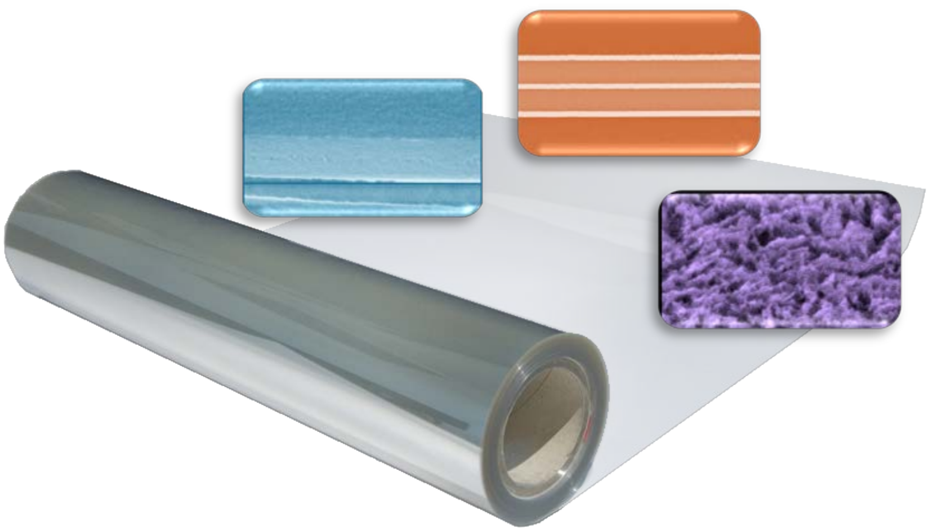
Vacuum plasma treatment and coating of fluoropolymer webs – challenges and applications

AIMCAL 2016



Cindy Steiner

John Fahlteich

Dresden, 01.06.2016

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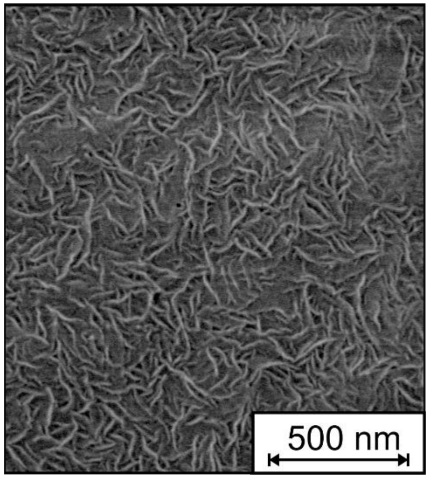
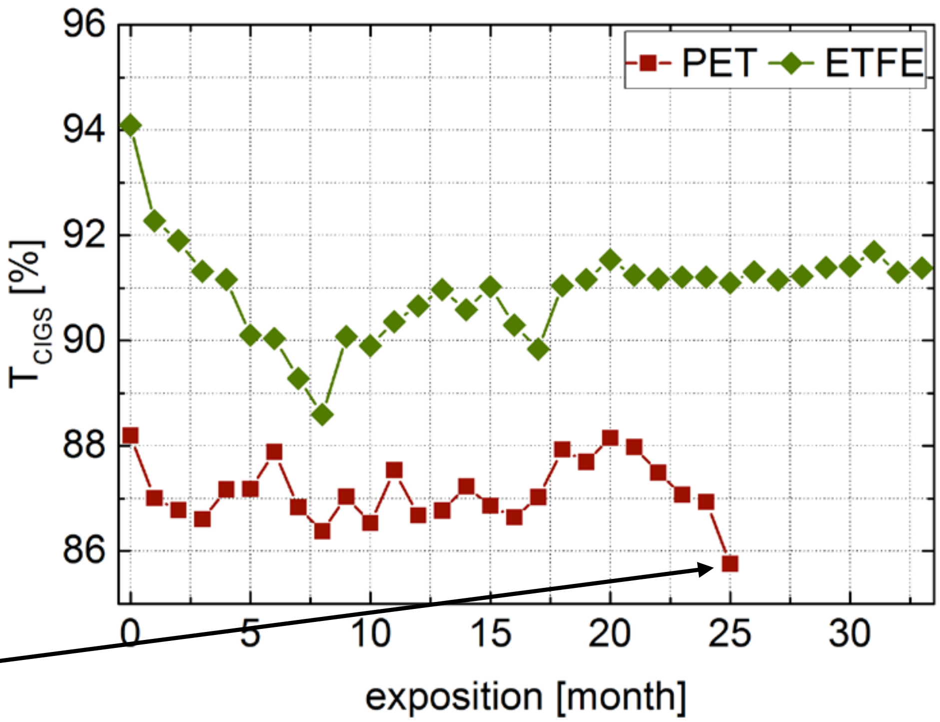
Ethylene Tetrafluoroethylene (ETFE)



semi-crystalline co-polymer of ethylene and tetrafluoroethylene

- high weathering stability and high transmittance



- low surface energy
- low elastic modulus
- strong shrinkage at high process temperatures

cracking
mechanical destruction

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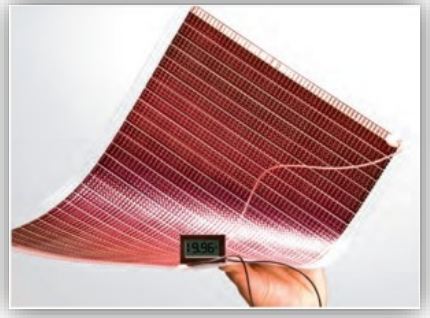
Applications and Requirements

electronic devices

flexible solar cell



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organic light emitting diode (OLED)

architecture

ETFE facades and roofs in Stadiums….

source: wikipedia

Manufacturing / processing

- roll-to-roll
- temperature
- tensile forces
- radiation

Application

- temperature / humidity at place of use
- mechanical load
- outdoor / indoor
- decorative aspects

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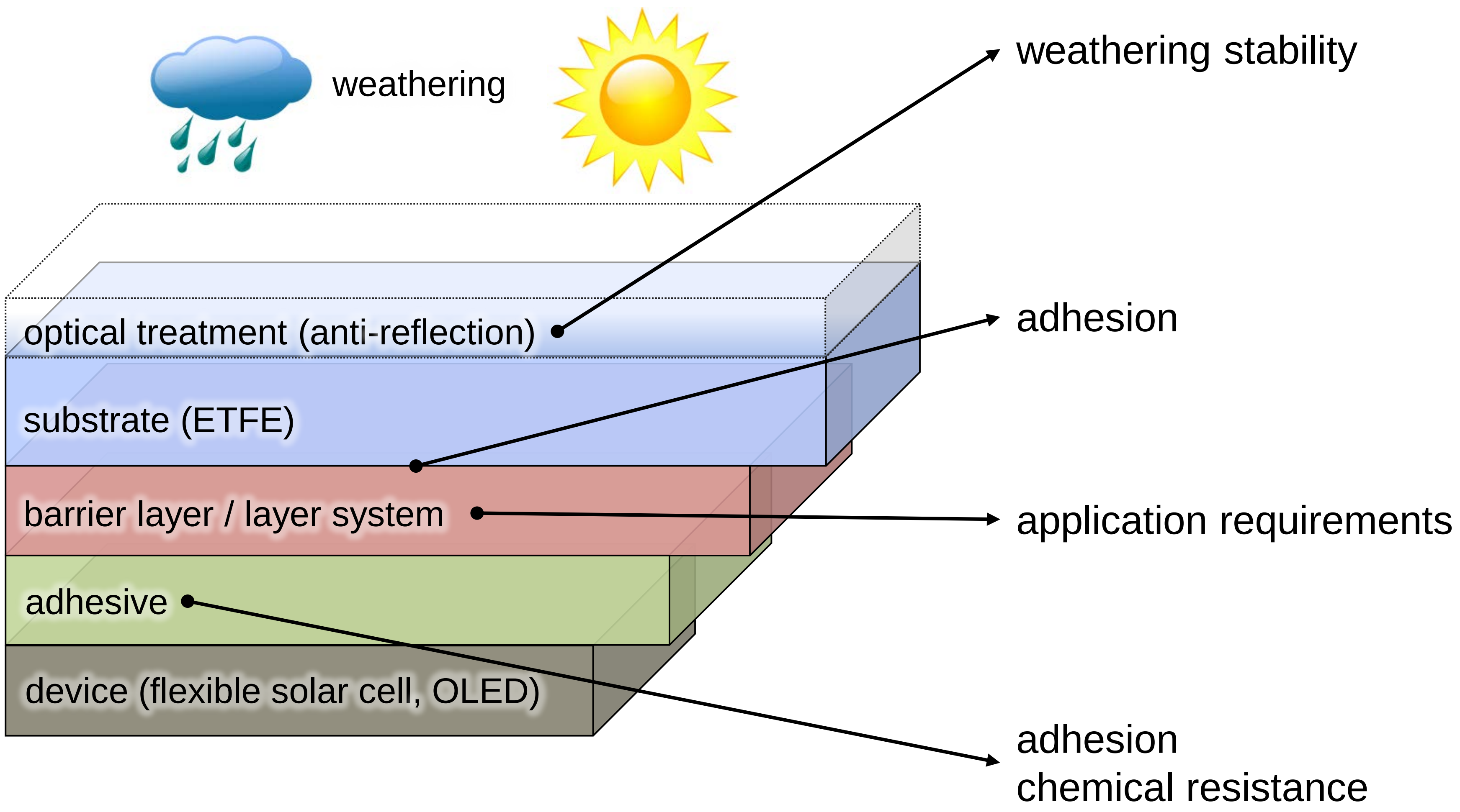
Challenge



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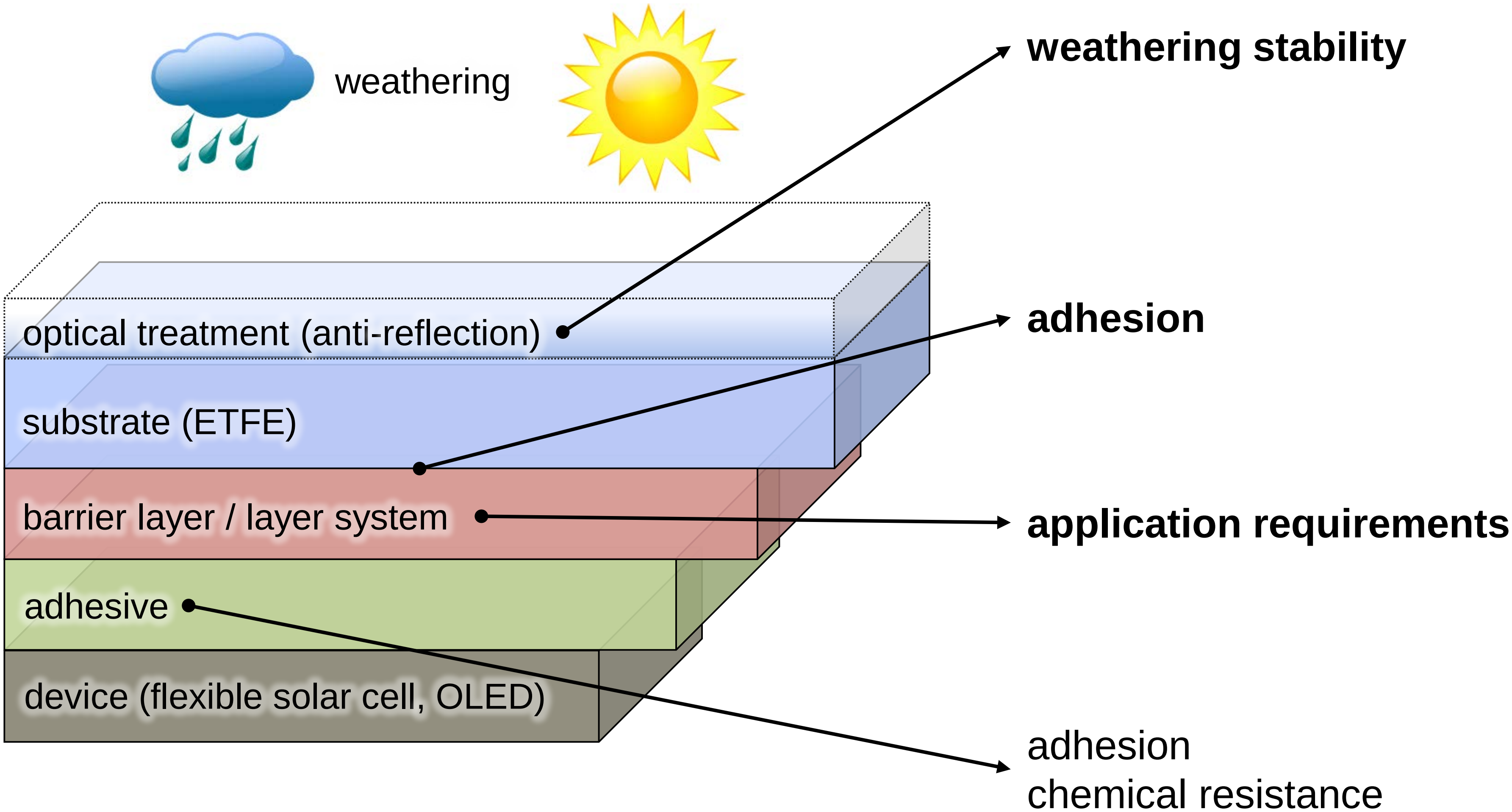
Challenge



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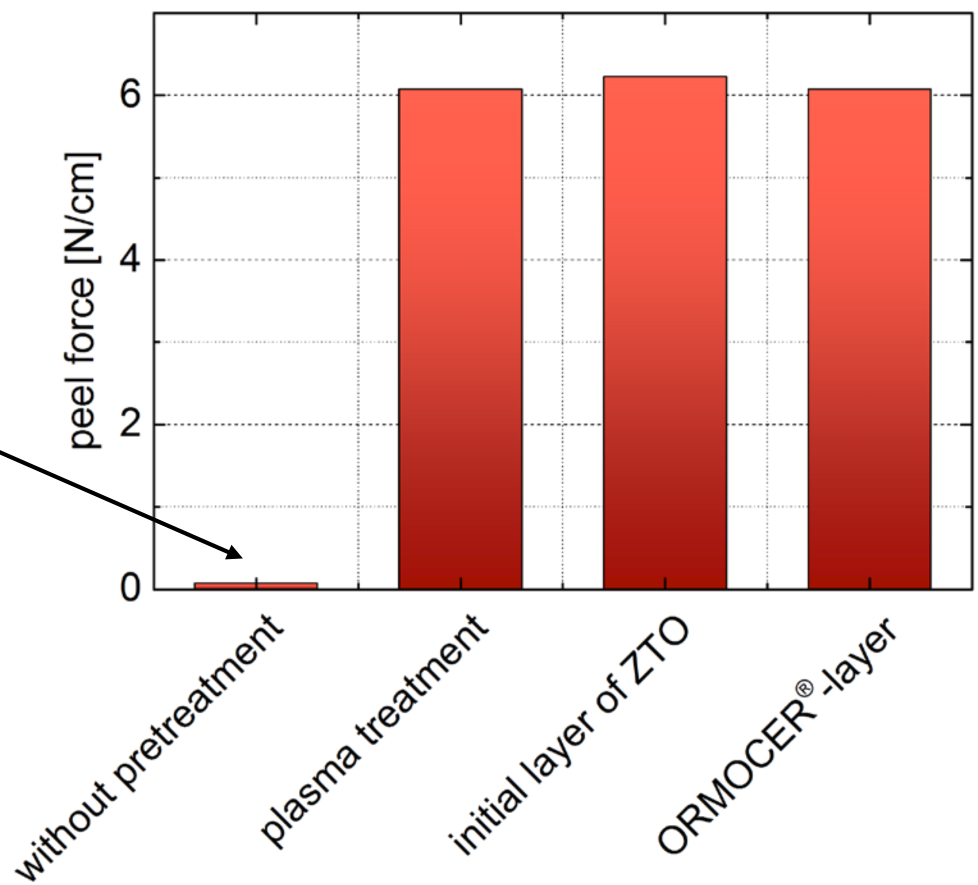
Layer adhesion – barrier oxides and ORMOCER®

substrate	layer material and thickness [nm]	peel force[1] [N/cm]
PET Melinex 400	ZTO 100 nm	> 12
ETFE ET6235-Z	ZTO 50 nm	7.2
	Al_2O_3 100 nm	< 0.5
	ORMOCER® 1000 nm	11.5



- three possibilities to improve adhesion of aluminum oxide
- ≥ 6 N/cm → destruction of adhesive

[1]90° Peel-Test according to IPC-TM-650

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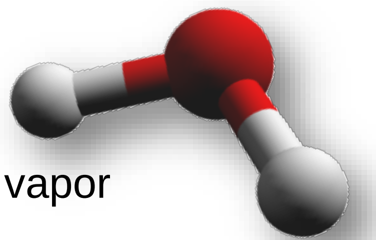
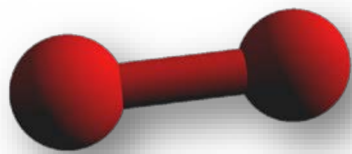
Transparent Permeation Barrier

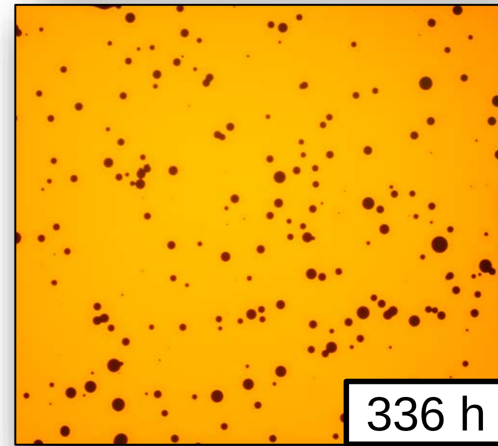
protection of electronic and organic devices against



water vapor



oxygen



- Water vapor transmission rate WVTR
- Oxygen transmission rate OTR

Oxygen	**1 cm³/(m²d bar)**	= $4.5 \cdot 10^{-5}$ mol/(m²d)	= $1.4 \cdot 10^{-3}$ g/(m²d)
Water vapor	10^3 cm³/(m²d bar)	= $5.6 \cdot 10^{-2}$ mol/(m²d)	**= 1 g/(m²d)**

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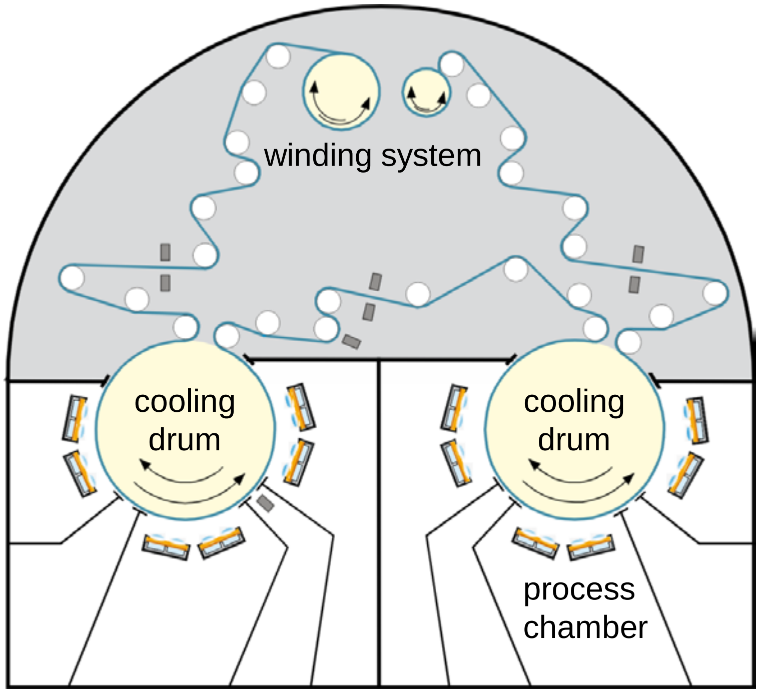
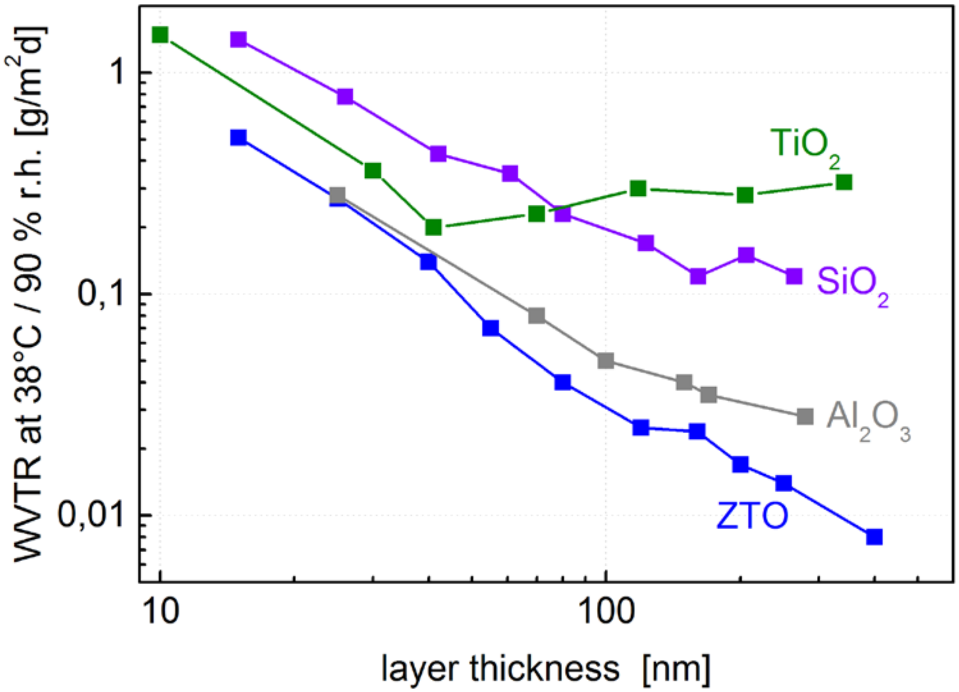
Layer materials



pilot scale roll-to-roll-coater

- six process chambers
- roll length up to 500 m
- roll width up to 650 mm

- sputtered layers on low-cost standard PET Melinex 400 CW



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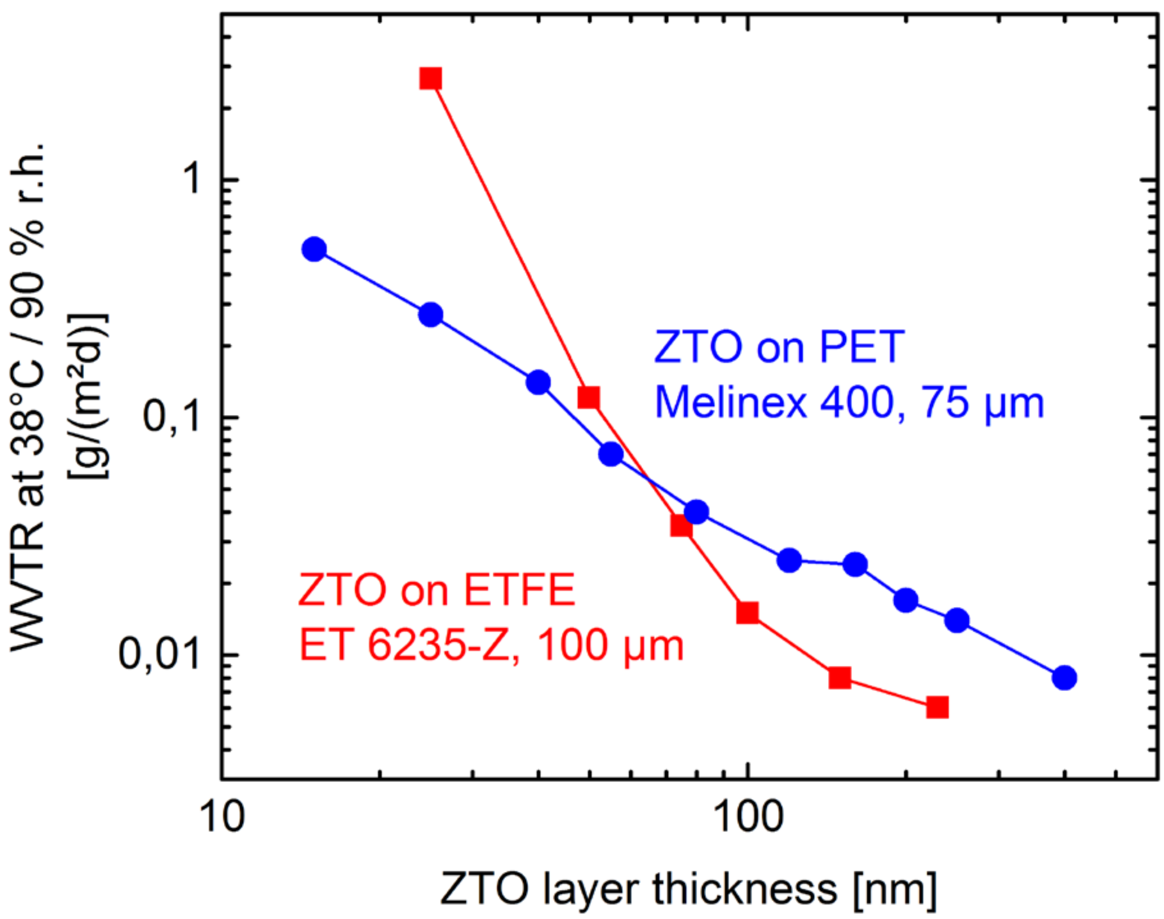
Barrier performance of single layers



- coulometric measurement
- Oxygen transmission rates – 150 nm ZTO: < 0.1 cm^3 / (m^2d bar) on **PET and ETFE**
- Layer thickness ↑ → crack onset strain ↓[1]

[1]more Details about dimensional stability of ETFE in presentation of O. Miesbauer from Fraunhofer IVV

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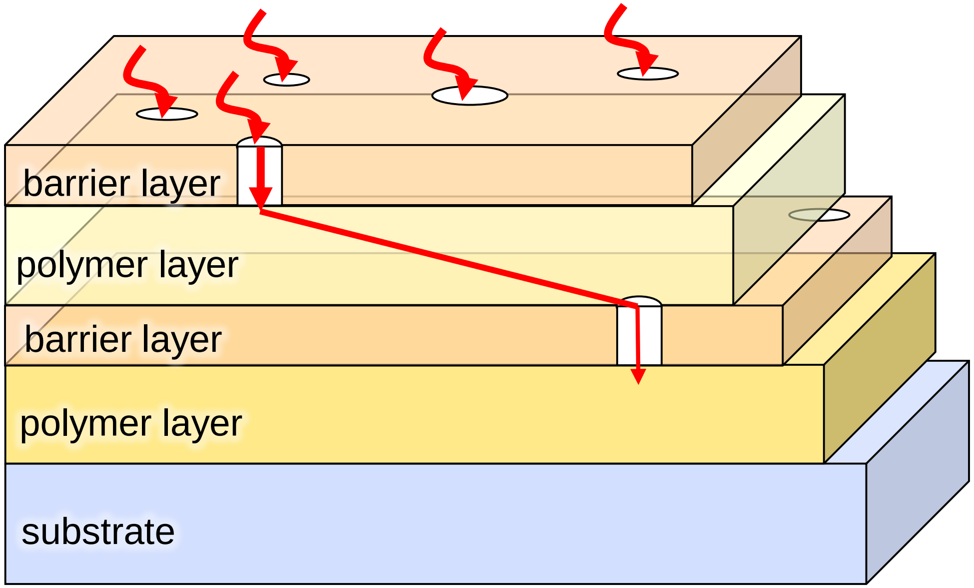
Barrier performance of layer systems

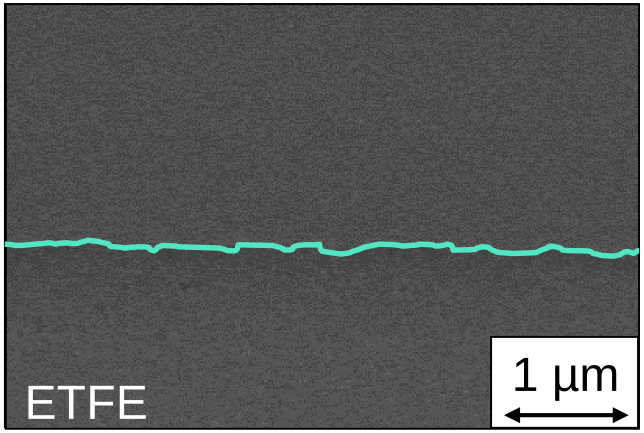


Tasks of second polymer layer

- interrupt growth of defects
- surface planarization and defect coverage
- reduce mechanical stress – improve flexibility

Tasks of first polymer layer

- Planarization of substrate
- UV-protection
- improved adhesion
  (> 11 N/cm ORMOCER® auf ETFE)



source: Fraunhofer FEP

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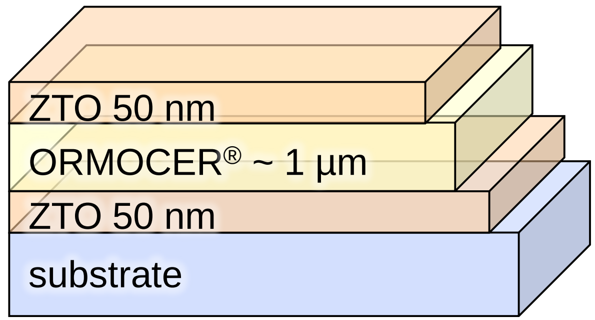
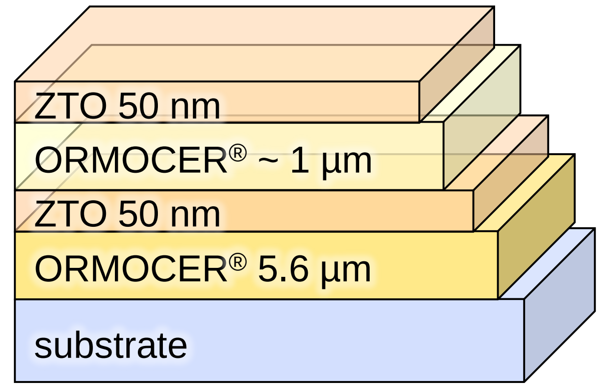
Barrier performance of layer systems





parameter			
Substrate	PET	ETFE	ETFE
WVTR [g/m²d]	0.002	0.035	0,002
OTR [cm³/m²dbar]	< 0.1	-	< 0.1
T_{CIGS} [%]	76.5	78.3	74.4

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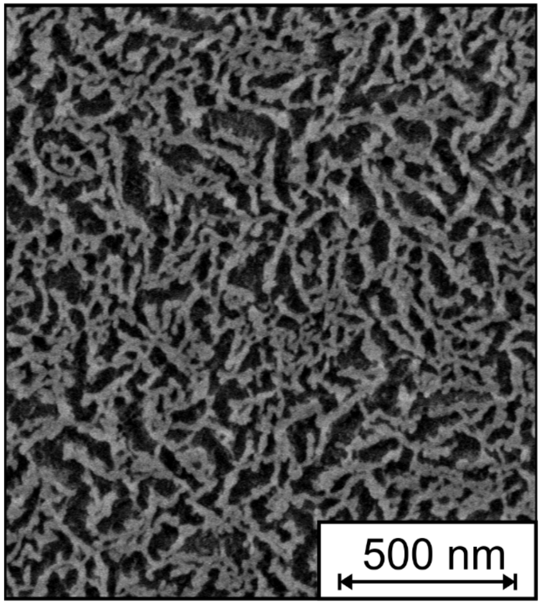
Anti-reflection (AR) properties by nanostructuring

- based on moth-eye-effect
  - structure size lower than wavelength of visible light → no scattering
  - refractive index gradient
  - without absorption and scattering
    - reducing reflection (R) results in transmission (T) increase
    - T + R = 100



  - stochastic structures
  - direct structuring of ETFE
  - plasma induced nanostructuring

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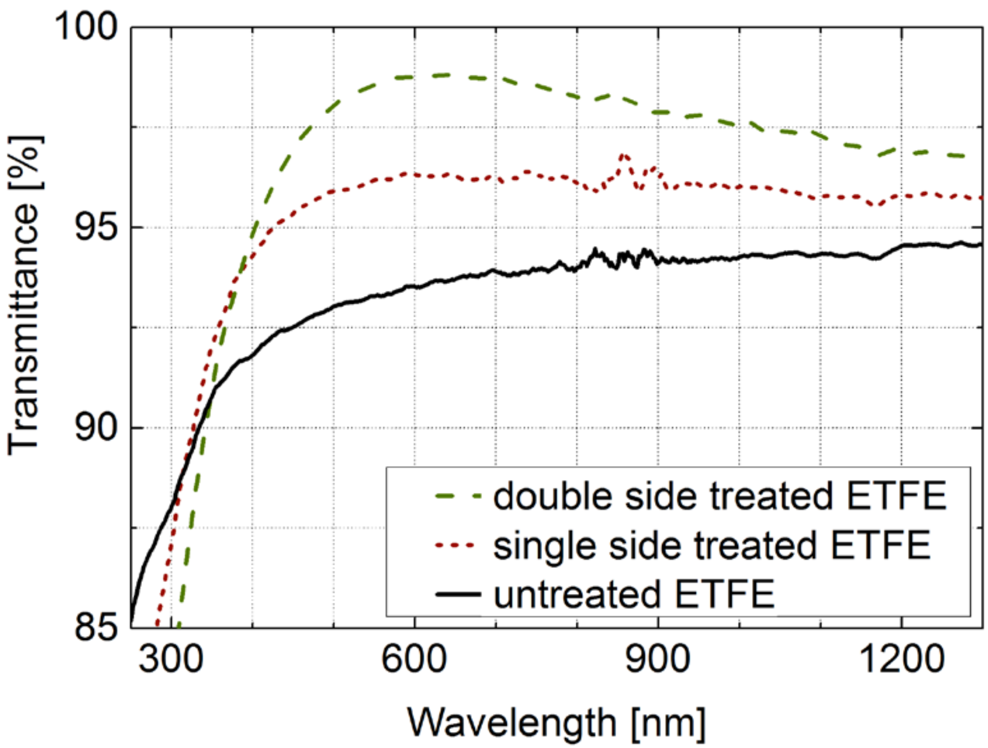
Optical Properties



- broadband AR-effect
- maximum in transmittance at 600 nm
  - untreated ETFE 93.7 %
  - single side treatment 96.3 %
  - double side treatment 98.7 %

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C. Steiner, S. Günther and M. Fahland, "Eigenschaften nanostrukturierter Fluorpolymerfolien," *10. ThGOT Thementage Grenz- und Oberflächentechnik*, Leipzig, 2014

Outdoor Weathering Equipment

- four racks with 25 samples (150 mm x 150 mm) per rack
- located in Dresden (Germany) on top of a roof with nearly 45° tilt and adjusted southwards
- samples in aluminum frames
- monitoring of climate data
- monthly measurement of optical properties of the samples

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C. Steiner, S. Günther and M. Fahland, "Characterization of nanostructured surfaces of fluoropolymers produced by reactive plasma treatment," in *14th International Confer-ence on Plasma Surface Engineering*, Garmisch-Partenkirchen, 2014.

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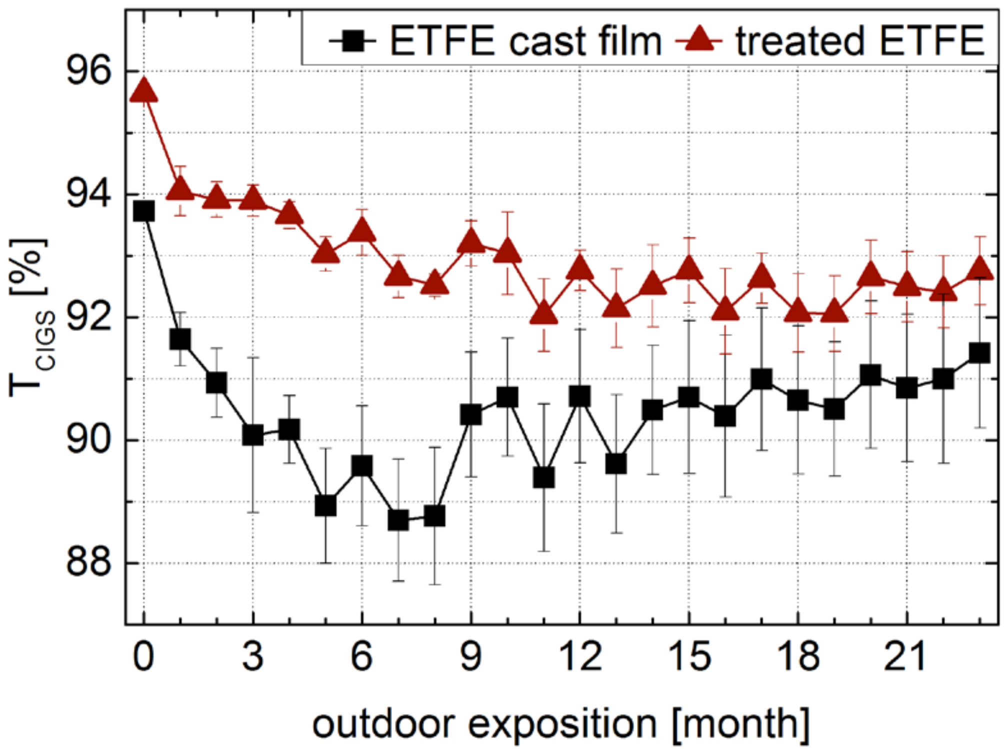
Results of Outdoor Weathering Test



- results without additional cleaning
- start of exposition in April 2014
- after 12 month → difference ≈ 2%
- transmittance ETFE increases after 9 months
  - less pollution
  - cleaning effect because of more rain

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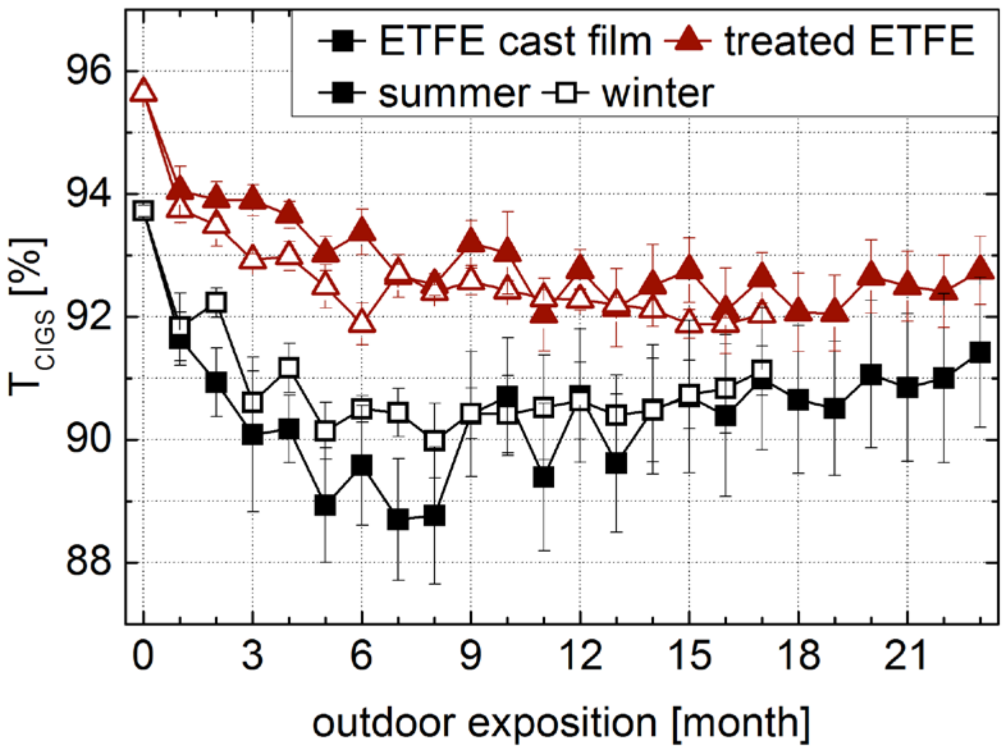
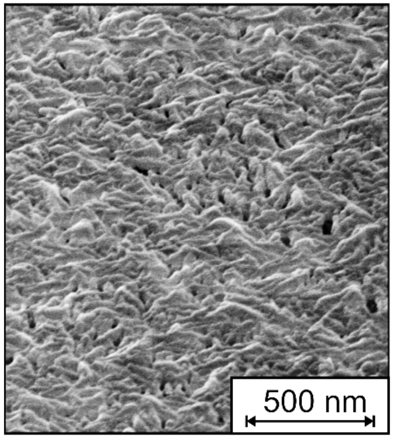
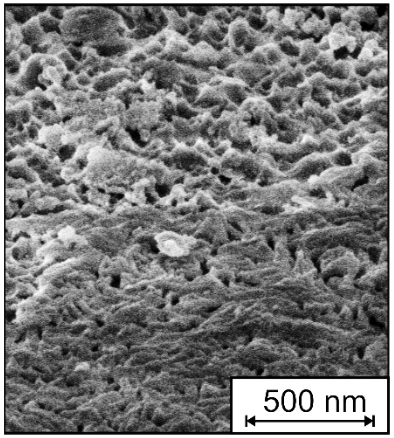
Results of Outdoor Weathering Test



- results without additional cleaning
- start of exposition in April 2014 and November 2014
- Independent of the start of exposition



original state



after 6 months

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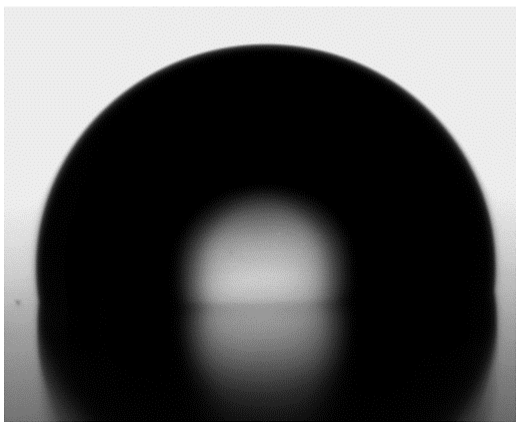
Wetting behavior of nanostructured ETFE

- static contact angle measurement with water

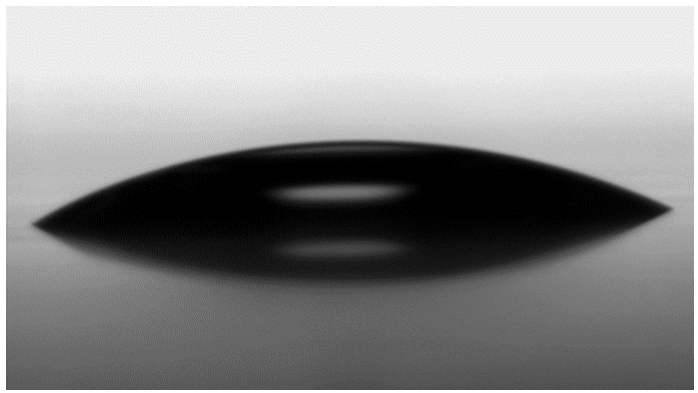
ETFE - cast film

~ 95°



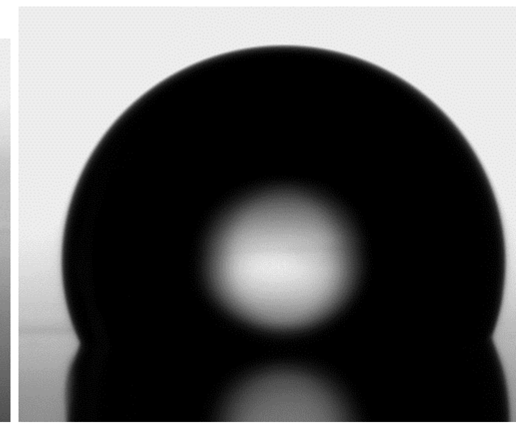
SiO_2 - top coat

~ 30°



TiO_2 - top coat

~ 110°



→ wetting behavior adjustable from hydrophilic to hydrophobic

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According to: C. Steiner, S. Günther and M. Fahland, "Eigenschaften nanostrukturierter Fluorpolymerfolien," *10. ThGOT Thementage Grenz- und Oberflächentechnik*, Leipzig, 2014

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Conclusion

- ETFE has specific requirements to processing and handling, but we show you:
  - pretreatments to improve layer adhesion
  - coating of transparent barriere layers
  - coating of layer systems including laque hardening at 120°C in R2R process
  - nanostructuring to
    - improve optical properties → AR-effect
    - adjust wetting behavior → hydrophilic to hydrophobic
  - weathering stability of nanostructures

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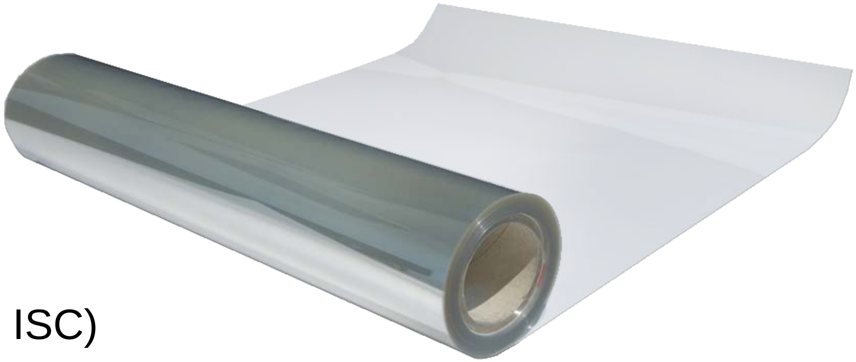
Thank you



- project partners for great co-operation, work and constructive discussions
- Dr. Sabine Amberg-Schwab (Fraunhofer ISC) for providing the ORMOCER®-lacquer
- Oliver Miesbauer (Fraunhofer IVV) for providing printed ORMOCER®-layers by roll-to-roll processing
- colleagues of Fraunhofer FEP for coating and material characterization

M. Eng. Cindy Steiner
Fraunhofer FEP
Winterbergstraße 28,
01277 Dresden, Germany
Tel: +49 (351) 2586 143
cindy.steiner@fep.fraunhofer.de
www.fep.fraunhofer.de

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