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Super-Low-Refractive-Index Hole Transport Layers with Perfluororesin for High-Outcoupling-Efficiency OLEDs

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ABSTRACT

One of the promising techniques for enhancement of outcoupling efficiency of OLEDs is to lower the refractive index of charge transport layers. In this study, we effectively lower the refractive index of HTL used for OLEDs by co-depositing a perfluororesin, which is stably evaporable by usual thermal deposition. We achieve a low refractive index of a co-deposited HTL of 1.56 (at 550 nm) without deteriorating its electrical properties. Using the HTL, we also demonstrate a 1.22-fold enhancement of the outcoupling efficiency of a phosphorescent OLED.

1 Introduction

Since the internal quantum efficiency of OLEDs reached ~100% by using phosphorescent emitter or TADF materials, further improvement of external quantum efficiency (EQE) of OLEDs has relied on the enhancement of outcoupling efficiency. It is well-known that there are many conventional techniques for outcoupling enhancement: for example, the use of a microlens array, a high-refractive-index substrate, and a dielectric multilayer mirror. However, because most existing techniques control the light propagation in OLEDs not by internal organic semiconductor layers but by external optical elements, they inevitably lead to the increase of process cost for device fabrication.

To develop a new technique for outcoupling enhancement with light propagation control by organic semiconductor layers, we have tried since 2012 the technique of co-deposition of perfluoro materials, which substantially decreases the refractive index of charge transport layers used for OLEDs [1]. Furthermore, we have investigated the electrical properties of the low-refractive-index co-deposited films with a hole transport material and a perfluororesin and applied the films to OLEDs for outcoupling enhancement. We found that the electrical properties are not deteriorated by the co-deposition of the perfluororesin and demonstrated the enhancement of outcoupling efficiency of an OLED [2]. This technique made it possible to lower the refractive index of HTL more substantially than the selection of existing low-refractive-index OLED materials [3]. However, the perfluororesin used in the above study was not stably evaporable by thermal vacuum deposition (chemical decomposition occurs), and the detail of the properties of the low-refractive-index co-deposited films has not yet been clarified.

In this study, we synthesized and adopted a perfluororesin, PBVE (Fig. 1) with a small molecular weight (M_w = 10,700), which has a high amorphousness and a low refractive index (1.34 at 550 nm). This PBVE can be stably evaporable by conventional thermal vacuum deposition without chemical decomposition. By co-depositing PBVE with a hole transport material 2-TNATA (Fig. 1) with a volume ratio of 50:50, we effectively lower the refractive index of the HTL to 1.56 (at 550 nm) without deteriorating its electrical property. We also demonstrate a 1.22-fold enhancement of the outcoupling efficiency of a phosphorescent OLED.

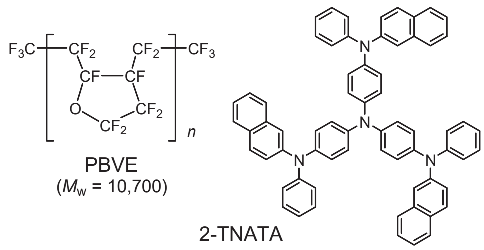

Fig. 1 Chemical structure of PBVE and 2-TNATA.

2 Results and discussion

Fig. 2(a) shows the ordinary and extraordinary refractive indices of neat and co-deposited films of 2-TNATA and PBVE with different vol% of PBVE. With increasing vol% of PBVE, the refractive indices were effectively lowered. With 50 vol% of PBVE, the refractive index is almost isotropic and reaches 1.56 (at 550 nm).

Fig. 2(b) shows the *J-E* characteristics of hole only devices using the co-deposited films with different vol% of PBVE: ITO/2-TNATA:PBVE (100 nm)/Al (100 nm). Even though the insulating material PBVE was co-deposited with 2-TNATA, the electrical properties of the co-deposited films with 25 and 50 vol% of PBVE were not deteriorated compared to that of the neat 2-TNATA film (0 vol%). This result indicates that we can apply these low-refractive-index co-deposited films to OLEDs without deteriorating their electrical properties.

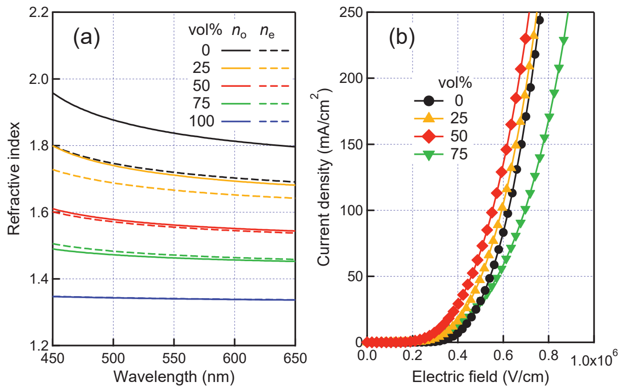

Fig. 2 (a) Ordinary and extraordinary refractive indices and (b) *J-E* characteristics of the 2-TNATA: PBVE neat and co-deposited films.

To explain why the electrical properties of the 2-TNATA: PBVE co-deposited films were not deteriorated, we assumed that co-deposition of 2-TNATA and PBVE causes phase separation. To investigate it, we measured the SAXS profiles of the 2-TNATA:PBVE neat and co-deposited films as shown in Fig. 3. The result shows that the co-deposited films have a periodic structure of electron density with $2\pi/q$ ~ 10 nm, which indicates the formation of the structures of nano-sized phase separation between 2-TNATA and PBVE. Furthermore, as seen in the cross-sectional images of the 50-vol% co-deposited films (see the inset of Fig. 3), we observed pillar-like structures vertical to the substrate surface. The formation of this well-organized pillar-like structures contributes to the retention of the paths of hole transport in the co-deposited films.

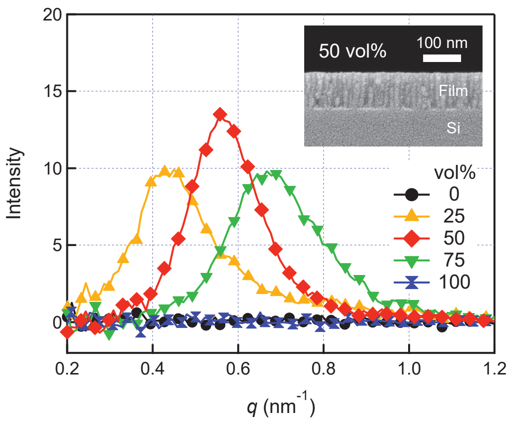

Fig. 3 SAXS profiles of the 2-TNATA:PBVE neat and co-deposited films. Inset: Cross-sectional SEM image of the 50-vol% film.

Fig. 4 shows the EQEs of the two phosphorescent devices A (reference) and B (with low-refractive-index HTL). The structures are A: glass/ITO (75 nm)/2-TNATA:HAT-CN (1 wt%, 20 nm)/2-TNATA (40 nm)/α-NPD (10 nm)/CBP:Ir(ppy)$_2$(acac) (8 wt%, 15 nm)/TPBi (65 nm)/LiF(1 nm)/Al (100 nm), and B: glass/ITO (75 nm)/2-TNATA:PBVE (50 vol%, 70 nm)/α-NPD (10 nm)/CBP:Ir(ppy)$_2$(acac) (8 wt%, 15 nm)/TPBi (60 nm)/LiF (1 nm)/Al (100 nm), where the thicknesses of HTL and ETL were optimized based on the optical simulations using *setfos* software. The *J-V* characteristics of the two devices are similar (see the inset of Fig. 4). In contrast, the EQE of the device B showed a 1.22-fold enhancement of EQE compared to that of the device A, demonstrating the effect of the low-refractive-index HTL as also confirmed by optical simulation.

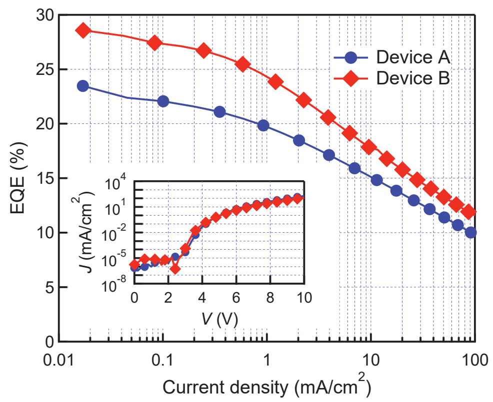

Fig. 4 EQE of the OLED devices A and B. Inset: Their *J-V* characteristics.

3 Conclusions

By co-depositing a perfluororesin PBVE with 2-TNATA (50 vol%), we actively lowered the refractive index of the films to 1.56 (at 550 nm) without deteriorating their electrical properties. Using this co-deposited film, a 1.22-fold outcoupling enhancement of a phosphorescent OLED is demonstrated.

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