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Micropatterning of emitting layers by microcontact printing and application to organic light-emitting diodes

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ABSTRACT

The microcontact printing (μCP) technique, which is a simple and low damage fabrication technique for thin films, was successfully applied to fabricate patterned emitting layers such as polyfluorene (PF). We fabricated micropatterns by transferring dried and uniform thin films, and observed strong electroluminescence (EL) from the fabricated organic light-emitting diodes (OLEDs) with the patterned emitting layers. The performance of the fabricated device was superior to that of a conventionally fabricated device. This demonstrates the well-controlled interfaces achieved by μCP. Furthermore, we succeeded in fabricating OLEDs with multiple emitting layers. These results show that this technique is promising for application to cost-effective, high luminance and multicolored OLED displays.

1. Introduction

Organic light-emitting diodes (OLEDs) have been studied for application to next-generation thin flat-panel displays since they were reported by Tang and VanSlayke in 1987 [1,2]. OLEDs have several characteristics such as high luminance, self-luminous and short response time. In general, OLEDs are industrially fabricated by a vacuum process, which needs large amounts of energy and materials. Therefore, current OLED production is very expensive, and the establishment of a cheap and controlled fabrication process is a key issue.

To solve this problem, printing techniques such as ink-jet printing and transfer-printing have been proposed [3–8]. However, the ink-jet printing technique includes photolithography steps because it needs banks for precise patterning of an emitting layer. Furthermore, the throughput of ink-jet printing is very low. On the other hand, the transfer-printing technique has an advantage because we can simultaneously pattern thin films on large-area substrates. However, little has been achieved at present in the fabrication of micropatterns of an emitting layer without using the vacuum process due to the difficulty of fabricating an emitting layer with uniform thin films and well-controlled interfaces. Choi et al. demonstrated micropatterning of an emitting layer using a printing process or a detachment process [6,7]. Yet, their processes include vacuum process in the fabrication of the emitting layer. Yim et al. demonstrated the fabrication of an emitting layer without using vacuum process [8]. Yet, they have not achieved micropatterning of the emitting layer. In addition, their process needs a sacrifical layer to transfer the emitting layer.

We have proposed a patterning technique using microcontact printing (μCP) [9,10]. μCP is an attractive technique for directly obtaining micropatterns below 10 μm with an etchingless process that minimizes material consumption. The μCP technique has been applied mainly to the patterning of self-assembled monolayers (SAMs) and catalysts for electroless deposition [11–13]. We succeeded in fabricating organic thin-film transistors (OTFTs) by applying μCP to the patterning of conductive polymers such as poly(3-hexylthiophene) (P3HT) and poly(3,4-ethylenedioxythiophene):poly(4-stylenesulfonate) (PEDOT:PSS) [9,10]. Recently, Bolognesi et al. have reported on μCP and have fabricated OLEDs with patterned emitting layers [14]. In this paper, we demonstrate micropattern fabrication of emitting layers such as polyfluorene (PF) by using μCP without a vacuum process. PF is regarded as a promising material for an emitting layer in OLEDs [15,16]. Our method has an advantage over the processes in the above-mentioned literature in that the performance of the fabricated device is superior to that of a conventionally fabricated device. Moreover, we present a simple and low damage technique for fabricating OLEDs with multiple emitting layers for application to multicolored displays.

2. Experimental

The procedure for fabricating OLEDs with multiple emitting layers is illustrated in Fig. 1. First, a patterned poly(dimethylsiloxane) (PDMS) elastomer stamp was fabricated using the nanoimprint method with a mold [17]. The mold was fabricated using conventional photolithography. The patterned PDMS layer with total thickness of ~50 μm was prepared on a hard glass substrate to prevent the sagging

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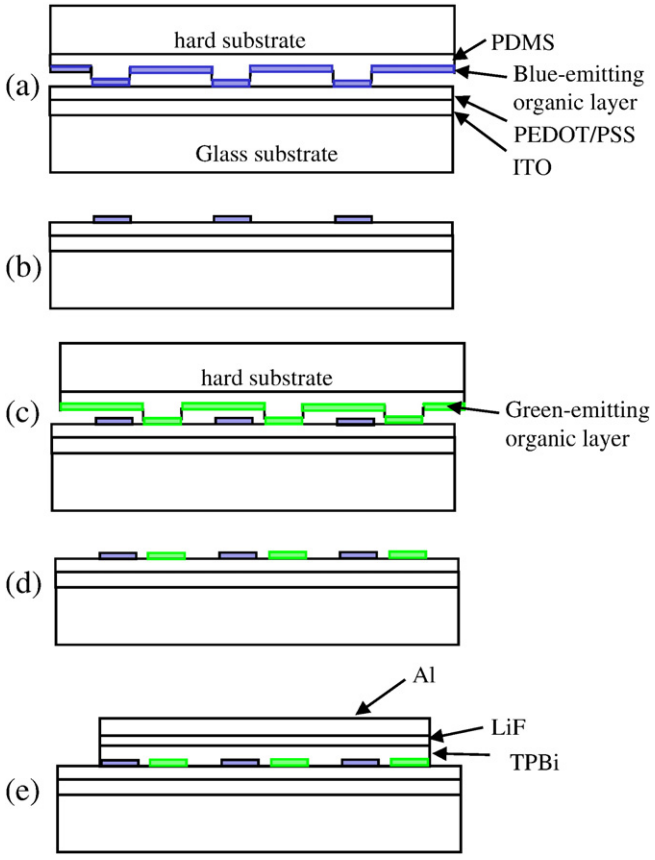

Fig. 1. Procedure for fabricating OLEDs with multiple emitting layers. (a) PDMS elastomer stamp coated with F8 for the blue-emitting layer is put on a glass substrate with ITO and PEDOT:PSS thin films. (b) PDMS elastomer stamp is removed from the substrate. (c) PDMS elastomer stamp coated with F8BT for the green-emitting layer is put on the substrate with alignment. (d) PDMS elastomer stamp is removed from the substrate. (e) TPBI, LiF, and Al thin films are sequentially stacked on the substrate. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

of noncontact regions. The height and widths of the PDMS steps were 3 μm and 50–2000 μm, respectively. Then, we spin-coated a toluene solution of poly(9,9-dioctylfluorene) (F8) as a blue-emitting layer on the PDMS. The concentration of F8 was 1 wt.%. Next, the PDMS elastomer stamp coated with F8 was put on the glass substrate covered with indium tin oxide (ITO) as an anode layer and PEDOT:PSS thin films (60 nm) as a hole-injection layer (Fig. 1a). The assembly of the PDMS elastomer stamp and the substrate was baked on a hot plate at 40°C for 20 min to enhance adhesion of the patterned F8 thin film to the substrate. Then, the PDMS elastomer stamp was removed from the substrate, leaving the F8 patterns for the blue-emitting layer on the PEDOT:PSS surface (Fig. 1b). Next, we spin-coated a toluene solution of poly(9,9-dioctylfluorene-benzothiadiazole) (F8BT) as a green-emitting layer on the PDMS. The concentration of F8BT was 1 wt.%. Then, the PDMS elastomer stamp coated with F8BT was put on the above-mentioned substrate with the alignment shown in Fig. 1c. Next, we fabricated the F8BT patterns for the green-emitting layer as well as those for the blue-emitting layer (Fig. 1d). After we fabricated the emitting layers, we annealed the substrate at 190°C. The glass transition temperatures for F8 and F8BT were 150–160°C. We improved contact with the PEDOT:PSS thin films of the underlayer by annealing at higher temperature than the glass transition temperature. Finally, 1,3,5-tris(N-phenylbenzimidazole-2-yl)benzene (TPBI) (40 nm) as an electron transport layer, and lithium fluoride (LiF) (2 nm) and aluminum (Al) (50 nm) thin films as cathode layers were sequentially stacked on the polyfluorene thin films using vapor deposition (Fig. 1e).

Electric characteristics of the fabricated OLEDs were measured with an electrometer (Keithley 2400 source/measure unit) in constant voltage mode with a step of 0.5 V and a delay time of 1 s between measurements. At the same time, the brightness was measured using a luminance meter (Topcon BM-9). Photoluminescence was measured with a 300 W high pressure Xe-lamp as an excitation source. All measurements were performed at room temperature in air without sample encapsulation.

3. Results and discussions

3.1. Micropatterning of emitting layers by μCP and fabrication of OLEDs

Fig. 2a shows the photoluminescent image of the F8 thin films fabricated by μCP. The 50-μm-wide micropatterns of the F8 thin films were clearly observed. The thickness of the F8 films was approximately 50 nm. Fig. 2b shows the electroluminescent image of the blue OLEDs with the patterned F8 thin films as emitting layers. We operated the OLEDs at 11 V bias voltage. The pixel size is 400 μm by 2000 μm. We observed strong electroluminescence (EL) in the fabricated devices with the patterned F8 thin films. EL spectra of the devices were measured with the Darsa Pro 5000 diode array analyze system. We confirmed that the illumination-wavelength was around 430 nm from the EL spectra, although the data are not presented here. One of the features of our μCP method is that we transfer dried and uniform F8 thin films onto a substrate. We measured the surface free energy from the contact angle of the solvent on the PDMS: 112° in water and 88° in diiodomethane (Kyowa Interface Science, DropMaster500). The surface free energy of PDMS was extremely low ($\gamma = 14\ \mathrm{mJ/m^2}$) and both toluene and F8 in the solution were chemically stable against the PDMS. The contact angle of toluene

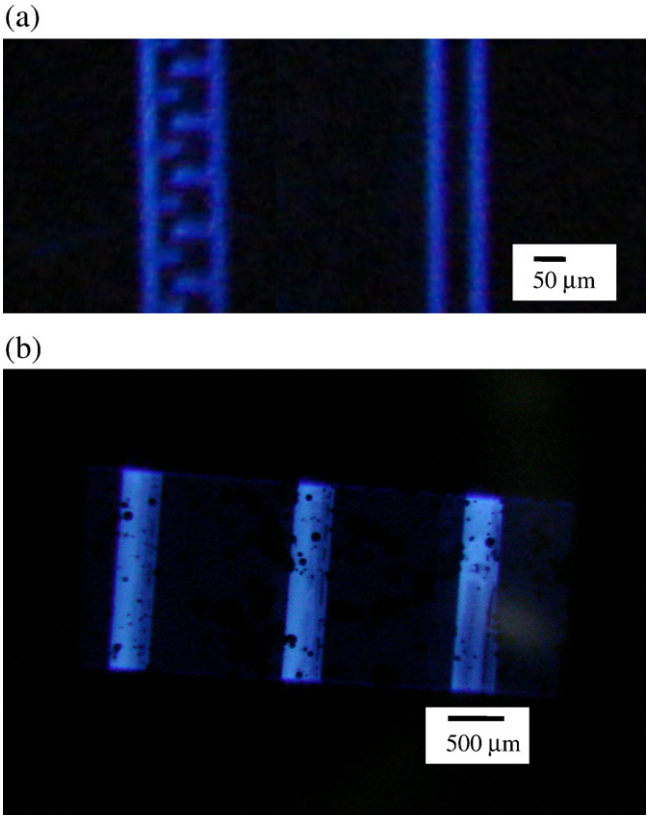

Fig. 2. (a) Photoluminescent image of the F8 thin films fabricated using μCP (50 μm lines in width). (b) Electroluminescent image of the blue OLEDs with the patterned F8 thin films as emitting layers (pixel size of 400 μm × 2000 μm).