IMRE/ETPL Flagship Project

Nanoparticulate Barrier Films & Gas Permeation Measurement Techniques for Thin Film Solar & Display Application Problems

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Outline

- Background
- Barrier Technology Development
  - Permeation Measurement system
  - Flexible Substrate
  - Flexible Encapsulation & Flex Test Results
  - Benchmarking
- Summary
Why Flexible Barrier Films

• **Drivers**
  - Flexibility – to form a variety of applications
  - Thin, light weight, and unbreakable
  - Large area, R2R processes, printing techniques
  - Manufacturing cost – reduction (50%)

• **Challenges**
  - Barrier properties ✓ IMRE IP
  - Thermal stability of the base substrate *(DuPont, Mitsui etc)*
  - Encapsulation ✓ IMRE IP)
  - Permeability measurements
    • ✓ IMRE IP
  - High Cost ✓ IMRE Solution
Projected Barrier Substrates Market

2+ high growth markets

Source: Solarbuzz, Displaysearch, EPIA, Konarka, GE, NanoIdent

Flexible Displays/ Lighting
Flexible Photovoltaics
Sensors/ Other
Barrier Requirements - Issues

10^6
10^5
10^4
10^3
10^2
10^1

OLED Display Lighting
Thin Film Solar Devices
Flexible LCD RFID Tag
Food Packaging
Plain Plastic Film

Permeation process through barrier coated plastic

Barrier Oxide Layers Water Vapour Desorption

Diffusion Plastic Substrate

Water Vapour Adsorption Grain Boundary Crack Pinhole
Permeation Measurement System

- IMRE permeation measurement system *(Patent pending)*
  - Quantitative measurements - H₂O & O₂ transport rates & diffusion coefficients
  - High sensitivity 10⁻⁶g/m².day
  - Automatic data recording system

- Barrier oxide films - Defect analysis
  - Pinholes, cracks etc

- Integration of sensor into device package *(Patent pending)*
  - Device failure analysis

- IMRE - Service based projects
Permeation Test - Principle

- Calcium is used as a sensor
- Sensor fabricated on organic coating or polymer/composites surfaces
- Water vapor permeation
  - through defects of oxide films
  - diffusion through organic films/substrate
- Calcium reacts with water vapor
  - Produces calcium hydroxide \([\text{Ca(OH)}_2]\)
- The rate of change of Ca resistance & 1/f noise and converted as WVTR under steady state conditions.
WVTR Calculation – Package Structure

Type A - Adhesive

Type B - Adhesive

40°C & 90% RH
Base Substrate Effect – Comparative Results

Test condition: 60°C & 90% RH
Base Substrate Effect – Comparative Results

Test condition: 60°C & 90% RH
Qualitative Analysis - Defects Analysis

- Sub-Micron Cracks 23 hours PET/ SiN (150nm compressive stressed film)
- Porous Film – 3.5hrs PET/ SiN (5nm)
- Micro size Pin holes - 6 hours PET/ SiN (30nm)
- Micro-Size Pinholes – 7.5 hours PET / SiN (60nm)
- Micro – Cracks 6.5 hours PET / SiN (90nm)
- Denser Multi-stack Film (Al$_2$O$_3$) – 585 hrs
Uniformity Analysis - Example

A1

17 hrs

110 hrs

240 hrs

764 hrs

A2

Calcium test @ 40°C & 90%
Line Defects

Calcium Test: 40°C & 95% RH @ 240 hrs (A1)
Line Defects

Calcium Test: 40°C & 95% RH @ 240 hrs (A1)
WVTR Measurement Results

SiN Barrier oxide - Thickness Dependence Studies

Calcium degradation Images @ 7.5 hrs 50°C & 90% RH
Calcium Sensor Integration with Organic Device

- Organic devices/OLED displays
  - Ensure the reliability of packaging
  - Estimation of device lifetime
  - OLED failure analysis & Degradation studies
- Patent pending

The small molecule based OLED luminescence against time. The insert figure shows water vapor transmission rate ($2 \times 10^{-3} \text{g/m}^2/\text{day}$) of OLED package under steady state condition at 60°C and 90% RH.
## Barrier Films - Characterization

<table>
<thead>
<tr>
<th>Barrier Films / stack</th>
<th>Deposition Process</th>
<th>Lag time</th>
<th>WVTR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polycarbonate (150 µm)</td>
<td></td>
<td>15 min</td>
<td>33 g/m²/day at 40ºC &amp; 90 % RH</td>
</tr>
<tr>
<td>PET (188 µm)</td>
<td></td>
<td>20</td>
<td>3 g /m²/day at 40ºC &amp; 90% RH</td>
</tr>
<tr>
<td>50 µm PET / Al₂O₃</td>
<td>Sputtering</td>
<td>29 hours</td>
<td>0.07 g/m²/day at 50ºC &amp; 90% RH</td>
</tr>
<tr>
<td>188 µm PET / SiN</td>
<td>Sputtering</td>
<td>8 hours</td>
<td>0.24 g/m²/day at 50ºC &amp; 90% RH</td>
</tr>
<tr>
<td>133 µm PC/undercoat/SiOx/Undercoat/ITO</td>
<td>Sputtering</td>
<td>60 hours</td>
<td>0.04 g/m²/day at 50ºC &amp; 90% RH</td>
</tr>
<tr>
<td>188 µm PET/undercoat/Al₂O₃</td>
<td>FCVA</td>
<td>3.5 hours</td>
<td>0.14 at 50ºC &amp; 90% RH</td>
</tr>
<tr>
<td>188 µm PET / undercoat / SiN</td>
<td>Sputtering</td>
<td>27 hours</td>
<td>0.10 g/m²/day at 50ºC &amp; 90% RH</td>
</tr>
<tr>
<td>188 µm PET / undercoat / SiN/Undercoat/SiN (3 layers)</td>
<td>Sputtering</td>
<td>200 hours</td>
<td>7.5 x 10⁻³ g/m²/day at 50ºC &amp; 90% RH</td>
</tr>
<tr>
<td>Multi-layer (2 layers) with PC Developed at IMRE.</td>
<td>Nanostructured barrier stack</td>
<td>2300 hours</td>
<td>2 x 10⁻⁶ g/m²/day at 60ºC &amp; 90% RH</td>
</tr>
</tbody>
</table>
IMRE Barrier Technology - Concept

- **Barrier stack**
  - barrier oxide layer and Nanoparticulate sealing layer
- **Nanoparticulate sealing layer**
- **Barrier Mechanism**
  - To seal pinholes in the oxide layer
  - To absorb & react with moisture & oxygen
- **Results**
  - Benchmarked with GE & Vitex
  - Good UV filter
  - Less layers, Cost savings
Surface Morphology – Nanoparticulate Interlayer

Plain Polymer (0.8nm RMS) - AFM  
Nanoparticulate interlayer (4nm RMS) - AFM

SEM Image of Nanoparticulate interlayer – 40000x
Proof of Concept – Lab Scale

<table>
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<tr>
<th>Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plastic Substrate</td>
</tr>
<tr>
<td>ITO</td>
</tr>
</tbody>
</table>

Calcium test @ 80°C & 90% RH
Lab Scale - Results

Calcium test @ 80°C & 90% RH
Flex Test – Results

IMRE Flex test machine – ASTM STD
Bending Cycles : 10,000 cycles
Radius of curvature: 25mm (of 50mm substrate)

2 Layer Barrier Stacks – Flex Test undertaken @ 60°C & 90% RH – Initial test results

2 Layer Barrier Stacks – Flex Test undertaken @ 60°C & 90% RH – Flagship Recent development
Scratch data for the sample A53

LC1 first crack, A53
70 mN

LC2 delamination, A53
215 mN
Scratch data for the sample HB2

LC1 first crack, 39 mN

LC2 delamination, 81 mN

2nd layer indication

LC3 Full delamination

369 mN
Comparisons of scratch data

<table>
<thead>
<tr>
<th>IMRE samples</th>
<th>Friction Co-efficient at the point of delamination</th>
<th>Scratch Hardness (GPa)</th>
<th>Critical load for delamination</th>
<th>Data from</th>
</tr>
</thead>
<tbody>
<tr>
<td>HB2</td>
<td>0.59</td>
<td>1.67</td>
<td>369 mN</td>
<td>CSM</td>
</tr>
<tr>
<td>A53</td>
<td>0.70</td>
<td>2.97</td>
<td>216 mN</td>
<td>CSM</td>
</tr>
<tr>
<td>HC</td>
<td>0.76</td>
<td>-</td>
<td>237 mN</td>
<td>CSM</td>
</tr>
</tbody>
</table>

From Literature

<table>
<thead>
<tr>
<th>Antiscratch layers on organic lenses</th>
<th>0.2</th>
<th>-</th>
<th>6 mN</th>
<th>Ref 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu thin films on oxidised silicon</td>
<td>-</td>
<td>2.58</td>
<td>0.25 N</td>
<td>Ref 2</td>
</tr>
</tbody>
</table>

A higher critical load means a higher scratch resistance ability or higher adhesion force between coating and substrates or between different coatings in the case of HB2

Single Barrier Stack - R2R Fabricated

- Test condition - 60°C & 90% RH
- Single barrier stack – 1 oxide layer + 1 sealing layer *(R2R fabricated)*
- Single barrier stack (without nanoparticle)
- Adhesion strength of nanoparticulate sealing layer onto Al₂O₃ is 48 N/m
- Transparency – 93% without ITO
Uniformity – Optical & Surface Roughness

Samples were acquired up to 60 meters (96% Transmittance)

Nanostructured Sealing layer by WebFlight R2R coated

DuPont base substrate
CPI Al2O3 barrier layer

UV-VIS Spectrophotometer Results

AFM - Results

3.765 nm (RMS)
External Test – CPI, UK

Quantitative Test Results

IMRE1 Button3 %Ca Degradation

WVTR = 1.51x10^{-6} g/m^2/day @ 60°C & 90% RH

Qualitative test results

IMRE 2 barrier stack tested at 60°C & 90% RH conditions – Size (50x50) mm. No Ca Oxidation up to more than 1000 hrs (after 1000 hrs permeation test cell delaminated)
Multilayer test results

- Barrier stack - 3 oxide layers + 2 nanoparticulate sealing layers
- Conventional barrier stack – 3 oxide layers + 2 acrylic polymer interlayers
- Transparency – 85% (with ITO)

IMRE – Test Results @ 80degC & 90% RH
Flexible Encapsulation – Results

- Passed 30k cycles of bending test (ASTM standard for smart card applications – 10k)
- Tested at ambient with a constant electrical stress at 8V

Flexible OLED fabricated using IMRE Barrier substrate and Encapsulation Technology (3 patents pending)
Summary

- **Permeation measurement system**
  - Integrated with device for failure analysis
  - Benchmarked with Mocon & General Atomics
  - Validated by Mitsui Chemicals

- **Nanostructured barrier stack**
  - Demonstrated optical, mechanical & barrier properties
  - Benchmarked with GE & Vitex
  - Validated by industries and test agencies

- **Exploring possible commercialization**
  - Established strong industrial partnership and collaboration
  - R2R manufacturing Know-how

FOLED light units for signaling in on emergency situation may be used in aircraft – Courtesy Philips
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