

# Thin Film Photopatternable Quantum Dot Downconverters with High Optical Density

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## ABSTRACT

We demonstrate a scalable fabrication method for tri-color high-resolution microLED and OLED displays using photopatternable InP-based QDs. Using photosensitive ligands, we demonstrate pixel resolutions of 10  $\mu\text{m}$  with EQE of >40% in <10  $\mu\text{m}$  thickness for green and red InP QDs. Reliability measurement is performed under accelerated conditions and modeled to calculate an expected lifetime of >10k hours for direct-view microLED operating conditions.

## 1 Introduction

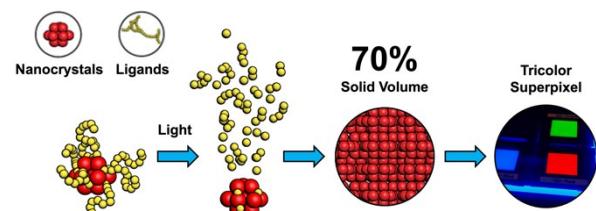
In recent years, micro light-emitting diode (microLED) technology has attracted widespread research attention due to advantages such as energy efficiency, high brightness, high dynamic range, and wide viewing angle. The application space for microLED displays is diverse, encompassing display sizes ranging from multi-story video walls down to <0.5 mm diameter microdisplays as seen in AR contact lenses (Biwa et al., 2019; Martin, 2022). Development of full-color microLED displays is being approached by a variety of architectures, including direct red, green, and blue emission as well as quantum-dot downconversion of blue or UV pumps. Each of these approaches may play a part in the future of microLED technology, as different applications may not culminate in a “one size fits all” solution. These different microLED architectures may have tradeoffs in cost, manufacturing complexity, efficiency, and color gamut.

One of the main challenges for microLED technology is to deliver on the promised efficiency gains while shrinking pixel size to enable the dramatic cost reductions necessary for adoption. LED chips are the largest cost contributor to microLED displays, and the cost scales with the total die area. Virey and Bouhamri have projected that die sizes in the range of 5-10  $\mu\text{m}$  will be required in order to address the high-volume markets for TVs, tablets, laptops, and smartphones. (Virey & Bouhamri, 2021) Furthermore, to address applications such as AR headsets, even smaller die sizes, in the range of  $\leq 2 \mu\text{m}$ ,

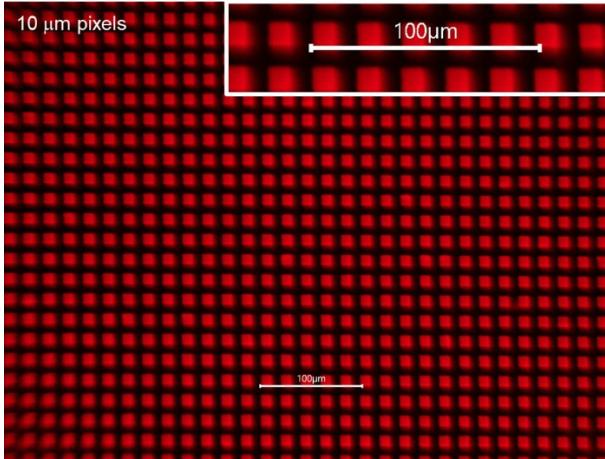
may be required.

With these stipulations in mind, quantum dot downconverters are an attractive method to ease manufacturing complexity and reduce cost.. However, these materials must demonstrate that they can meet the needed resolution while maintaining high efficiency, optical density, and reliability under operating conditions. Traditional quantum dot (QD) photoresists combine QD with a conventional photoresist material to provide a photopatternable functionality. Because the QDs are dispersed in a photoresist and due to the low inherent absorption strength of InP, these materials may be limited to pixel sizes greater than 25  $\mu\text{m}$ . Likewise, traditional ink-jet lithography is also limited to pixel sizes larger than 25  $\mu\text{m}$ .

In contrast to traditional QD photoresists, direct optical lithography of functional inorganic nanomaterials (DOLFIN) enables direct photopatterning of optically dense QD films. (Wang et al, 2017) In this process, a substrate is coated with an ink made of nanoparticles that are functionalized with a photosensitive ligand. As shown in Figure 1, the ink is then selectively modified via exposure to a patterned light source and the substrate is treated with a developer solution, which removes either material type, by which multilevel patterns may be formed.



**Fig. 1.** In the DOLFIN process, photocatalyzable ligands are used to create a nanoparticle ink. Under exposure to light, these ligands are removed and a fully dense nanoparticle layer at up to 70% solid volume is formed.



**Figure 2:** 10  $\mu\text{m}$  InP red quantum dot pixels patterned with a film thickness of 5  $\mu\text{m}$  at an optical density of 1.3.

The high volume density of nanoparticles enables films with greater than 2x decreased thickness for the same optical density (OD) as compared to QD-photoresist (Etheridge et al, 2021). Figure 2 shows an example of red InP QD photopatternable ink coated on top of a matrix of SU8 wells on glass and photopatterned with the DOLFIN technique to produce an array of 10  $\mu\text{m}$  pixels at 10  $\mu\text{m}$  pixel pitch. The coated quantum dot layer is 5  $\mu\text{m}$  thick at an OD of 1.3.

For DOLFIN processing to create commercially competitive materials, the films must not only possess the high OD and good patterning properties demonstrated previously, but also show high conversion efficiency of the pump wavelength to the downconverted wavelength. This value is measured as the percentage of emitted downconverted photons over incoming blue photons, also known as External Quantum Efficiency, or EQE, as shown in Equation 1.

$$\text{EQE}(\%) = \frac{\text{\# of emitted downconverted photons}}{\text{\# of pump photons}} \quad (1)$$

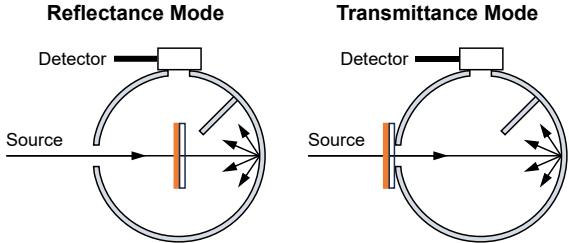
Additionally, to verify the compatibility of the DOLFIN processed films with microLED technology, the layers patterned through direct optical lithography must also retain good reliability under blue flux.

Therefore, this work seeks to demonstrate the viability of this process through measurement of the conversion efficiency and reliability of photopatternable quantum dot inks.

## 2 Experiment

### 2.1 Measurement of External Quantum Efficiency

Red and green InP-based quantum dots from Nanosys, part of Shoei Chemical, were formulated into photopatternable inks and blade coated onto glass slides. The EQEs of the green and red QD films were measured



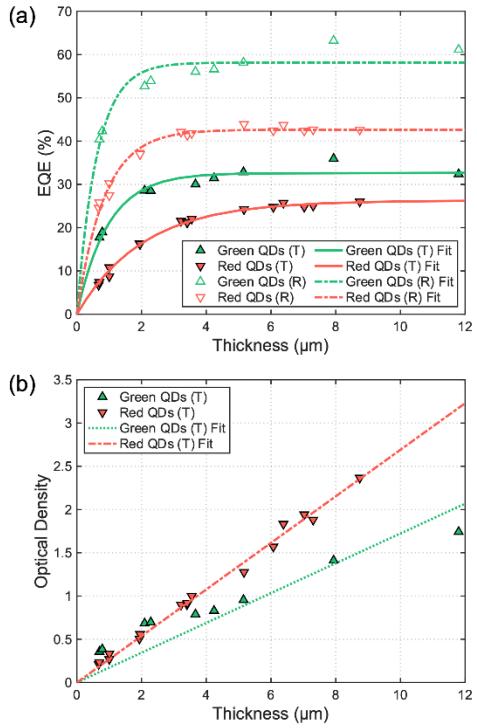
**Figure 3:** Schematic of integrating sphere setup: (a) Reflectance mode; (b) Transmittance mode.

using a Thorlabs M455F3 (455 nm) fiber-coupled LED, a Thorlabs FL457.9-10 laser line filter, a Labsphere 3P-GPS-060-SF integrating sphere, and an Ocean Insight OCEAN-HDX-VIS-NIR spectrometer. The measurements were carried out in both reflectance and transmittance configurations as illustrated in Figure 3.

Because of the importance of the measurement geometry on the measured EQE, both reflectance mode and transmittance mode measurements are shown. In a real device, the QD film will be coated onto a microLED, somewhat akin to a transmission mode measurement instead of in a reflective geometry. However, photoluminescence (PL) is uniform in all directions, and half the emitted photons are emitted backwards and not captured by the integrating sphere in a transmission mode measurement. In a real device, the back-emitted photons would be largely reflected by the microLED which is not strongly absorbing to sub-bandgap light, producing a geometry closer to the reflectance mode EQE.

### 2.2 Reliability Testing

To evaluate the reliability of the QD films under high blue flux accelerated conditions, the QDs were drop-cast directly onto Luxeon Z LED chips with a flip-chip architecture. The blue light intensity of the LED chips was calculated from datasheet values of flux, assuming the 1  $\text{mm}^2$  chip size as the area of illumination (Lumileds, 2021). At the low currents used in this testing the radiometric power was fit to a linear relationship of Power (mW) = 1.2923 \* I (mA) where I is the forward current. LEDs were run at 1 mA, 5 mA, and 10 mA, respectively, corresponding to 1.3, 6.5, and 13 mW/mm<sup>2</sup> blue flux. The integrated strength of the downconverted emission was monitored over a period of time under stress conditions. The stress tests were carried out in a nitrogen environment inside a glove box to simulate encapsulated device conditions. The LED flux was measured in a Labsphere STAGE-RTL-T reflection-transmission stage and the emitted LED spectra were captured at every measurement point with an OCEAN-HDX-VIS-NIR spectrometer. Control blue LEDs with no QD films were measured at each test point to ensure the oxygen-free environment did not cause LED degradation at these test currents.

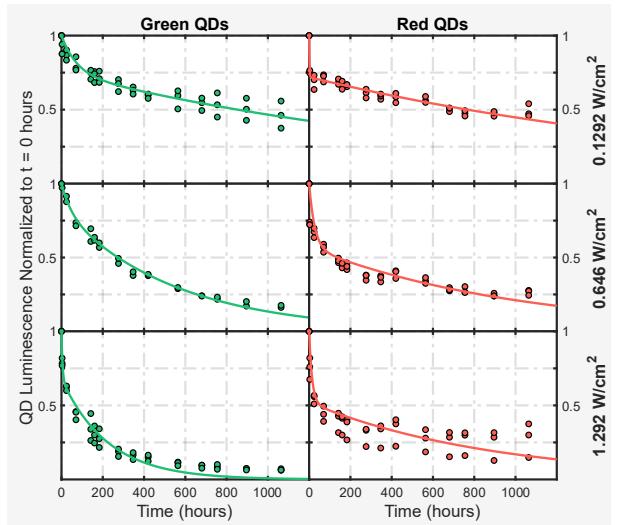


**Figure 4:** (a) EQE in transmission and reflectance mode and (b) OD of green and red InP dense photopatternable QD films as a function of film thickness.

### 3 Results and Discussion

The EQE of green and red photopatternable QD films is shown as a function of film thickness in Figure 4. Due to effects of light absorption, the EQE asymptotes at thicknesses above approximately 6  $\mu\text{m}$  (Figure 4a). Due to the high retained PLQY of these films as shown previously (Etheridge et al, 2021), EQEs above 40% (reflectance mode) can be observed for red QD films and above 50% for green at a layer thickness of only 6  $\mu\text{m}$ . In transmittance mode, the max EQE is in the range of 25% for red QDs and 35% for green QDs. The OD of both green and red QD films increase linearly with increasing film thickness (Figure 4b), with both films yielding an OD of 1 at thicknesses less than 6  $\mu\text{m}$ . While the red films are more absorbing compared to green, the higher EQE values can be attributed to higher internal PL quantum yields for the green quantum dots.

The reliability of both green and red QDs were measured in an on-chip configuration as described in section 2.2. While the reliability of CdSe quantum dots in an on-chip configuration has been well established, (Shimizu, 2017) to our knowledge, this is the first on-chip reliability measurement of dense InP quantum dot layers. The blue LEDs were run at a variety of currents to simulate operating conditions in a range of 0.13 to 1.3  $\text{W}/\text{cm}^2$  (approximately 77k to 770k nits). This approach allowed reliability testing to be conducted under

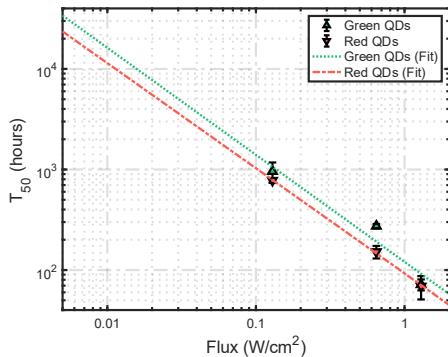


**Figure 5:** Reliability (downconverted intensity normalized to initial downconverted intensity) of green and red dense photopatternable QD films drop-cast directly onto an LED as a function of blue power.

significantly accelerated degradation compared to typical operational parameters of OLEDs (~500 nits) or microLED displays (~5000–50k nits). For thicker, dilute quantum dot films, accelerated lifetime testing at high blue light fluxes has been used to predict long-term lifetimes in typical blue flux operating conditions. (Jen-La Plante, 2023) We have adapted this technique to LED-level testing in order to predict expected lifetimes for our films in operating conditions for direct-view microLEDs. Because excitonic transfer through FRET between adjacent quantum dots may lead to lower reliability of dense quantum dot films compared to dilute films, it is important to validate that the reliability of dense quantum dot color converting layers for microLEDs can be sufficient for typical operating conditions.

Figure 5 describes the degradation rates of both green and red photopatternable QD layers at different blue intensities. Multiple LEDs were tested for each QD color and blue flux, and their intensities (normalized to  $t=0$ ) were plotted as a function of time. As expected, the degradation rates for both QD films increase rapidly with increasing blue flux.

The decay in PL intensities of both our photopatternable quantum dot inks were found to have two distinct phases, a rapid initial degradation followed by a slower decline. Thus, the reliability trends were fitted to a dual exponential function,  $y = Ae^{-Bx} + (1-A)e^{-Cx}$ , where the free parameters A, B, and C were optimized using a least-squares algorithm. The trend lines shown in Figure 5 were calculated based on the average decay rates for a given LED and blue power. However, in the subsequent analysis, each LED is treated separately, and fitted with its own decay function.



**Figure 6:** Variation of QD film lifetime as a function of blue power.  $T_{50}$  refers to the average operation time of a given LED when the downconverted emission intensity of the QD film drops to 50%. The error bars represent the standard error for each LED data set.

LED lifetimes were characterized by evaluating the time taken for each LED to decay to 50% of its initial emission intensity ( $T_{50}$ ) based on their respective fit functions. While  $T_{90}$  has been previously reported by others, the acceleration factors used here lead to such fast initial degradation that our fits give higher fidelity to a model of 50% degradation. Figure 6 shows the variation in  $T_{50}$  for green and red formulations as a function of blue intensity on a log-log plot. As expected, a negative correlation is observed between the LED lifetimes and blue intensity. These trends can be extrapolated to estimate the lifetime of LEDs at lower powers characteristic of typical direct-view displays. For reference, a state-of-the-art smart watch (2023 Apple Watch Ultra) operates in the range of  $\sim 3000$  nits. This level of luminance can be roughly estimated to require a blue pump power of approximately  $\sim 0.005$  W/cm<sup>2</sup> based upon the established relationship between luminance and blue pump power for typical solid state lighting applications. Due to the small number of LEDs tested these should be used only as rough estimates. Based on our fits the estimated  $T_{50}$  lifetimes for green and red photopatternable InP QD films at a blue flux of 0.005 W/cm<sup>2</sup> are 34k and 24k hours, respectively, while at 0.01 W/cm<sup>2</sup> blue flux the  $T_{50}$  lifetimes are 16.2k hours for green and 11.4k hours for red.

#### 4 Conclusions

As microLED technology progresses, it is important to consider all the engineering parameters which must be simultaneously optimized to meet all requirements for commercialization, including patterning, optical performance, and reliability. In this study, it was demonstrated that an InP-based QD downconverter film that can be photopatterned at  $<10$   $\mu$ m lateral resolutions can reach transmission EQEs above 30% and reflectance-mode EQEs of  $>55\%$  at layer thicknesses of

$<10$   $\mu$ m, opening the way to QD downconverter applications at small pixel sizes. Simultaneously, a 10  $\mu$ m film thickness is demonstrated to have optical densities of over 2 for red and over 1.5 for green. With these photopatternable QD inks, it is shown that the QD layers have an estimated lifetime of  $>10k$  hours under typical operating conditions, based on accelerated reliability testing in an on-chip configuration. This already appears close to sufficient for direct-view microLED applications, and as the reliability of InP QDs continues to improve, it is anticipated that the stability and performance of photopatternable InP QD inks will enhance further.

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