High Optical Density
Quantum Dot Pixel Color Conversion Films for Displays

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Abstract

Quantum Dot downconverters will enable high-resolution, bright, and wide color gamut displays for all display formats. We have developed a method to directly photopattern densely packed InP/ZnS Quantum Dots that achieve an optical density of 2 at sub 10 µm thicknesses while preserving high photoluminescence quantum yield.

Author Keywords

Quantum Dot Downconverters; Optical Density; Photolithography.

1. Objective and Background

A macroscopic view of the display market shows growing interest in high resolution, wide color gamut, bright, and fast refresh rate displays. One promising candidate in this arena are micro-LED displays, they have earned this interest from the real-world energy savings associated with the established LED technology and the ability to create the high resolution displays for applications in smartphones and wearables. Furthermore, micro-LEDs are showing the ability to address the needs of the Augmented Reality (AR) and Virtual Reality (VR) display markets due to their superior energy efficiency, refresh rate, and brightness. Currently, micro-LED display manufacturers produce individual red, green, and blue LEDs, then attempt to install them without a single error over millions of pixels to create tricolor displays. As can be inferred from this description, making a tricolor micro-LED display effectively triples the total number of steps compared to a monochrome display, increasing the processing cost as well as reducing throughput. One solution is the use of color converters to transform monochrome displays into their tricolor counterparts [1,2].

Current industrial solutions to address tricolor micro-LED displays include 1) ink jet printing of Quantum Dot (QD) downconverters, 2) incorporating QD downconverters into photo-resin and patterning using photolithography, and 3) using micron scale pick-and-place machines to attach red, green, and blue LEDs. These approaches are aimed at addressing the needs of micro-LED manufacturers by achieving sub 5 µm x 5 µm lateral resolutions, high conversion efficiencies/brightness, and high production throughput. Each one of these approaches have been developed by industry research groups and show promise, however each solution has its own limitations preventing the immediate adoption as illustrated in Figure 1. For inkjet printing, Figure 1b, the ink droplet size and the serial deposition mechanic prevents easy access to resolutions below 50 µm for each sub pixel. Companies such as Kateeva and ITRI have demonstrated micro-LED displays using 50 µm x 50 µm LED pixels for TVs, however at these pixel sizes micro-LED displays will have a difficult time to be cost competitive with OLED [3]. To date no company has demonstrated inkjet printing at the 5 µm x 5 µm lateral resolutions required for many micro-LED applications [4]. A major limitation for QD bound in photo resins, Figure 1c, is that a 30 µm-thick film is needed to fully convert all blue backlight into red or green due to the high concentration of non-absorbing organic additives. Further, 5 µm pixels would result in excessively narrow downconverter pillars that would collapse, limiting the achievable resolutions. To address this issue, companies such as Nanosys and Nanoco are currently developing different QD downconverters with higher absorption. With such QDs still in development, we have seen reports that scale up will be a challenge [5,6]. For pick-and-place methods, Figure 1d, the limitation is speed and throughput. For instance, a single Oculus "Quest" VR headset micro-LED display consists of 2.3M pixels [7]. With current pick-and-place speeds, a single display would take ~100 hours to make. Several companies are working to reduce this assembly time down to ~1 hour through methods such as laser lift-off, fluidic assembly, electrostatic arrays, and elastomeric stamping. However, even with these methods applied, downconverted red and green pixels still offer a 3x advantage in assembly time and corresponding reduction in cost. In addition, using blue LEDs with red and green downconversion avoids the driver complexity needed to drive red, green, and blue pixels made of different semiconductors at differing turn-on voltages [8,9].

To address the unmet needs of the micro-LED downconverter market, NanoPattern Technologies, Inc. (NPT) is commercializing high resolution QD inks for display makers that will convert single color displays into full color displays as a plug-and-play solution that does not require a redesign of their pixel architecture (Figure 1a). This is enabled by patterning a QD film with extremely high packing density while preserving a high photoluminescence quantum yield (PLQY). To accomplish this, the coordinated ligands surrounding the QDs were engineered not only to improve suspension of the QDs into a solvent but also to decompose into volatile constituents upon photoirradiation. The approach is inspired by the work done by Wang et al [10,11] where different ligand chemistries were investigated to enable patterning of the QDs. This paper will focus on the community and NPT's efforts to develop a QD downconverter film that is able to achieve an optical density (OD) of 2 and lateral resolution of 5 µm while preserving PLQY. In this report, we will demonstrate an OD of 2 with varying approaches and QD materials selections compared to the QD encapsulated in a conventional photoresin.

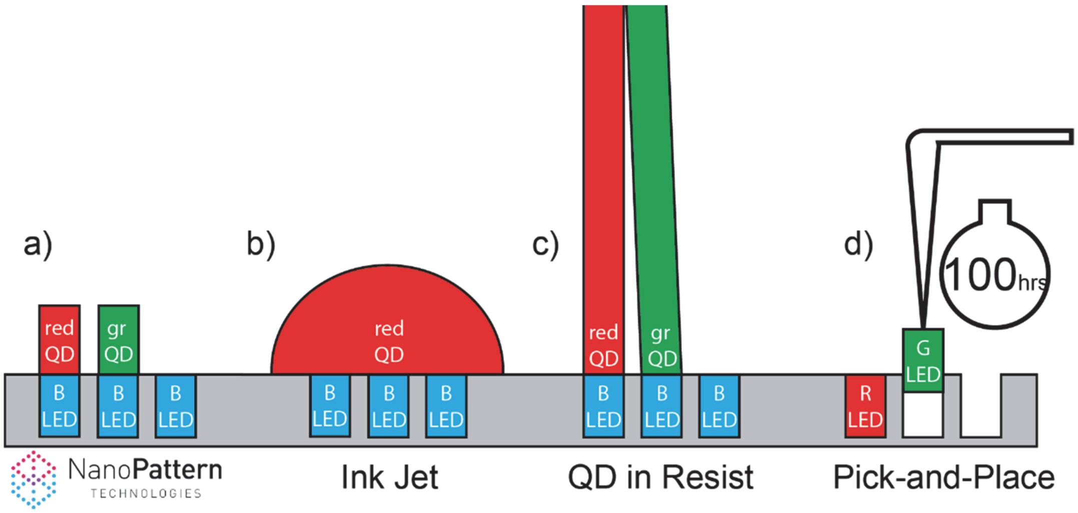

Figure 1. Illustrations of competitor shortcomings for making tricolor micro-LED displays compared to the a) NPT method for: b) inkjet printing, c) photolithography, or d) pick-and-place methods.

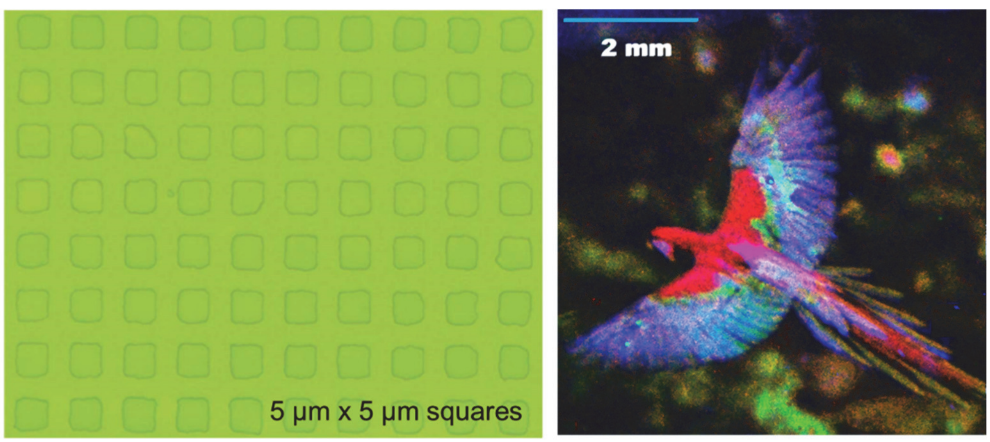

Figure 2. Patterning features of the NPT ink demonstrated as (left) 5 µm x 5 µm square patterns with 5 µm thickness and (right) a tri-colored image of a bird composed of red, green, and blue quantum dots showcasing the ability to multipattern [10].

2. Results and Discussion

In this study, to demonstrate high resolution capabilities, InP/ZnS based QDs were converted into photopatternable inks using NPT's proprietary process. The films were coated via blade coating and patterned using a conventional contact lithography system with 365 nm light. The 5 µm lateral resolution can be seen in the left image of Figure 2. In an earlier study meant to demonstrate the ability to pattern multiple layers, QD inks were used to produce the tricolored image in Figure 2 right [10].

To compare optical properties, 650nm emitting InP/ZnS based QDs were suspended inside of a conventional photoresin, coated using blade coating onto a surface, and patterned. By changing the concentration in solvent and by changing blade coating conditions, film thicknesses ranging from 1 µm to 20 µm were coated to investigate the linearity of the optical density (OD). The patterned films were developed and placed inside of an integrating sphere and excited with a collimated light at 470 nm to measure the degree of absorption and emission. The OD of the film is calculated using Equation (1).

$$\boldsymbol{OD = log_{10}\frac{I_0}{I}} \tag{1}$$

Where I_0 is the intensity count of the excitation beam integrated from 460 nm to 489 nm and I is the intensity count of the transmitted peak integrated from 460 nm to 489 nm. Furthermore, the OD of the QD film is studied from the perspective of a model presented by Osiniski et al [12] in which the OD of a QD film as a function of thickness is calculated assuming that the path of light traveled is the thickness of the film. The OD model used is shown in Equation (2).

$$\boldsymbol{OD} = \frac{\boldsymbol{\mu f t}}{\ln\left(\mathbf{10}\right)}, \quad (2)$$

where t is the optical path length (cm), μ is the bulk-like material property intrinsic absorption coefficient (cm^{-1}) for the InP/ZnS core-shell QD used in this study as calculated from the values given in Table 1 by Osinski et al,[12] and f is the volume fraction of the QD in the film. In this comparison, the optical path length is assumed to be the film thickness, and the volume fraction is adjusted to maximize fit of the model to each data set. The resulting experimental and model prediction values of OD as a function of thickness for the InP/ZnS film are shown in Figure 3a.

By making the ligands themselves photoactive, the photoresin commonly used to prevent dissolution of the QDs is eliminated allowing for near ideal random packing of spherical particles at 65 vol% as estimated by the model. By reaching high packing density, the OD of the film was demonstrated to improve by a factor of 2 at the same thickness when compared to a QD film suspended in a photo resin.

A critical topic that is important for us to demonstrate is the actual conversion efficiency of the downconverter film because the dense packing of the QDs enabled by NPT's technology inevitably decreases the interparticle distances increasing the potential for non-radiative recombination through FRET (Förster Resonance Energy Transfer) as indicated in Equation (3) as well as other energy transfer mechanisms [13,14].

$$\boldsymbol{E_f} = \frac{\mathbf{0.211}\boldsymbol{\kappa^2 \varphi J(\lambda) n^{-4}}}{\mathbf{0.211}\boldsymbol{\kappa^2 \varphi J(\lambda) n^{-4}} + \boldsymbol{r^6}} \quad (3)$$

where E_f is the FRET efficiency, κ is the orientation factor, φ is the solution PLQY, $J(\lambda)$ is the spectral overlap integral, n is the volume weighted average refractive indices of the QD, and r is the core separation distance. Consequently, the PLQY of a densely packed QD film will decrease as interparticle distance, r, decreases. The spectrum of the QD film is shown in overlay with the QD suspended in resist in Figure 3b.As demonstrated in Figure 3b, the PLQY can be preserved even in high density films. Although many of the energy transfer mechanisms cannot be avoided, careful control of the ligand, core, and shell properties can mitigate most energy transfer losses. As synthesis protocols of InP based QDs improve, the full width half maximum (FWHM) of the emission spectrum and the base solution PLQY will improve. These improvements will continue to narrow the deviation between the solution PLQY and densely packed film PLQY by 1) statistically eliminating non-radiative cores and 2) reducing the energy transfer losses due to excitons from smaller InP cores moving to larger InP cores.

Industries looking towards commercializing InP quantum dots have reasonable avenues to achieve high PLQY levels in films. As with other materials, such as CdSe QDs, the percolation of advanced synthesis techniques will benefit the InP quantum dots community and lead to materials with near-unity quantum yield. While CdSe/CdS and InP/ZnS have seemingly disparate chemistries, we have shown that dense InP/ZnS quantum films can reach 50% absolute PLQY, and it stands to reason that as the quality of source particles improve, the film values should rise as well. For instance, in 2019 Hanifi et al. showed that high quality CdSe/CdS quantum dots can achieve 99.6% PLQY in thin films. They achieved this by the careful shell growth around nearly uniform-sized CdSe cores. These steps were taken in order to minimize the impact from non-radiative energy processes in order to maximize the PLQY in films [15]. This result shows that dense quantum dot films can achieve high PLQY.

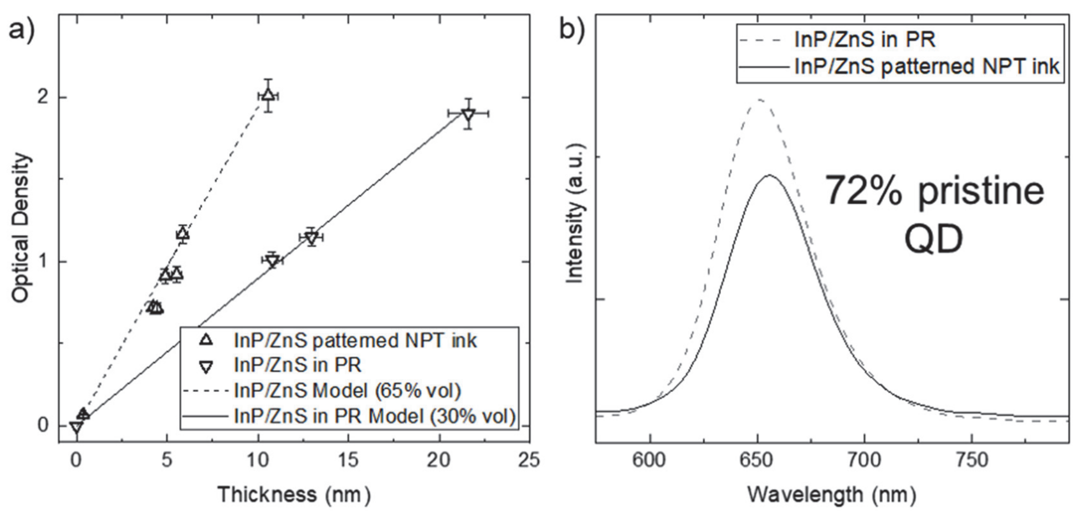

Figure 3. a) Optical Density of the patterned QD film as a function of thickness. Dotted lines are models based off of the work by Osinski et al.[12]) and b) PLQY Data represented as: overlay of the (dashed) Quantum Dot suspended in photoresist and the (solid) patterned film spectrum as well as the PLQY.

3. Impact

In this work, we have demonstrated that an InP/ZnS downconverter film can reliably reach an OD of 2 at sub 10 µm thicknesses while preserving the PLQY of the film. This assuages concerns that the PLQY could not reach needed efficiencies at high densities due to the increased interparticle energy transfer. Furthermore, we find that the model reported by Osinski et al [12] shows an excellent match to experiment. Considering the model assumes that the light travel length is the thickness of the film, it is possible to even further increase the OD of the film by increasing scattering and reflection of the excitation blue photons within the film. The findings in this paper show a clear path to QD downconverters for micro-LED display applications. The QD ink demonstrated in this study features: 1) sub 5 µm lateral resolution, 2) OD of 2 at sub 10 µm thicknesses, 3) conventional photolithography compatibility, and 4) stable PLQY. With further optimization, it is possible to reach the performance needed to commercialize high OD QD pixel color conversion films for displays. In addition to microLED displays, higher OD with thinner downconverters is an attractive feature for all displays utilizing downconverters. For an example, the next generation of TVs that can achieve BT.2020 coverage of over 95% using QD downconverter pixels can improve energy efficiency with a higher OD film because it minimizes lateral loss of photons to the black matrix material [16].

4. Acknowledgements

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