Blue OLEDs Fabricated by Close-Space Sublimation

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Abstract

A close-space sublimation process (CSS) was used for the deposition of blue emitting layers (EMLs) with a host-dopant composition. Blue EMLs with a uniform dopant distribution were obtained using a pair of host and dopant with matching evaporation characteristics. Blue OLED devices fabricated via CSS with improved performance were demonstrated.

Author Keywords

Blue OLED; close-space sublimation; evaporation temperature; doping profile.

1. Introduction

Vacuum thermal evaporation (VTE) is a standard process for manufacturing full-color, high-resolution organic light emitting diode (OLED) displays, such as those used for smartphone screens. In this process, a fine metal mask (FMM) is needed to produce an array of pixels with side-by-side RGB subpixel arrangement. The pixel density achievable is around 600 ppi (pixel per inch), which is limited by the finite thickness of the FMM and the oblique shadowing effect caused by the line-of-sight nature of VTE. Furthermore, material utilization is low due to the long throw distance associated with VTE. Close-space sublimation (CSS), which is an alternative version of VTE, allows the transfer of an organic film from a donor substrate to a receiver substrate held in close proximity. Thus, CSS ensures much higher material utilization along with a much faster deposition rate compared to VTE. Furthermore, recent studies have showed that CSS, due to its conformal deposition characteristics, can significantly lower the shadowing effect associated with VTE when used with FMM.^[1-3]

A critical issue of the CSS is the deposition of the emitter laver (EML), which typically has a host-dopant composition. To ensure a uniform concentration of dopant molecules in the host matrix throughout the thickness of the film, the dopant and host molecules must co-evaporate at a fixed rate ratio as they are transferred from the donor substrate to the receiver substrate. This condition is difficult to meet for blue EMLs, because most common hydrocarbon molecules used as the host tend to evaporate at a lower temperature compared to the amine dopants due to their large difference in molecular weight. Hence, these hosts and dopants may evaporate at significantly different rates at a given temperature, resulting in partial segregation of the host and dopant molecules in the CSS-deposited EML. In this study, we evaluated a series of amine molecules as dopant with a prototypical hydrocarbon as host. We were able to identify a host-dopant pair that full-fills the conditions of co-evaporation in producing a uniformly doped EML with no apparent segregation throughout the layer thickness.

2. Experiments and Results

Blue EML materials selected for this study are: BH (9-(*naphthae-ne-l-yl*)-10-(4-(*naphthalen-2-yl*)phenyl)anthracene) as host; BD1 (*N*,*N*,*N'*,*N'-tetra-p-tolylpyrene-1*,6-diamine), BD2 (*N*,*N'-bis*(dib-

enzo[*b*,*d*]*furan*-4-*yl*)-*N*,*N*'-*diphenylpyrene*-1,*6*-*diamine*), and BD3 (*N*,*N*'-*diphenyl*-*N*,*N*'-*bis*(6-*phenyldibenzo*[*b*,*d*]*furan*-4-*yl*)*pyrene*-1,*6*-*diamine*) as dopant.^[4] Shown in Figure 1 are their molecular structure and weight. Following the procedure for CSS deposition reported previously, we used a thin tantalum foil (10 µm) as the heating element as well as the substrate for the donor film. All the donor films were deposited on the Ta foil by conventional VTE in a separate chamber.^[5] As shown in Figure 2, the Ta foil with the donor film was clamped and tensioned between two copper electrodes. The temperature of the Ta foil (monitored by a thermocouple placed at the center of the foil) was controlled by passing current through it. The heating rate was maintained between 0.6 and 1.0°C/s with a power source and the deposition rate was monitored with a quartz crystal monitor (QCM) held about 5 mm above the donor film area. The area of the donor film was 177 mm².







Figure 2. Setup for CSS deposition using a Ta foil as the heating element.

Figure 3 shows the temporal profiles of Ta foil temperature and the evaporation rate for BH, BD1, BD2, and BD3. With a nearly constant heating rate, the evaporation rate and the onset temperature for CSS deposition vary with the donor film composition. A notable feature is that there are more than one peak in the evaporation rate curve. This is particularly apparent for host BH with a main peak at 176°C and a smaller peak at 149°C. For dopants BD1, BD2 and BD3, the main peak occurs at 167°C, 215°C and 234°C, respectively, with only a minor peak at a lower temperature. This two-stage evaporation behavior has been previously observed in the evaporation of Alq₃ film and attributed to a two-layer film structure with different morphological phases.^[6] It is likely that what was observed here for BH is due to phase

transition occurring in the film. The evaporation rate drops after first peaking at 149°C as the film (with a glass transition temperature T_g of 120°C) has completed the transition from an amorphous phase to a more crystalline phase. It can be seen that the main rate peak of BH (176°C) overlaps most closely with that of BD1 (167°C), suggesting this pair is likely a good choice for CSS deposition.



Figure 3. The temporal profiles of the evaporation rate and Ta foil temperature for BH, BD1, BD2 and BD3 deposition.



Figure 4. The temporal profiles of the evaporation rate and Ta foil temperature for doped films.

Figure 4 shows the temporal profiles for three doped donor films containing 8% of BD1, BD2 and BD3 as dopant in BH host. The BD1-doped film exhibits the characteristic double peak of the neat BH film, whereas the BD2 and BD3 doped films both show a new peak corresponding to the evaporation of the dopant at a higher temperature (216°C and 227°C, respectively). This is in addition to the double peak of the BH host. These rate profiles clearly indicate that BD1 with an evaporation temperature closest to that of BH is more likely to yield a uniformly doped film compared to BD2 and BD3.



Figure 5. The apparatus and temperature profile for the radiation heating CSS process.

For OLED device fabrication, we used radiation heating rather than electrical heating for the CSS deposition as radiation heating can provide a more uniform temperature profile on a large substrate. For our setup, the donor substrate was a 200 um silicon wafer and a halogen lamp was used as the heating source. Figure 5 shows the schematics of the radiation CSS setup with a Si wafer held above a 250 W halogen bulb and a typical donor substrate temperature vs. time profile. In this process, the Si wafer can be heated up to 250°C in 5 seconds, which is sufficient to completely evaporate the donor film. To avoid residue heating due to the proximity of the donor and receiver substrates with a 1 mm gap, immediately after the CSS deposition, the lamp was turned off and the receiver substrate with the CSS-deposited film was moved away from the Si donor substrate.

For an assessment of the uniformity of dopant concentration in the CSS-deposited films, we compare the PL spectra of the CSS-deposited films with that of the VTE-deposited films of identical host-dopant compositions. As shown in Figure 6, for BH:BD1, the PL spectrum of the CSS-deposited film is practically identical to that of the VTE-deposited film, showing only BD1 dopant emission. Clearly this indicates uniform dopant distribution in the host. In contrast, the PL spectra of CSS-deposited BH:BD2 and BH:BD3 films exhibit not only dopant emission but also host emission, indicating non-uniform distribution or segregation of BD2 and BD3 dopants in the BH host. These results corroborates with the evaporation rate profiles of the doped films in Figure 4.

To evaluate the distribution of dopants across thickness the CSSdeposited films, we used an Al film (deposited on top of the CSS films) as PL quencher to gauge the variation of host dopant composition. Figure 7 shows the normalized PL spectra of BH:BD1, BH:BD2, and BH:BD3 CSS-deposited films with and without the Al overlayer. It can be seen that BH:BD1 is the only sample showing almost identical PL spectra with or without Al. In contrast, both BH:BD2 and BH:BD3 films exhibit host BH peak at 430 nm, which is more pronounced with the Al layer. These PL profiles indicate segregation of host and dopant during CSS deposition with the BH evaporation prior to that of the less volatile BD2 or BD3.



Figure 6. Normalized PL spectra of doped CSS-deposited and VTE-deposited films.



Figure 7. Normalized PL spectra of doped CSS-deposited films with and without Al.

We fabricated blue OLED devices of the following layer structure ITO|HATCN (10 nm)|HTL (40 nm)|EML (30 nm)|ETL (30 nm)|Liq (2 nm)|Al, where EML was BH:BD1 (8%) deposited by CSS. The other layers were deposited by VTE in a separate chamber. Brief exposure of the CSS donor film to atmosphere was

incurred during fabrication. As shown in Figure 8, the efficiency of the blue OLED device with a CSS-deposited EML (Device 2) is significant lower than that of the reference device with a VTEdeposited EML (Device 1). We suspect that the air exposure of the donor film and resulting moisture accumulation may be the cause for the reduced efficiency. However, we found that we were able to partially recover the efficiency by subjecting the donor film to a pre-heating step prior to CSS deposition. This pre-heating step presumably removes any moisture accumulated on the donor film. In Figure 8, Device 3, which was prepared with a donor film preheated for 2 minutes at 90°C, shows a much improved efficiency over Device 2, although still below the reference Device 1. We believe that with further process development and control of atmospheric exposure, CSS devices with performance comparable to that of the VTE devices can be achieved.



Figure 8. The performance of blue devices with EML deposited by CSS and VTE.

3. Conclusion

In this study, we investigated the close-space sublimation (CSS) for fabricating blue OLED devices. By selecting an appropriate pair of host (BH) and dopant (BD1) with comparable evaporation profiles, we demonstrated the utility of the CSS process in producing a blue emitting layer with a uniform dopant distribution. We further demonstrated blue OLED devices with modest efficiency and determined that atmospheric exposure during the CSS process can play a critical role.

4. Impact

CSS is an alternative process for the production of OLED displays. Our results have demonstrated the utility of CSS and the critical process steps needed to produce blue OLEDs.

5. References

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