Final Report
DOE SSL Grant (No. DE-EE0006673)
Advanced Light Extraction Structure for OLED Lighting

Project Team:
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Subcontractor: OLEDWorks, LLC

Project Period:
September 10, 2014 to April 30, 2017

Summary:

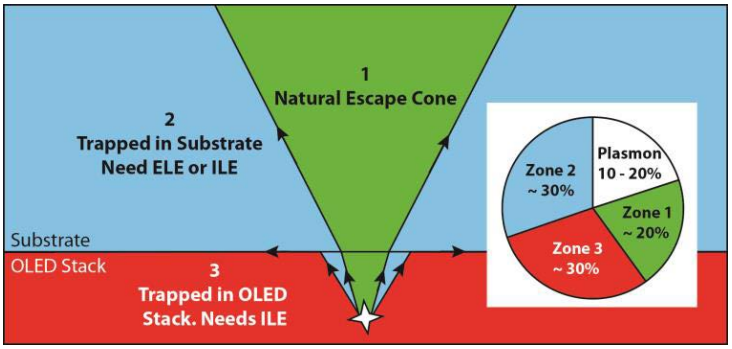
This is the final scientific and technical report for the DOE SSL Grant No. DE-EE0006673 titled "Advanced Light Extraction Structure for OLED Lighting". During this project, we successfully demonstrated the following:

- Developed a process to make a graded index IEL (Gen 3)
- Developed a formulation comprising HRI material with scatterers (Gen 2)
  - Modified the formulation to be compatible to OLED manufacturing processes
  - Improved the adhesion – Developed a formulation that would adhere to the glass substrate
- Developed slot-die deposition capabilities – important deposition method in industry
- Developed a process to analyze the index gradient in a transparent film
- Developed IR analytical method to quantify the degree of cures in films
- Demonstrated as high as 2.7x EQE gain
  - Built 72 devices at OLEDWorks – 26 Gen 2 and 46 Gen 3

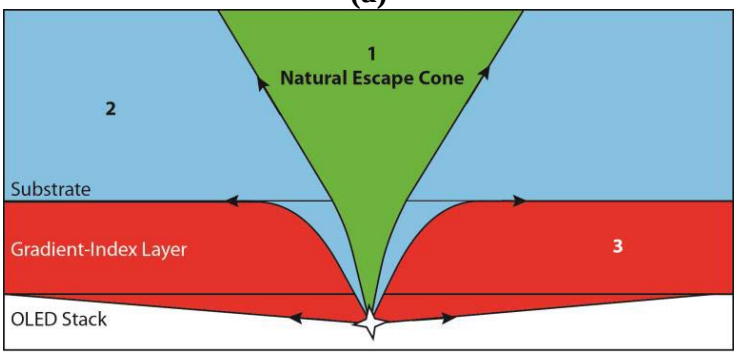
Introduction

The innovation proposed in this grant is to demonstrate a novel internal light extraction (ILE) design that can maximize the energy efficiency of Organic Light Emitting Diode (OLED) lighting devices without negatively impacting the device voltage, efficacy or angular color dependences. Even though, OLEDs have unique features compared to its inorganic counterparts, LEDs, in terms of technology development and market readiness levels, it still lags LEDs by several years. The main challenges as identified in the National Research Council's 2013 Assessment on Solid State Lighting, are the cost of the materials and the low light extraction efficacy [1]. Improving the light extraction will improve both the $/Klm and lm/W, two important metrics DOE uses to measure the cost effectiveness of a light source.

Based on the initial success of applying Pixelligent's nanocomposite as the high index smoothing layer that demonstrated high light extraction efficiency, we believe that by redesigning the same elements of that proven light extraction scheme, a new scheme that is both simpler to manufacture and more effective at extracting light can be created. The proposed innovation is based on Pixelligent's High Refractive Index (HRI) formulation to create an Internal Light Extraction layer (IEL) that will have a graded-index layer, embedded with sparely populated light scatterers. This layer will be situated between the transparent conductor, i.e., indium tin oxide (ITO) and the substrate. The proposed structure not only provides much improved light extraction efficacy but is also cost-effective, simple to manufacture,and compatible with existing OLED manufacturing processes. Pixelligent Technologies, LLC collaborated with OLEDWorks LLC, a major US based OLED lighting manufacturer on this project.



(a)



(b)

Figure 1: a) A much simplified illustration showing the three major zones of light distribution in an OLED device and the inset shows the rough break down of all four light loss mechanisms; b) the same three zones when an gradient-index layer is inserted.

Project Activities

The goal of the project is to develop the processes for creating a full graded-index structure with embedded light scattering centers and together with our partner, OLEDWorks, demonstrate the performance in a 4" by 4" prototype white OLED lighting panel. The technical plan is to create the graded-index layer based on Pixelligent's HRI nanocomposite with a simple manufacturing process. The optimum scatterers particles will be investigated and incorporated in the HRI formulation. Once the process to create the gradient-index layer with desired profile is optimized and the scatterer concentration is identified, the IEL integrated substrates will be sent to OLEDWorks to be integrated in to the test panel for device performance testing.

The delieverables for the project are: (1) Build the gradient-index layer with a 0.25 refractive index difference in a film embedded with scatterers with low surface roughness and compatible with OLED manufacturing; and (2) Demonstrate a 4" by 4" 2.5 in^2 white OLED test panel with 70% light extraction efficiency, with the proper color temperature (3000 K) and angular emission spectra (< 0.004 angular spectral shift compared to a white OLED standard).

Technical Results Summary

Gradient-index Film Formation

Pixelligent's High Refractive Index (HRI) nanocomposite formulation is comprised of Pixelligent's proprietary nanocrystals and a UV curable polymer that was developed in SBIR Grant No. DE-FOA-0000969. The refractive index of the HRI formulation can be tuned from 1.60 to 1.85 at 400 nm based on the loading of the nanocrystal in the formulation. (Figure 2) Therefore, in this project, we explored ways to create a thin layer of film whose refractive indexes will decrease going from top to the bottom of the layer.

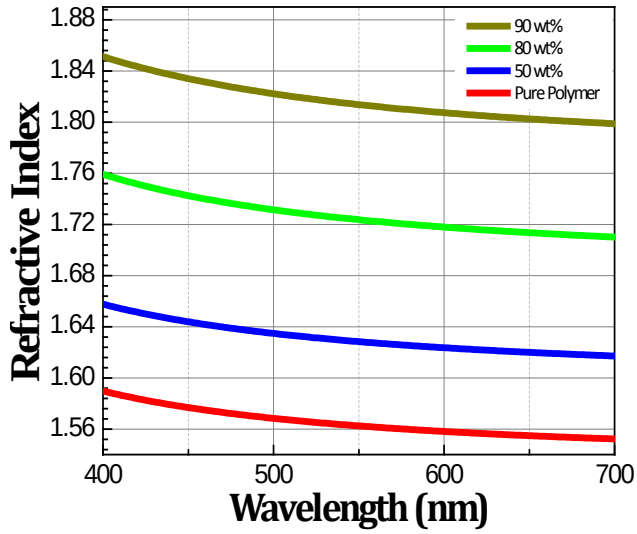


Figure 2 - Refractive Index vs. wavelength as a function of nanocrystal loading.

Characterization of Index Gradient

Since there was no analytical method to determine the gradient distribution within the IEL, an in-house mathematical method (which we have nicknamed "the Fresnel solver") was developed. This mathematical formula uses the transfer matrix method which is capable of calculating the transmittance of thin film stacks with an arbitrary number of layers using complex refractive index and different wavelengths while simultaneously determining the refractive index profile through the thin film and substrate.

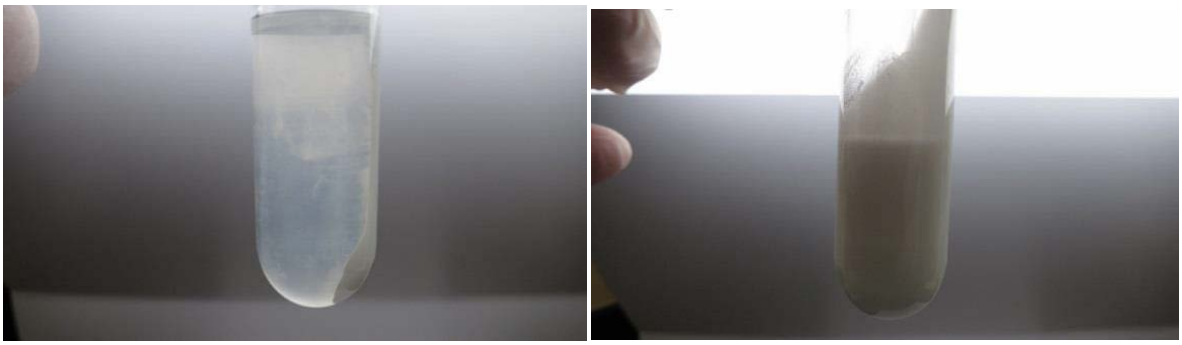
Creating Gradient-Index Film with a Sufficient Index Span

We explored a wide range of parameters to find the optimal condition for obtaining a graded index. Some of the parameters explored were the thickness of the film and processing conditions. The films that were clear and uniform were tested to determine gradient using Fresnel solver.

Introduction of Scattering Centers

As part of the project, our goal was to incorporate scatterers into our HRI matrix to act as scattering sites. Several scatterers were tested as potential candidates.

We were able to suspend scatterers into our HRI formulation to give an opaque suspension. Initially the scattering particles settled in a short period. However, by extensive formulation work, we were able to develop a process to make a stable formulation, which we refer to as the Gen 2 formulation. The stability of the formulation was tested by centrifugal methods where the settling time at 1150G was extrapolated to a settling time at 1G. Additional scale-up efforts of Gen 2 was performed under the SBIR Phase II grant. (Figure 3)



(a) **(b)**

Figure 3 - (a) Unstable slurry of scatterers after centrifugation (b) Stable slurry of scatterers after centrifugation.

One of the milestones to complete was to perform device testing on a 4” by 4” inch glass substrate and slot-die was the intended deposition method chosen since it matches closely with manufacturing processes. Extensive effort was invested in optimization the slot-die process. An example of a 2 micron thick Gen 2 IEL coated by slot-die is shown in figure 4. The thickness of the coated films as a function of shuttle speed and viscosity was mapped out. The capillary number is $Ca = \mu SV/\gamma$, where μ is the viscosity of the formulation, SV is the shuttled speed, and γ is the surface tension of the formulation. It is known that for a slot-die coater, below a critical capillary number Ca*, the film thickness is controlled by shuttle velocity only and above the Ca*, the film thickness is controlled by shuttle velocity and viscosity. The branched behavior has been observed.

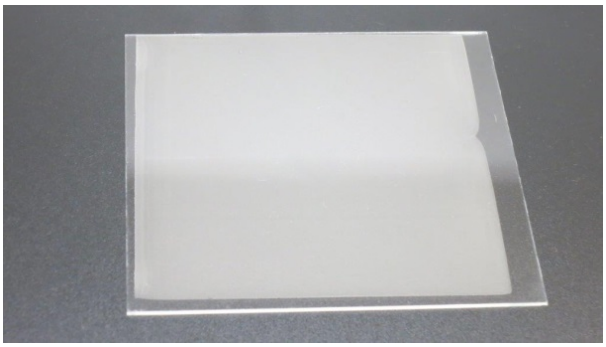


Figure 4 - Photo of a 4” by 4” glass substrate coated with scattering layer using Pixelligent’s in-house slot-die coater.

Once we were able to successfully coat a uniform film, Gen 2 was incorporated into the Gen 3 process. The fresnel solver analysis is capable of determining the gradient only for a transparent film and we were not able to find an alternative method to determine the gradient of a film containing scatterers. Hence we determined the process for creating gradient in the film by using the transparent HRI film and then assumed that process should be the same for the film with scatterers. The film coating process using Gen 2 formulation was similar to the formulation without scatterers. Successful devices were built using this process.

Modeling and Simulation

When we applied for the project there was no software available to simulate high refractive index scattering layers in an OLED device. The only approaches that had even been discussed involved making approximations that would severely limit the usefulness of the modelling work

but allow the simulation to be run quickly. We had hoped to do an "accurate" model (a direct solution of Maxwell's equations) that would allow us to optimize scatterer size, type, and concentration, along with the refractive index of the binder. Several things happened during the course of the project that convinced us to change the planned work:

- First, the solution of Maxwell's equation for a scattering layer turned out to be too computationally intensive even to be run a few times to find the optimal scattering amount. We did get the simulation to run but that required having only a few scatterers in a small area so that we could not really trust the results. With significant additional budget and the use of supercomputers we could have gotten this to work.
- Second, we decided to test many of the issues experimentally rather than through simulation.
- Third, Setfos came out with a module that allowed for the simulation of high index scattering layers.

For these reasons we tried Setfos. Initial work in this area has focused on verifying the device improvements possible with the use of the Gen 2 IEL, the scattering layer in the graded index films, before moving onto simulating the multi-layer IEL. OLEDs were simulated via schematics provided by OLEDWorks.

OLED Device Integration and Testing

Pixelligent has made 6 runs comparing Gen 2 and Gen 3 (PC-170622, MH2-170119, MH2-170105, MH2-170112, PC1-161116, MH2-170126) and 1 run with only Gen 3 devices (MH2-160802), with all of these devices being OLEDWorks' optimized white made on 2.5" glass. The major issue that we found was there was a lot of variation within each run and this made a comparison between Gen 2 and Gen 3 difficult as this variation was much larger than the difference between the efficiency of Gen 2 and Gen 3. An example of this can be seen in the plot below for PC-170622 (note this graph shows the controls with external light extraction). (Figure 5) This run consisted of 10 Gen 2, 8 Gen 3, 5 OW ITO Controls (3 yielded), 2 Commercial ITO controls, and 7 Forced Gen 3 (0 Yielded, Forced Gen 3 has an additional high index layer so that the gradient can be directly measured). At the extreme the Gen 2 devices ranged from an EQE above 100% to below 60%, much greater than the 5 – 10% increase in efficiency expected for Gen 3 compared to Gen 2.

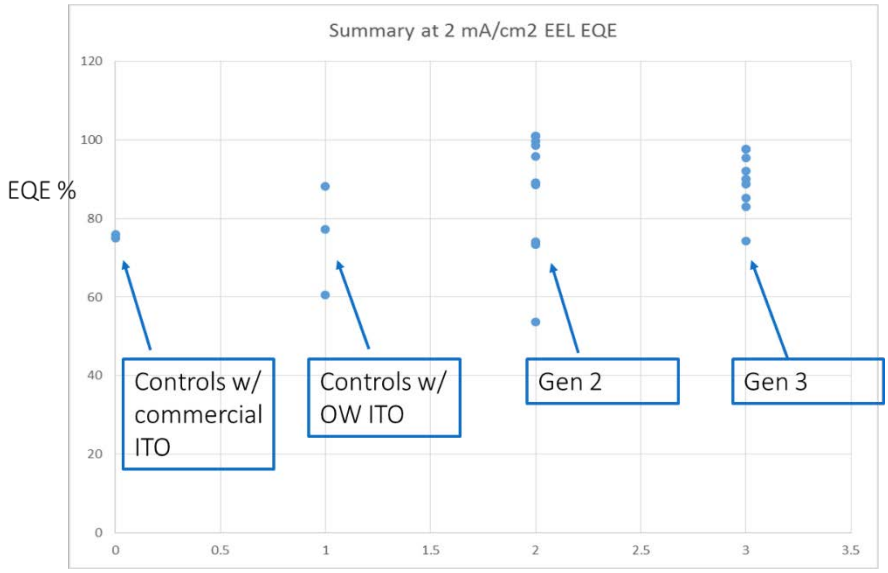


Figure 5 – The variations in the EQE for controls, Gen 2 devices and Gen 3 devices within run PC-170622.

Source of Variation

OLEDWorks believes the major source of variation come from when they deposit ITO. Ordinarily OLEDWorks buys substrates with commercially deposited and patterned ITO. For example in the plot above there were two controls with commercial ITO and these devices had an EQE (with external light extraction) of 75.9% and 75.1% for an average of 75.5% with a variation of about 1.06% ((75.9 – 75.1)/75.5) and OLEDWorks has informed us that this is a typical result. For the controls with ITO deposited at OW 2 of the 5 devices did not yield and the other 3 had an EQE of 88.1%, 60.6%, and 77.3% for an average of 75.3%. In this case the lowest performing device is about 19.5% below the average ((75.3-60.6)/75.3) and the highest performing devices is about 17% above the average ((88.1-75.3)/75.3). Because there are so few devices and the devices do not exhibit a normal distribution we have not done a lot of statistical analysis.

The suspected mechanism for the variation has to do with defects. In OLEDWorks facilities the ITO deposition tool is in a “non-clean” area. In addition when OLEDWorks deposits ITO they also perform other steps where contamination can occur. We also know that when Pixelligent deposits the extraction layers we do not have a clean environment either. So there are numerous points in the manufacturing where defects can be deposited (note that for future work Pixelligent is purchasing a clean environment.)

The defects are physical protrusion in the device that lead to microshorts or current leakage (in a small area some of the current flowing directly from the cathode to the anode without going through the organic layers). As this current is not producing light it lowers the efficiency of the device. This is the most important mechanism of how the defects affect the EQE measurements.

OLEDWorks performs the efficiency measurement by measuring the amount of light (intensity as a function of wavelength) from a portion of the OLED panel at several angles (0°, 15°, 30°, 45°, 60°, 70°) and comparing that to the current flowing through the device at a given voltage. No matter where the shorts are located they will lower the efficiency of the device because in the area of the short more current will be flowing than expected, resulting in less than expected current flowing through the areas of the device that are emitting light. If the shorts are located in the area of the OLED where the light is being measured then the effect on efficiency will be greater because there will be less light being emitted than would be expected if there were no shorts.

It is also theoretically possible for there to be a defect that blocks the flow of current in some areas of the device and with no (or less light being emitted in those areas). In this case there would be more than the expected amount of current flowing through the rest of the device. If one of these defects occurred outside the portion of the device that was being measured then it could result in a device that appeared to be more efficient than it actually was. We believe that this kind of defect is relatively rare and the device would be noticed because it would not be uniform when lit.

The result of this is that we believe that when we see very high efficiencies these are likely to be the result of our excellent light extraction but the lower efficiencies are likely to be the result of the shorts, which we know to be present. Supporting this hypothesis is a run where we had low variation in the performance of the devices even though OLEDWorks deposited the ITO. Please see the plot below from run MH2-160802. (Figure 6) The EQE of the Gen 3 devices ranged from 97.5% to 102% and the two controls with OLEDWorks’ ITO were 36.5% and 40.3% (without external light extraction). These devices had lower defects and this resulted in the greater uniformity but still resulted in a large improvement ~2.6X in EQE.

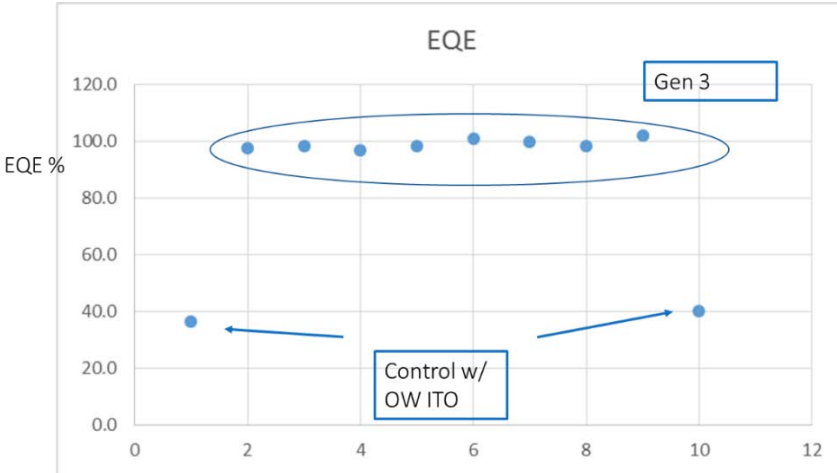
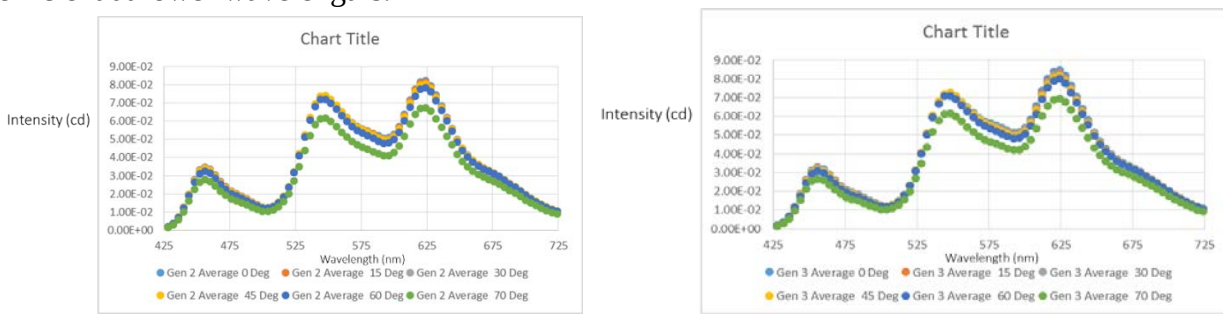


Figure 6 – The EQE measured for Gen 3 OLED devices in run MH2-160802.

Data Analysis

For all of the runs where we could compare Gen 2 and Gen 3 we created an average of all of the Gen 2 and Gen 3 runs. For the PC-170622 run the Gen 2 and Gen 3 averages are below. (Figure 7).

We then divided the Gen 3 average by the Gen 2 average. For the PC-170622 run this ratio is below. (Figure 8) Here we see that the Gen 3 is more efficient at wavelengths above 575 nm and less efficient below. This analysis is still subject to the problems imposed by the large amount of variation in the device performance. So we cannot necessarily rely on this data to tell us that Gen 3 is 3% more efficient at 625 nm and 5% less efficient at 450 nm. For the 6 runs that we did comparing Gen 2 and Gen 3 in 2 cases the Gen 2 was more efficient and in 4 cases Gen 3 was more efficient. However in all of the cases there was the same basic wavelength dependence shown below. That is the Gen 3 was relatively more efficient at higher wavelengths and relatively less efficient at lower wavelengths.



(a) **(b)**

Figure 7 – The averages of the EQE of Gen 2 and Gen 3 devices in relation to intensity for run PC-170622.

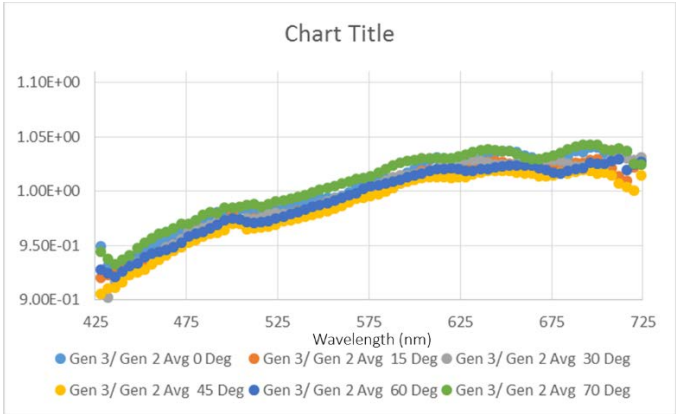


Figure 8 - Gen 3 average divided by the Gen 2 average for run PC-170622.

We believe that this is due to the fact that the Gen 3 samples that we have prepared have higher absorbance at all wavelengths but especially at lower wavelengths. This is not an inherent feature of Gen 3 light extraction structure but rather represents the current stage of our process. We are able to measure the Gen 2 and 3 absorbance at Pixelligent before any processing. What really matters is the absorption of the extraction layers in the functioning device and that absorption will be higher than what is measured below because the processing of the device (mainly heating the substrate for ITO deposition) will increase the absorption especially below 550 nm. However the absorption in the device is more difficult to measure so the values measured at Pixelligent represent the minimum absorption added by the extraction layers.

The absorption data can be used to estimate how much light is lost due to the extra absorption from the Gen 3 extraction layer. Performing a rigorous analysis would be complicated because the scattering particles mean the light will not take a straight path through the extraction layer and light at different angles will also have different path lengths. It is also complicated to figure out how many times the light will pass through the extraction layer. The simplest assumption to make is that the light passes through the extraction layer at least one time (which must be true for all light that is extracted) and to use this same correction for all angles of emitted light. In that case the 1 Pass Corrected Intensity (θ,λ) = Intensity $(\theta,\lambda)/(1-A(\lambda))$.In reality the light would, on average, make more than one pass through the extraction layer. If the light makes two passes through the extraction layer the 2 Pass Corrected Intensity (θ,λ) = Intensity $(\theta,\lambda)/(1-A(\lambda))$^2.

Depending on the wavelength and details of the assumptions, the corrections could offer as low as a 1.5% improvement for Gen 3 relative to Gen 2 and as high as a 15% improvement. We have not calculated the overall improvement integrated over all wavelengths. This shows that the additional absorption added by the Gen 3 layer as compared to the Gen 2 layer is significant, especially for blue light. Also the absorption in the actual devices is likely to be greater than the absorption data used here, which was taken immediately after the films were made and before any processing occurred.

MH2-170112

One of the more successful runs was MH2-170112. (Figure 9) Only 1 out of 10 devices did not yield and that was one of the controls. All 8 devices with Pixelligent's IEL (4 Gen 2 and 4 Gen 3) were successfully fabricated. While the OW control appears to be less efficient (have a lower EQE, 25.4%) than a typical control (EQE ~40%), the rest of the devices were more consistent than other runs. (Table 1) The devices with Pixelligent extraction layers had EQEs that range from 97.4% - 109% with 6 of the 8 devices between 104% and 109%. Also these devices had high EQEs. The Gen 3 devices had an average EQE of ~107%. When compared to a typical OW control

with an EQE just under 40% this is about 2.7X improvement in EQE. In this case it does not make sense to compare to the one control from this run, which had an EQE of 25.4% (which would give an EQE enhancement of greater than 4). The Gen 2 devices had an average EQE of ~102%.

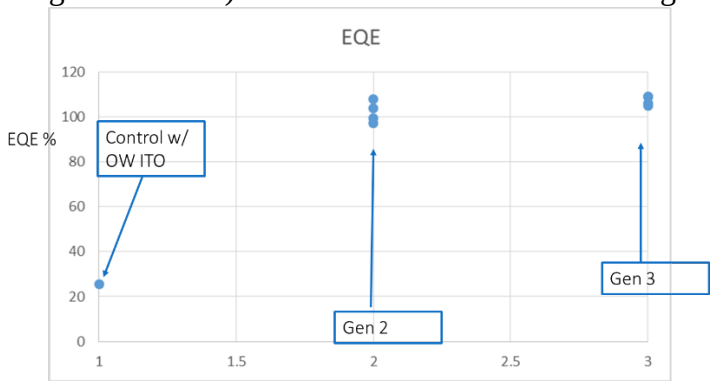


Figure 9 – The variation in the EQE measured for Gen 2 and Gen 3 devices in run MH2-170112.

Figure 10 shows the ratio of the Gen 3 average to the Gen 2 average. Again we see that the Gen 3 is relatively more efficient at longer wavelengths. When these devices were made we did not understand the importance of the relative absorption between Gen 2 and Gen 3 so we did not measure the absorption at that time and therefore cannot correct for the absorption.

Table 1. The EQE measured for each device within run MH2-170112

Type	Pix I.D.	EQE
120216-A6	Gen2	97.4
120216-A8	Gen2	99.5
120216-A9	Gen2	108
120216-A10	Gen2	104
OW Control	OW	
120216-C6	Gen3	109
120216-C7	Gen3	105
120216-C8	Gen3	106
120216-C10	Gen3	109
OW Control	OW	25.4

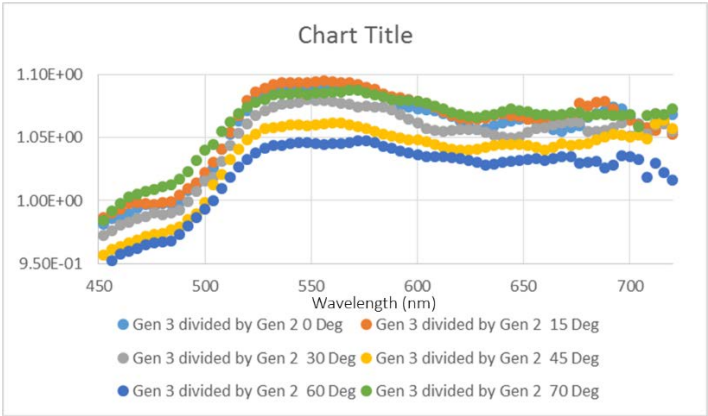


Figure 10 – Gen 3 average divided by the Gen 2 average for run MH2-170112.

The Importance of Blue Light

Because the Gen 3 has relatively more absorption in the blue, correcting for absorption gives relatively greater efficiency in the blue. Because fluorescent blue emitters are used, every

additional blue photon extracted potentially saves 4 electrons, whereas every additional red and green photon extracted saves only 1 electron.

Conclusion

We have demonstrated a significant improvement in light extraction. This improvement comes from a combination of the proper scatterers contained in a high index binder. This project represents, to the best of our knowledge, the first such demonstration in the world. In this program we successfully created a stable high index formulation with scatterers. We were able to coat this formulation using inkjet printing, spin coating, and slot die coating. Through a combination of formulation and process improvements we were able to create low defect coated substrates that OLEDWorks was then able to use fabricate very efficient OLEDs. These OLEDs had uniform color as a function of angle with up to a 2.7X improvement in light extraction. We were also able to create a process for creating and verifying a gradient index.

Due to significant variation in device performance we have not been able to determine the added efficiency that comes from having a gradient index in addition to scatterers contained in a high index binder. The evidence slightly favors that having the gradient index does improve efficiency in the 5 – 10% range. It is also difficult to tell the difference because the current Gen 3 samples that Pixelligent makes have more absorption than our Gen 2 samples. Both samples have more absorption than is desirable and it should be possible to make samples with much lower absorption. This is good news because even with this current high level of absorption we have been able to make practical OLED devices with the most efficient light extraction yet shown and we have a way to continue to boost this efficiency.

Bibliography

[1] National Research Council, "Assessment of Advanced Solid State Lighting," The National Academies Press, 2013.