Chapter-6

LIGHT OUT COUPLING EFFICIENCY ENHANCEMENT OF ORGANIC LIGHT EMITTING DIODES BY USING MgF₂-NANOSTRUCTURED FILM PRODUCED BY RAPID THERMAL ANNEALING

Early in 1990’s the OLEDs were fabricated using small molecule fluorescent organic and polymeric materials [14]. The internal efficiency ($\eta_{\text{int}}$) of OLEDs fabricated on these materials was limited to 25% only. This is due to the fact that once the organic molecule is excited both singlet and triplet excitons are formed with a ratio of 1:3. Radiative decay of triplet excitons to ground singlet state is forbidden and hence $2/3$rd of excitons loose their energy non-radiatively. Therefore light is generated by only singlet excited states hence $\eta_{\text{int}}$ is 25%. Later on the $\eta_{\text{int}}$ of OLEDs was improved significantly which is now near 100%, by means of harvesting both singlet and triplet excitons to decay radiatively. This is possible by means of using both fluorescent and electro-phosphorescent materials as emissive layer with a suitable energy transfer mechanism. But the external efficiency $\eta_{\text{ext}}$ remains near 20% only. This is due to the fact that light produced in OLED is a result of radiative decay of exciton light in organic emissive layer ($n \approx 1.67$) then it cross the ITO and glass substrate to come out from the device for which refractive indexes are $n \approx 2$, $n \approx 1.55$ and $n \approx 1$, respectively [205-209]. Due to this difference in refractive indices losses
occur at glass-air boundaries. According to classical ray optics about 30% light is lost at the substrate-air interface and 50% light is lost at organic-ITO, ITO-glass edges [210,211, 80]. Only ~20% of generated light is coupled out from the device. Rest 80% light is lost due to the combined effect of total internal reflection (TIR) and wave-guiding at boundaries of different refractive index materials. In this way, a very small fraction of light is coupled out from the device as useful light and rest of the light gets trapped inside the device or reflects towards edges. All these optical losses are one of the major obstacles for development of high efficiency organic light emitting devices.

Along with enhanced internal efficiency and color purity, it is necessary to extract maximum amount of produced light outside the device. Light generated in emissive layer has to travel through the number of layers of different refractive indexes before it comes out from the device as shown in fig. 6.1.

Fig 6.1: Schematic diagram showing energy losses in OLED at different interfaces.
Extensive amount of research have been done by the researchers to enhance light extraction efficiency of OLEDs by using various techniques which includes, use of micro-lenses, micro-cavities, spherically shaped substrates, photonic crystals, use of high refractive index substrates and brightness enhancement films etc. [212-214]. Yang et. al. have reported 60% enhancement in out coupling efficiency using micro-lens arrays [215]. Do et. al. have used two dimensional photonic band gap structure to extract the trapped light [216]. Some other techniques have also been used by the researchers like textured surface, metallic nano wire arrays, nanostructured ITO etc. [217-219]. These techniques are very effective but their fabrication requires high precision which is difficult to control. High fabrication cost and essential accuracy in fabrication limits their use for large scale. One other method that has been suggested for improved light extraction in OLEDs is the use of anti-reflection layer such as magnesium fluoride (MgF$_2$). MgF$_2$ is best known for its good optical properties like high transparency in visible as well as UV and IR region. Furthermore, low refractive index and low cost make it suitable for using as antireflection coating on various optical components for e.g., beam splitter, prisms and solar cells etc. In previously reported work, about 1.5 times enhancement in light extraction efficiency was achieved by using thermally evaporated MgF$_2$ film with thickness of quarter-wave on the backside of glass substrate [220].

In this chapter, significant improvement in external efficiency of OLEDs is achieved by applying nano-porous MgF$_2$ antireflection thin film instead of uniform MgF$_2$ film from outside the device. A novel, faster, easier and relatively low-cost method that can be used on a large scale is described for the fabrication of nano-porous magnesium fluoride (MgF$_2$) films. Further, nano-structured ITO layer was also produced by using the rapid thermal
processing (RTP) method. Results were also compared with uniform MgF$_2$ film coated on the backside.

6.1 Methodology

6.1.1 Fabrication of Nano-Porous MgF$_2$ and ITO Films On The Glass Substrate

As shown in Fig. 6.2, on the backside of pre-cleaned ITO-coated glass substrates a 200 nm MgF$_2$ film was deposited by thermal vapor deposition under vacuum by maintaining the pressure at $10^{-5}$ Torr. MgF$_2$ coated ITO substrates were then treated thermally using RTP system at 300 °C for 1200 sec under the vacuum of $10^{-4}$ Torr.

Fig 6.2: Schematic diagram of deposition and thermal treatment of MgF$_2$ thin film.
Temperature was increased up to 300°C in 3 sec only by maintaining the heating rate of 100 °C s$^{-1}$. Once the temperature was reached to 300°C, it was kept constant for 1200 seconds and then allowed to cool down at room temperature rapidly (Fig. 6.3). During this thermal processing MgF$_2$ and ITO are rapidly heated. The nano-porous MgF$_2$ and ITO films were then characterized by atomic force microscope (AFM) and UV-Vis spectroscopy.

6.1.2 Fabrication of OLEDs

Three types of devices were fabricated to study the effect of nano-porous MgF$_2$ on to the light out coupling efficiency of OLEDs. Different layers of organic materials were deposited on the ITO side of the substrates. Thin films of α-NPD, Alq$_3$ followed by LiF/Al were thermally evaporated under vacuum to function as HTL, EML and anode. All devices named A, B and C were fabricated under same condition with same configuration of ITO/α-NPD/Alq$_3$/LiF/Al. Thicknesses of all layers were also identical in all the devices. Detailed configurations of all three devices are given below in table 6.1.
<table>
<thead>
<tr>
<th>Device</th>
<th>Configuration</th>
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<tbody>
<tr>
<td>A (reference device)</td>
<td>Glass substrate/ITO/α-NPD (350 Å)/Alq₃(280 Å)/LiF (10 Å)/Al (1000 Å)</td>
</tr>
<tr>
<td>B (with uniform MgF₂)</td>
<td>MgF₂ thin film (2000 Å)/glass substrate/ITO/α-NPD (350 Å)/Alq₃(280 Å)/LiF (10 Å)/Al (1000 Å)</td>
</tr>
<tr>
<td>C (with nano-porous MgF₂)</td>
<td>MgF₂ nano-porous film (2000 Å, RTP)/glass substrate/ITO nano-porous (RTP)/α-NPD (350 Å)/Alq₃(280 Å)/LiF (10 Å)/Al (1000 Å)</td>
</tr>
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</table>

### 6.2 Result and Discussion

#### 6.2.1 Characterization of Nano Porous MgF₂ Thin Film

MgF₂ thin film prepared by the thermal vapor deposition followed by RTP is first characterized by AFM and UV-Vis spectroscopy discussed below.

Fig. 6.4 (a) and (b) show the AFM images of MgF₂ thin films before and after thermal treatment, respectively. It can be seen that after RTP, MgF₂ film shows fine granular structure with size range of 300 nm to 500 nm as compared to the uniform film before RTP. Thermal treatment also affected ITO coating on the other side of the substrates. Fig. 6.4 (c) and (d) shows the AFM images of ITO films before and after RTP, respectively. After RTP, ITO film was also found to be consisting of grains of average size 400 nm approximately but this effect is less prominent compared to MgF₂. This may be due to the reason that ITO melts at higher temperature as compared to MgF₂ [221, 222]. The presence of nano-structures on both sides of glass substrates lead to enhancement of the light extraction.
efficiency of the OLEDs. Fabrication of nano-structured substrates using RTP is a low-cost method and can be applied at large scale.

Figure 6.4: Atomic force microscopic (AFM) images of MgF$_2$ film coated on the backside of glass substrate: (a) without RTP, (b) with RTP nano-structured film and ITO coated on the other side of glass substrate, (c) without RTP, (d) with RTP nano-porous film of ITO, respectively.
To study the effect of RTP on transmittance, spectra were recorded for ITO coated glass substrate, ITO glass substrate with MgF$_2$ coating on the back side before and after RTP using UV-Vis spectrophotometer. Figure 6.5 shows the transmittance spectra of ITO coated glass substrate, without MgF$_2$, with uniform MgF$_2$ and nano-structured MgF$_2$. After deposition of MgF$_2$ as anti-reflection coating transmittance was found to be improved in visible range of 400-700 nm. RTP leads to further improvement in transmittance of the MgF$_2$ coated substrate. For sample with nano-structured MgF$_2$ coating, measured transmittance was approximately 88% as compared to 83% and 79% for samples with uniform MgF$_2$ and without MgF$_2$.

![Figure 6.5: Transmittance spectra of ITO coated substrates without MgF$_2$, with MgF$_2$ RTP treated MgF$_2$](image)
6.2.2 Device Characterization

Reference device, with uniform MgF$_2$ and device with nano-porous MgF$_2$ were characterized by Electroluminescence (EL) measurements at varying voltages. Fig. 6.6 (a) to (c) shows the EL spectra of devices without MgF$_2$, with uniform MgF$_2$ and with nano-porous MgF$_2$ coated on the backside of the substrates, respectively.

![Figure 6.6](image)

*Figure 6.6: Electroluminescence intensity curve of OLEDs versus voltages: (a) without MgF$_2$, (b) with uniform and (c) with nano-porous MgF$_2$ and ITO structures coated on the backside and front side of the glass substrate, respectively.*
Reference device (device A) shows approximately 1449 EL intensity at 9 V whereas, device with uniform coating of antireflection material MgF₂ (device B) shows better EL intensity at 9 V but best brightness was found in device which was having nano-porous coatings on the backside of the substrate (device C).

Fig. 6.7 (a) and (b) represent the EL comparison of all three devices at 7 V and 9 V, respectively. It is clear from the figure that EL intensity at 7 V was improved by 1.3 times in case of uniform MgF₂ whereas in case of nano-porous MgF₂ this enhancement was 4.8 times. At higher voltage also, EL intensity was improved by 1.5 times and 3.1 times in case of MgF₂ and RTP-treated MgF₂.

Figure 6.7: Comparison of luminescence intensity of OLEDs at (a) 7 V and (b) 9 V with and without RTP.

Luminescence versus voltage for all three devises, i.e., without MgF₂, with uniform and nano-porous MgF₂ is shown in fig 6.8. Above 8 volts, the enhancement in luminescence
Observed was more than 3 times with nano porous films. Luminescence at 9 V for Device A, B and C was 1450, 2130 and 4460, respectively.

Figure: 6.8: Luminescence verses voltage characteristics for all three OLEDs.

Enhanced performance can also be represented in terms of current efficiency and power efficiency. Fig. 6.9 (a) and (b) represent the current efficiency and power efficiency for all three devices A, B and C. Current efficiency for device A, B and C at 9 V was 2.9, 3.7 and 8.4, respectively. Power efficiency was also found to be improved for nano-porous MgF$_2$ in comparison to uniform MgF$_2$ and reference device. Power efficiency for devices without MgF$_2$, with uniform MgF$_2$ and nano-porous MgF$_2$ was 0.95, 1.30 and 2.9, respectively (see Fig 6.9 (b)).
Figure 6.9: (a) Current efficiency and (b) Power efficiency curves of all three devices.
At 9 V, there was 1.3 times enhancement in current efficiency for device with uniform MgF$_2$ whereas in case of nano-porous MgF$_2$ this enhancement was three times. Similarly power efficiency was improved by 1.4 times in case of uniform MgF$_2$. This enhancement is more than three times after RTP treatment of the substrates. This upgraded performance of the devices can be explained as follows. Earlier energy losses takes place at different interfaces in OLEDs (see fig. 6.1). Without any alteration in substrate only 20 % of generated light is coupled out from the devices due to the loss occurred at different boundaries of organic-ITO, ITO-glass and glass-air [80]. On travelling from glass ($n=1.55$) to air ($n=1$) amount of light travelled out can be calculated by the simple relation given below [223].

$$\eta = \frac{1}{2n^2} \times 100 \quad (6.1)$$

Where, $\eta =$ amount of light escape from the device

$n =$ effective refractive index of the material

Rest of the light is lost due to total internal reflection (TIR) at glass-air boundary due to large difference in refractive indexes. This refractive index contrast between different layers is the main reason for optical losses in OLEDs. Exciton decay take place in emissive layer which is made up of high refractive index material ($n_{Alq3} \sim 1.7$). Light produced due to this exciton decay propagates in all directions in order to escape from the device to air ($n=1$). However, only few amount of light photons whose incident angle ($\theta$) is smaller than the critical angle ($\theta_c$) could come out from the device, as shown in fig 6.10.
Figure 6.10: Schematic diagram showing critical angle at interface of two different refractive index material.

Remaining light experiences TIR and escape from the edges of the device or get trapped into the device and converts into the heat which further results in device instability and thus affect the lifetime of OLEDs. 80% of generated light is lost and can’t be used because of this mismatch of refractive index. After coating MgF$_2$ on the backside of ITO coated substrates this high difference in refractive index can be reduced. Refractive index of MgF$_2$ ($n=1.37$) is less than glass and higher than the air ($n_{\text{glass}}>n_{\text{MgF}_2}>n_{\text{air}}$) which leads to reduced refractive index difference and hence more amount of light escape from the device. Due to antireflection coating of the MgF$_2$ results in enhancement in light out coupling at glass-air boundary [220]. After applying MgF$_2$ coating 27% of light can couple out from the device into the atmosphere. This can be calculated using mathematical relationship given in equation 6.1. Thus improved EL intensity and current efficiency and power efficiency were observed in case of uniform MgF$_2$. EL intensity and device efficiency can further be improved by fabricating nanostructured MgF$_2$ by the means of RTP. Moreover, RTP also results in nanostructured ITO thus this additional factor further enhances the out coupling efficiency. Further, due to RTP the MgF$_2$ and ITO layers become disordered/rough therefore these surfaces will act as scattering surfaces and the light loss due to TIR will
decrease. Remarkable EL and efficiency enhancement was observed with nano-porous MgF₂ coating on the backside of the nano-structured ITO substrate, given in Fig. 6.7 and 6.9, respectively. Fig. 6.11 represents the ray diagram of light propagation at the different boundaries in the device and substrate-air boundary. In device C, light travels through the modified boundaries of nano-porous MgF₂–air and nano-porous ITO–glass. The nano-porous structure the MgF₂–air results in disordered or irregular edge which works as scattering structure for the incident photons coming from the emissive layer. This discontinuous and disordered boundary changes the angle of incidence (θ) and pores generated as a result of thermal shock scatter the light. These nano sized pores act as scattering centres and deviates the propagation path of incident light rays coming from the emissive layer of the device [224].

Figure 6.11: Schematic diagram of OLED structure with MgF₂ and ITO nanoporous structures on the back front side of the glass substrate illustrating the ray optics diagram with light out-coupling.
Pores in film of MgF₂ and ITO causes Rayleigh scattering for green light of the device which leads to reduced wave guiding effect and total internal reflections [225]. Therefore as a result of disordered boundary and nanoscale scattering centres, significant amount of light extracted from the OLED.

Furthermore, nano-scaled unsystematic structures of MgF₂ on the back side and ITO from the inside of the glass substrate effectively scatter light without any wavelength dependency. On both side of the glass substrate, i.e. ITO-glass and glass-air boundary, path of travelling light changes and thus trapped light at both interfaces coupled out more effectively.

In OLED, device travels through various layers of different refractive indices. From emissive layer or organic material \((n_{\text{org}} = 1.6\text{~}1.7)\) it passes through ITO \((n_{\text{ITO}} = 1.8\text{~}2.0)\) and glass substrate \((n_{\text{glass}} = 1)\) and finally leaves the substrate to enter in the free space \((n_{\text{air}} = 1)\). Amount of light extracting out from the device can be calculated by the relationship, 
\[
\eta = \frac{1}{2n^2} \times 100
\]
Before any modification, 20% of generated light can escape from the device (device A) because light is directly coming out in air from glass. Since refractive index difference is high therefore losses occur are also high and thus brightness is low. Whereas after antireflection MgF₂ coating, the optical barrier reduces due to lower refractive index of MgF₂ \((n_{\text{MgF2}} = 1.37)\) as compared to glass and light extraction efficiency improves to 27%. Addition of porosity in this MgF₂ film further reduces the refractive index, as reported in earlier literature [226]. The refractive index of MgF₂ reduced from 1.37 to 1.13 due to porous structure produced by RTP. This further reduced barrier in refractive index enhances the light extraction at glass-MgF₂-air boundary to 40%. Again nanostructured
ITO also helped in escaping the trapped light at ITO-glass interface and support the enhancement in light out coupling. The successful scattering due to nanostructured surface and reduced refractive index, extraction efficiency reaches to 60% approximately and results in three times enhancement in brightness. This enhanced brightness helps in improving current and power efficiency enhancement. Hence, nano-structured substrates produced by the RTP are efficient, low-cost way to improve the external efficiency of the OLEDs. Also this method can be applied to produce nanostructure substrates at large scale.

6.4 Conclusions

Nanoporous MgF$_2$ and ITO coated substrates were successfully produced using physical vapor deposition followed by thermal treatment for OLED application. Significant enhancement of about 60% in light-out-coupling efficiency was observed with nanoporous MgF$_2$ and ITO coated substrates. Enhanced light out-coupling efficiency resulted in improved current and power efficiency by 2.9 and 3 times as compared to the reference device, respectively. The method of RTP was found to be very useful, cost-effective and easy to produce large area nano-structured substrates for display devices.