Latest Progress of Solution-Process OLED Materials with Small Molecule Based Emission Layers

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ABSTRACT

Recent progress of materials and inks for the ink-jet printed OLED is reported. Newly developed HIL ink with reduced viscosity gives flat shape in pixels and is the best practice for high-resolution panel. Device performance is improved by new emitters with deep and sharp emission and durable skeleton.

1 Introduction

Inkjet-coated OLEDs are attractive for the manufacture of high-performance medium- and large-sized displays. In these days, all-printed OLEDs without vapor deposition ETLs is also developed. [1, 2] Mitsubishi Chemical Group (MCG) is actively developing HIL/HTL/EML materials and inks applicable to soluble OLEDs.

To realize soluble OLEDs, HIL/HTLs must be resistant to the solvent of the ink used for the application of the next layer. We have been continuously developing charge transport polymers applicable to soluble OLEDs and have a library of polymers with a wide range of ionization potentials and hole mobilities for printed organic electronic devices. [3]

The p-doping technique is often used in OLEDs to help hole injection from the anode. The p-dopant in our HIL ink has excellent thermal and chemical stability, solubility in organic solvents, and high doping ability [4]. However, in printed OLEDs, p-dopants may diffuse into adjacent layers during baking. This diffused p-dopant has a negative impact on device characteristics. We have taken a unique approach to this diffusion problem.

OLED displays are expanding their applications, and further improvements in brightness, durability, and color gamut are required. Our emission layers contain emitter and host materials, all of which are small molecule materials. Since all these materials are small molecules, we can easily control the energy levels, charge balance, and other factors necessary for high brightness and durability. Improvement of emitter materials is still essential for higher brightness and color gamut. Emitter materials are required to have deep and narrow luminescence. Since the report of Hatakeyama et al. [5-7] polycyclic multiple resonance (MR) thermally activated delayed fluorescence (TADF) emitters have attracted much attention because of their narrow emission.

In this paper, we report and discuss the development of our printed OLED materials and inks and the recent progress of device performance at MCG.

2 Development and Result

2.1 HIL/HTL Polymer and Ink

Materials used for HIL/HTL of printed OLEDs are better suited for polymers than small molecules because they need to be insoluble in the solvents used in the inks in the upper layers.

Fig. 1 shows typical fabrication process of the printed OLEDs. To insolubilize, making HIL and HTL needs to be heated by 200°C or higher. EML film, on the other hand, does not need to be heated at such high temperatures. ETL and cathode are formed by evaporation under vacuum. For stable jetting in ink-jet process, it is important not to increase the viscosity, and therefore, it is required to reduce the average molecular weight of HIL/HTL polymer.

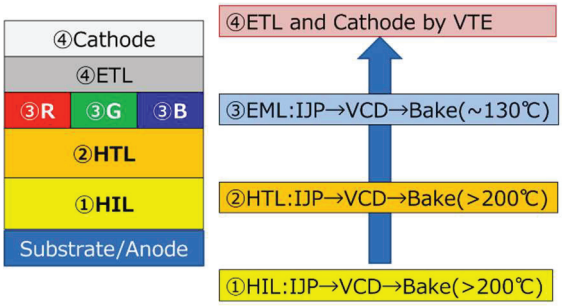

Fig. 1. Fabrication process

A new HIL material was developed and applied to the ink. As shown in Fig. 2, the newly developed HIL ink has a lower viscosity than the conventional standard ink, which is advantageous for inkjet application to pixels with higher resolution.

The uniformity of film thickness in the pixel banks was also examined. Two inks were printed on substrate with pixel bank structures by using Dimatix Material Printer (DMP2831). The thickness of the bank was 0.7um. The printed inks were dried in vacuum chamber under 1 Pa and annealed at 230 degrees Celsius for 30 minutes. We measured the film profile using stylus profiler (KOSAKA ET-200).

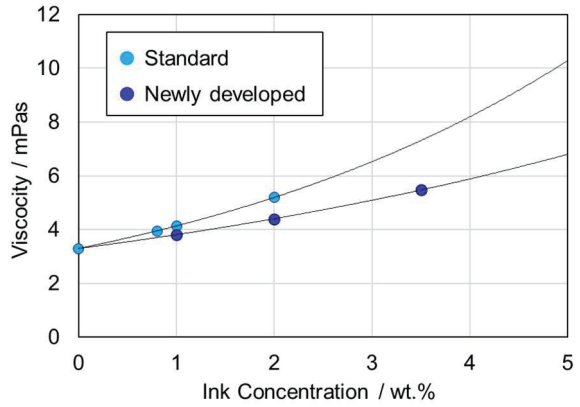

Fig. 2. Viscosity vs. Ink concentration

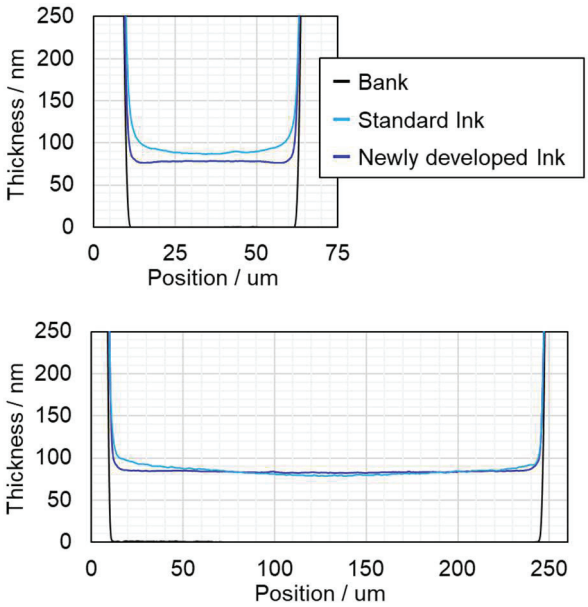

Fig. 3. Film uniformity of HIL inks pixel bank

As shown in Fig. 3, the newly developed ink has high uniformity in both the long and short axis directions within the pixel bank.

2.2 *p*-Dopant

In fabricating the printed OLEDs, the diffusion of *p*-dopant causes some issues. As shown in the Fig.4, the conventional *p*-dopant is diffused to the neighbor layers when baking at high temperature, resulting in worse device properties such as efficiency and lifetime. We have successfully designed and developed new *p*-dopants that do not diffuse while maintaining high doping strength.

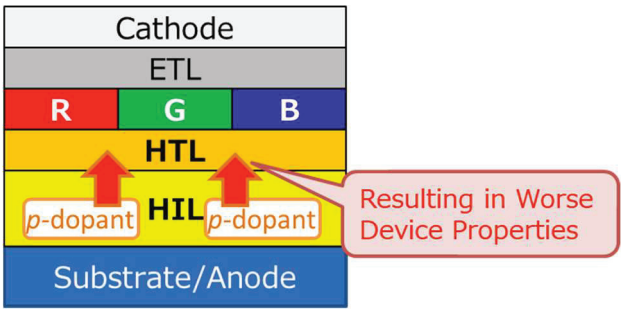

Fig. 4. Conventional *p*-dopant

The amount of *p*-dopant diffusion was measured by ToF-SIMS analysis. In devices using conventional *p*-dopants, the presence of *p*-dopants was confirmed not only in the HTL but also in the EML. On the other hand, in the device using our new *p*-dopants, there was no diffusion at all as in the case of forming HTL / EML by vapor evaporation. There was a strong negative correlation between the amount of *p*-dopant in the EML and the OLED device properties. The efficiency is improved by preventing the diffusion of *p*-dopants. The impact of this new technology on the lifetime was very significant, and it was confirmed that the lifetime was tripled by applying the no-diffusible *p*-dopant (Fig. 5).

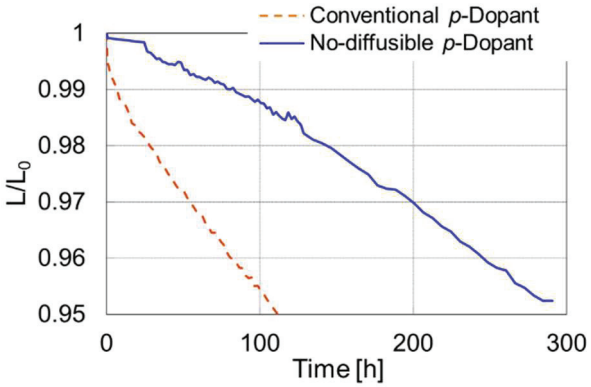

Fig. 5. Lifetime curve of OLEDs

2.3 Red Emitter

In order to realize a next generation display with a wide color gamut, RGB emitters are required to have sharp emission spectra. In the red region, the longer the emission wavelength, the more the quantum yield drops significantly according to the energy gap law. [8, 9] In addition, a red emitter with a broad spectrum has disadvantage in terms of efficiency because emission in the infrared region is wasted. Therefore, a deep-red emitter with a narrow FWHM is useful for both high efficiency and wide color gamut. Fig.6 shows the spectra of our newly developed skeletal red emitter and the conventional material.

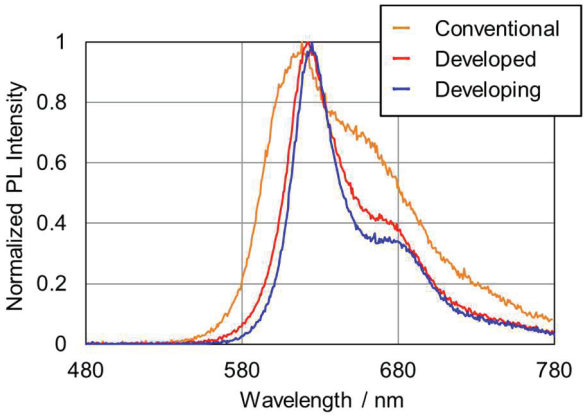

Fig. 6. Photoluminescence spectra

At IDW21 we reported a deep red emitter with newly developed skeleton. [10] We have successfully developed a new deeper red emitter with a narrower FWHM. Fig. 6 shows photoluminescent spectra of red emitters. The new red emitter makes it possible to achieve both high luminance and deep color coordinate of x=0.68 in CIE1931 in top emission device.

2.4 Design of EML with Narrower FWHM Emission

To achieve higher brightness and color gamut, we are developing emission layers with fluorescent emitters with narrower FWHM than conventional phosphorescent emitters. 75% of the triplet must be converted to a singlet in the emission layer to achieve higher efficiency with fluorescent emitters. In Fig.7, the energy transfer through the triplet-to-singlet conversion in the luminescent layer under development is schematically illustrated.

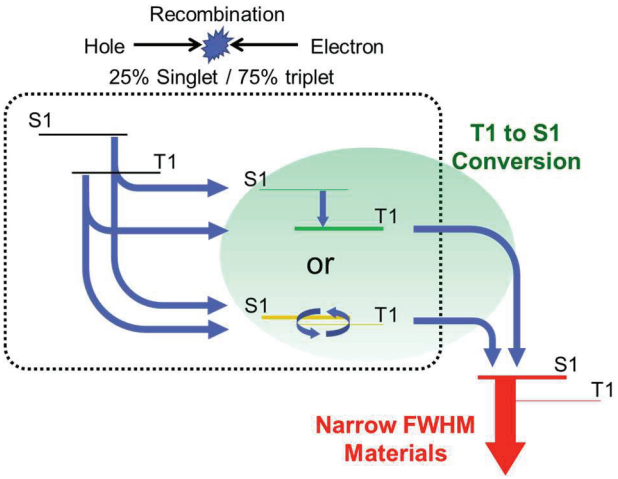

Fig. 7. Energy transfer scheme in small molecule based EML

To apply fluorescent emitters with full usage of excitons, the host material of the emitting layer is required to play three roles: (i) charge transport, (ii) energy transfer, and (iii) energy conversion. It is difficult to realize all three roles with a single material. Mixture of several materials with separate functions, such as the small molecule-based emission layer we are developing, can be a solution.

Fig. 8 shows EL spectra of bottom emission devices using developing and conventional emission layers with the following configuration: IZO (50 nm)/HIL (105 nm)/HTL (120 nm)/EML (70 nm)/ETL (20 nm)/Al (80 nm). The device using the developing emission layer shows a narrow emission with a FWHM of 36nm, which is narrower than the 64nm of the conventional emission layer. The chromaticity improved from (0.32, 0.65) to (0.28, 0.69) and the current efficiency improved by 8%.

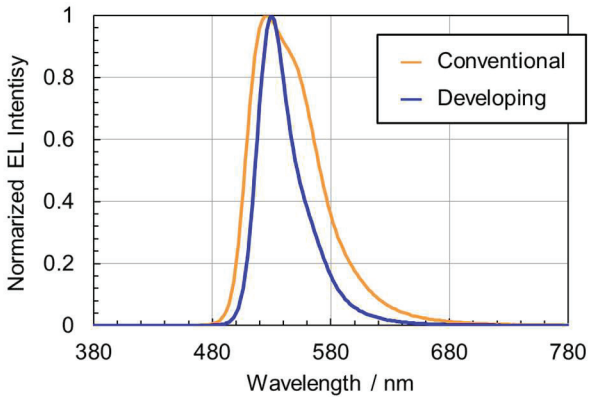

Fig. 8. EL spectra of bottom emission device

3 Summary

The typical performance of top emission devices obtained by combining our latest technologies described above is shown in Table 1.

Table1. Top-Emission Device Performance.

Color	Efficiency at 1000 cd m^{-2} [cd A^{-1}]	LT95 at 1000 cd m^{-2} [h]	CIE (x, y)
Red	47	30,000	(0.68, 0.32)
Red (New HIL)	52	30,000	(0.68, 0.32)
Green	113	25,000	(0.23, 0.73)

Our HIL/HTL polymer library has a wide range of ionization potential and hole mobility. These polymers have a low average molecular weight and a narrow molecular weight distribution, so stable jetting is possible even with high-concentration inks. Newly developed HIL material and ink gives the improved film uniformity and suitable for inkjet application to pixels with high resolution.

No-diffusible *p*-dopants were developed as a key

technology for improving device performances and stabilizing manufacturing of the printed OLEDs. Our *p*-dopants have a great effect on extending the lifetime of devices.

The newly developed deep-red emitter skeleton showed high PLQY and very narrow FWHM. Our new emitter gives not only higher efficiency and better color coordinate, but also better viewing angle dependence.

We are developing light-emitting layers utilizing fluorescent emitters to achieve higher brightness and wider color gamut. By efficient transfer of excitons generated in the emission layer to the emitter, devices with narrower line widths and higher brightness are expected to be realized.

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