Various Approaches for High-Barrier Film Development

From Low Cost Production to High-End Applications

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AIMCAL
Web Coating & Handling Conference
from 30 May – 2 June 2016
Dresden, Germany
Outline

- Production of high barrier films
- Newest results
- Summary and outlook
Aim of High Barrier Film Development

Requirements of Products and Performance of Barrier Films

- Water vapor transmission rate (WVTR) [g / m² · d] 23°C / 85% RH
- Oxygen permeability [cm³ / m² · d · bar] 23°C / 50% RH

- Inorganic photovoltaics
- Organic photovoltaics
- OLEDs
- Sensitive food
- Single inorganic coatings
- Polymers
- Multilayer structures roll-to-roll 2016
- Vacuum insulation panels

Source: va-Q-tec
Requirements for Barrier films Depend on Application

- Compatib le
- Climate stable
- Low cost
- Large area production
- Oxygen
- Water

END PRODUCT
- Lifetime
- Environment
- Stresses
- Cost

Barrier to gases
Water Induced Degradation of OLED on Plastic Films

1. Water permeation perpendicular through the barrier films
2. Side-ingression through adhesive layers (bulk material)
3. Water permeation through the interfaces
Water Induced Degradation of OLED on Plastic Films

1. Water permeation perpendicular through the barrier films
2. Side-ingression through adhesive layers (bulk material)
3. Water permeation through the interfaces

John Fahlteich, Encapsulation of flexible Electronics, LOPE-C 2016, Munich, Germany
High Barrier Film Development

Basic Principles of Permeation

Solution-diffusion model

\[ P = D \times S \]

“Defect-dominated” permeation mechanisms

SEM picture: Defects due to anti-blocking particles
SEM picture: Defects resulting due to thermal stress
SEM picture: Porosity and surface roughness

Inorganic layer coatings: Al, AlO_x, SiO_x

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High Barrier Film Development

Ultrabarrier Stack: Alternating inorganic/organic layers

Vitex material: Four dyads

Affinito J. and Hilliard D. “A New Class of Ultra-Barrier Materials”, SVC, 2004

Inorganic layers with high intrinsic barrier properties

Extended diffusion path-length

Filling of defects

Protective and smoothing layers:
Elimination of nano- and micron-sized particulates
High Barrier Film Development

Ultrabarrier Stack: Alternating inorganic/organic layers

Optimization of multilayer films for low permeability and long time lag

- Increase of number of dyads
- Integration of active absorbers into multilayers
High Barrier Film Development

Ultrabarrier Stack: Alternating inorganic/organic layers

Time Lag Effect: Time dependent permeation data

No inorganic layer

~ 1.5 dyads

~ 3 dyads


Multilayer Approach for High Barrier

Fraunhofer POLO® Multilayer Barrier

Polymer substrate:
- Mechanical carrier
- Flexible

Inorganic coating:
- O₂ and H₂O barrier
- Brittle and porous
- ZnSnOₓ (ZTO), AlOₓ, SiOₓ

Hybrid polymer lacquer:
- Provides flexibility
- Planarizes the surface
- Effectively “decouple” defects
- Probable filling of pores

Langowski, H.C., Lope-C, 2009
J. Fahlteich et al., SVC, 2012

http://www.polo.fraunhofer.de/
Fraunhofer Polymer Surfaces Alliance POLO®
Multilayer Approach for High Barrier

Barrier Lacquer ORMOCER®

Inorganic coating, 80 – 100 nm

http://www.polo.fraunhofer.de/
Fraunhofer Polymer Surfaces Alliance POLO®
Multilayer Approach for High Barrier: Low-cost

Laminated Multilayered Structures

- Higher mechanical stability
- Thicker structures

**Challenge:** Proper adhesive selection
**Thermal stability problem:** 85°C/85%RH
High Barrier Film Production

Coating Technologies: Roll-to-Roll Deposition Processes

Reactive Sputtering

E-beam evaporation

Thermal evaporation
High Barrier Film Production

Roll-to-Roll Processes: Atomic layer deposition (ALD)

R2R-ALD plant, unwinding unit and reactor

- Spatial-ALD (S-ALD) → R2R processing at economically viable speeds
- deposition of well-defined, conformal, homogeneous, and almost pinhole-free layers at the atomic/subatomic level
- modified Chemical Vapor Deposition (CVD) process
- deposited in cycles, atom layer by atom layer
- extremely high layer quality

Application areas:
Diffusion barriers I Injection, transport, and blocking layers for OLEDs, OPVs I TCOs e.g. AZO I Passivation and buffer layers for OEs and CIGS solar cells I Dielectric materials I Optical coatings, e.g. for light out-coupling in OLEDs I Improvement of wetting characteristics for subsequent processes I Anti-bacterial coatings I Anti-corrosion coatings on metal foils I SAMs (Self Assembled Monolayers)
High Barrier Film Production

Coating Technologies: Roll-to-Roll Processes

Lamination / Lacquering under Clean-Room Environment

- Protection from dust particles
- Enclosed, filtered air
- Flow controller
High Barrier Film Production

Biggest Challenges

- **Substrate quality:**
  - Cleanliness, surface roughness

- **Thermal and mechanical stability:**
  - Substrate and barrier layers

- **Production processes:** Low cost

- **Process conditions:**
  - Temperature, Pressure (lamination)
  - Web-speed, web tension
  - Dust-free coating, no contact on coated side

- **Quality Control:**
  - Inline (layer thickness, crosslinking degree)
  - Off-line (permeation, adhesion, bending stability)
Outline

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- Newest results
- Summary and outlook
OPV Encapsulation

Project goals:
- **OPV Lifetime**: Up to 20 years
- **OPV Cost**: 0.7 € / wp
- **Efficiency**: 8 - 10%

Encapsulation Requirements

- **WVTR**:
  \[ < 5 \times 10^{-4} \text{ [g/(m}^2\text{·d)]} \]
  \((23^\circ\text{C} / 50 \% \text{ RH})\)

- **O}_2\text{ Permeability}**: 
  \[ < 1 \times 10^{-3} \text{ [cm}^3\text{/(m}^2\text{·d·bar)]} \]
  \((23^\circ\text{C} / 50 \% \text{ RH})\)

Transparency
- Low cost
- Weatherability
- Mechanical stability
- Flexibility

SUNFLOWER- "Sustainable Novel Flexible Organic Watts Efficiently Reliable" (FP7-ICT-2011-7, Grant number: 287594)
Coordinator: Dr. Giovanni Nisato, CSEM, Switzerland
Novel Barrier Structures for OPV Encapsulation

Barrier Layers on Weatherable Substrates

- Lowest WVTR: $5 \times 10^{-4} \text{ g/(m}^2\cdot\text{d)}$ (23°C / 85 % RH)
- No barrier loss (1000 cycles, bending radius 5 mm)
- Transparency: 90% (> 450 nm)
- Low cost, large-scale production: e-beam deposition and lamination processes
- < 10 €/m² (in up-scale scenario)
Novel Barrier Structures for OPV Encapsulation

Integration of Adhesives

![Graph showing WVTR (water vapor transmission rate) over time for different adhesives and PET layers.](image)

**WVTR (extrapolated):**
- Adhesive-1: $1.2 \times 10^{-3}$ g/(m²·d)
- Adhesive-2: $0.7 \times 10^{-3}$ g/(m²·d)
- Adhesive-3: $0.6 \times 10^{-3}$ g/(m²·d)
OPV Integration in Windows, Window Blinds, Hand bags,…
Goals related to high barrier films

- Water barrier: $10^{-5} \text{[g/(m}^2 \cdot \text{d}]}$
- Compatible to encapsulation

OPV Encapsulation
Pilot Line Organic Electronics

SMARTONICS (2013-2017) Dev. of smart machines, tools and processes for precision synthesis of nanomaterials with tailored properties for OEs (NMP.2012.1.4-1, 310229) Prof. S. Logothetidis, AUTh, GR
OPV Encapsulation

Ultra-High Barrier at lower costs!

WVTR

\(23^\circ\text{C}, 50\% \text{ RH} \):
\(2 \times 10^{-5} \text{ g/(m}^2\cdot\text{d)}\)

\(38^\circ\text{C}, 90\% \text{ RH} \):
\(1 \times 10^{-4} \text{ g/(m}^2\cdot\text{d)}\)
## Barrier Performance Overview

(a) Inorganic barrier layer: e-beam

<table>
<thead>
<tr>
<th>Structure</th>
<th>WVTR [g/(m²·d)] (23°C / 85 % RH)</th>
<th>O₂ Permeability [cm³(STP)/(m²·d·bar)] (23°C / 50 % RH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P + SiOₓ</td>
<td>0.3</td>
<td>0.1</td>
</tr>
<tr>
<td><strong>Multilayer Structures</strong></td>
<td><strong>Mocon® Aquatran®</strong></td>
<td><strong>Mocon OX-TRAN®</strong></td>
</tr>
<tr>
<td>1 P + SiOₓ + ORM + SiOₓ</td>
<td>2 x 10⁻³</td>
<td>&lt; 5 x 10⁻³</td>
</tr>
<tr>
<td>2 1 / Adhesive / 1</td>
<td>5 x 10⁻⁴</td>
<td>&lt; 5 x 10⁻³</td>
</tr>
</tbody>
</table>

(b) Inorganic barrier layer: reactive sputtering

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<tr>
<th>Structure</th>
<th>WVTR [g/(m²·d)] (23°C / 85 % RH)</th>
<th>O₂ Permeability [cm³(STP)/(m²·d·bar)] (23°C / 50 % RH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P + ZTO</td>
<td>0.01</td>
<td>0.05</td>
</tr>
<tr>
<td><strong>Multilayer Structures</strong></td>
<td><strong>Ca - Test</strong></td>
<td><strong>Mocon OX-TRAN®</strong></td>
</tr>
<tr>
<td>3 P + ZTO + ORM + ZTO + ORM + ZTO (25 nm)</td>
<td>2 x 10⁻⁵</td>
<td>&lt; 5 x 10⁻³</td>
</tr>
</tbody>
</table>

**P**: Polymer substrate, **ZTO**: Zinc-Tin-Oxide
Summary and Outlook

- **High barrier production by multilayer approach**
  - Low permeability and long time lag
  - Defect-dominated permeation mechanism, substrate selection
  - Good defect coverage and smoothing effect by ORMOCER®s

- **Barrier adhesive integration by lamination:**
  - Increased number of dyads, cost-effective, longer time lag, high barrier performance

- **Demonstration of a long-lasting, low cost, flexible OPV:**
  - Weatherable PET substrates
  - Integration of barrier adhesives

- **Fraunhofer POLO® barrier film at low inorganic barrier layer thicknesses!**
  - Cost reduction and enhanced mechanical stability

- **Standardisations needed for high barrier measurements!**
  - Necessary for further development of ultra high-barrier films
Thank you for your interest!

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Material development