Latest Technology of Ink Jet Printed OLEDs with Small Molecule Based Emission Layers

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ABSTRACT

We are accelerating the development of inks for the printed OLEDs. Small molecules including electron or hole transport type for EML and polymers with reduced the molecular weight for HIL/HTL have been developed as the best practice for high-resolution panels. Further, no-diffusible p-dopants and deep-red emitter have been developed.

1 Introduction

We are developing inks for HIL, HTL, and EML. In the printed OLEDs, HIL / HTL must be insoluble in the upper layer ink solvents. We have plenty of insolubilizable polymer libraries of a wide range of the properties to show a wide range of ionization potential (IP) and the desired hole mobility. Polymers have IPs around 5.1-5.3 eV, which is suitable for HIL, and IPs around 5.4-5.6 eV, is suitable for HTL. [1]

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. 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.

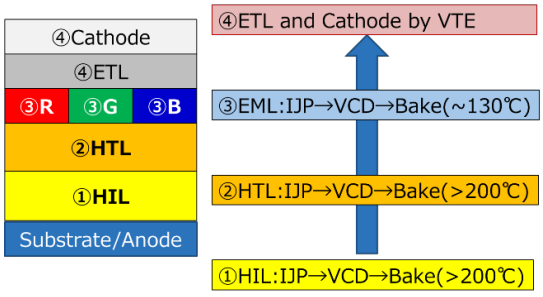

Fig.1 Fabrication Process

HIL ink contains *p*-dopant to help the hole injection from anode. The *p*-dopant system we developed has attributes like thermal and chemical stability, good solubility in organic solvents, and high doping strength. [2] However, in the printed OLEDs, *p*-dopant can be diffused to the adjacent layers at the baking process. The diffused *p*-dopant adversely affects the device properties. We have taken a unique approach to this diffusion issue.

We also have many types of small molecules that can be suitably used for the host materials of EML. Each small molecule has ability to inject and/or transport electron or hole charge, to generate and confine exciton. All small molecules also have qualified high solubility, low crystallinity, high thermal and electrical durability.

For emitter materials, technological progress in red is particularly required. Narrowing the full width at half maximum (FWHM) of red is effective for both high efficiency and wide color gamut. We found a new skeleton with a narrow spectral width.

Recently, research on all-printed OLEDs without vapor evaporation ETL has become active. [3] As shown in the fig.2, eliminating the vapor evaporation ETL is also important in terms of cathode connection. We have found that small molecule based EML is suitable for the ETL-free device structures.

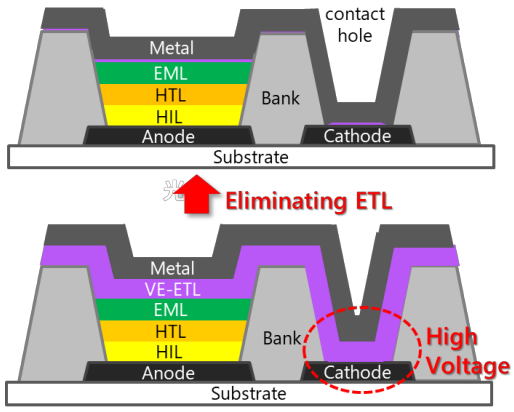

Fig.2 All-printed OLED

In this paper, our recent progress on HIL / HTL polymer, no-diffusible *p*-dopant, red emitter with narrow FWHM, carrier balance control of EML, and solvent parameter to improve film shape as key technologies for high-performance printed OLEDs is reported and discussed.

2 Development and Result

2.1 HIL / HTL Polymer

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. 3 shows viscosity vs. solid concentration of a small molecule ink and some polymer inks. In generally, sable ink jetting is difficult for high-viscosity inks, and lower-viscosity inks are required. Therefore, there is a limit to the concentration of the polymer inks. On the other hand, small molecule EML inks with low dependence of viscosity on concentration can be produced at a higher concentration than polymer inks. In particular, manifacturing high resolution displays requires higher density inks to prevent ink mixing at adjacent pixels. In particular, manifacturing high resolution displays requires higher density inks to prevent ink mixing at adjacent pixels. We succeeded in lowering the average molecular weight of the platform polymer by developing a new skeleton in which the hole mobility does not change even if the average molecular weight is lowered. Our new HIL / HTL polymers can provide high concentration inks while maintaining a favorable viscosity for ink-jet process.

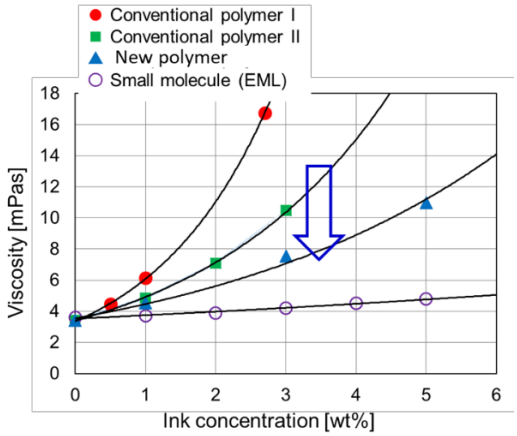

Fig. 3. Viscosity vs. ink concentration

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.

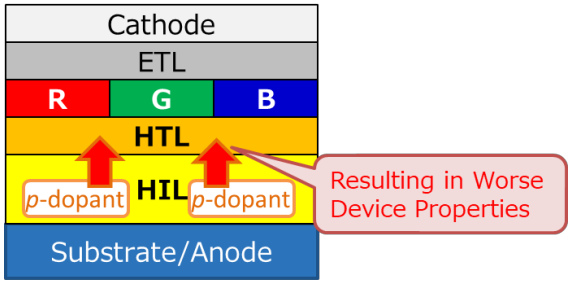

Fig. 4. Conventional *p*-dopant

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).

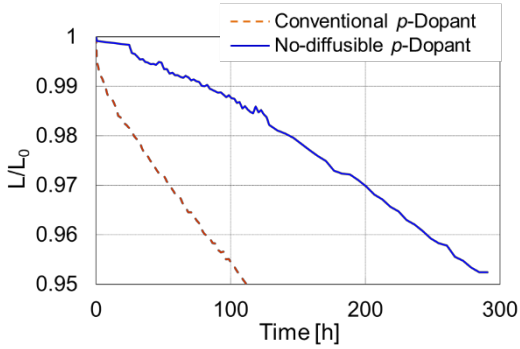

Fig. 5. Lifetime curve of OLEDs

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. [4] 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.

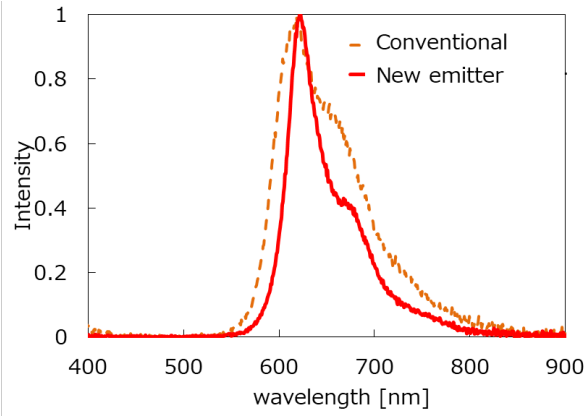

Fig. 6. Photoluminescence spectra

The luminescence properties were measured in a 1x10^-5 M toluene solution at an excitation wavelength of 380 nm. By this method, the PLQY of our new red emitter exhibited 0.79 at λ_{max} 621 nm and FWHM 44 nm. The PLQY of the conventional material was 0.80 at λ_{max} 615 nm and FWHM 90 nm. By applying a new skeleton, we have succeeded in lengthening the wavelength and narrowing the spectrum while maintaining a high quantum yield.

2.4 Carrier Balance Control

Our EML inks contain emitters, electron transport materials (e-host) and hole transport materials (h-host), all of which are small molecules. Therefore, we can control the carrier balance by changing the e/h host ratio according to the properties of the common layer such as anode, HIL / HTL, ETL, and cathode. Fig. 7 summarizes the OLED device characteristics when the e/h host ratio is changed. The devices rich in h-host had a longer lifetime and increasing e-host was effective in improving EQE.

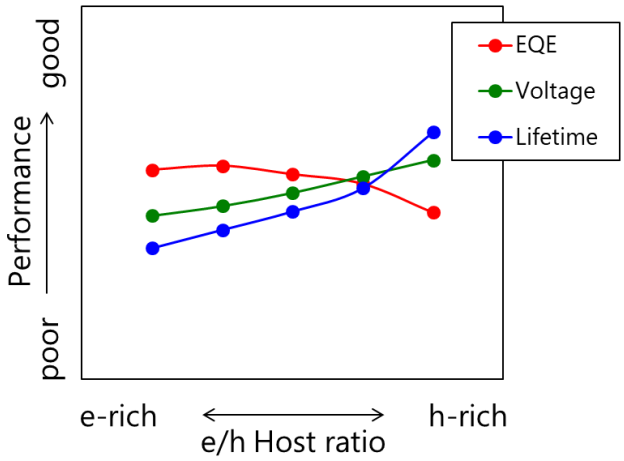

Fig. 7. Device performance vs. e/h host ratio

We compared the performance of the following OLED devices A and B. The results show that the e/h mixed host system is suitable for ETL-free device structures.
Device A: IZO(50)/ HIL(110)/ HTL(160)/ EML(80)/ Vaper evaporation ETL(20)/ Al(80) (unit: nm).
Device B: IZO(50)/ HIL(110)/ HTL(160)/ EML(100)/ NaF(3)/ Al(80) (unit: nm).

The HIL / HTL / EML for devices A and B were all formed using the same inks. In device A, an organic ETL was formed by vacuum evaporation at 20 nm. In device B, instead of eliminating the organic ETL, the EML was thickened by 20 nm to 100 nm. The efficiency of device B maintained 90% of device A. The lifetime of devices A and B was almost the same. It is considered that e-hosts included in our mixed host system improves compatibility with various cathodes.

2.5 Uniformity in Bank

To apply the OLED materials for displays, we need to dissolve the materials to the solvent and print it to the substrate by using an ink-jet printer or others. Furthermore, to separate red, green, and blue OLED finely, the substrate has pixels divided by the liquid-repelled wall, which is called bank. The OLED inks are usually printed in the pixels surrounded by the bank and dried to form the organic thin films. On the other hand, the flatness of organic thin films quite affects to the OLED performance, especially the current efficiency and EL spectrum. Therefore, the film uniformity in pixel is the key parameter for OLED display performance.

The film shape near the bank edge is very difficult to control since the structural parameter and surface condition of the bank edge region is quite different from the center region. The self-pinning at bank wall and ink flow by Laplace pressure are a quite key factor to determine the film shape near the bank edge.[5] These two phenomena make the film thickness near the bank edge higher. The self-pinning occurs at bank wall because of the bank shape, the change of surface energy, the change of ink viscosity, the change of contact angle, and so on. On the other hand, the ink-flow by Laplace-pressure occurs from the center region to the bank edge region because of the surface tension of the ink, the surface curvature of the ink, the self-pinning at the bank wall, and so on. The film shape near the bank edge is attributed to a lot of complex parameters, however we found that surface tension (ST), viscosity (VC), and vapor pressure (VP) of the solvent has a certain correlation to the film shape.

We prepared a few kinds of HIL ink, where the same HIL material dissolved at different solvent. By using Dimatix Material Printer (DMP2831), these inks were printed on the substrate with pixel bank structure. The thickness of the bank was 1.5um. The printed inks were dried in vacuum chamber under 1 Pa and annealed at 230 degrees Celsius for 20 minutes. We measured the film profile using stylus profiler (KOSAKA ET-200).

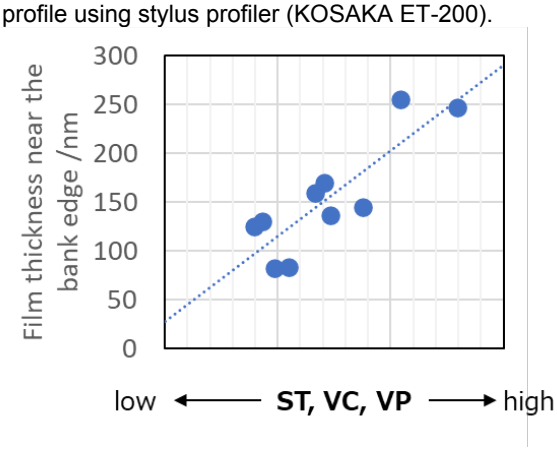

Fig. 8 Film thickness near the bank edge vs parameter relating to ST, VC, and VP

Fig. 8 shows the film thickness near the bank edge

dependent on the solvent parameter relating to surface tension, viscosity and vapor pressure. We have improved the HIL film profile by adjusting this parameter finely.

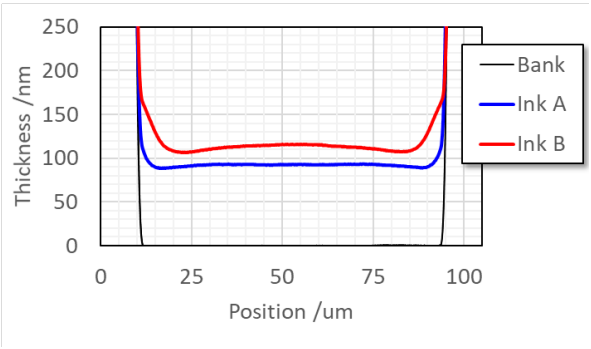

Fig. 9 HIL film profiles

Fig. 9 shows the HIL film profile formed using ink A and ink B. The solvent of ink A was adjusted finely to get the flat HIL film by using solvent parameter relating to ST, VC, and VP. On the other hand, the HIL film profile using ink B is almost flat at the center region, but the thickness near the bank edge is too high because the solvent parameter was not adjusted for film thickness.

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]	CIEx,y
Red	47	26,000	(0.67, 0.33)
Green	116	15,000	(0.26, 0.71)

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.

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 emitters are effective not only for high efficiency and wide color gamut, but also for reducing viewing angle dependence.

One of the advantages of the small molecule based EML is the ability to optionally mix three or more materials for carrier balance control in the devices. It was shown that this advantage is effective not only for improving OLED performances but also for compatibility with common layers and electrode structures.

The flatness of the organic film in the pixel is very important to get printed OLED panel with high performance. To gain good flatness, the film shape near the bank edge has to be controlled. Adjusting the solvent parameter achieved the good film shape near the bank edge, resulting in the good flatness of the organic film.

References

[1] K. Iida, K. Ishibashi, Y. Shoji, K. Nagayama, Y. Oshima, H. Gorohmaru, “Key technologies in soluble OLED materials,” Proc. IDW ’19, pp. 825-828 (2019).

[2] H. Seima, N. Haase, K. Scheible, H. Heil, E. Böhm, H. Buchholz and H. von Seggern, “Photoactivation of an ionic *p*-type dopant used in a triarylamine based hole transporting material for enhancing conductivity of solution processed films,” Synth. Met., Vol. 230, pp. 105-112 (2017).

[3] a) N. Aizawa, Y. Pu, M. Watanabe, T. Chiba, K. Ideta, N. Toyota, M, Igarashi, Y. Suzuri, H. Sasabe and J. Kido, “Solution-processed multilayer small-molecule light-emitting devices with high-efficiency white-light emission,” Nat. Commun. Issue 5, Article number 5756 (2014). b) T. Yamada, N. Akino, Y. Tsubata, D. Fukushima, S. Amamiya, and J. Sekihachi, “Latest Development of High-performance OLED Material Suitable for Printing,” J. SID, Vol. 48, No. 1, pp. 845-848 (2017).

[4] a) S. Okada, K. Okinaka, H. Iwawaki, M. Furugori, M. Hashimoto, T. Mukaide, J. Kamatani, D. Igawa, A. Tsuboyama, T. Takiguchi and K. Ueno, “Substituent effects of iridium complexes for highly efficient red OLEDs,” Dalton Trans., Issue 9, pp. 1583-1590 (2005). b) N. Sako, K. Iida, K. Ishibashi, Y. Shoji, K. Nagayama, Y. Oshima and Y. Bando, “Advanced Materials Development for Ink-Jet Printed OLEDs,” J. ICDT, Vol. 50, Issue 51, pp. 332-334 (2019).

[5] D. Fukushima, S. Tanaka, H. Kakimoto and T. Yamada, “Latest Development of Soluble OLED Material for Printed Display,” J. SID, Vol. 51, Issue 1, pp. 387-390 (2020).