Recent Advances in Research and Development of Microfluidic Organic Light-Emitting Devices

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Liquid organic semiconductors (LOSs) have been an attractive class of functional materials for next generation organic electronic devices. In 2009, a liquid organic light-emitting diode (Liquid OLED), which consists of LOS in the active layer, was proposed by Xu and Adachi. Although several papers have reported on an improvement in device performance, from the viewpoint of the device architecture, there are challenges associated with multi-color electroluminescence (EL) emissions. In order to integrate multiple individual liquid OLEDs on one substrate, we have developed multi-color microfluidic OLEDs which have single-μm-thick microchannels sandwiched between two electrodes. This paper presents a brief overview of the authors’ own recent progress on the microfluidic OLED technologies, including fabrication methodology for electro-microfluidic devices and demonstration of multi- and white-color EL emissions using pyrene-based LOSs. We believe that the proposed microfluidic OLEDs can be promising for novel liquid-based device applications.

Keywords: Microfluidic OLED, Microfluidic WOLED, Liquid OLED, Liquid organic semiconductor

1. Introduction

Organic light-emitting diodes (OLEDs) have been widely studied [1,2] since Tang and VanSlyke reported the first thin-film OLED in 1987 [3]. Currently, OLED display and lighting, which have several advantages in self-emission, wide view-angle, light weight, and fast response time, have reached the stage of commercialization. Typical architectures of the standard OLEDs are composed of the multi-layered solid-state organic semiconductor films sandwiched between two electrodes. In the case of OLED display application, red, green, blue, and white (RGBW) emitting layers have been precisely formed on one substrate using a wide range of patterning technologies such as the vacuum deposition through a shadow mask [4], screen printing [5], gravure printing [6], and ink-jet printing [7]. White EL emissions, which require a broad range of emission spectrum, have been obtained by employing appropriate emitting layer architectures, including stacked multilayers [8], blended-layers based on the host-guest system [9], and striped-layers [10].

Recently, solvent-free organic fluids such as liquid organic semiconductors (LOSs) have attracted great interest for their wide range of applications in next-generation organic electronic devices [11-13]. In 2009, Xu and Adachi proposed a liquid OLED consisting of LOS as the emitting layer [14]. The use of liquid emitting layers is expected to be potential benefits for
offering flexibility in device structure because liquid materials can easily change their shape. In addition, the LOS-based emitting layer is not vaporized during constant voltage application. Although the device performances have been improved [15,16], from the viewpoint of device structure, there are technical challenges associated with multi-color light emissions on one substrate. In the present technology, liquid OLEDs are simply fabricated by sandwiching a single liquid emitter between two electrode-patterned glass substrates. Therefore, development of the integration methodology for multiple liquid OLEDs on a flexible substrate is an important step for novel liquid-based display applications.

During the past few decades, microfluidic devices, which are also called lab-on-chips, have become powerful tools for biological and chemical analysis because of their significant advantages on fast chemical reactions and lower sample consumption [17]. The μm-scale fluidic channels and chambers are precisely fabricated in several materials such as silicon, glass, and polymer substrates using microelectro mechanical systems (MEMS) technology. Many research groups reported on the fabrication methodology for microchannel structures with the embedded electrodes [18,19]. Therefore, MEMS-based electro-microfluidic technology can become an attractive candidate for future flexible liquid-based display devices which consist of high-resolution liquid emitter patterns.

Toward next-generation display, our research group has proposed multi-color microfluidic OLEDs that combined liquid OLEDs with electro-microfluidic devices [20-26]. The concept of the microfluidic OLED display is shown in Fig. 1. In order to obtain the individual multi-color emitting layers on one substrate, LOS-based emitters are injected into the single-μm-thick microchannels which are sandwiched between the anodes and cathodes. When a direct current (DC) voltage is applied to the target light-emitting pixels, the holes and electrons are injected into LOSs from the anode and cathode surfaces, respectively. Consequently, electroluminescence (EL) is generated by the recombination of the holes and electrons. White light emission that widely covers the visible light wavelength is produced by the simultaneous greenish-blue and yellow EL emissions.

This paper describes an overview of the recent progress in the microfluidic OLED technology. The following topics are given: Fabrication methodologies for single-μm-thick electro-microfluidic devices; Multi-color EL emissions with pyrene-based LOS; White color EL emission from the integrated greenish-blue and yellow emitting layers; Flexible microfluidic OLED sheet and ribbons. We hoped that our microfluidic OLED technology can contribute the development of not only liquid-based display, but also several research fields.

2. Single-μm-thick-electro-microfluidic device

In this section, we describe the fabrication methodology for the microfluidic OLEDs. In order to integrate individual multiple liquid OLEDs on one substrate, we fabricated single-μm-thick electro-microfluidic devices using MEMS process and heterogeneous bonding technology through the use of amine- and epoxy-terminated self-assembled monolayers (SAMs) [20-24].

Figure 2 shows the design of a prototype microfluidic OLED that consists of a 3 x 3 array of light-emitting pixel in SU-8-based microchannels. Indium tin oxide (ITO) anodes and cathodes are formed on glass and polyethylene naphthalate (PEN) substrates, respectively, and 1000 to 1500 wide microchannels are sandwiched between the anodes and cathodes. Liquid emitting layers are obtained by injecting fresh LOSs into the
microchannels from the inlet holes formed on the cathode substrate, while the used emitters are collected from the outlet holes.

The fabrication process of the microfluidic OLED is shown in Fig. 3. The detailed information could be found in our previous work [20-24]. The ITO-coated glass and PEN substrates were used as the anode and cathode substrates, respectively (Fig. 3 (a) and (d)). The electrode patterns were obtained using photolithography and wet etching with an aqua regia solution (Fig. 3 (b) and (e)). The inlet and outlet holes were mechanically formed on the cathode substrate (Fig. 3 (f)). Single-μm-thick SU-8-based microchannel structures were formed on the anode substrate using photolithography process (Fig. 3 (c)). Subsequently, according to the heterogeneous bonding technique reported by Tang and Lee [27], the anode and cathode substrates were bonded using epoxy- and amine-terminated SAMs. 3-Glycidoxypropyltrimethoxysilane (GOPTS) and 3-aminopropyltriethoxysilane (APTES) solutions were used for the anode and cathode substrates, respectively. In the case of the anode substrate, ITO surfaces were covered by the sacrificial resist in order to prevent chemical reaction between the ITO anode and cathode during the bonding process. After the surface treatments were carried out using vacuum ultraviolet irradiation in the presence of oxygen gas (VUV/O3), the anode and cathode substrates were modified with GOPTS and APTES, respectively (Fig. 3 (g) and (h)). The unbound APTES and GOPTS molecules and the sacrificial resist were removed by rinsing the substrates with organic solvents. Finally, the anode and cathode substrates were bonded under a contact pressure of 1.5 MPa at 140 °C for 5 min (Fig. 3 (i)).

The ITO and APTES-modified ITO surfaces were analyzed using a photoemission yield spectroscopy in air (Riken Keiki, Co.,Ltd., AC-2), and the work functions of the anode and the cathode embedded in the fabricated electro-microfluidic device were estimated to be 4.77 eV and 4.55 eV, respectively [23]. APTES modification can be useful for reducing the work function because the amine groups in the APTES-SAM are electron donating in nature [28].

3. On-demand multi-color microfluidic OLEDs

This section presents the performance of the fabricated electro-microfluidic device (described in Fig. 2. Design of a prototype microfluidic OLED that consists of single-μm-thick SU-8 microchannels sandwiched between ITO anodes and cathodes.

Fig. 2. Design of a prototype microfluidic OLED that consists of single-μm-thick SU-8 microchannels sandwiched between ITO anodes and cathodes.

Fig. 3. Fabrication process of the microfluidic OLEDs. The anode and cathode substrates are separately fabricated and then bonded using the heterogeneous bonding techniques.
in section 2) using LOS-based emitters. In 2015, we used a pyrene-based LOS, 1-pyrenebutyric acid 2-ethylhexyl ester (PLQ), not only as the greenish-blue liquid emitter, but also as the liquid host [23]. The pyrene derivatives have been widely studied for blue emissive materials of the solid-state OLEDs [29].

Chemical structures of PLQ and guest dopants are shown in Fig. 4 (a). The HOMO and LUMO levels of PLQ are located at 5.8 eV and 2.6 eV [16]. 5,6,11,12-Tetraphenyltetracene (rubrene) and tetraphenyldibenzo-periflanthene (DBP), which have been used as the emitting layers of the solid-state OLEDs, were selected as yellow and red guest dopants. For preparing the liquid emitters, both PLQ and guest emitter were dissolved and mixed in dichloromethane (CH2Cl2) solution, and then CH2Cl2 was only evaporated in a vacuum oven at 80 °C for 5 h [23]. Here, 2 wt% rubrene, and 0.4 wt% DBP were doped into the host PLQ. In addition, 0.25 wt% tributylmethylphosphonium bis(trifluoromethanesulfonyl)imide (TMP-TFSI) was also doped into the liquid emitters to enhance carrier injection [15].

Figure 4 (b) shows the PL spectrum of the host PLQ and the absorption spectra of PLQ, rubrene, and DBP. It can be seen that PLQ has a strong UV absorption feature, and the PL spectrum of PLQ has spectral overlaps with the absorption spectra of the guest emitters. The multi-color liquid emitting layers were found to be formed on-demand by injecting the prepared liquid emitters into the microchannels (inset of Fig. 4 (c)). For evaluating the PL spectra of the prepared liquid emitters, 365-nm UV light was used for exciting only the host PLQ. Rubrene-doped PLQ and DBP-doped PLQ showed yellow and red PL spectra, respectively, under 365-nm UV light irradiation, as shown in Fig. 4 (c). This indicates that Förster energy transfer can take place effectively from the host PLQ to rubrene and DBP due to the spectral overlap between the host PL spectrum and the guest absorption spectra.

When a DC voltage was applied between the anodes and cathodes, the 6-µm-thick microfluidic OLED with PLQ, rubrene-doped PLQ, and DBP-doped PLQ successfully exhibited multi-color EL emissions (Fig. 5). The target light-emitting pixels are simply controlled by passive matrix addressing. In the case of the host-guest system, the HOMO and LUMO levels of rubrene and DBP are reported to be within the HOMO-LUMO gap of the host PLQ [30], which suggests that electrons and holes were trapped by the guest emitters, and therefore the excitons were generated by the direct recombination as well as the energy transfers from the host PLQ [31]. From the EL demonstrations, PLQ can be useful as the liquid host as well as the greenish-blue emitter.

The luminance of the 6-µm-thick microfluidic OLED with PLQ was measured to be 26.0 cd/m² at 61 V [23]. In comparison with state-of-the-art solid-state OLEDs, the performance of our microfluidic OLED is still in a research stage. For improving the EL performance, we have investigated the optimized device architecture. We also demonstrated that the microfluidic OLED has unique luminescence recovery characteristics [23]. The degraded emitting layer was simply replaced by reinjecting fresh liquid emitter into the target microchannels. Pure red, green, and blue liquid emitters are required for full-color display applications. It was found that 5,12-diphenyltetracene (DPT)-doped PLQ can be used as a green liquid emitter [23].

On the other hand, the development of a wide bandgap LOS-based host materials is important step in order to obtain deep-blue emissions. Currently, our research group has synthesized a novel naphthalene-based LOS (1-naphthalene-acetic acid 2-ethylhexyl ester (NLQ)) [26]. Blue EL emission was demonstrated from the NLO-based emitting layer doped with 9,10-diphenylanthracene which is well-known as blue fluorescent material.

Recently, several researchers have focused on development of liquid-based liquid emitting devices using not only LOSs, but also electrochemiluminescence (ECL) solutions [32-34]. ECL is a light-emitting phenomenon generated by electrochemical reactions. The ECL solution typically consists of the emissive materials dissolved in organic solvents. Our electro-microfluidic device can exhibit multi-color ECL emissions of fluorescence materials and thermally activated delayed fluorescence (TADF) materials as well as EL emissions of the LOS-based emitting layers [22]. In the chemical and biological fields, the use of OLEDs has been reported as excitation sources for fluorescent detection systems. Currently, we have studied to apply the electro-microfluidic devices as the on-demand EL and ECL excitation.
We believe that on-demand multi-color microfluidic OLED using the host PLQ can contribute the development of not only liquid-based display, but also the chemical and biological fields.

4. Microfluidic WOLED technology

In this section, we describe our recent progress on the microfluidic WOLED that exhibit white EL emission via simultaneous greenish-blue and yellow emissions. In 2015, we fabricated the integrated sub-100-μm-wide microchannels sandwiched between common transparent electrodes in order to obtain white light emission that widely covers the visible light wavelength [24].

Figure 6 (a) shows the photograph image of a prototype 6-μm-thick microfluidic WOLED which was fabricated in accordance with the fabrication methodology for the electro- microfluidic devices (described in section 2). The SU-8-based microchannel widths were designed to be 60 μm, while the space distance between the microchannels was 40 μm. Here, PLQ was used as the greenish-blue liquid emitter, while 2,8-di-tert-butyl-5,11-bis(4-tert-butylphenyl)-6,12-diphenyltetracene (TBRb) was chosen as a yellow guest dopant [24]. PLQ and 2 wt% TBRb-doped PLQ were injected alternately into the microchannels sandwiched between the ITO anode and cathode.

The fabricated microfluidic WOLED with PLQ and TBRb-doped PLQ exhibited a broad spectrum ranging from 420 nm to 750 nm, as shown in Fig. 6 (b). The obtained EL spectrum from the microfluidic WOLED is in good agreement with the synthetic EL spectrum of the 1000-μm-wide electro-microfluidic device with PLQ and TBRb-doped PLQ under the same driving voltage [24]. Therefore, the excitons of greenish-blue and yellow emitters were produced from the integrated 60-μm-wide microchannels in
the same way as the 1000-μm-wide microchannels. It is found that the microfluidic WOLED with PLQ and TBRb-doped PLQ shows the Commission Internationale de l’Éclairage (CIE) coordinates of (0.40, 0.42) which is within the white region and nearly corresponds to warm-white (Fig. 6 (c)). We have studied that white balance of our microfluidic WOLED can be simply tuned by varying microchannel-width ratios for PLQ and TBRb-doped PLQ [24].

5. Flexible microfluidic OLED technology

This section presents the flexible microfluidic OLEDs that have flexible microchannel structures sandwiched between the ITO anode and cathode [22]. The use of liquid emitters is expected to provide flexibility in display architecture. In addition, the emitting layers of the microfluidic OLEDs are simply formed by injecting liquid emitters into the microchannels without a vacuum process, which enables the realization of large-area display applications. However, it is difficult for the glass-based microfluidic OLEDs to obtain flexible emitting layer structures. Therefore, we used the ITO-coated polyethylene terephthalate (PET) films as both the anode and cathode substrates. Furthermore, toward future large-area display, a belt-transfer exposure technique was used for patterning the SU-8 microchannels on the flexible substrate.

The fabrication process of the anode substrate is shown in Fig. 7. ITO anodes were formed on the PET substrate using screen printing with the resist ink and the wet etching with an aqua regia solution (Fig. 7 (a) and (b)). After the resist ink was removed with organic solvents, SU-8 was spin-coated on the substrate to obtain a 4.5-μm-thick layer (Fig. 7 (c) and (d)). The substrate was aligned with a film photomask and then exposed with UV lamp using the belt conveyor at the speed of 11.6 m/min.

Fig. 8 (a) shows photographic image of the fabricated flexible microfluidic OLED using the heterogeneous bonding technique (described in section 2). The flexible microfluidic OLEDs with PLQ exhibited greenish-blue EL emissions at the light-emitting pixels in a curved state (Fig. 8 (b)). Furthermore, similar current density-voltage (J-V) curves were confirmed in the flat and curved states (with a radius of 3 cm), as shown in Fig. 8 (c). This result indicates that in both states, holes and electrons were similarly injected into the emitting layer, and excitons were generated by their recombination. From J-V characteristics, it can be seen that the current density was proportional to the applied voltage up to 40 V in an Ohmic behavior ($J \propto V$) and then increased proportionally to the square of the voltage ($J \propto V^2$). This result is presumed to be the space charge limited current (SCLC) behavior [15].

Recently, we fabricated the microfluidic OLED ribbons that can be integrated into free-formable textile devices, as shown in Fig. 8 (d) [25]. We expect that the proposed flexible microfluidic OLEDs will be a highly promising technology for future unique flexible...
6. Conclusion

In this paper, we describe the fabrication methodology and the performance evaluations of the microfluidic OLEDs. LOSs are a potentially suitable material for novel flexible organic electronic device applications. The microfluidic OLEDs with the LOS-based emitting layers have already realized unique properties such as on-demand multi-color EL emissions and luminance recovery features. However, the research and development regarding device performances and LOS materials are still at early stage. Therefore, we have been investigating the device architectures and new molecular design strategies. We expect that the proposed microfluidic OLEDs are applicable for next-generation display.

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