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Background

The past few years have witnessed rapid growth in the market share of solid state lighting (SSL), including light emitting diodes (LEDs) and Organic light emitting diodes (OLED). SSL is a paradigm-shifting technology that can potentially reach nearly 100% energy conversion efficiency. The luminous efficacy of radiation (LER) of SSLs, measured as lumens per watt (lm/W), can potentially achieve a two-fold increase over the most efficient lighting devices currently in use today. The theoretical upper limit of LED efficacy is above 400 lm/W [1] and today the record efficacy for commercial LEDs is 200 lm/W by Cree Inc., greatly surpassing the best fluorescent lamps; the current record for OLED is 156 lm/W by NEC Lighting, [2] albeit on a small substrate with non-scalable technology. In addition, SSL is far superior to conventional lighting in terms of reliability and lifetime compared.

OLED technology offers several unique advantages: They are inherently ultrathin film devices that can be deposited on any smooth large area substrates, even flexible substrates, enabling dramatically different form factors; the devices themselves can reach near 100 percent internal quantum efficiency; the colors of the devices are easily tunable from blue to near infrared to provide broad band full spectrum white, by simply varying the doping; and the devices induce minimal temperature rise, even when operated at very high brightness. In terms of technology development and readiness levels however, OLEDs lag their inorganic counterparts by several years.

Challenges Facing OLEDs

The main challenges that are facing the market adoption of OLED technology, as identified in the National Research Councils' 2013 Assessment on Solid State Lightings, are the cost of the materials and the low light extraction efficacy.[2] Given the fact that the LER of current commercially available OLED lighting is ~ 20-30%, significant near-term cost reduction can be achieved by the improvement of the light extraction efficiency of the device.

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White Paper: Pixelligent Zirconia Nanocrystals for OLED Applications

The overall external quantum efficiency for a typical OLED device structure shown in Figure 1 can be described as: [4]

$$\eta_{EQE} = \gamma \eta_{exc} \chi \eta_{coupling}$$

where γ is the electron–hole charge balance factor, η_{exc} is the ratio of radiative to non-radiative recombination of excitons (η_{exc} = 1/4 and 1 for fluorescence and phosphorescence based OLED materials respectively), and χ_p is the intrinsic quantum efficiency for radiative recombination (including both fluorescence and phosphorescence). And $\eta_{coupling}$ is the light extraction efficiency of the device. Currently, the light extraction efficiency of OLED lighting devices is only ~ 42% and overall panel efficiency is only 23% according to the 2013 DOE Multi-Year Program Plan according to. [2]
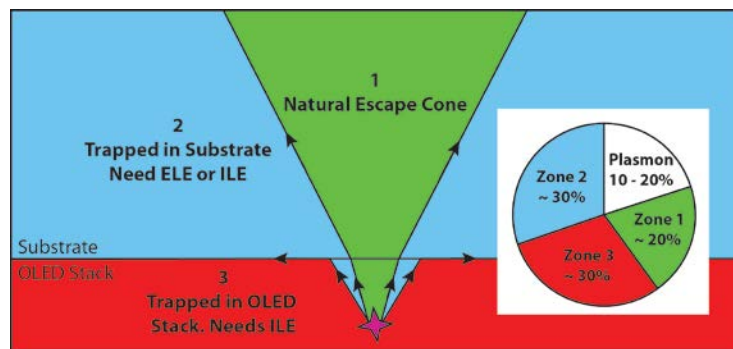

Figure 1: A much simplified illustration showing the three major zones of light distribution in an OLED device and the inset shows the rough break down of all four light loss mechanisms.

The root cause of the light loss is the mismatch of the refractive indexes of the OLED active materials, the anode material, i.e. indium tin oxide (ITO), and the substrate, i.e., glass. When light travels from a material with a high refractive index into a material with low refractive index, if the incident angle is larger than a critical angle, it experiences total internal reflection (TIR). As a result, the light produced can be trapped either in the OLED stack or the substrate. The three major zones of the light distribution in a typical OLED lighting device are shown in Figure 1. The mechanisms that were not included in Figure 1 are the plasmonic loss that occurs at the cathode surface and absorption in organic layers. Due to the large number of interfaces in an OLED device, the losses by TIR at these interfaces quickly add up and the total
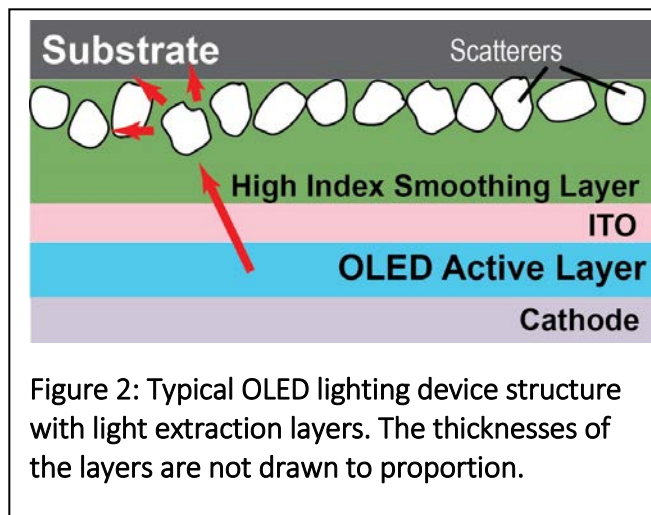
light extraction efficiency is only ~ 20 - 25% without any light extraction scheme. The light that undergoes TIR is absorbed and turned into heat, reducing the reliability and lifetime of the device.

Many approaches have been proposed to improve the light extraction efficiency of OLEDs at different interfaces. The majority of extraction research and development falls into three categories:

- External light extraction: surface modification at the glass/air interface including substrate shaping, scattering layers, and micro-lens patterns;
- Internal light extraction: effective index of refraction modification, photonic crystal, buckling structure, or scattering layers within the OLED device;
- Cathode refinement: patterning, topography and microstructures to inhibit plasmonic losses at the metal cathode surface;

The common theme of all these approaches is to avoid smooth interfaces to suppress TIR and disrupt the resulting wave-guide modes. [4]

Figure 2: Typical OLED lighting device structure with light extraction layers. The thicknesses of the layers are not drawn to proportion.

Significant advancements in efficacy can be made through internal extraction techniques alone. However, integration of the light extraction structure within the OLED structure presents additional challenges. As an example, Figure 2 shows a common internal light extraction scheme with light scatterers, where the direction of emitted light is randomized by the light scatterers. The scatterers are usually inorganic particles with high refractive index and have to be larger than the light wavelength to scatter light efficiently. The large size of the scatterers compared with the layer thickness results in high surface

roughness of the scattering layer which lowers the yield and reliability of the OLED devices to unacceptable levels.

Therefore, a smoothing layer is critical to enable the light scattering scheme. The smoothing layer must have surface roughness less than ~2 nm to avoid negative impact on yield and reliability. It must also have high refractive index, >1.7, preferably >1.8, close to that of ITO, with high transparency, to avoid index mismatch with ITO and allow the light to be transmitted to the scatterers.

Aside from the index and transparency, the smoothing layer must be able to cost-effectively meet the following requirements:

- Compatibility with OLED device structures without affecting the scattering uniformity;
- Compatibility with OLED materials, including chemical, mechanical and thermal compatibility;
- Compatibility with the OLED lighting manufacturing processes, including compatibility with common low-cost coating techniques, low volatility, no out-gassing, high thermal stability, and compatibility with laser patterning and lithography processes;
- Compatibility with OLED operation conditions, including maintaining performance over standard temperature and humidity ranges.

A similar smoothing layer is required for light extraction schemes where grid patterns or photonic crystals are involved. Before Pixelligent developed its proprietary nanocrystal based formulation, a material that meets all these requirements did not exist, causing a major barrier for OLED efficacy improvement.

Figure 3: DOE projection on the cost of materials on processed substrates ($/m^2)
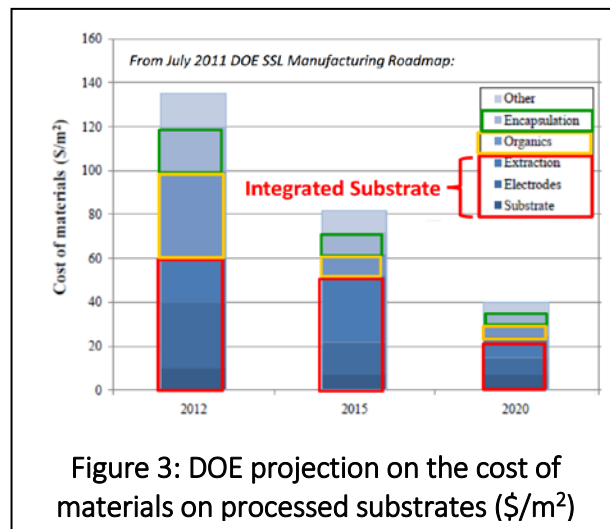
In addition to the performance and compatibility, the cost of the Pixelligent's material is in line with the DOE projection. As indicated in the DOE 2011 SSL Manufacturing Roadmap, the performance improvement must be associated with cost requirements as well. The contribution of the extraction layers to the total product cost is projected to be less than $10/m^2$ by 2020, a 90% reduction from current technologies while simultaneously doubling the extraction efficiency. Because of the inherent scalability of Pixelligent's nanocrystal manufacturing process and because only a very thin layer is required, we estimate that additional cost to the extraction structures will be able to approach and ultimately exceed the DOE 2020 target. The benefit of much improved yield and LER will significantly out-weight the additional cost. More importantly, a nanocomposite material with tunable refractive index that is compatible with OLED manufacturing introduces new degree of freedom of design to the light extraction structures, for example, an integrated scattering/smoothing layer or a single graded index layer. In the latter case the scattering layer is no longer necessary and the cost of the light extraction layer itself can be reduced.

Significance of Pixelligent's High Index Nanocomposites

Most polymers have refractive indexes less than 1.6, while many inorganic materials possess high refractive indexes greater than 1.6. For example, TiO_2 has a refractive index of ~ 2.6 in the visible spectrum, and is the material with the highest refractive index in the visible spectrum. However, bulk inorganic materials require high temperature growth processes, which is impractical for the OLED manufacturing processes. Most of the materials used in OLEDs are polymers, which are very easy to process and integrate into complex device structures. Combining the advantages of both material systems, nanocomposites composed of inorganic nanocrystals with polymer matrices are great candidates for high refractive index materials for OLED manufacturing.

Nanocrystals are particles of a material, typically tens of nanometers or smaller, that retain the stoichiometry and crystal structure of their bulk counterpart. Nanocrystals have been the focus of accelerated scientific studies for the past two decades because they often demonstrate novel (sometimes undiscovered) properties as a result of the reduced sizes. Moreover, nanocrystals can be surface treated with various capping agents and dispersed into polymer matrices to form nanocomposites that can be used in applications where bulk materials are impractical or novel and integrated functionalities are

required. When nanocrystals are dispersed into an optically transparent polymer, the refractive index of the resulting nanocomposite, assuming the diameters of the nanocrystals are much smaller than the wavelength of the light, is approximated as: [7]

$$n_{eff} = n_{nano} \times v_{nano} + n_{poly} \times (1 - v_{nano})$$

where n_{nano} and n_{poly} are the refractive indexes of nanocrystals and the polymer matrix respectively, and v_{nano} is the volume loading of the nanocrystals. The nanocomposite combines the high refractive index of the inorganic material and the ease of processing of the polymer, creating a new class of materials that is ideally suited to be used as high refractive index layers for OLED light extraction.} Although many previous attempts to produce high refractive index nanocomposite have been focused on TiO_2 for its high bulk refractive index, [8] Pixelligent has chosen to pursue ZrO_2 for a number of reasons, including:

- ZrO_2 nanocrystals are chemically inert and a stable material in the nanocrystal form; nano-sized TiO_2 is photo-chemically active and is actually sometime used as photo-catalyst;
- ZrO_2 has a much larger bandgap, ~ 5.8 eV, and has very little absorption down to deep UV region, TiO_2 has a bandgap of ~ 3.4 eV and its absorption tail stretches into the visible spectrum;
- The refractive index of ZrO_2 has a much smaller wavelength dependency than TiO_2, i.e. high Abbe number. This is a direct result of the large bandgap of ZrO_2; and
- ZrO_2 can be perfectly dispersed into a large variety of solvents, monomers, and polymers

The concept of combining inorganic nanocrystals with polymer matrices to produce high refractive index nanocomposites has been around for a while. However, there are few commercial products for such a material. The barrier to market entry can be mainly attributed to two factors, dispersion and scalability of the nanocrystals:

1. Dispersion in the polymer matrix: To minimize the light loss due to Rayleigh scattering, the size of the nanocrystals has to be less than one tenth, frequently significantly less than one tenth, depending on the application, of the working wavelength. It must also be free of agglomerations. Without a proper capping and dispersion technology, it is difficult to reduce the light scattering and the resulting nanocomposites often look cloudy or even opaque.

2. Scalability for commercialization: Many nanocrystals and nanocomposites show promising results in the laboratories but are not commercially viable because the materials are difficult to manufacture at commercial scale while simultaneously meeting cost and batch to batch uniformity necessary for a commercial product.

In the past few years, Pixelligent Technologies LLC has developed high quality sub-10 nm ZrO_2 nanocrystals with precisely engineered surface chemistry. The capping agents on the nanocrystals can be tailored to be compatible with a broad array of solvents, monomers and polymers. The sub-10 nm particle size is only about one fiftieth of the wavelength and is comparable to the size of polymer molecules. At this size range, the nanocrystals induce minor, if any, amounts of scattering, even with very high loading and large layer thickness. In addition, Pixelligent's nanocrystals manufacturing technology is inherently scalable. Funded through an $8.3M NIST Technology Innovation Program (TIP), Pixelligent
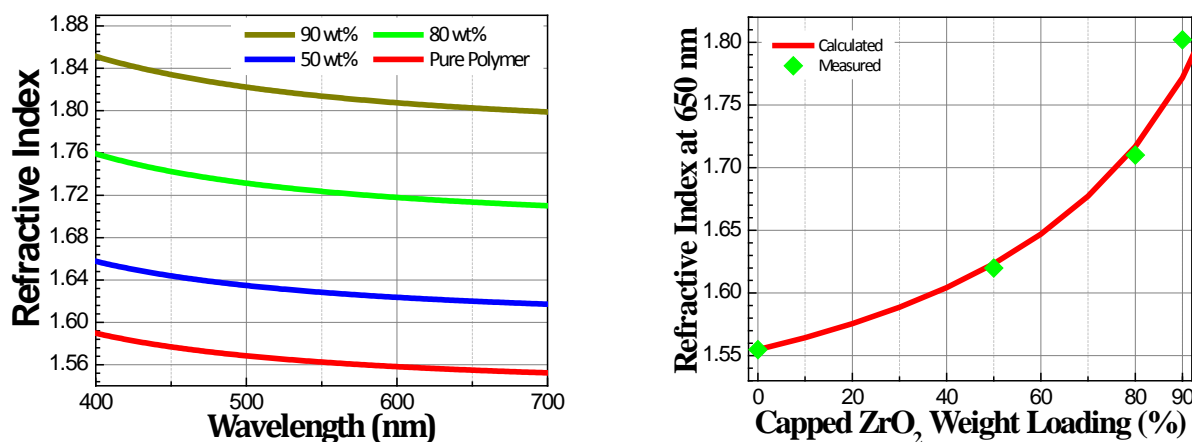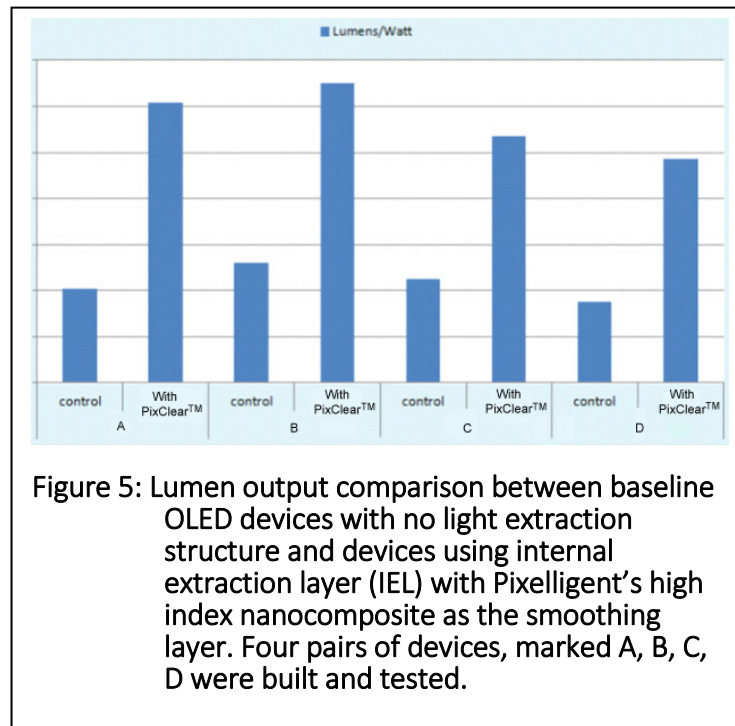

achieved a remarkable 10,000-fold scale-up in three years and currently has a 5 ton/year capability and is further scaling up our production capacity. This level of production will satisfy the initial market demand while meeting cost targets.

a)   b)

Figure 4: a) Refractive indexes of the acrylic/capped ZrO_2 nanocrystal nanocomposite films with different nanocrystal loading as measured with Woollam M2000 ellipsometer; and b) The calculated refractive as a function loading vs. the measure values. The near perfect match also indicated the high quality of the dispersion.

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Figure 5: Lumen output comparison between baseline OLED devices with no light extraction structure and devices using internal extraction layer (IEL) with Pixelligent's high index nanocomposite as the smoothing layer. Four pairs of devices, marked A, B, C, D were built and tested.

Pixelligent's nanocrystals, therefore, have overcome the two key challenges in commercially applying nanocrystals as high refractive additives. The quality and versatility of our nanocomposites have attracted many customers in the lighting and display industry. The initial results performed by our industrial partners have demonstrated that our nanocomposite can provide the high refractive index required for the light extraction applications and the material is largely compatible with the manufacturing process of OLED lightings. Preliminary results carried out by a partner showed that Pixelligent's high index nanocomposite is capable of tripling the lumen output (Group A in Figure 5), when compared to a standard white OLED panel fabricated in the lab while meeting the surface roughness requirement when coated on top of the scattering layer, note that the gain showed in the figure was the raw lumen gain and was not adjusted for color-point shift.

Summary

Pixelligent's proprietary ZrO_2 nanocrystals synthesis and superior dispersion technology has enabled the optical grade high refractive index nanocomposite that can potentially meet all requirements by the OLED manufacturing process for the light extraction applications in solid state lighting. Pixelligent is currently funded by a DOE SBIR Phase I Grant and DOE SSL R&D Grant to explore different approaches to use our nanocomposite for OLED light extraction to meet DOE performance and cost targets.

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