Ultra-high Barrier Plastic

MSE5420 Flexible Electronics
Martin Yan, GE Global Research
Outline

- Introduction to plastic substrate and need for barrier
- Barrier technologies
- WVTR measurement technologies
- Summary
Evolution of Display Technology

Source: Displaybank’s presentation on 2007 Flexible Display & Microelectronics Conference

September 30th, 2008
OLED Technology

- iRiver SPINN A/V Player
- Kodak EasyShare LS633 Camera
- Sony XEL-1 11” OLED TV
- DZ7086 OLED watch by Diesel
- Nokia Prism Mobile Phone
- Kodak EasyShare LS633 Camera
- Light

Cathode
n-layer
p-layer
Anode

September 30th, 2008
Flexible OLED Display

High information content

Low power consumption

Light weight, compact

Large area display (active matrix)

Video rate

Full color

Excellent viewing angle

Source: UDC presentation on 2007 Flexible Display & Microelectronics Conference
Replace Glass with Plastic Substrate

**NOW**

- Glass Substrate

**FUTURE**

- “Roll-Up Displays”

**Plastic Advantages**

- Rugged.
- Thinner.
- Lighter.
- Enable flexible display.
- Enable R2R processing.
Energy Consumption for Lighting: Year 2001
22% of the total electricity generated in the U.S. was used for lighting!

Source: U.S. Lighting Market Characterization Volume I:

Need to replace incandescent with more efficient light technology!
Organic Electronics (OE) Advanced Technology Program at GE Global Research

Technologies:
• OLED Devices
• Low Cost Manufacturing
• High Barrier Substrate

High barrier substrate enables R2R OLED manufacturing.
OLED Offers Novel Features

Mechanical Flexibility  Thin and Light  Transparent

Color Tunability
Flexible OLED Product Concepts

UDC’s Flexible Display Concept

Polymer Vision’s Flexible Display Concept

Source: Best Life Magazine – February 2006
Opportunity for Plastic Substrate

- **Flex.Display**
  - OLED
  - LCD

- **Digital Paper**
  - E-paper
  - Postage

- **Lighting**
  - General lighting
  - Back lighting

- **Solar Cell (PV)**
  - Thin Film PV

**Barrier Plastic Film**

**Major Players**: Samsung, Pioneer, Bridgestone, Fujitsu, Fuji Xerox, Toppan, DNP, E-Ink, TOYOTA, National, LG, IMES, Sharp, Sanyo, Kaneka, Canon
Challenges for Flexible OLED Substrate

The Problem

- **OLED**
- **Polymeric substrate**
- **Transparent electrode**
- **H₂O, O₂**

Commercial available polymeric substrate

![Graph showing permeation rates.](image)
Substrate Requirement
- Key Properties

Moisture/Oxygen Permeability
- H$_2$O: low $10^{-6}$ g/m$^2$/day
- O$_2$: < $10^{-3}$ cc/m$^2$/day

Thermo-mechanical stability
- Shrinkage: < 20 ppm/hr @150°C
- Bending diameter <= 1"
- Adhesion: ≥ 4B

Transparent Conductor
- Low Conductivity, Low Transmission Anode
- High Conductivity, High Transmission Anode
- Low Temp. Plastic
- High Temp. Polycarbonate
- < 40 Ohm/ sq
- > 90 %T

Optical Transmission
- > 80 %T
Barrier Substrate Development at GE Global Research

Technology Development at GE

- Plastic Substrate Film
- Ultra-high Barrier Coating
- Chemical Resistant Coating
- Transparent Conductor Coating

Enable

Integrated Plastic OLED Substrate

- Transparent electrode
- Graded ultra high barrier
- Chem resistant layer
- High heat polycarbonate
- Chem resistant layer
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Material Options for Transparent Hermetic Barrier

Moisture Permeability

Log Thickness (meters)

Time to Reach 50% of Outside RH

Ref. Traeger

SILICONES

EPoxyeS

FLUORO-CARBONS

GLASSES

METALS

10 nm continuous glass-like coatings would exceed the needs

OTR through Perfect SiO2 Barrier:

10nm ⇒ 10^{-24} cc/m^2/day

\[ T = \frac{d}{2} \sqrt{ \frac{k}{D_{w}} } \]

Ref. Deal & Grove, J. Appl. Phys. 36 (12), 3770 (1965)
Defect-Driven Moisture Permeation

Barrier performance of single layer inorganic coating is defect limited

Non-Fickian Diffusion

~ 100 defects/mm²

Defect Imaging w/ Acetone

20x

~1mm
Ultra-high Barrier: Single Layer Approach

– Uni. Of Colorado: Atomic Layer Deposition of AlO$_x$
– Dow Corning: Plasma Enhanced Chemical Vapor Deposition of SiO$_x$C$_y$
– Symmorphix: Sputtering of AlSi$_x$O$_y$

Source: Symmorphix's presentation on 4th Flexible Display and Microelectronics Conference
Ultra-high Barrier: Multilayered Approach

Concept for Multilayer UHB

Source: VITEX’s presentation on 5th Flexible Display and Microelectronics Conference
Permeation Simulation: Multilayered Barrier

Assumptions:
- 2 perfect barriers
- each barrier has 1 defect
- defects are offset/decoupled

Fick’s Law:
Continuity:
Diffusion Equation:

\[ J(x,t) = -K \frac{\partial n(x,t)}{\partial x} \]
\[ \frac{\partial n(x,t)}{\partial t} = -\frac{\partial J(x,t)}{\partial x} \]
\[ \frac{\partial^2 n(x,t)}{\partial x^2} = K \frac{\partial^2 n(x,t)}{\partial x^2} \]

Flux Ratio = \frac{\text{Flux}_2 \text{ Layer System}}{\text{Flux}_1 \text{ Barrier System}}

Work in this regime to achieve Ultra-High Barrier
Ultra-high Barrier: Graded Approach

GE's Graded Ultra High Barrier

Organic zone

Inorganic

Cross-sectional TEM of Graded UHB

XPS Spectrum of Graded UHB

Continuous composition transition
Graded Ultra-high Barrier Plastic Film

Parallel plate PECVD

High T Lexan® film

Low temperature PECVD process is compatible with plastic substrates
Base Film Surface Quality is Critical

Ultra-high Barrier Performance

Start with an ultra-smooth surface!

Bare Lexan Substrate

Ultra-high barrier coating

Smooth Coating Substrate
Flexible OLED substrate

The Problem

- OLED
- Commercial available polymeric substrate
- Polymeric substrate
- Transparent electrode
- H₂O  O₂

The Solution

- OLED
- GE Barrier Substrate
- Graded ultra high barrier
- Chem resist layer
- High heat polycarbonate
- H₂O  O₂

3,530 hrs at 23°C 40%RH

12 mm

Proved that high barrier substrate is possible
GE’s Graded Barrier Plastic Performance

<table>
<thead>
<tr>
<th>Specification</th>
<th>Key USDC Specifications*</th>
<th>GEGR Performance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture Barrier</td>
<td>$10^{-6}$ g/m²/day</td>
<td>low $10^{-5}$ to mid $10^{-6}$ (at 23°C 50 % RH)</td>
</tr>
<tr>
<td>Chemical Resistance</td>
<td>acid, solvent, alkali</td>
<td>Pass</td>
</tr>
<tr>
<td>Electrical Conductivity</td>
<td>$\leq 40 \ \Omega$/Sq</td>
<td>40.3 $\Omega$/Sq</td>
</tr>
<tr>
<td>Optical Transparency</td>
<td>$&gt;80%$</td>
<td>82 %</td>
</tr>
<tr>
<td>Mechanical Flexibility</td>
<td>bend around 1” radius</td>
<td>Pass</td>
</tr>
<tr>
<td>Thermo-Mechanical Stability</td>
<td>200°C for 1hour</td>
<td>Pass</td>
</tr>
<tr>
<td>Adhesion</td>
<td>$\geq 4B$</td>
<td>4B</td>
</tr>
<tr>
<td>Dimension stability</td>
<td>$&lt;20$ ppm/hr at 150°C</td>
<td>4 ppm/hr</td>
</tr>
<tr>
<td>Average surface roughness</td>
<td>$&lt;5$ nm</td>
<td>0.6 nm</td>
</tr>
</tbody>
</table>

* Subset of complete USDC specification list

15 cm square flexible OLED lighting Device on high heat polycarbonate substrate with graded UHB
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WVTR measurement technologies

• Capacitive or Resistive (humidity sensor)
• Spectroscopy (mass spectroscopy, fluorescence quenching)
• Calcium degradation (optically or change in resistance)
• Radioactive (tritium)
Commecially Available Gas Permeation Measurement

Detection limit for H₂O: 5×10⁻³ g/m²/day


Fourier transform Infrared (FTIR) Spectrometer
Calcium Corrosion Test: GE’s Setups

Ca test @ 23°C / 50%RH

Ca Test @ 60°C 90% RH

Detection limit for H₂O: 1×10⁻⁵ g/m²/day
Tritium Test: GAT’s Setup

General Atomics Tritium Test

Source: RALF DUNKEL, ROKO BUJAS, ANDRE KLEIN, AND VOLKER HORNDT, PROCEEDINGS OF THE IEEE, VOL. 93, NO. 8, AUGUST 2005, pg 1478-1482

Detection limit for $H_2O$: $2 \times 10^{-7} \text{ g/m}^2\text{/day}$
OLED Device Test

Universal Display Corporation
OLED Shelf Lifetime Test @ 60°C 85% RH

Glass/Glass control

Device on GE sample

Glass/Glass control

Device on GE sample

w/o desiccant

w/ desiccant

Source: GE’s presentation on 4th Flexible Display and Microelectronics Conference