Barrier Films for Quantum Dot Encapsulation

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QDEF Development Process

Fundamental Technology Development

3M CRPL

SEMS CRAL CRML

Product Development

CRL

Business Group: Multiple Divisions with Applied Development Engineering Teams

Industrial
From purification to aerospace – changing how industry works

Safety & Graphics
From protecting people & information to enhancing visual & design communication

Electronics & Energy
Enabling tomorrow’s lifestyle today with power, communications and electronics

Consumer
From simplifying life at home to keeping you organized at work

Health Care
From preventing infections to making smiles brighter

nanosys
Outline

• Trends in Display Market – OLEDs and QD-LCD
• Quantum Dots (QD) – Benefits
• Need for Encapsulation
• 3M™ UltraBarrier Films
• 3M™ Quantum Dot Enhancement Film (QDEF)
• Edge Ingress
• QDEF: Production and Future Developments
Trends in Displays

• Wider Color Gamut – allow for enriched colors in displays
• Lower Power Consumption
• Curved Features

Two Options- OLED or Quantum Dot (QD) displays

Expanded use of Organic Light Emitting Diodes (OLEDs)  
(http://www.idtechex.com) OLED display market: 2016 - $16bn  
2026 - $57bn

QD market: 2016 – $0.4 bn  
2026 - $11 bn

Small Area (Cell Phones, Hand Helds) – OLEDS
Large Area (HDTV, monitors) – OLEDS* or QDOT** LCD TV

*4K OLED TVs were recently launched by LG and Panasonic
** Samsung 60” flat and 78” curved 4K SUHD TV – Quantum Dot Display

3M Quantum Dot Enhancement Film (QDEF) – Widens gamut ranges for HD LCD displays  
with lower power consumption and flexibility (curved) options
What is a Quantum Dot?

Nanosys – QD manufacturer

- **Nano-semiconductor**
  - Highly efficient, inorganic light converter
  - Important to isolate dots: overlapping band states lead to non-radiative e-h recombination

- **Core and shell structure**
  - Core – Optically active
  - Shell – Isolates core and improves efficiency*
    - 1-2 monolayers of ZnS can increase $\eta_{PL}$ by 2-3X
    - Narrow emission spectra for each particle
      - FWHM < 40 nm

- **Changes in size drive changes in emission wavelength***
  - Narrow size distributions = narrow emission spectrum
  - Advanced synthetic techniques control size and distribution

Why use Quantum Dots in LCDs?

- QDs can increase the color gamut of an LCD
  - Standard color filters pass broad distributions of red and green light
  - QD produces narrow green and red distributions – sharper colors

![Diagram showing the effect of QDs on LCD color gamut](image)

White LED BLU * Color Filters = LCD Spectral Output

Standard System

White LED

QD Film with Standard Color Filters

Light Guide Plate

Blue LED

QD Film

Spectral Output of Quantum Dot BLU

Color Filters

LCD Spectral Output

Overlap ➔ Washed Out Color

Separation ➔ High Color Gamut!

High color gamut with high efficiency
White Point Control Example

- White point can be controlled by changing the total concentration of QDs (case shown) or by changing G:R dot ratio.

Can additionally tune spectrum through QD size changes.
Encapsulation Need for QD

CdSe degrade with oxygen exposure (not as sensitive to $\text{H}_2\text{O}$):

- Loss in Photoluminescence after hours of exposure to air
- Shift in Photoluminescence peak to lower energies -

Photo emission spectra for CdSe/ZnS QD with different air exposure times

Correlated to the appearance of $\text{SeO}_2$ x-ray photo emission peaks.

Variables for degradation:

1) Ligand with the QD
2) Shell Layer – Provides some protection
   ZnS does not consistently provide needed encapsulation


WVTR around $10^{-2}$ to $10^{-4}$ g/(m$^2$day) needed for top encapsulation
## TFE vs Film Encapsulation

### Thin Film Encapsulation (TFE)

<table>
<thead>
<tr>
<th>Encapsulation</th>
<th>Encap. Process</th>
<th>Application to Device</th>
<th>Favorable Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>TFE</td>
<td>Some Vacuum Deposition</td>
<td>Direct deposition</td>
<td>Vacuum Deposited Devices (OLEDs)**</td>
</tr>
</tbody>
</table>

### Coated Film Encapsulation

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<tbody>
<tr>
<td>Film</td>
<td>Vacuum Deposition</td>
<td>Lamination/Adhesive</td>
<td>Non-vacuum Deposited Devices (QDOT)</td>
</tr>
</tbody>
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**3M™ UltraBarrier Films: ideal traits for Flex OLEDs – e.g. thin barrier layers**
3M™ UltraBarrier Film (FTB3-50)

Polymer Multi-Layer (PML) constructions on flexible polymers - acrylate layers separated by inorganic oxides

- Roll-to-Roll processing
- Polymer (acrylate): Organic Vapor Deposition
- Oxides: PVD (Sputtering, Evaporation)
- Required barrier performance dictates number of layers
- Applications: Display, Solar, Wearables
- Ideal for flexible products (inorganic barrier layer thicknesses of 10’s of nm)

Note: Strong repeatable correlation has been found between OTR and WVTR.
3M™ UltraBarrier Film Performance

For QDEF application: WVTR of $10^{-2}$ to $10^{-4}$ g/(m²•day) needed
  → Less complicated (few layers) UltraBarrier structure

Typical WVTR values (50 °C, 100% Rh):
  Mocon (Permatran 700) - <5 x $10^{-3}$ g/(m²•day) (below detection level)
  Mocon (Aquatran I) - low-mid $10^{-4}$ g/(m²•day) (at or below detection level)

**Ca Measurement Data (60 °C, 90% Rh)**

Values from stoichiometric modeling, Optical Trans. Data

Blue: standard QDEF barrier film
Red: two-ply laminate barrier film (OLEDs)

High transmission (>90%)
QDEF Construction

- 3M UltraBarrier Film
- Amino Silicone Oil with Red and Green Quantum Dots
- QD in 2 Part Epoxy Matrix Layer
- Matte finish for Anti-wetout

Total thickness of 210 um (110 um from the barrier films)

QDEF Integration

- Into existing LCD Manufacturing Processes as a replacement of the Diffuser Film
- Between LED Light Guide Panel (LGP) and Light Control Films (3M Brightness Enhancement Films (BEF))
- BEF and Polarizer remain
Quantum Dot Enhancement Film (3M™ QDEF) performance

Enabling Full Color Gamut With Standard LCDs

<table>
<thead>
<tr>
<th>Device</th>
<th>% of NTSC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original</td>
<td>77.3%</td>
</tr>
<tr>
<td>QDEF Modified</td>
<td>106.7% (↑38.0%)</td>
</tr>
</tbody>
</table>

Deep greens and emeralds

Stunning, best-in-class reds

<table>
<thead>
<tr>
<th>QDEF Peak Wavelength (Red, Green)</th>
<th>Adobe RGB</th>
<th>Adobe RGB</th>
<th>DCI-P3</th>
</tr>
</thead>
<tbody>
<tr>
<td>530nm</td>
<td>530nm</td>
<td>540nm</td>
<td></td>
</tr>
<tr>
<td>630nm</td>
<td>610nm</td>
<td>630nm</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Standard LCD (White Light)</th>
<th>Adobe RGB</th>
<th>Adobe RGB</th>
<th>DCI-P3</th>
</tr>
</thead>
<tbody>
<tr>
<td>76%</td>
<td>76%</td>
<td>73%</td>
<td></td>
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</table>

<table>
<thead>
<tr>
<th>With QDEF</th>
<th>Adobe RGB</th>
<th>Adobe RGB</th>
<th>DCI-P3</th>
</tr>
</thead>
<tbody>
<tr>
<td>98%</td>
<td>92%</td>
<td>96%</td>
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</table>

NTSC: National Television System Committee Television STD
Adobe RGB: Printed Media
DCI-P3: Movie Projection
Energy Savings with QDEF

- QD are 10 to 15 percent more efficient than conventional white LEDs and color filters in achieving the sRGB standard (72% NTSC) color gamut
- With QD, can use more transmissive color filter – Less light needed from Blue LED
- More energy savings from larger color gamut

Energy Savings: Case study of 55” LCD HDTVs → QD films result in an average power savings of 46% over existing LCD technologies
Encapsulation of Devices

Edge Ingress Through the Matrix Materials

QDEF Construction

Water and oxygen exposure through an exposed edge that causes a visual appearance change over a small area

85°C/500hour, Air, UV Exposed

Black line overlaid at corner represents maximum ingress predicted by model (white lines are 1 mm apart)

85°C/500hour, Air, Contrast Enhanced

Yellowing along edge is evidence of oxidation in epoxy

UV source

Detector
QDEF Edge Ingress Data

- Measured (Microscope) edge ingress as a function of time and temperature
  - Edge ingress occurs rapidly at first then slows to a near asymptotic value
  - Edge ingress appears to reach a maximum ~1.2 mm
  - Temperature dependent – higher temps result in greater/faster ingress

**Modified Exponential Fit**

\[
x(t) = x_\infty \left(1 - e^{-t/\tau}\right)^{1/4}
\]

- \(x\) = ingress distance
- \(x_\infty\) = ingress asymptote
- \(t\) = time
- \(\tau\) = time factor

Measured data indicates that at operating temperatures of 50°C or lower edge ingress distance will be about 1mm or less
Oxygen Limited Diffusion Theory

QDEF matrix diffusion equation modeled

\[ \frac{dC}{dt} = D \frac{\partial^2 C}{\partial x^2} - K_1 C \]

- \( D \) = oxygen diffusion coefficient
- \( K_1 \) = oxidation rate constant

- Oxidation of QDOT material due to oxygen diffusion is the hypothesis for ingress
- Matrix polymer also oxidizes (degrades) consuming oxygen - involves many components and is usually solved using a closed loop oxidation mechanism where different products initiate, propagate and eventually terminate
- Because QDOT ingress appears to reach steady-state, the model only includes one rate constant (\( K_1 \)). It is expected over long periods of time, the polymer available for oxidation will be consumed.
Production of QDEF

• In full production
• Significant sales in TV and Large Monitor Applications

Further Developments of QDEF

• Improvements to QD Matrix to minimize edge egress
• Increased Production Rates/Machine Capacities
  - QD fabrication
  - Barrier film fabrication
Summary

- Quantum Dot films increase the color gamut of an LCD Display
  - QDs produce narrow green and red light distributions
- Quantum Dots require encapsulation
  - Photoluminescence decreases with oxygen exposure
  - Blue shift in PL Spectra with oxygen exposure
- 3M™ UltrabARRIER films used to encapsulate QD in 3M™ QDEF
  - Mocon (Permatran) WVTR \(<10^{-3}\) g/m²/day
  - Ca Measurements WVTR in \(10^{-5}\) g/m²/day
- Side Ingress of oxygen through QD matrix material causes some side discoloration - at operating temperatures of 50°C distance about 1mm or less
- 3M™ QDEF Quantum Dot films are the most efficient route to high color gamut LCD Displays
  - Works within current LCD architecture
  - Offers design freedom to efficiently achieve a variety of target color gamuts
  - Adobe RGB or DCI-P3 color gamuts can be efficiently attained
  - Currently in mass production