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Barrier Films for Quantum Dot Encapsulation

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ABSTRACT

Quantum Dot Enhancement Films (QDEF) increase the color gamut of standard LCD displays by roughly 50% through optical down conversion of blue light to narrow bandwidth red and green light. 3M's barrier film technology encapsulates and stabilizes the environmentally sensitive light-emitting materials, thereby enabling excellent white point and brightness stability, and product lifetime. In this presentation, we will present a general overview of 3M QDEF, discuss barrier film development for 3M QDEF, and compare 3M QDEF product performance to standard LCD displays.

INTRODUCTION

The expanded use of light sensitive materials such as quantum dots and organic light emitting diodes (OLEDs) in the display industry have pushed for the use of high performance water and oxygen barrier constructions with high levels of transparency. In particular for small handheld devices, the OLED based display market continues to dramatically grow with projections that suggest domination in small-scale applications [1]. In contrast for large area displays (e.g. television applications), the large volume use of OLED is in question due to yield issues and potentially more cost effective options.

Quantum Dot Enhancement Films (QDEF) combined with standard Liquid Crystal Display (LCD) (Blue) back lighting elements is an option heavily explored in the industry. The QDEF films used to achieve high color gamut levels at high power efficiencies. The color performance of these QDEF displays has previously been shown to match that for the OLED displays [2]. With such high performance, the QD-LCD market is forecasted to be over $300M by 2018 [3].

The quantum dots in these constructions are sensitive to oxygen and, as in the case of the OLED devices, will degrade with exposure to air and thus require protection with barrier constructions. Since OLED devices are typically made with vacuum-based processes, Thin Film Encapsulation (TFE) (moisture/oxygen barrier) layers are commonly deposited directly onto the organic layers in vacuum using a costly, multi-layered construction. In contrast, quantum dots are typically synthesized from solution using non-vacuum, colloidal methods making it inconvenient to use TFE vacuum methods for protection. Instead, barriers films are typically attached to quantum dot/matrix materials to encapsulate the structures. In this manuscript, we will describe the beneficial use of 3M barrier films in the 3M QDEF application.

BARRIER FILM CONSTRUCTION

The 3M UltraBarrier^{TM} films are comprised of polymer multi-layer (PML) constructions on flexible polymers with acrylate layers separated by inorganic oxides prepared by physical vapor deposition (PVD) methods (see Figure 1). The number of layers used in the constructions is dictated on the required barrier performance for the product. All layers are made in a roll-to-roll processing manner using various polymer-based films as substrates again dependent on the application. Multi-layer 3M UltraBarrier films are nearly pin hole free and barriers with transparencies greater than 90% and very low water and oxygen transmission rates of up to 5×10^{-6} g/m^2/day. These films are designed for photovoltaics, displays, and organic based electronics. In particular to 3M, these barrier layer structures are ideal for flexible products in each of these fields.

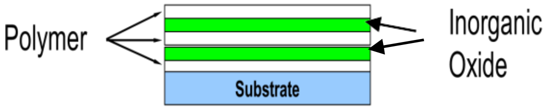

Figure 1. PML structure

3M has optimized the layer construction such that the inorganic barrier layer thicknesses are in the order of 10's of nm. In comparison, many TFE structures have barrier layers with thicknesses in the 100's of nm to 10's of microns. The thinner inorganic layers allow for enhanced flexibility over the TFE option making them ideal for foldable and flexible electronic-based applications such as flex OLED displays.

Quantum Dots

Colloidal Quantum Dots (QD) in QDEF act to convert a portion of the high energy blue light from a light emitting diode (LED) source to lower energy red and green light as is depicted in Figure 2. In these products, the high efficiency dots are CdSe based with ZnS capping or shell layers. The QD emission wavelength is dependent upon the size of the QD as is shown in an article by Yuan, et. al. [4]. When struck by blue photons (~ 445nm), 7nm diameter quantum dots fluoresce, producing red (~ 620 nm) light and 3nm diameter dots fluoresce, producing green (~ 535 nm) light. The ability to precisely control these sizes leads to light emission which is spectrally narrow (FWHM ~ 30 nm, measured using fluorescence) to primary red, green and blue peaks enabling displays with high color gamuts. The relative mix of red and green QDs combined with their location in the backlight determine the display white point. The narrowness of the QD peaks contrast with much broader features from light produced by a YAG phosphor (yttrium, aluminum, garnet) converted blue LED light processed through color filters (Figure 3). The broad features limit the ability to ideally separate the color output, generate smaller color gamuts and lead to less vivid display colors. The ZnS shell material, with a higher band gap than the core material, serves to shield the photo-generated electrons and holes from the outer nanocrystal surface where surface defects exist which can lead to nonradiative electron- hole recombination. The shell also greatly extends the lifetime of the quantum dots by making them less susceptible to the chemical changes surrounding the quantum dots.

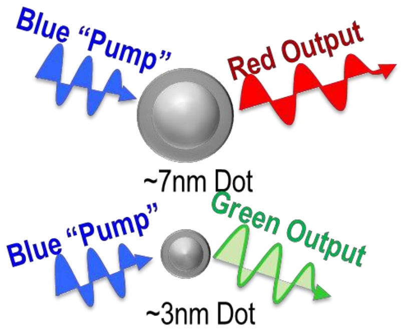

Figure 2. Light emission from quantum dots.

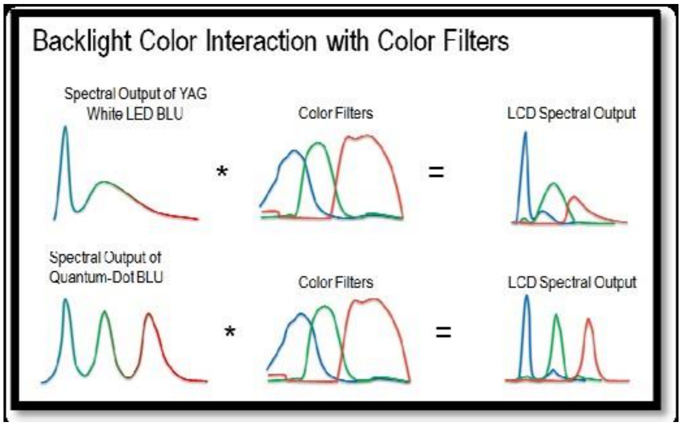

Figure 3. Light conversion from a conventional "white" YAG LED and quantum dots.

Soon after fabrication, the QD are incorporated into a polymer matrix. The matrix is an epoxy polymer formed from a 2-part epoxy amine resin. The QD matrix material is required to have several properties including holding the barrier films in place and very low optical absorption to keep the overall luminance high.

Barrier Film Requirements for QD

If left unprotected under ambient conditions, the photoluminescence intensity of the QD-polymer matrix will degrade due to photo-oxidation of the CdSe during days of exposure. B. O. Dabbousi et. al. [5] have shown the formation of selenium oxides characterized by the appearance of a SeO_2-related x-ray photoemission peak at 59 eV after an 80 h exposure to air in both bare CdSe and 0.65 monolayer ZnS overcoated samples. In addition to loss of photoluminescence (PL) intensity, a shift in the emission spectrum to lower wavelengths with the decrease size in the CdSe portion of the dots has also been observed [6,7]. In one case [6] emission peaks were found to shift from roughly 585 nm to 555 nm after only 51 s for unencapsulated QDs. After a blue shift of about 40 nm (60-180 s), the emission of the QD was observed to be fully photobleached with the CdSe core size decreasing by about 1nm (almost two layers of CdSe).

By sandwiching the QD-polymer matrix between two glass cover slides and sealing the edges, it has been shown that intensities can be maintained over several weeks without significant losses [4]. These examples demonstrate that long term stability for the CdSe QD can be obtained with proper encapsulation. Barrier films are the most attractive method of encapsulating due to weight, robustness and flexibility.

It has been observed that the CdSe quantum dots are more sensitive to oxygen exposure than water vapor. So in contrast to other barrier film applications where water vapor transmission rates (WVTR) are more closely monitored, for QDEF applications, barrier film performance optimization should focus on obtaining the lowest Oxygen Transmission Rates (OTR). For the 3M Ultrabarrier films, a strong repeatable correlation has been found between OTR and WVTR. Since significantly more measurements of WVTR have been made in our labs, we will discuss WVTR in this manuscript.

The encapsulation requirement of the QD matrix will depend on a number of variables; 1) the ligands that form the coordination sphere stabilizing the QD, 2) the shell layer used (materials, integrity and thicknesses), and 3) the polymer matrix materials [5,6]. In particular, use of a ZnS shell layer leads to the formation of $ZnSO_4$ as a photo-oxidation product formed on the surface of the ZnS providing a surface barrier for photo-excited carriers [8]. In the Bol et al. studies [6], passivation of QD surface ligands with 3 monolayer thicker ZnS capping layers can extend the luminescence lifetime but by only 1-2 min while the results from Dabbousi et. al. suggest that in some instances even a 1.3 monolayer thick ZnS can eliminate any oxidation up to 80 hours of air exposure [5]. For display applications requiring quantum yield (QY) > 90%, capping layers do not consistently provide the needed protection and separate encapsulation layers/materials are required and thus additional encapsulation methods are needed.

Proper curing of the polymer matrix is essential to enhance crosslinking, limiting permeability of the matrix and maintaining required separation distances between quantum dots. Quantum dots in too close proximity are subject to recombination through overlapping defect states.

The actual OTR and WVTR requirements of barrier films for QD encapsulation have been becoming less stringent as improvements to both the QD capping layer efficiency and polymer matrix materials have been improved. At present, 10^{-2} to 10^{-4} g/m^2/day WVTR values correlate to the OTR performance typically needed, values that are significantly less challenging than those required for solar cell and OLED applications. Because of these low restrictions, less complicated barrier structures are utilized in combination with the multi-layered QD structures to achieve stability.

For the 3M UltraBarrier films for QDEF applications, WVTR values are below 1 x 10^{-3} g/m^2/day, significantly below the 5 x 10^{-3} g/m^2/day detection limit of the commonly used Mocon Permatron 700 measurement system. From Ca ingress tests, calculated WVTR values in the range of 10^{-4}–10^{-5} g/m^2/day are typically observed. Figure 4 displays optical loss data from the Ca ingress tests for the standard barrier films used for QDEF (blue) and a two-ply laminate barrier film (red) with an increased number of barrier layers using 60 °C, 90% Rh test conditions. With the additional barrier layers, WVTR values are decreased from the 10^{-5} range to 10^{-6} range, allowing for use in applications that are more demanding for higher barrier performance than QDEF such as OLEDs.

In terms of transparency through the barrier films, values greater than 90% are needed for these display applications. Figure 5 shows a transmittance spectrum for 3M Ultrabarrier Film demonstrating the high transmission (>90%) across the visible wavelengths.

3M$^{\text{TM}}$ QDEF Product Construction

The development of 3M QDEF was based on a 3M partnership with Nanosys, a leader in the development of QD technology for displays. The 3M$^{\text{TM}}$ QDEF [9] is a stack of three layers: an upper barrier film, a middle polymer matrix material layer containing quantum dots dispersed in polymer, and a lower barrier film (See Figure 6).

The number of quantum dots and the ratio of green to red dots are determined by the color specifications of the display, the degree of light recycling in the back light unit, the properties of the color filters and the overall thickness of the film. For anti-wet out to other films in the optical stack, the barrier films are designed with a matte finish for the outer surface of the QDEF. The total target thickness for the QDEF construction is 210 um, 110 um from the barrier films. There is also a 360 um thick product for larger displays (TVs).

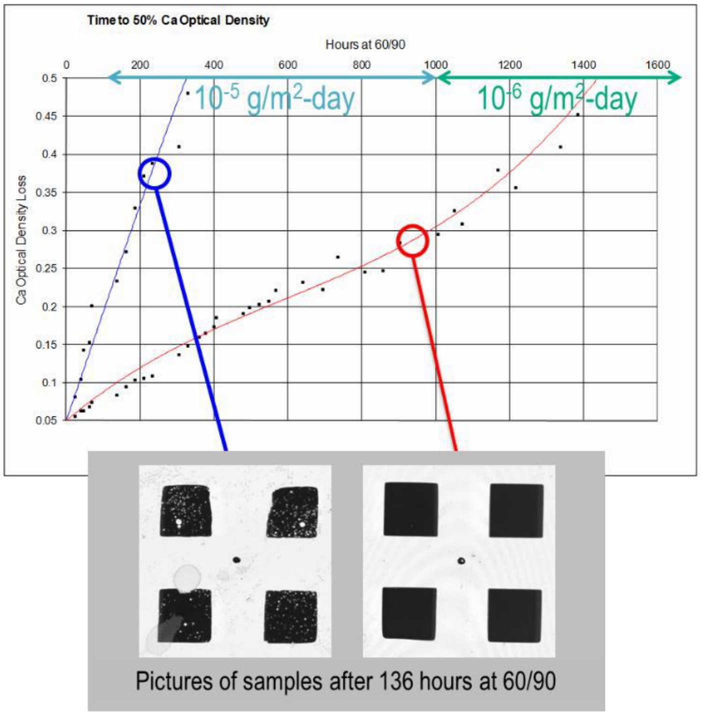

Figure 4. Optical Loss data from Ca test samples made using 3M UltraBarrier films and a two-ply version of these films.

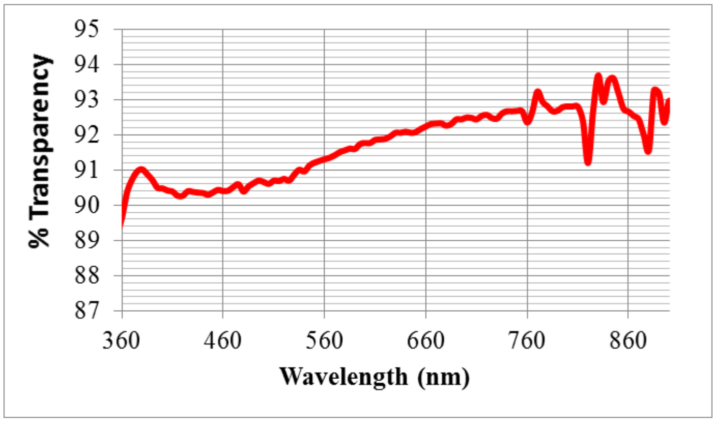

Figure 5. Spectral transmittance (transparency) for the 3M Ultrabarrier.

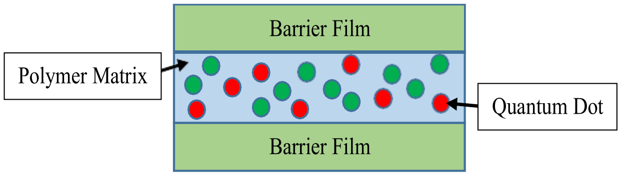

Figure 6. 3M QDEF schematic film construction.

Alternative approaches to barrier films for encapsulation of the quantum dots include glass tubes (rails) that require positioning close of the LED source. This leads to high temperature/high flux environments for the quantum dots which detrimentally affect both efficiencies and lifetimes. These solutions are also not flexible, nor practical for smaller display sizes with limited bezel areas since their use requires reconfiguring current display manufacturing processes.

Because 3M QDEF has diffusive properties, it can be integrated into existing LCD manufacturing processes as a replacement of the diffuser film, as is shown in Figure 7. The diffuser is commonly positioned in the backlight between the light guide and the light control films that direct and recycle light. The backlight unit's other components such as the reflector, the prism film such as 3M's Brightness Enhancement Films (BEF) and the reflective polarizer remain in place. The ability to be integrated with existing LCD architectures makes the 3M QDEF more cost efficient than other high color gamut solutions.

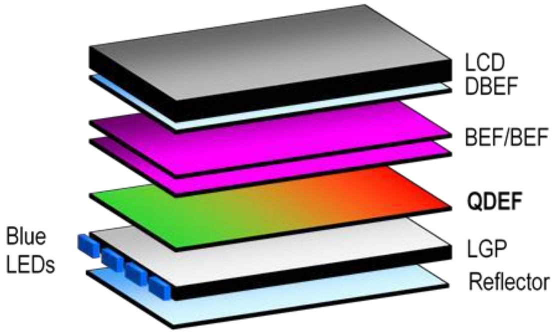

Figure 7. 3M QDEF in LCD display architecture.

In terms of product performance, a number of different color gamuts are used to define references for color saturation in the display industry, the most commonly used are summarized in Table I. The color gamuts of larger color gamut displays are usually described in terms of the Adobe RGB or Digital Cinema Initiatives DCI P3 standards. Adobe RGB is closely associated with printed media, while DCI P3 is more aligned with video creation. Although Adobe RGB offers a slightly wider range of greens, DCI P3 is a larger gamut offering both enhanced reds and greens when compared to the sRGB standard. REC 2020 is presently the proposed standard for ultra-high definition displays coving a very larger gamut area.

Table 1. Common Color Gamuts

Gamut	Common Purpose	Relative Size (%)
NTSC (1953)	National Television System Committee. Analog television STD.	100
sRGB	“Standard and Internet color gamut	87.2
Rec 709	Current HDTV standard. Identical primaries to sRGB	110.9
Adobe RGB	Common in high end displays. Useful for coverage of printing color space. Output supported by many DSLR cameras.	101.7
DCI P3	Current digital camera and movie projection standard	109.5
REC 2020	Proposed standard for UHD content	150.2

Figure 8 shows the color gamuts for a standard LCD display and the same display with the 3M QDEF product. A significant increase into the green and red regions with the use of the QDEF allows for richer green and reds in the displays as is shown in Figure 9. The standard display covers 77.3% of the NTSC gamut while with the QDEF, the gamut is 106.7% of the NTSC standard, an increase of 38% in coverage. Table 1 displays the increased coverage of the different color gamuts (92-98%) with the use of the QDEF product.

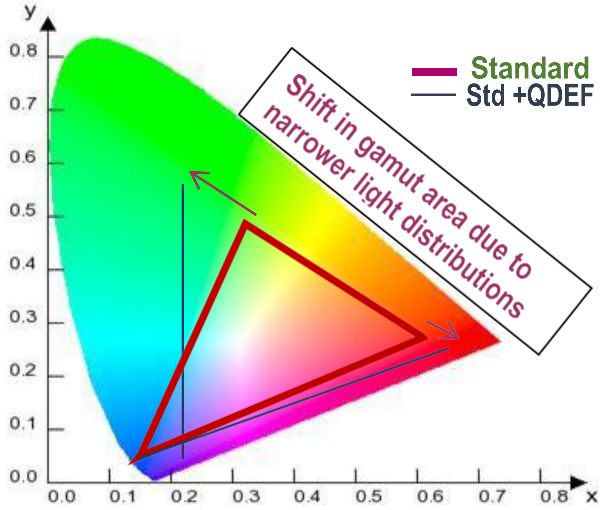

Figure 8. Color Gamuts for Standard LCD and LCD with 3M QDEF product

(a) (b)

Figure 9. LCD displays without (a) and with (b) 3M QDEF.

In addition to the enhanced color gamut range, for high definition displays, the blue LED back lights with quantum dots are significantly more efficient than conventional white LEDs with color filters. A case study of 55” LCD TVs has concluded that QD films result in an average power savings of 46% over existing LCD technologies [10].

The QD matrix material has a WVTR ~5-100 g/m^2/day, 5 to 7 orders of magnitude greater than the permeability of the QDEF barrier film (10^{-4} – 10^{-5} g/m^2/day.) Thus, the edge ingress of oxygen through the QD matrix can play a significant role in the appearance of the QDEF display device over long periods of time. Figure 10 shows a photograph of an aged QDEF film heated at 85°C for 500 hrs. The image was created by shining UV light through the device to show the defective region (roughly 1mm wide) near the edges of the film where QDs areoxidized thus having no red and green light emission and the blue appearance. In the rest of the area of the film, the QDs convert the light into the emitted green color. A number of measurements of the amount of ingress at different temperatures have been made and are plotted as a function of temperature and exposure time in Figure 11. The lines represent modified exponential fits to the curves with $x=x_\infty(1- e^{-t/\tau})^{1/4}$ where x is the position of the ingress edge, x_∞ is the ingress at an infinite time, and τ is a time factor dictated by the temperature. Reasonable fits to the data points can be observed with a predicted maximum length of ingress of oxygen of 1.2 mm. For many applications, this level of ingress is acceptable but is an area for improvement through the testing of different matrix material formulations.

CONCLUSIONS

3M UltraBarrier films for QDEF were reviewed for use in the protection of sensitive films from oxygen and water vapor. It was shown that the addition of QDEF to standard LCD displays can increase the color gamut by roughly 50% and energy savings of greater than 40% can be achieved over other high definition display solutions. Further improvements to the QDEF are to decrease side ingress of oxygen and water vapor through the QD matrix using improved materials.

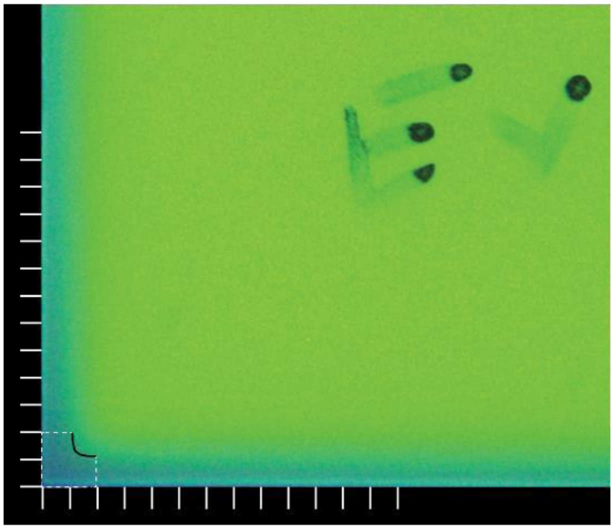

Figure 10. Edge ingress (blue edge) appearance in aged display (white lines represent 1mm).

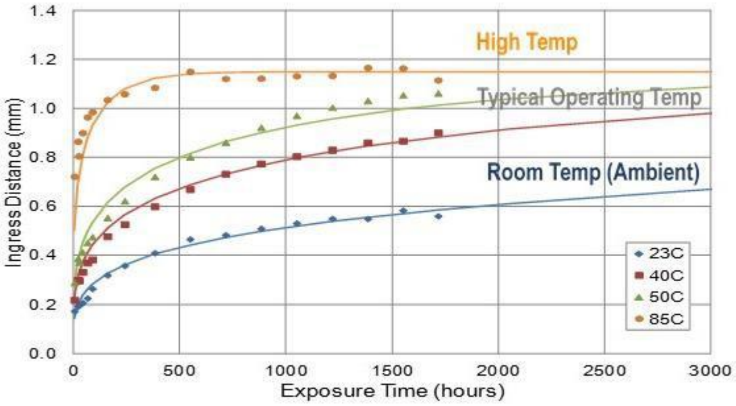

Figure 11. Side ingress through Matrix Adhesive with icons representing measured data and line representing modified exponential fits to the data.

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FOR FURTHER INFORMATION

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