# ROLL-TO-ROLL TECHNOLOGY ON PILOT SCALE FOR TRANSPARENT ULTRA-HIGH MULTILAYER BARRIERS

Fraunhofer POLO

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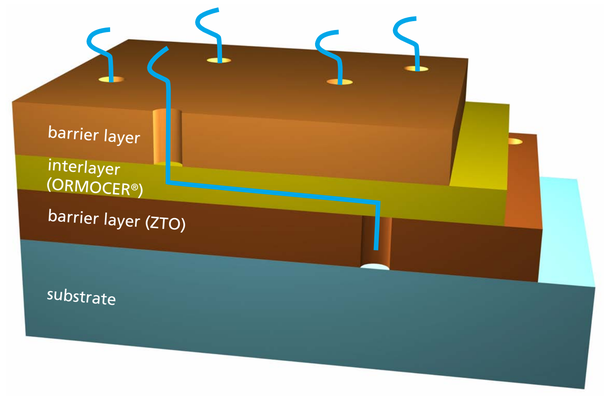
## INTRODUCTION

Flexible organic electronic devices (OLED and OSC) have to be protected from water vapor and oxygen in order to guarantee a long lifetime. A **water vapor transmission rate below $10^{-5}$ g/(m²d)** is needed to achieve sufficient protection for 10000 hours shelf lifetime.
The Fraunhofer Polymer Surfaces Alliance POLO® has developed a technology for coating polymer films with a layer system that is almost impermeable to water vapor and oxygen, without significantly impairing the flexibility and optical transparency of the film.
The technology is based on oxide layers deposited by **reactive dual magnetron sputtering** which are separated by an intermediate polymer layer.
The intermediate polymer layer consists of a novel inorganic-organic hybrid polymer, a so-called ORMOCER®, deposited by **reverse gravure printing**. The intermediate layer interrupts defect growth in the oxide barrier layer and provides ideal conditions for deposition of the second oxide barrier layer.



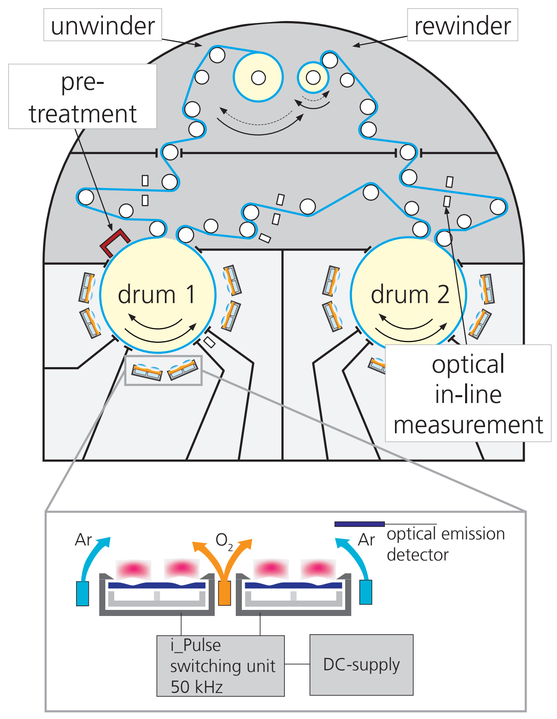

**Tasks of the interlayer:**

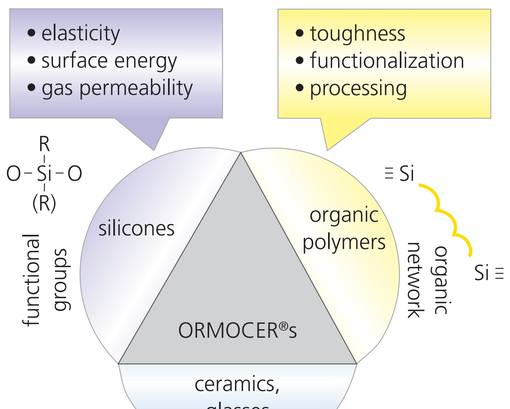
- interrupt growth of defects
- reduce mechanical stress compared to thick single layers
- cover particles with polymer layer and smoothen the substrate surface
- lengthen the path of diffusion for long defect distance in barrier layers

## TECHNOLOGY AND PILOT SCALE COATING MACHINES

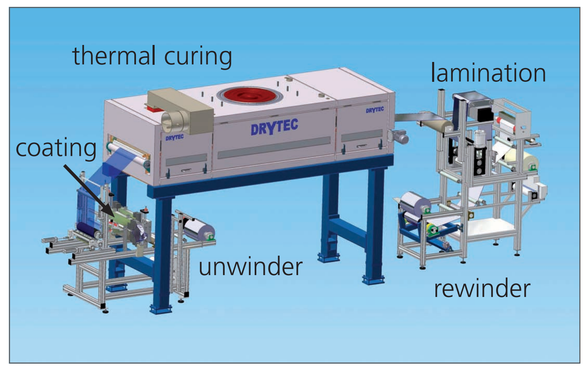
| *coFlex® 600* | |
|---|---|
| coating width [mm] | 600 |
| web speed [m/min] | 0.1 ... 100 |
| coating stations | 6 |
| base pressure [Pa] | $<10^{-3}$ |
| typical roll length [m] | up to 1000 (@ 75 µm) |
| substrate thickness [µm] | 12 ... 200 |
| substrate materials | polymers, thin metal foils,textiles |

- dual-magnetron-sputtering from metal target (Zn-52 wt.% / Sn-48 wt.% → $Zn_2SnO_4$ (ZTO))
- reactive gas flow control based on optical emission of excited metal atoms in plasma
- other materials: $Al_2O_3$, $SiO_2$, $TiO_2$,…



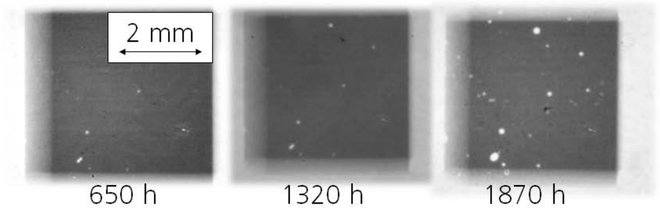

- ORMOCER® synthesized in sol-gel process
- roll-to-roll application as thermally curable lacquer
- very smooth surface

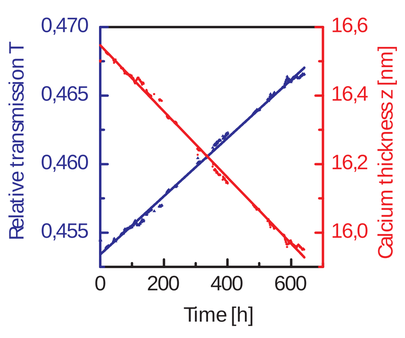


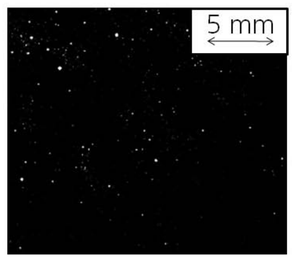

| | |
|---|---|
| coating width [mm] | 400 (up to 460 possible) |
| web speed [m/min] | 0.5 … 30 |
| typical roll length [m] | 600 (@ 75 µm) |
| features | corona pre-treatment, web cleaning, handling of liners, contact-free winding, thermal and UV-curing |

## PROPERTIES OF THE MULTILAYER BARRIER

### WATER VAPOR TRANSMISSION RATES (CA-TEST)



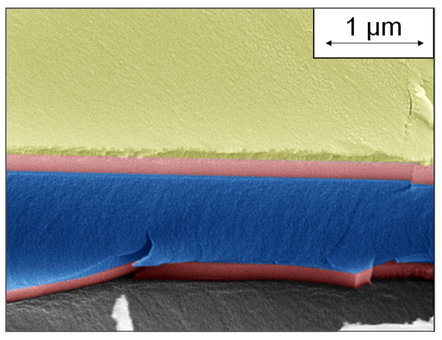

large area overview after 1730 h

- Ca directly deposited on barrier with glass encapsulation on top
- measured optical density on at least nine 7 mm² spots at both 23°C / 50% r.h. and 38°C / 90% r.h.

### PROPERTY TABLE

| Property | Unit | Value |
|---|---|---|
| Layer stack | | ORMOCER® – 1000 nm<br>ZTO – 180 nm<br>ORMOCER® – 1000 nm<br>ZTO – 180 nm<br>PET Melinex® 400 CW – 75 µm |
| roll width | mm | 400 |
| roll length | m | up to 500 |
| roughness average | nm | 0.25 |
| peak-to-peak roughness | nm | 2.5 |
| visual light transmission | % | 82 |
| visual light absorption | % | < 1 |
| WVTR (Ca-Test)@ 23°C / 50% r.h. | g/(m²d) | $(5.5 \pm 2.7) \cdot 10^{-5}$ |
| WVTR (Ca-Test) | g/(m²d) (38°C / 90%) | $(2.0 \pm 1.3) \cdot 10^{-4}$ |
| WVTR (HiBarSens®) | | $(3.8 \pm 0.4) \cdot 10^{-4}$ |
| WVTR (Aquatran®) | | $< 5 \cdot 10^{-4}$ |
| OTR (Oxtran® 2/21) @ 23°C / 0% r.h. | cm³/(m²d bar) | $< 5 \cdot 10^{-3}$ |

### MULTIFUNCTIONAL LAYER STACKS



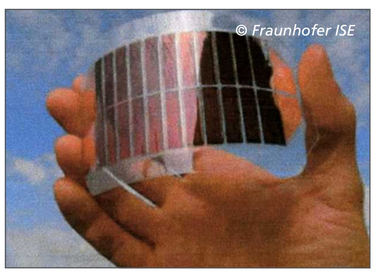

ITO conductive layer (100 nm)
$SiO_xC_yH_z$ protection layer (60 nm)
ZTO barrier (180 nm)
ORMOCER® (1000 nm)
ZTO barrier (180 nm)
PET substrate

| | |
|---|---|
| WVTR (Ca-Test) @ 23°C / 50% r.h. | $9 \cdot 10^{-5}$ g/(m²d) |
| WVTR after chemical etching of ITO | $< 3 \cdot 10^{-4}$ g/(m²d) |
| resistance ITO: | 90 Ω |

- patented TCO top-coat with etch protection
- mechanical and chemical protection with ORMOCER® top layer
- adaption to different substrates (e.g. fluoric polymers)

## SUMMARY AND OUTLOOK

| Technology / Property | HAD evaporation | MF sputtering | all-in-vacuum multilayer | ORMOCER® multilayer |
|---|---|---|---|---|
| typical deposition rates [nm·m/min] | 4800 | 100 | 100 | **100 (sputtering) 3000 (ORMOCER®)** |
| typical web speed (approx.) | 450 m/min | 1 m/min | 1 m/min | **1 m/min + 3 m/min** |
| typical total layer thickness [nm] | 5 ... 20 | 10 ... 300 | 100 + 400 + 100 | **180 + 1000 + 180** |
| lowest WVTR on PET (38°C / 90%) | 0.5 g/m²d | $10^{-2}$ g/m²d | $5 \cdot 10^{-3}$ g/m²d | **$2 \cdot 10^{-4}$ g/m²d** |
| development status | industry proven | | in development | **pilot production** |





A roll-to-roll technology for manufacturing an ultra-high multilayer permeation barrier film has been demonstrated achieving a water vapor transmission rate of $2 \cdot 10^{-4}$ g/(m²d) and below. The film has been manufactured on pilot scale for 400 mm wide and up to 500 m long rolls. A comparison of the WVTR using different measurement methods could show reproducible low water permeation among different samples on one roll and also among different manufactured rolls. Multifunctional layer stacks with a conductive top layer and a chemical protection layer have been tested as substrate for flexible OLED and OSC devices to show the feasibility of the barrier film for flexible electronics application.

Current and upcoming tasks are the adaption of the optical properties of the layer stack to the desired application and the increase of productivity to reduce the manufacturing cost for the film. Also the adaption to other substrates like fluoric polymers for solar application is in focus of the current and future work.

## CORRESPONDING CONTACT AND ACKNOWLEDGEMENTS

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