayer stacking without the damage caused by organic solvents, high-performance OLEDs could be fabricated with solution-based small molecules employing a low cost process. In this study, the performance of the multilayered OLEDs manufactured by the contact printing process is significantly enhanced than that found in spin-coated devices.

1. Introduction

Organic light-emitting diodes (OLEDs) are the natural choice for the next generation of display systems, because of their advantages in self-emission, low power consumption, high contrast ratios, high speed operation, ultra-thinness, and overall flexibility [1,2]. In spite of the potential benefits of OLEDs, they are still small and expensive to fabricate for commercial displays, compared to liquid crystal displays (LCD). Solution processes have been developed for the deposition of their organic and metal layers, since the solution-based thin film deposition methods allow for the potential of low cost roll-to-roll processing for flexible organic electronics [3–5]. Nevertheless, one of great challenges facing the fabrication of solution-based OLEDs is in the difficulty in obtaining high-performance devices, because of the problems found in multilayer stacking due to the dissolution of the preceding organic layers by the organic solvents used during the spin-coating of the next layers [6,7].

In order to overcome this multilayered structure limitation in the solution processes, various printing methods have recently been studied, such as using curable layers, orthogonal solvents, polarity, solubility, and so on [8–11]. However, these methods are limited to specific materials that have to be chosen for their specified properties, such as their crosslinkability, restricted energy levels, or solvent compatibility. The contact printing process is quite independent of the above limited specific materials when stacking organic layers for multilayered OLEDs. Yim et al. have reported upon the fabrication of multilayer organic electronic devices with well defined organic–organic interfaces accomplished by transfer printing [12]. The study suggested that functional multilayered conjugated-polymer structures could be fabricated. We propose to use this technique for various organic materials in order to enhance the performance of multilayered OLEDs based on small molecules.

In this study, we adopted a solution-based small molecule, 4,4′,4″-tris(N-carbazolyl)-tri-phenylamine (TCTA) for

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the hole transporting layer (HTL). In addition, TCTA has a high triplet energy level (2.7 eV), which can play the role of an exciton blocking layer (ExBL) in phosphorescent OLEDs [13]. In addition, TCTA has good solubility and film forming properties, as well as good adhesion to the next organic layer. In order to study the effect of the printing process on the device performance, an emitting layer (EML) was processed by contact printing and spin-coating onto a small molecule layer. Although thermal evaporation was used after formation of an EML, this is needed as an assured method for measurement and analysis of a completed device utilizing the printing process. These results would be a possibility of the layer transfer process for high-performance OLED in low-cost process, and next step is working in progress for all-printing process. Finally, the enhanced performance of OLEDs fabricated without intermixing problems by using contact printing was studied, which demonstrates a suitable process that can fabricate high-performance OLEDs based on solution-processes with a low-cost method.

This contact printing technique utilizes a planar poly(dimethylsiloxane) (PDMS) elastomer. The PDMS stamps are suitable for a repeatable process since they are characterized by their low adhesion, durability, and elasticity. When the next layer is printed onto the preceding layers mounted on a substrate, the intermixing problem between the layers does not occur since the organic solvents are completely dried before the transfer.

2. Experiment

In order to fabricate the stamps, PDMS (Sylgard 184, Dow Corning Co.) was poured onto a plain silicon wafer substrate. The PDMS was then cured in an oven at 70 °C for over 3 h. The PDMS stamp can then be easily peeled-off from the master since the PDMS has a good elasticity and a low surface energy.

In order to fabricate the OLED devices, indium-tin-oxide (ITO) coated glass was sonicated in acetone, methanol and deionized water; and then cleaned in an oxygen plasma. Poly(ethylenedioxythiophene):poly(stylenesulfonate) (PEDOT:PSS) as a hole injection layer (HIL) was then spin-coated onto the ITO substrates to a thickness of 30 nm and annealed at 115 °C for 10 min on a hot plate in order to remove the solvent. Subsequently, TCTA as a HTL with a 0.5 wt.% in toluene was spin-coated at 2500 rpm to obtain a thickness of 25 nm, then annealed at 150 °C for 30 min on a hot plate. Next, the prepared plain PDMS stamps were treated using oxygen plasma in order to enhance their surface energy for a better wetting of the EML on the PDMS. Poly(N-vinylcarbazole) (PVK) based green emitting material was used for the EML (Fig. 1d). After a few drops of the EML solution suspended in chlorobenzene were applied to the surface of the PDMS stamps, the stamps were spin-coated at 3000 rpm in order to obtain a thickness of 30 nm, and then dried. Fig. 1 shows the schematic illustration of the contact printing process. The EML coated PDMS stamp was then brought into contact with the TCTA coated substrate at 80 °C for 20 s. The PDMS stamp was then carefully peeled-off, leaving the EML on the substrate. After releasing the layer, the substrate was annealed at 150 °C for 30 min on a hot plate.

We compared our device to spin-coated EMLs on TCTA coated devices in order to define the effect of the EML printing process has on the device.

Reference device 1: ITO/PEDOT:PSS (25 nm)/EML (30 nm, spin-coated).
Reference device 2: ITO/PEDOT:PSS (25 nm)/TCTA (25 nm)/EML (30 nm, spin-coated).
Reference device 3: ITO/PEDOT:PSS (25 nm)/TCTA (50 nm)/EML (30 nm, spin-coated).
Contact printing: ITO/PEDOT:PSS (25 nm)/TCTA (25 nm)/EML (30 nm, contact-printed).

In order to examine the dissolution problems of the EML solvent on the TCTA layer, the TCTA was spin-coated at 2500 and 800 rpm to obtain thicknesses of 25 and 50 nm, respectively, and then annealed. Subsequently, the EML was spin-coated to a thickness of 30 nm on the TCTA layer. Finally, in order to study the effect on the electroluminescence (EL) efficiencies of the spin-coated and contact-printed devices, we deposited layers of 10 nm 4,4′-di(triphenylsilyl)-biphenyl (BSB) as a hole blocking layer (HBL), 45 nm 4,7-diphenyl-1,10-phenanthroline (Bphen) as an electron transport layer (ETL), 0.8 nm lithium-fluoride (LiF) as an electron injection layer (EIL), and 100 nm aluminum as a cathode using thermal evaporation. The emission area of the devices was 5 mm × 5 mm. The current–voltage characteristics were measured using a Keithley 237 High-Voltage Source-Measure Unit (Keithley Instruments, Inc.), the EL efficiency was measured using a PR-670 SpectraScan Spectroradiometer (Photo Research, Inc.) in a dark box.

3. Results and discussion

Fig. 2 shows the current density and the luminance as a function of the applied voltage. The multilayered OLEDs using spin-coating were fabricated as reference devices with the same organic layers and metal layers under the same conditions. The turn-on voltage of the contact-printed device was lower than the spin-coated devices: 5.1 and 6.2 V, respectively. The luminance of the contact-printed device was also enhanced compared to the spin-coated devices at the same voltage, since the contact-printed device has a higher current density than the spin-coated devices. The spin-coated devices have the interlayer dissolution issue when the EML solvent chlorobenzene is spin-coated onto the top of the TCTA interlayer. The dissolution test was examined by measuring the thickness of the remaining TCTA layer after the spin-coating of the chlorobenzene on the 25 and 50 nm TCTA layers. As a result, only the thickness of the PEDOT:PSS layer was measured without the TCTA layer. Fig. 2 shows that the *I–V* curves of Refs. [2,3] are almost the same as Ref. [1]'s without TCTA layer. This interlayer dissolution by the organic solvent affects the current–voltage characteristics, since the thickness of the TCTA is insufficient to play the role of the HTL. However,