Vacuum roll-to-roll technologies for transparent barriers on polymer webs

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Outline

- The need for transparent barrier films

- Vacuum coating technologies
  - Single barrier layer: HAD-AlOx-process
  - Single barrier layer: Sputtering
  - Multilayer: Sputtering + ORMOCER®
  - Multilayer/all-in-vacuum technology: Sputtering + PECVD

- Summary
The need for transparent permeation barrier films

- Harmful gases: water vapor, oxygen
- Food packaging
- Flexible solar cells
- Flexible organic light emitting diodes

Single layers vs. multilayer stacks
Permeation barrier: requirements

- Water Vapor Transmission Rate (WVTR) [g/(m²d)]
- OLED
- OPV
- flexible LCD
- inorganic solar cells
- packaging

- Sputtering + PML
- evaporation
- ALD
- Sputtering / PECVD
- Polymer films
- Sputter + ORMOCER®

- Note:
  defects vs. average permeation rate

- OLED with darkspots

- multilayer
- single layer
Encapsulation technologies

- **glass- / glass**
  - rigid

- **glass / film**
  - rigid

- **film / film**
  - flexible

- **thin film direct encapsulation**
  - rigid or flexible (depending on substrate)
Further requirements for barrier films

- optical properties
- mechanical resistance
- temperature stability
- UV-stability
- weather stability

- added functions
  - electrode layer
  - light management

200 nm Al$_2$O$_3$ on PET after 100 h damp heat test (85°C / 85% r. h.)
Vacuum coating technologies for transparent barrier films

- Water vapor
- Oxygen

permeation barrier layer

polymer film

permeation barrier layer stack

polymer film

➢ Vacuum coating technologies continue to be enabling technologies for transparent permeation barrier concepts
Vacuum roll-to-roll coating
Pilot roll coater novoFlex® 600

- flexible substrates (polymer webs, thin metal foils)
- 600 mm deposition width
- web speed 0.1...600 m/min
- double side coating
- 5 coating stations
- combination of evaporation, sputtering and PECVD
Transparent Barrier Film: Concise R&D Roadmap

- **HAD-ALOX** (1): packaging, superior productivity
- **Single layer sputtering** (0.001)
- **Multilayer: sputtering + ORM** (0.0001): high-barrier for flexible optoelectronic
- **Multilayer: all-in-vacuum** (0.005)

R&D, pilot, industrial

WVTR in g/(m²·d)

"ORM:" ORMOCER® by Fraunhofer ISC
Hollow cathode Activated Deposition process (HAD AlOx process)
Plasma system for web coaters

Plasma system, ready to be installed into a web coater with 2850 mm web width
Reactive Magnetron Sputtering

- Suppression of arcing
- Increased plasma density and ion bombardment of the substrate surface
- Long term stability
magPECVD – interlayer in multi layer barriers

- different plasma sources used:
  - dual magnetron with titanium targets
  - hollow cathode
- process pressure similar to reactive sputtering
  - in-line combination with reactive sputtering possible
- very high deposition rates for plasma-polymer layers: up to 400 nm·m/min
Pilot sputter roll coater *coFlex® 600*

- **flexible substrates** (polymer webs, thin metal foils)
- **600 mm deposition width**
- **web speed** 0.1...100 m/min
- **6 coating stations** (dual magnetrons)
- **Pulsed Magnetron Sputtering**
- **Magnetron PECVD**
## Properties of sputtered single layers

<table>
<thead>
<tr>
<th>property (300 nm thick layer):</th>
<th>ZTO</th>
<th>Al₂O₃</th>
<th>ZnO</th>
<th>SiO₂</th>
<th>TiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>dynamic deposition rate at 7.2 W/cm² [nm·m/min]</td>
<td>- 95</td>
<td>50</td>
<td>90</td>
<td>40</td>
<td>26</td>
</tr>
<tr>
<td>refractive index (550 nm)</td>
<td>-</td>
<td>1,95</td>
<td>1,65</td>
<td>1,93</td>
<td>1,48</td>
</tr>
<tr>
<td>arithmetic average roughness Rₐ on Melinex 400 [nm]</td>
<td>-</td>
<td>0,9</td>
<td>0,9</td>
<td>5,3</td>
<td>1,5</td>
</tr>
<tr>
<td>Peak-to-Peak roughness Rₜ [nm]</td>
<td>-</td>
<td>10</td>
<td>9</td>
<td>45</td>
<td>16</td>
</tr>
<tr>
<td>WVTR [g/(m²d)]</td>
<td>-</td>
<td>0,01</td>
<td>0,03</td>
<td>0,035</td>
<td>0,15</td>
</tr>
<tr>
<td>structural properties</td>
<td>dense, am</td>
<td>dense, am</td>
<td>column, pc</td>
<td>dense, am</td>
<td>column, am</td>
</tr>
</tbody>
</table>

- Al₂O₃ and ZTO: low roughness, low permeation, suitable for use in multilayer barrier
Barrier performance of different single layers

- measured using coloumometric sensor at 38°C / 90% r.h. on 104 cm² sample area
- substrate PET, 12 µm (evaporated layers) or PET, 75 µm sputtered / PECVD layers
Multilayer-technology using ORMORCER®s as interlayer

Made in roll-to-roll modus

Available on pilot-production scale
Multilayer-technology using ORMORCER®s as interlayer

<table>
<thead>
<tr>
<th>Properties</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>substrate material</td>
<td>PET (Melinex 400 CW, 75 μm)</td>
</tr>
<tr>
<td>WVTR</td>
<td></td>
</tr>
<tr>
<td>at 38°C/ 90% r.h. (Aquatran)*</td>
<td>&lt; $5 \times 10^{-4}$ g/(m²d)</td>
</tr>
<tr>
<td>at 38°C/ 90% r.h. (HighBarSens)*</td>
<td>$4 \times 10^{-4}$ g/(m²d)</td>
</tr>
<tr>
<td>at 38°C/ 90% r.h. (calcium mirror test)</td>
<td>$2 \times 10^{-4}$ g/(m²d)</td>
</tr>
<tr>
<td>at 23°C/ 50% r.h. (calcium mirror test)</td>
<td>$8 \times 10^{-5}$ g/(m²d)</td>
</tr>
<tr>
<td>OTR**</td>
<td></td>
</tr>
<tr>
<td>at 23°C / 0% r.h. (OX-TRAN 2/21)</td>
<td>&lt; $5 \times 10^{-3}$ cm³/(m²d bar)</td>
</tr>
<tr>
<td>(below measurement limit)</td>
<td></td>
</tr>
<tr>
<td>VLT*** (spectrum adaptable to application)</td>
<td>82%</td>
</tr>
<tr>
<td>roll width</td>
<td>max. 460 mm</td>
</tr>
<tr>
<td>roll length</td>
<td>max. 500 m</td>
</tr>
</tbody>
</table>

*) The water vapor transmission rate was measured on a large area (≥ 100 cm²) at different positions on the film; **) Oxygen transmission rate; ***) Visual light transmission

Made in roll-to-roll modus

Available on pilot-production scale
Barrier Performance – measured in different labs

- inter lab round robin for POLO® barrier
- sample size:
  - 50 cm² - Aquatran® (2 labs)
  - 134 cm² - HiBarSens®
  - 100 cm² - Tritium-Test

Measurement Partners:
Multifunctional Stacks – conductive barrier substrate

- ITO conductive layer (100 nm)
- ZTO barrier (180 nm)
- ORMOCER® (1000 nm)
- ZTO barrier (180 nm)
- PET substrate

Properties:

- WVTR (Ca-Test) @ 23°C / 50% r.h.: 8·10^{-5} \text{g/(m}^2\text{d)}
- WVTR after chemical etching of ITO: < 3·10^{-4} \text{g/(m}^2\text{d)}
- Resistance ITO: 90 \text{Ω}

- patented TCO topcoat with etch protection
- mechanical and chemical protection with ORMOCER® top layer
- adaption to different substrates
  - different type of PET
  - PEN
  - fluoric polymers (under development)
Multi layer stacks with a PECVD-layer as interlayer

- “all-in-vacuum” approach
- interrupt growth of defects
- cover defects with polymer interlayer
- reduce mechanical stress compared to thick single layer
- “tortuous path“ of diffusion

400 nm

ZTO, 100 nm

SiOₓCᵧHᶻ, 400 nm

ZTO, 100 nm

1000 nm
All-in vacuum deposition of barrier layer stack

in-line combination of PECVD and sputtering processes

Multifunctional layer stack
⇒ barrier layer stack
⇒ conductive layer
## Layer properties

<table>
<thead>
<tr>
<th>properties of the all-in-vacuum multi layer</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>substrate</td>
<td>PET Melinex 400 CW, 75 µm</td>
</tr>
<tr>
<td>barrier layer material</td>
<td>ZTO</td>
</tr>
<tr>
<td>barrier layer thickness</td>
<td>100 nm</td>
</tr>
<tr>
<td>interlayer material</td>
<td>SiO$_x$C$_y$H$_z$</td>
</tr>
<tr>
<td>Interlayer thickness</td>
<td>200 … 600 nm</td>
</tr>
<tr>
<td>optical transparency (VLT)</td>
<td>up to 84 % (depending on stack)</td>
</tr>
<tr>
<td>minimum WVTR (38°C / 90% r.h.)</td>
<td>5·10^{-3} g/(m²d)</td>
</tr>
<tr>
<td>number of layers per run</td>
<td>3 and more</td>
</tr>
<tr>
<td>web speed</td>
<td>0.5 … 1 m/min</td>
</tr>
</tbody>
</table>

- multifunctional layer stack
- current field of research: suppression of particle generation in PECVD
WVTR under strain

- minimum WVTR: $1.5 \cdot 10^{-3}$ (23°C / 50%) and $5 \cdot 10^{-3}$ (38°C / 90% r.h.)
- postponed WVTR increase to higher strain with multilayers
- barriere performance restored partially after relaxation of multilayer (elastic strain range)
Summary

HAD-ALOX 1 packaging, superior productivity

Single layer sputtering 0.001

Multilayer: sputtering + ORM 0.0001

Multilayer: all-in-vacuum 0.005

R&D objectives:
- reduce defects
- improve barrier
- UV stability
- extended choice of substrates
- added functions (light management, electrode)
- test strategy
- integration into final product
- reduce coating cost

WVTR in g/(m² d)

"ORM:" ORMOCER® by Fraunhofer ISC
Encapsulation Competence Dresden
Applied research and contract development

Roll-to-Roll deposition of barrier layers on polymer webs and flexible devices

Research & Development
Barrier & Devices
Academics & Industry
- joint in Dresden

Barrier testing, lifetime testing, encapsulation and device interaction

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Acknowledgment

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I thank you for your kind attention.

For further questions: Please visit us at the exhibition hall 2, booth 2.090 (joint booth with Organic Electronic Saxony)

You can meet me there on Wednesday 10 AM thru 3 PM.