Quantum Dots for Thin Film Optical Conversion

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Abstract

In this paper we explore the properties of Cd-free Quantum Dot based thin film conversion layers as applied to LED chips. We show current optical & reliability performance of such layers in on-chip applications and explore the possibilities that such a QD conversion layer as applied through liquid deposition processes can enable. We also explore the limits of such a system in terms of minimum thickness for full conversion.

Author Keywords

Quantum Dot, Thin Film Conversion.

1. Introduction

Quantum Dots have many unique properties as optical down converter materials. Narrow spectral emission and precise wavelength tunability have previously attracted interest to enable tuning of the optical output of white LEDs. This has already been used by ams OSRAM to add nuance to LED lighting products. Red Quantum Dots were added to the red end of the lighting spectrum to finely tune the output with significant efficiency gains while maintaining very high optical performance. The release of these Quantum Dot enabled LED products was a clear demonstration of the viability of quantum dot converters for on chip LED applications [1]. The initial advances in On-Chip use for lighting applications were based on Cadmium containing Quantum Dot materials but this technology has limitation due to the RoHS regulations on Cadmium use and customer acceptance of even very low levels of heavy metals. These limitations have spurred on the development of Cd-free alternatives [2]. Cd-free Quantum Dot materials are the focus of this work.

Beyond lighting applications, this same spectral purity and precise wavelength tunability have also clear potential with respect to improving the color gamut in display applications. In addition to the emission properties, the high absorption and nanometer scale dimensions open the possibilities to use quantum dot conversion in areas that were previously impossible to address with phosphor-based conversion due to limitations of phosphor dimension and absorption strength.

The possibility to create dense QD films can enable thin converting films that are compatible with LED front end type chip processes such as photolithography and etching. This can allow the conversion technology to move more toward front end LED wafer and chip processing instead of being a separate process in a backend package environment. A more streamlined converted LED production process is then possible. QD conversion enabled LED products including smaller chip size and mini/micro-LED applications are an area where this can contribute value.

2. Experiment

QD Film Formation:

Colloidal Quantum Dots from native growth solutions can be tuned by adjustment of solvent, ligand and QD concentrations for different deposition methods such as spin coating, drop casting and ink jet printing.

For the purposes of on chip testing in this work, we used a QD solution tailored for drop casting. Since a uniform conversion layer is desired, one of the challenges in this case is to avoid coffee ring type effects where the QD solids are deposited towards the edge of the chip. A custom solvent mixture was devised that is able to control Marangoni Flow in the droplet as it is dried, thus making it possible to achieve very homogeneous, dense QD layers directly on the chip or wafer surface. Chips coated in this way can be seen in Figure 1.

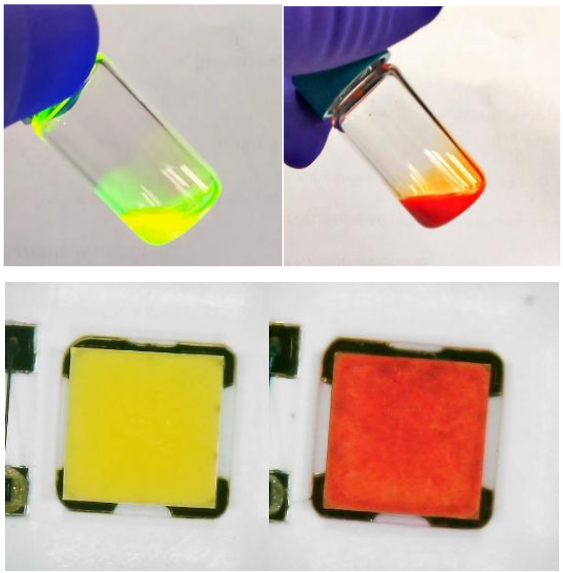

Figure 1. Quantum Dot formulations for Red and Green QD films formed from drop casting and curing QD solutions on blue emitting sapphire flip chips

QD Optical Performance in Film:

The Photoluminescent Quantum Yield (PLQY) for quantum dots can be affected by many different factors ranging from the surrounding chemical environment, concentration effects and drive condition. Extremely high PLQY with values up 100% are often quoted in the literature but this is typically for very dilute, low concentrations systems that are pumped at very low excitation levels. In the case of dense QD films, effects from self-absorption become more evident. Other factors such as coupling between the QDs can also play a role.

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Aiming for application relevant devices, dense QD films using the methods described above were generated and characterized. This resulted in On-Chip QD Films with a measured PLQY ~75% at flux levels of 1.2 W/cm².

This high PLQY value at an appreciable pump flux is in part enabled by relatively low flux droop observed in the Cd-free QD used. A remarkably flat response was measured in the QD architecture used and seen to surpass Cd-based QD performance under similar test conditions – particularly for very high flux levels as shown in Figure 2.

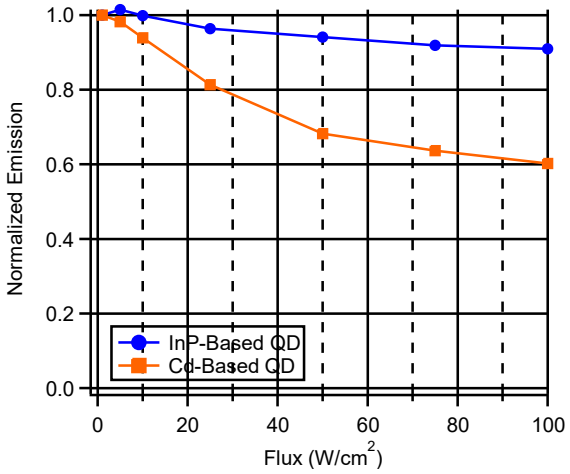

Figure 2. Comparison of flux droop curves of Cd based and InP based QD films up to 100W/cm²

This maintenance of brightness at higher flux level promises to open up higher flux applications areas for Quantum Dots. Loss of PLQY is due to non-radiative processes that typically generate heat or can contribute to negative surface chemistry that damage the QDs. In this case, the reduction of these non-radiative processes over this flux range hints that these materials could perform reliably even under higher flux conditions.

Reliability Results:

The Quantum Dots used in this study were optimized for stability at the nanoparticle level. Both particle passivation layers as well as surface chemistry and solution formulations are critical in both achieving stable material performance for handling and for the making of high-quality Quantum Dot films. In order to further stabilize the Cd-free QD film performance for On-Chip LED testing, metal-oxide films were deposited on top of the Quantum Dot film. Sample preparation included drop casting a QD solution directly onto the LED chip. A bakeout was performed to dry and set the QD layer and to ensure that outgassing of the QD conversion layer would not be an issue in the deposition chamber. Multiple types of metal oxide coatings have been applied; all show improved stability compared to uncoated samples.

Figure 3 highlights the stability achieved in final QD coated On-Chip LED Performance. The LED devices were stressed in HTOL conditions that are relevant for future applications. Samples for test were operated in a 50°C oven and removed periodically for measurement. The test vehicle for samples shown in Figure 3 is a standard chip and package found in commercial indoor illumination; they were driven such that the blue light flux density the QD film experienced is 1.2 W/cm². For these data, the coating film consisted of a single layer of a metal-oxide film. The same QD sample was run through the same sample preparation and coating process and the results confirm that this straightforward coating can repeatably impart improved stability. One can easily imagine more complicated coating stacks, tuned to a particular application area, also adding additional stability beyond what is shown here. The trials were also conducted with different QD synthesis batches and confirmed that the materials and QD films can also be done reproducibly.

The corresponding spectra from each measurement point are also shown in Figure 3. First note that the QD film thickness was somewhat low such that the blue light is not fully converted. Here, it can be seen that the QD emission intensity initially increases then is rather steady over 1000 hours of testing. This initial variation or brightening is a common effect that can also be engineered and minimized in the case it proves critical for an application. The emission wavelengths are observed to be stable with time. Also note the blue light level only varies minimally with time indicating that there is no significant change to QD absorption over the duration of the test.

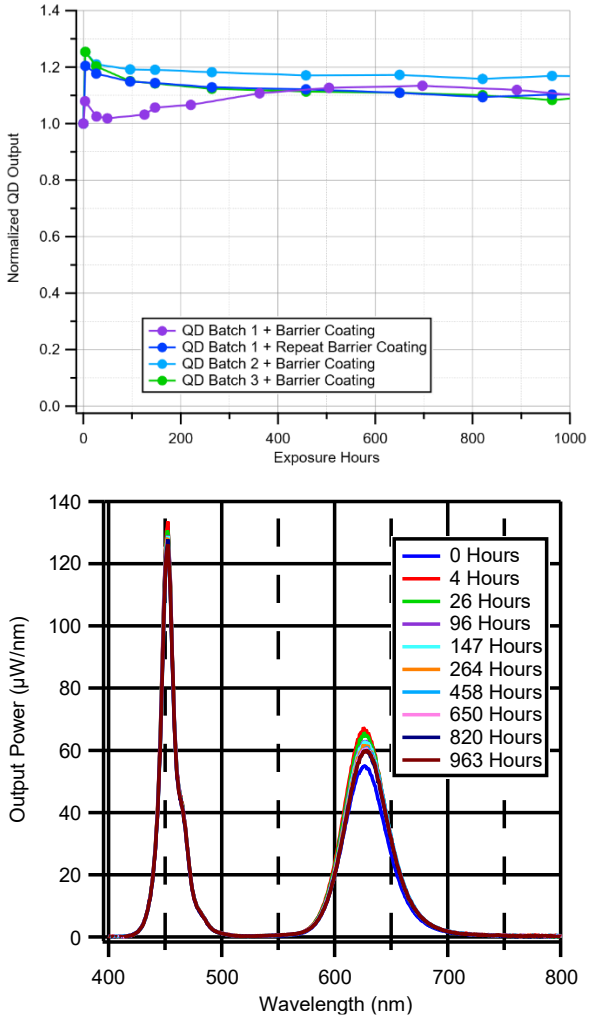

Figure 3. Robustness tests of an oxide coated Quantum Dot layer on chip in air pumped at 1.2W/cm² showing very stable operation over 1000 hours of operation

3. Thin Film Limits

Material Properties:

A primary consideration for on-chip conversion layers is the issue of thickness. Ideally, conversion layers should be as thin as possible. When calculating conversion layer thickness, it is not sufficient to simply think about the amount of pump light that must be absorbed, but rather the determining factor to establish the desired thickness is dictated by color points. For example, if 90% coverage of the Rec. 2020 gamut is desired, then this sets requirements for the requisite blue, green, and red color points to achieve such gamut coverage. The color point of each converted color is a function of the emission linewidth, the emission wavelength, but also the degree of conversion, which is in turn a function of both the degree of absorption as well as the photoluminescence quantum yield of the converters.

For further calculations of how to actually achieve such a system, we assume that the conversion layer needs to have an OD of approximately 2.0, which corresponds to 99% absorption. Examining absorption properties of various QD materials, the two most reported on systems involve either CdSe or InP cores. The band gaps of these materials are ideal for achieving emission in the visible part of the spectrum. Comparing then the bulk absorption properties of these core materials, as well as common shell materials for each of these systems, we see in Figure 4 that according to literature - InP has the strongest absorbance.

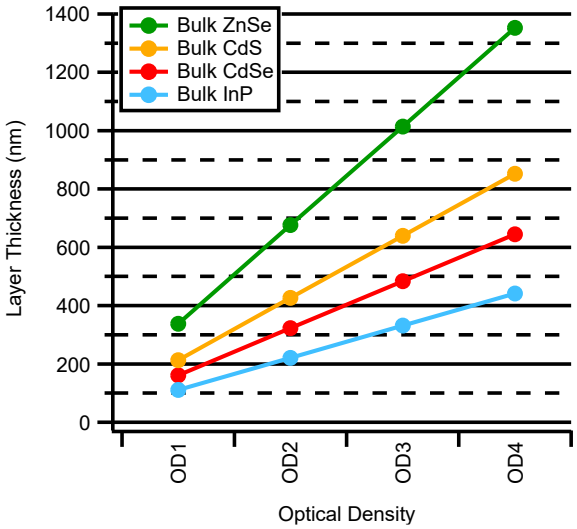

Figure 4. Calculated conversion layer thickness of common QD materials as derived from bulk materials properties at a wavelength of 450 nm as reported in literature [3-9]. Layer thicknesses assume a solid, bulk conversion layer.

InP is predicted to be able to achieve OD = 2 with only a conversion thickness of 220 nm. However, we need to take into account packing density for a nanoparticle system and that InP QDs alone are typically not stable enough, nor bright enough for use directly as conversion layers. Typical shell systems include ZnSe, ZnS and alloys thereof are required around the InP core. At 450 nm ZnSe is somewhat absorbing, but since this wavelength is very near the bulk bandgap, significant deviations can be found. It should be noted that ZnS is not shown in Figure 4, this is because ZnS has a bulk bandgap near 340 nm [5] which means that at 450 nm it is not absorbing. This further complicates the calculations for ZnSe because in QDs it can often be found as an alloy with ZnS such that depending on the ratio of Se to S in a ZnSeS alloy, the absorptions strength can change greatly. However, assuming a simple shell system with no alloys, and an InP core with both ZnSe and ZnS shells, the overall thickness of a conversion layer can subsequently be estimated as a funciton of thickness from both shells. Simulations were ran in varying both ZnSe and ZnS thicknesses to assess the limits to film thickness achievable for different QD shell architectures [3] as shown in Figure 5.

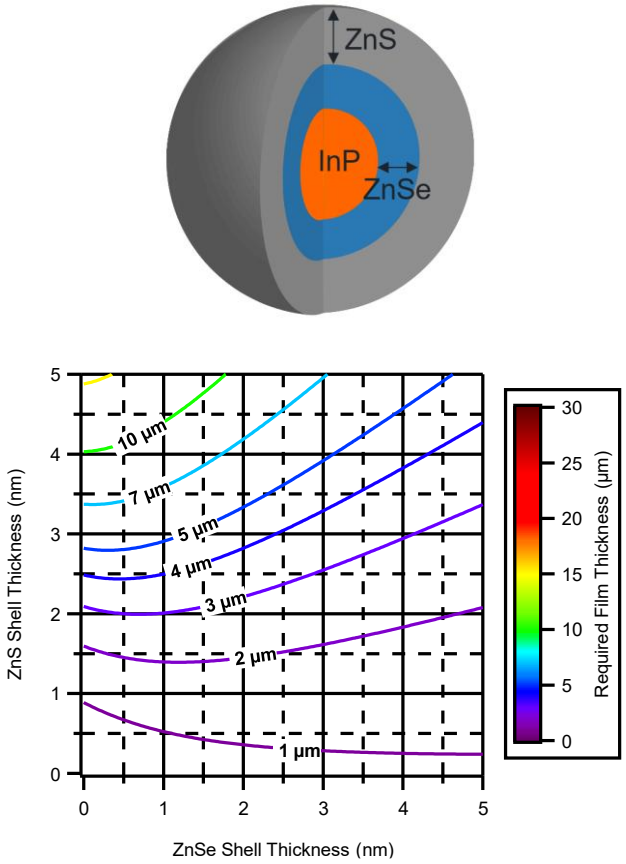

Figure 5. Schematic of Core Shell QD architecture and calculated conversion layer thicknesses for InP/ZnSe/ZnS QDs as a function of shell thickness for red QDs. Thicknesses indicated on contour lines correspond to an optical density of OD_{450} = 2.0

From these calculations, full conversion, as defined by OD_{450} = 2, can be achieved in a QD layer of a few microns thickness. It should be noted that these calculations shown in Figure 5 assume a hexagonal close-packed conversion layer is achieved through particles that are perfectly homogenous with identical size. Of course, real-world conversion layers will be formed with imperfect packing due to size inhomogeneities. In this regard, these calculations should be regarded only as a best-case scenario under ideal conditions. Real films achieving OD_{450} = 2.0 will then be thicker than these models suggest but it is nonetheless useful as guidance for where the limits of such a system might be.

4. Conclusion

We have demonstrated the feasibility of robust, thin film Cd-Free Quantum Dot conversion layers applied directly to the LED chip. This can enable the tight integration of optical conversion materials with front end LED type processing and in dimensions that are relevant for mini and MicroLED applications. Optical properties are maintained at levels that are useful for application in the On-Chip film at relevant pump flux levels. Furthermore – stability of such films has been shown to also be in a range suitable for application.

5. Acknowledgements

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6. References

1. "Quantum Dots from ams Osram make LEDs even more efficient", Press Release 20th May 2019 link
2. M Kessler, J Treadway, D O'Brien, J Owen, E Chan "Cadmium-Free QD Building Blocks for Human Centric Lighting", DOE funded project, Final Report 2024
3. B. Mangum "QD downconverted μLED devices", Proc. SPIE PC12906, Light-Emitting Devices, Materials, and Applications XXVIII, PC1290602 (13 March 2024); https://doi.org/10.1117/12.3004213
4. S. Adachi and T. Taguchi. Optical properties of ZnSe, Phys. Rev. B 43, 9569-9577 (1991)
5. S. Ozaki and S. Adachi. Optical constants of cubic ZnS, Jpn. J. Appl. Phys. 32, 5008-5013 (1993)
6. S. Adachi. Optical dispersion relations for GaP, GaAs, GaSb, InP, InAs, InSb, AlxGa1−xAs, and In1−xGaxAsyP1−y, J. Appl. Phys. 66, 6030-6040 (1989)
7. D. E. Aspnes and A. A. Studna. Dielectric functions an tical parameters of Si, Ge, GaP, GaAs, GaSb, InP, InAs, and InSb from 1.5 to 6.0 eV, Phys. Rev. B 27, 985-1009 (1983)
8. S. Ninomiya and S. Adachi. Optical properties of wurtzite CdS, J. Appl. Phys. 78, 1183-1190 (1995)
9. S. Ninomiya and S. Adachi. Optical properties of cubic and hexagonal CdSe, J. Appl. Phys. 78, 4681-4689 (1995)