Recent Developments in Sol-Gel Processing - Multifunctional and Active Surfaces through Sol-Gel Processing and Wet Chemical Deposition Techniques

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INSIDE & ON TOP
MATERIAL SOLUTIONS
by Fraunhofer ISC

Fraunhofer
ISC

Contents

Fraunhofer ISC Overview – „It´s a material world“

Material-based solutions

Materials Chemistry
- Sol-Gel
- coatings
- Barriers
- Med. Preparate
- Particles

Application Technology
- Mikro-Optics/ Elektronics
- Glass
- Dental/ Micromedicine

Services
- Analytics (ZAA)
- CeDeD Device Development
- IZKK

ZfAE

Center for Applied Electrochemistry

CeSMa

Center Smart Materials

370 Employees
23,5 Mio € Budget
rd. 8100 m² total area of which
rd. 5800 m² labs and technical space

4 sites centrally located within Germany

Fraunhofer-Center HTL

HT Lightweight Materials, Bayreuth

Project Group IWKS

Materials Recycling and ressources, Alzenau/ Hanau

Fraunhofer ISC - Core Competencies

Materials

- Glass/ Ceramics
- Nanoparticles
- Inorganic Fibers
- Battery Materials
- Adaptive Materials
- ORMOCER®e

Processing

- (Wet) Coatings
- Roll-to-Roll
- Clean room
- Pilot plants
- Upscaling areas
- Demonstrators

Solutions for industrial partners

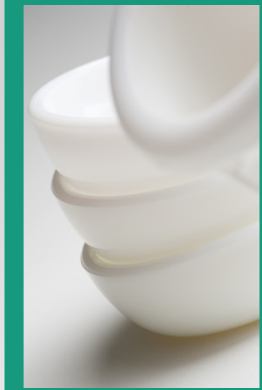
Analytics

- Materials characterisation
- Failure analysis
- Quality control
- Thermooptical measuring devices

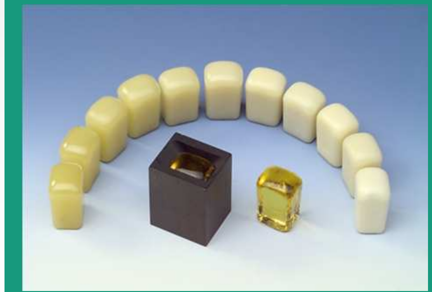
MATERIAL SOLUTIONS
INSIDE & ON TOP

Glass Technologies

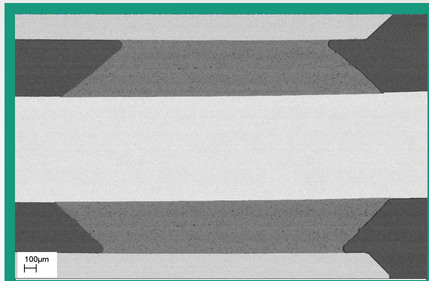
- Glass processing
- Glass production
- Pilot plant glass manufacturing devices



- REACH compliant glasses
- Porous glasses
- Optical glasses



- (Dental) glass ceramics

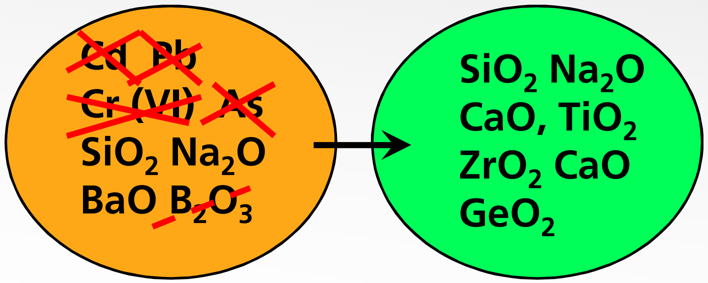


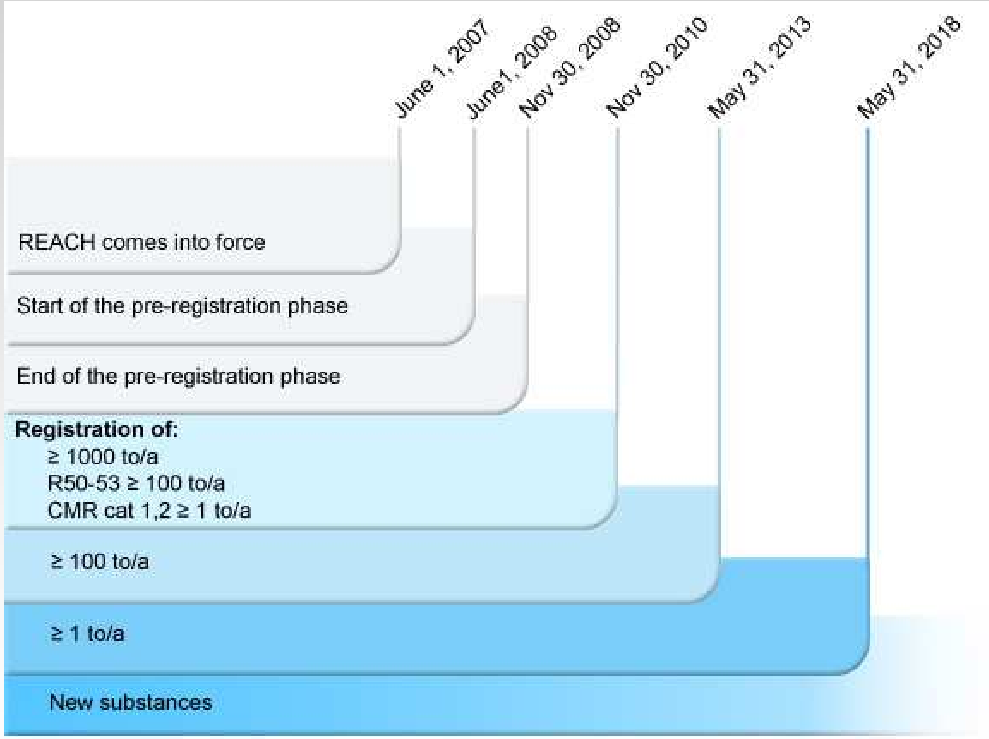
- Solder glass
- Joining technologies

Glass and REACH

REACH: Registration, Evaluation, Authorisation of Chemicals, (EU-Regulation Nr. 907/2006 - EU L 396 dated 29.05.2007)

- Consulting
- Analysis
- Substitution

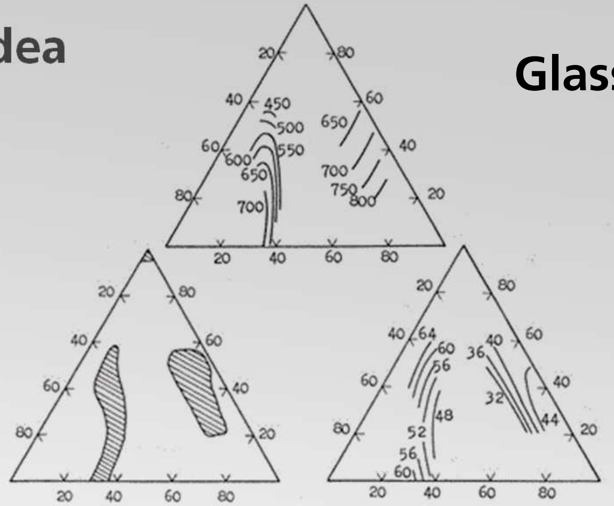




Source: Sigma Aldrich

Lead-free Glass Colours

Initial idea



Glass system

... production

... final application !

... analytical results

New Class of Lead-free Ceramic Colors

Physical properties of best glass system

- glass system: ZnO, Al_2O_3, B_2O_3, T_g = 740 K
- melting temperature range: 800-900 K
- high brillance
- hydrolytic class HGB 1
- acid resistance
- contains oxides of Si, Zn, B, P, Na, Ti, Al and Ca
- colours: blue, green, white, black
- tunable thermal expansion
- screen printable

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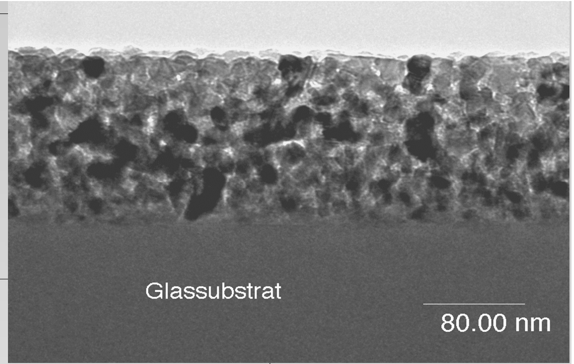
Properties of Coatings and Substrates

Atmosphere, weathering (O_2, water, light)



Porosity
Functional Groups
Si-OH-Content
Thickness
Curing Conditions
(T, Irradiation)

Coating

Surface Energy

Chemical Composition

Thermal Coefficient of Expansion

Mirohardness   Elastic Moduli

Residual Stresses, Tensile Strength

Interface

Graded Layer

Primer?, Chemical Bonds, Interdiffusion

Surface Condition

(Smoothness, Functional Groups)

Surface Energy

Thermal Coefficient of Expansion

Elastic Moduli

Residual Stresses, Tensile Strength

Substrate

Sol-Gel Processing – Nucleation and Growth

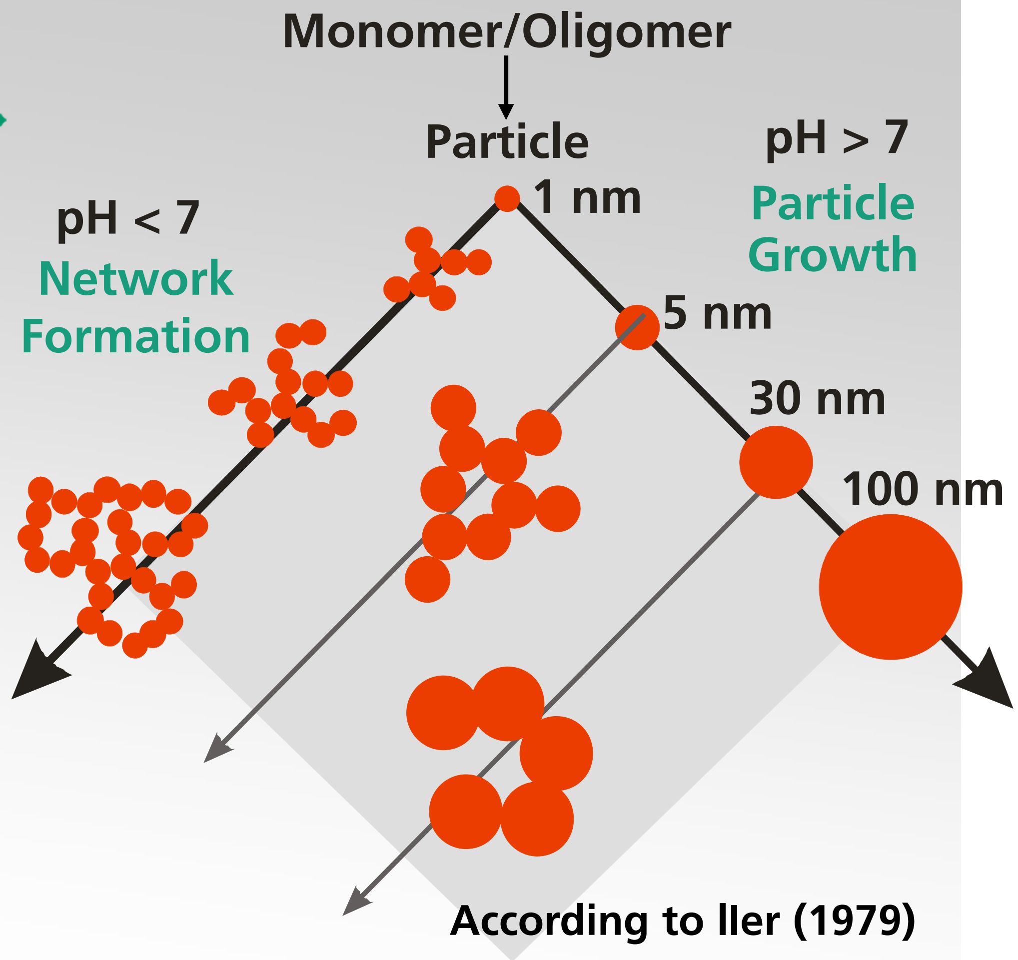
particle growth and network formation largely depend on the pH-value of the solution

pH < 7

- gel formation: continuous solid network with solvent trapped in the pores

pH > 7

- particle growth: colloidal solution (sol state)
- salts enhance aggregation of particles at pH 7 – 10



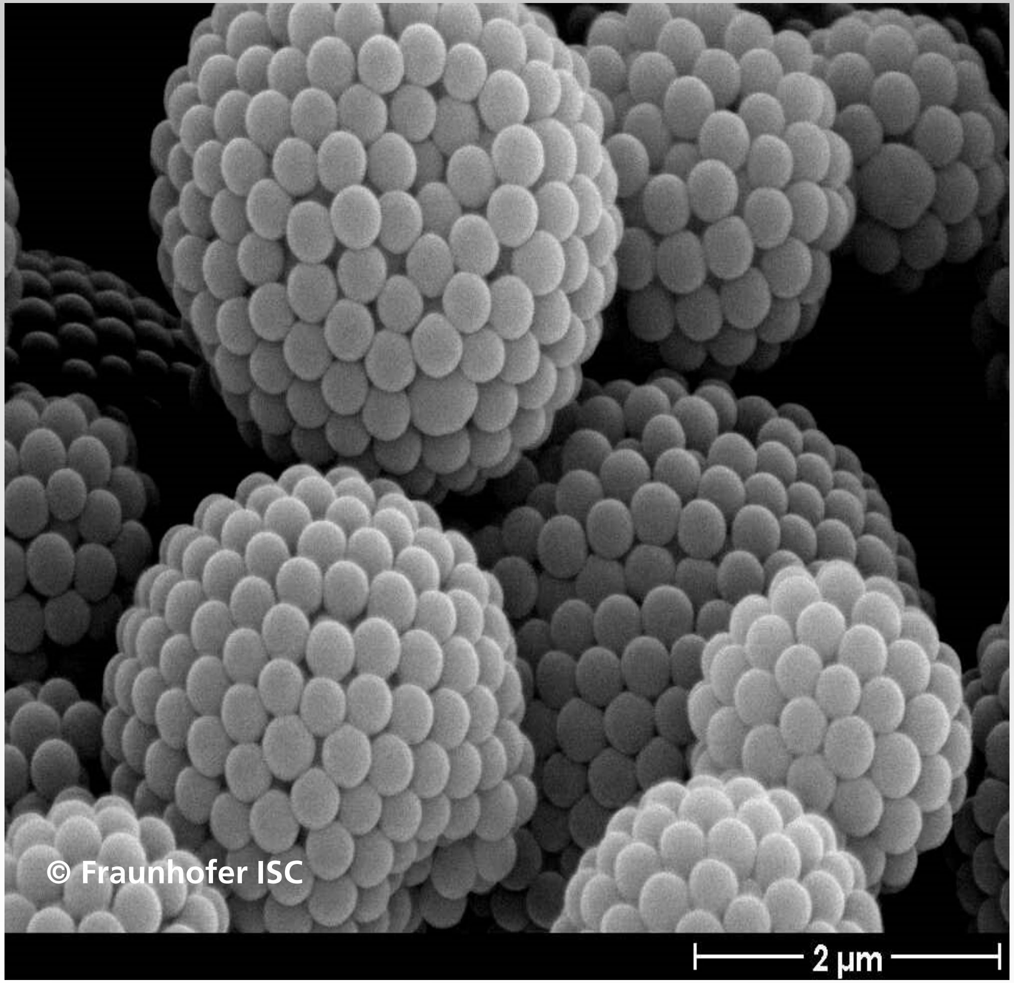
Redispersible Nanopowders

Spray drying of surface modified silica sols (SiO_2)

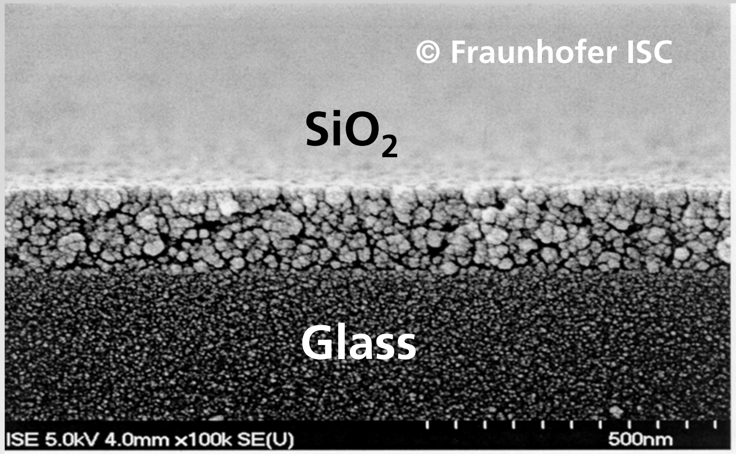
redispersible in various solvents

processing of nanocomposites

application of particle mixtures of different size and type to increase packing density, improve X-ray scattering



Increase of Energy Efficiency through AR coatings



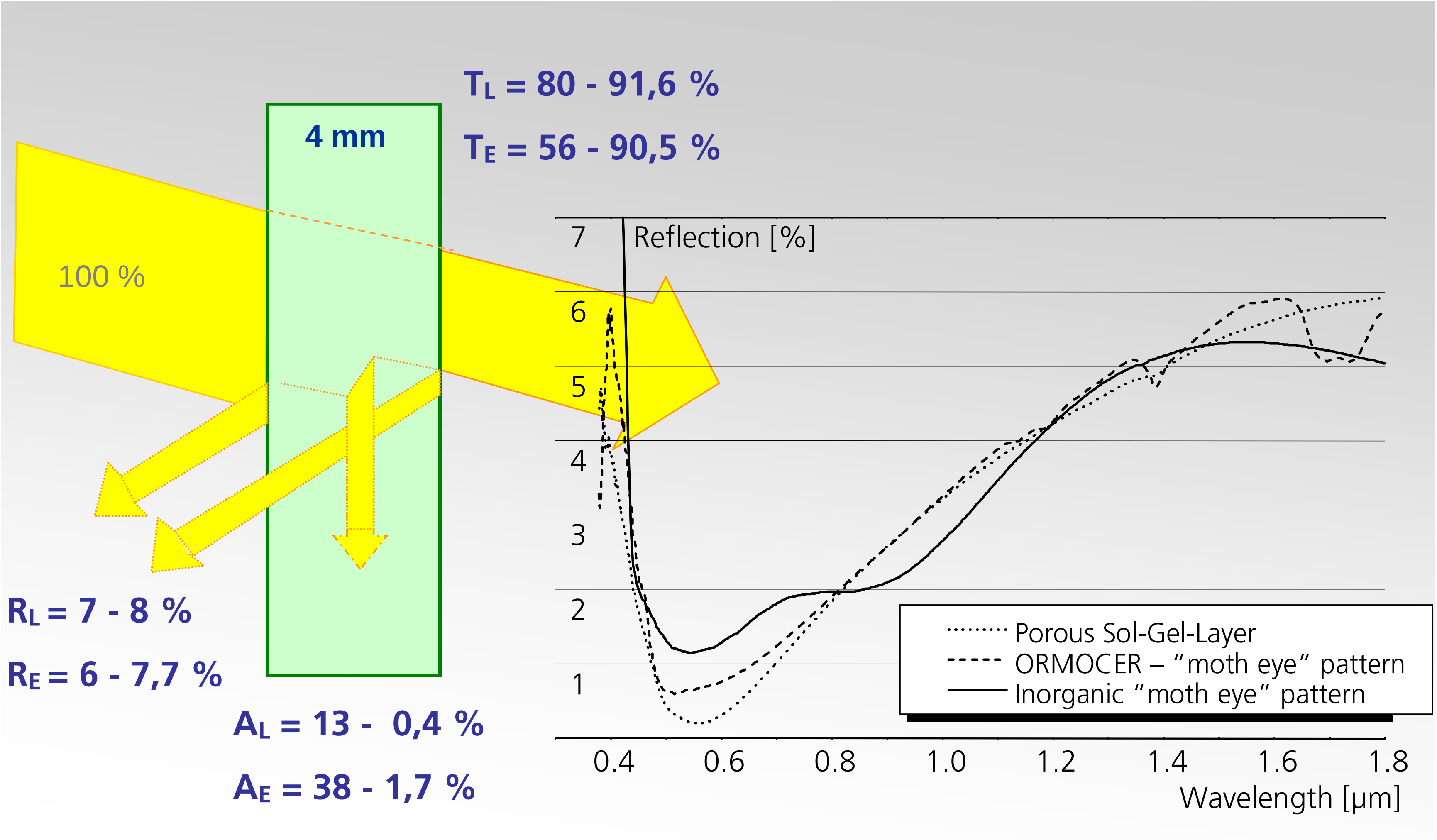
SEM image (100.000 x)

Layer thickness	120 nm
Porosity	45 %
Refractive index	1.24

Increase of energy efficiency: 6 %/a (PV)

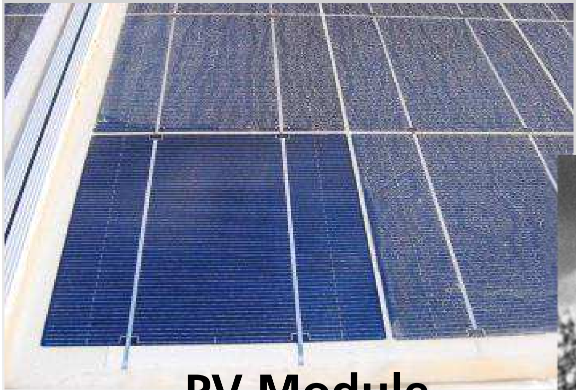
Thermal collectors: 10 % / a

Optical Properties of Glasses

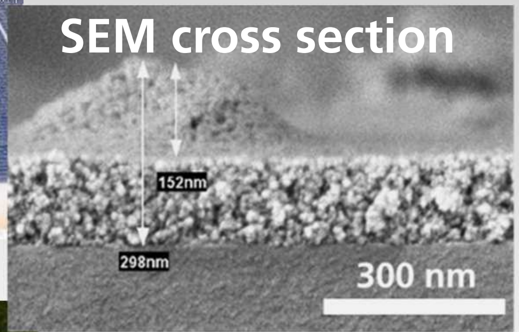


Applications of Nanostructures

Antidust coatings



PV-Module



Greenhouses

Cologne cathedral

Triple glazing units with higher light transmission

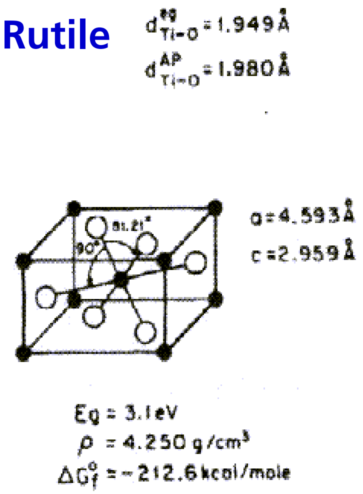
Feel-good glass

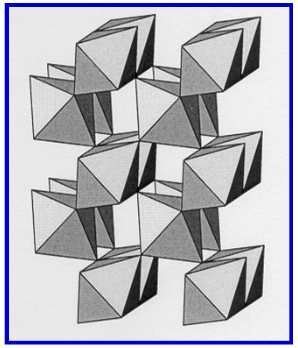
Antireflective

Crystal Growth of Titanium Dioxide

TiO_2 polymorphs: Brookite, Anatase, Rutile, TiO_2 B

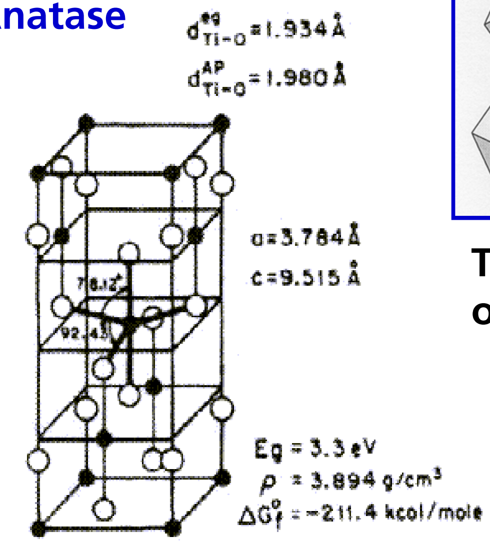
Rutile

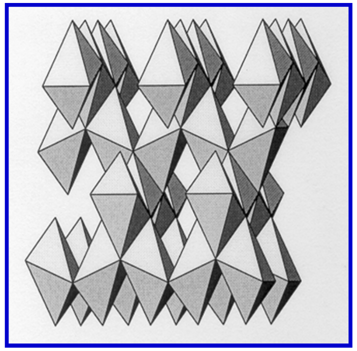




TiO_6 octahedra share edges and corners

Anatase



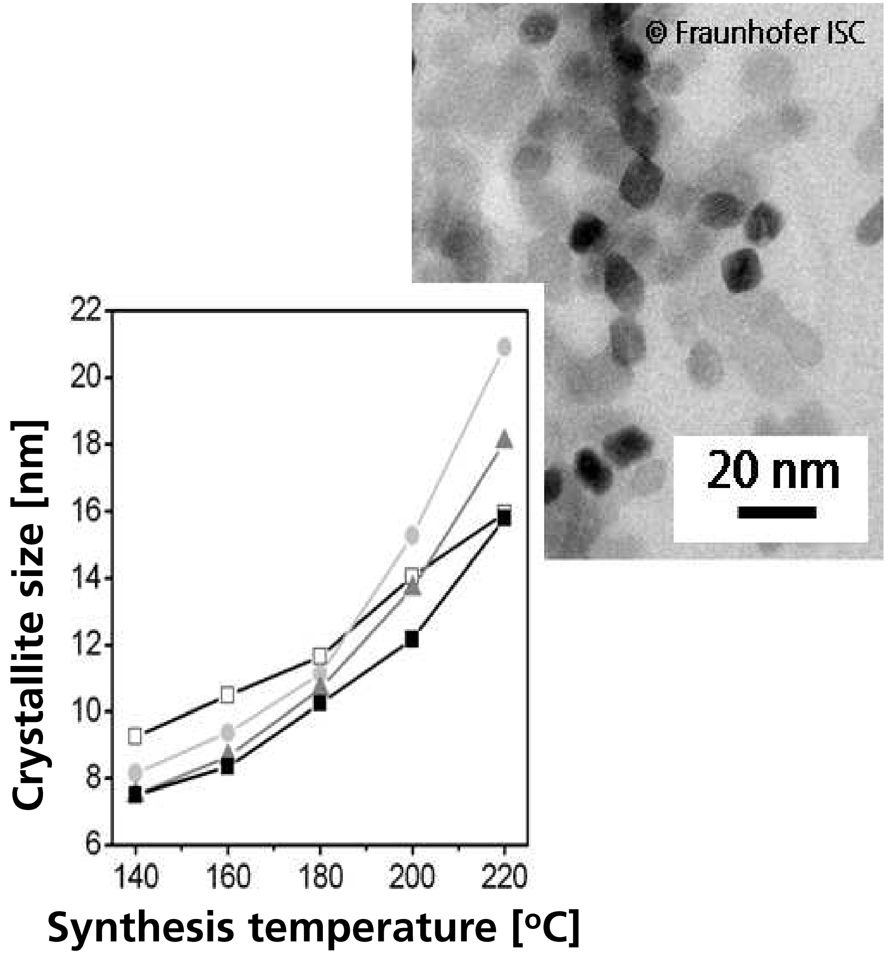


TiO_6 octahedra only share edges

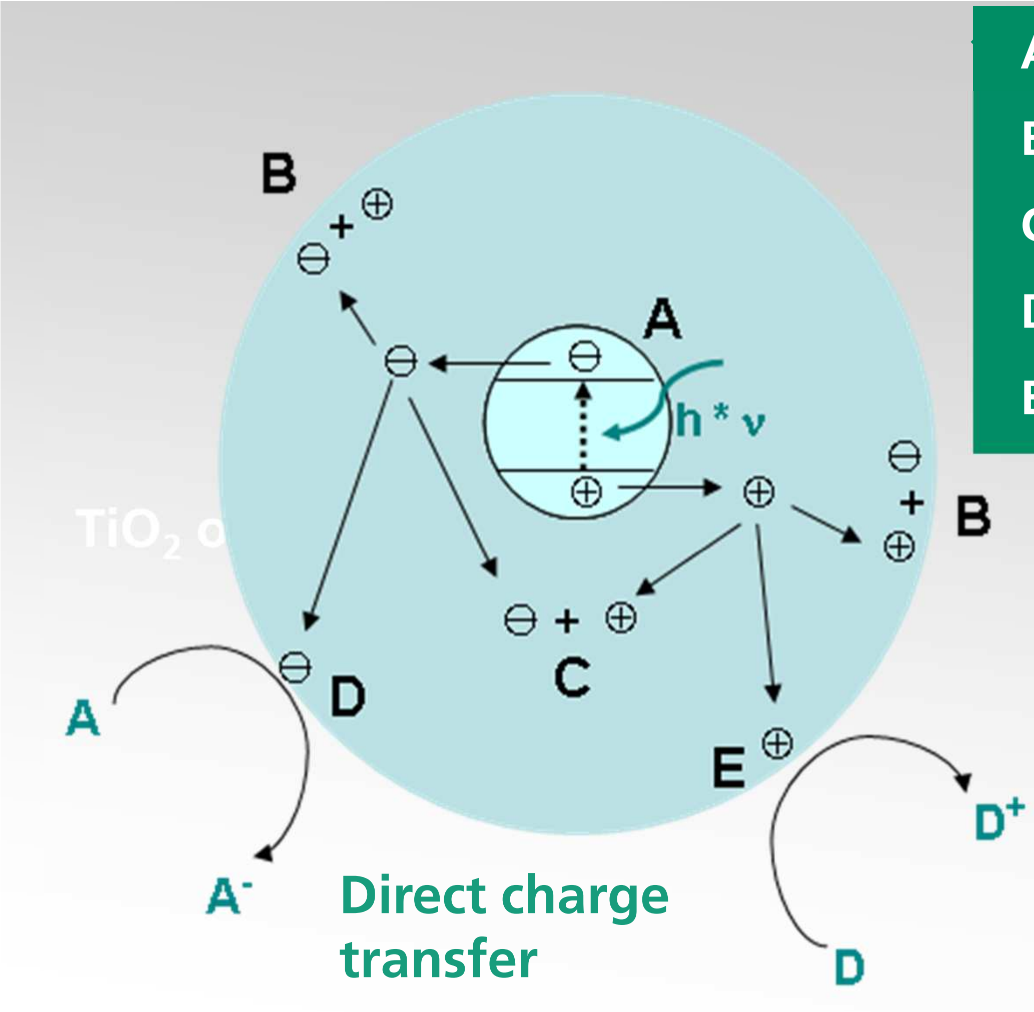
H. le Roux, L. Glasser, J. Mater. Chem., 1997, 7(5), 843 - 851
A. L. Linsebigler, G. Lu, J.T. Yates Jr., Chem. Rev. 1995, 95, 735

Hydrothermal Synthesis of Nanocrystalline TiO_2-Dispersions

Anatase –
tailorable particle size
redispersible in water or alcohol



Nanocrystalline Particles – Photocatalytic Effect



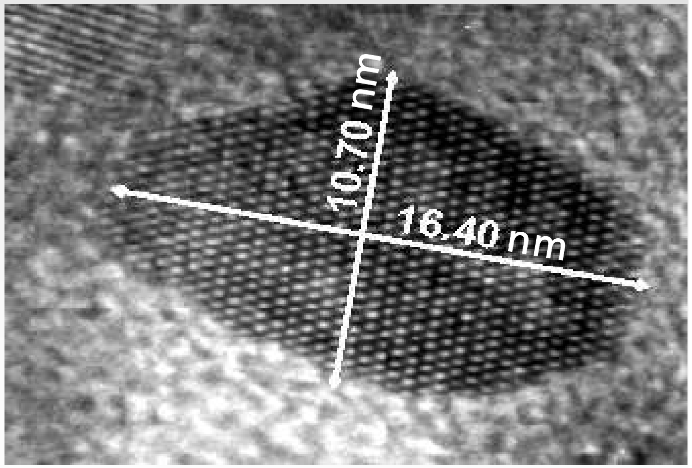
A: Charge carrier generation

B: Surface recombination

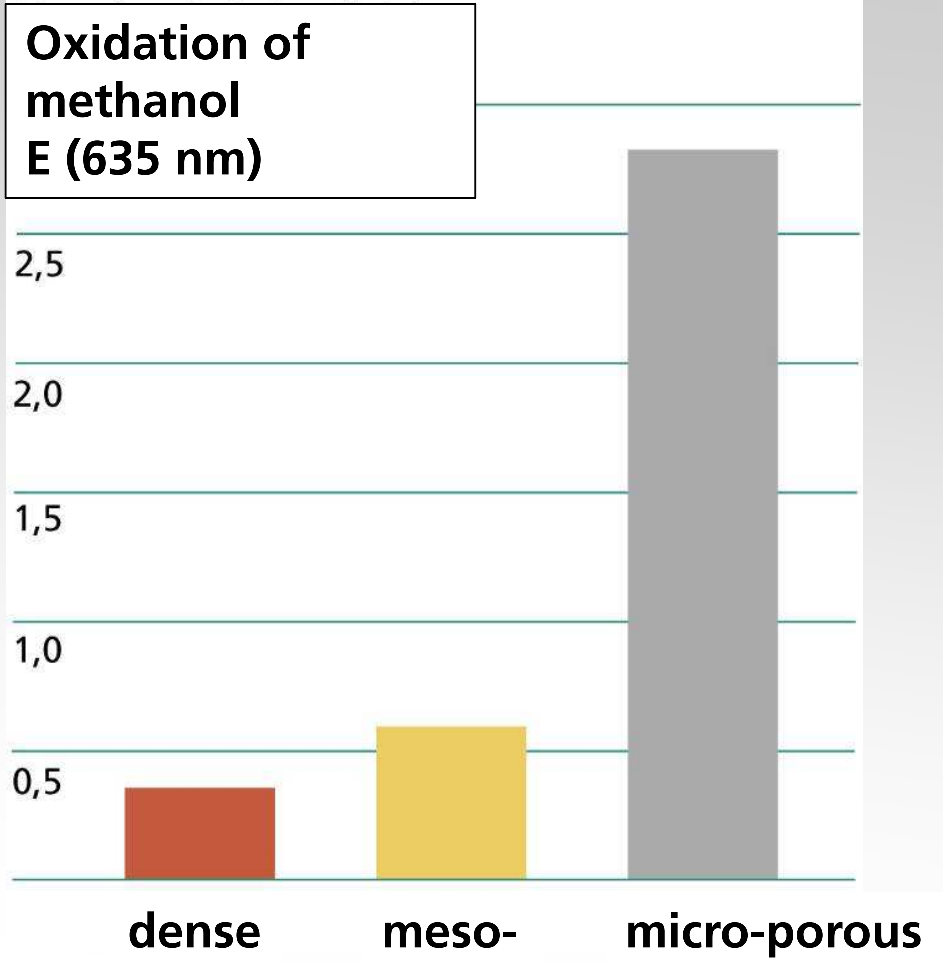
C: Internal recombination

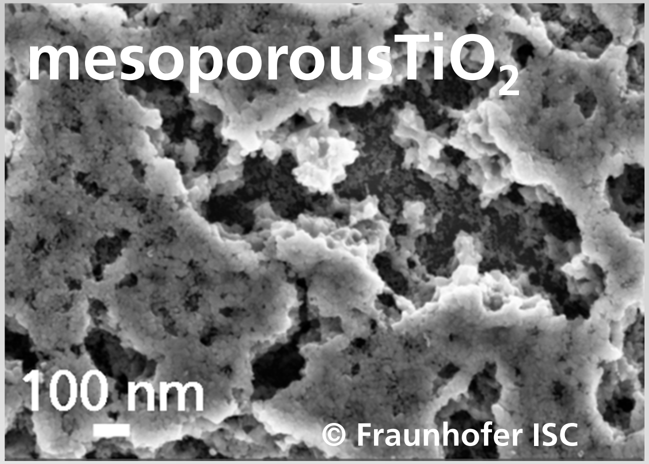
D: Reduction of acceptors

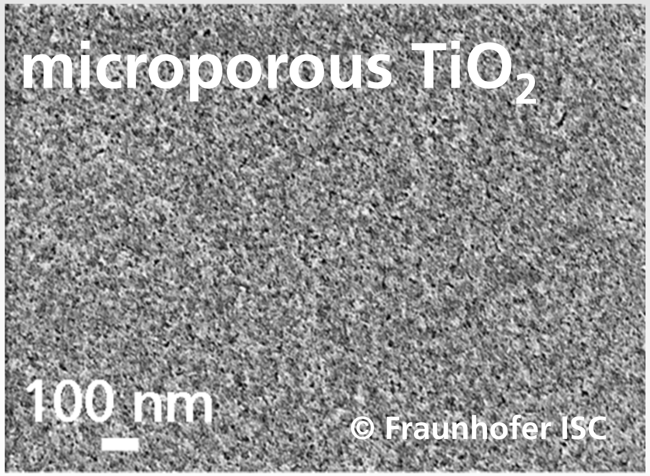
E: Oxidation of donors



Photocatalytic Activity of Porous TiO_2-Coatings







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Plastics with Photocatalytic Surfaces

Surface modification during processing/forming

arm chair parts

left : coated

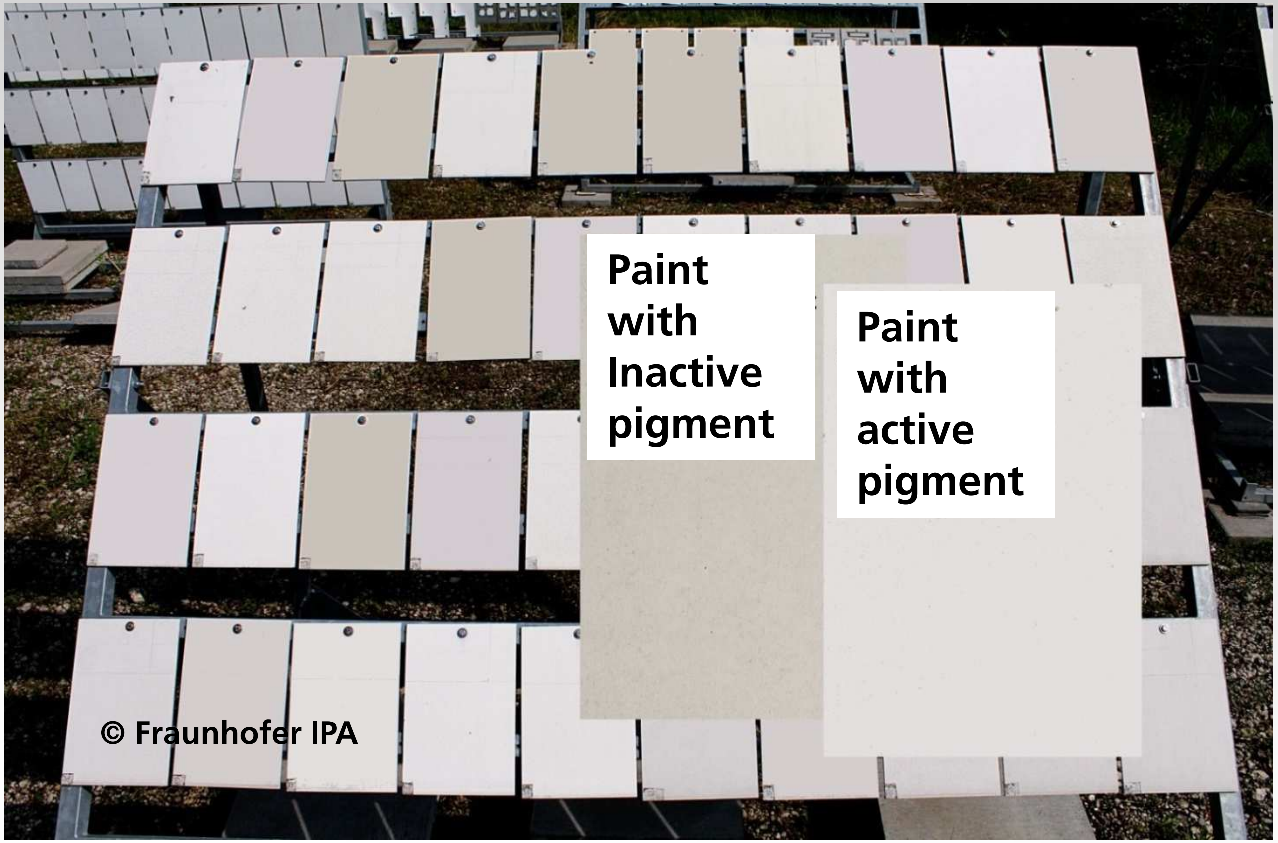
right: non-coated

- **after 2 years exposure time**
- **at ambient conditios**
- **reduced growth of algae**
- **antimicrobial effects**
- **self-cleaning surfaces**

Façade Panels Equipped with Photocatalytic Paint

Exposure conditions

- 2 years
- 45° south
- highly traffic loaded street in Stuttgart



Degradation of Organic Substances on Interior Paints

Daylight

Dark

Methylene Blue

Coffee

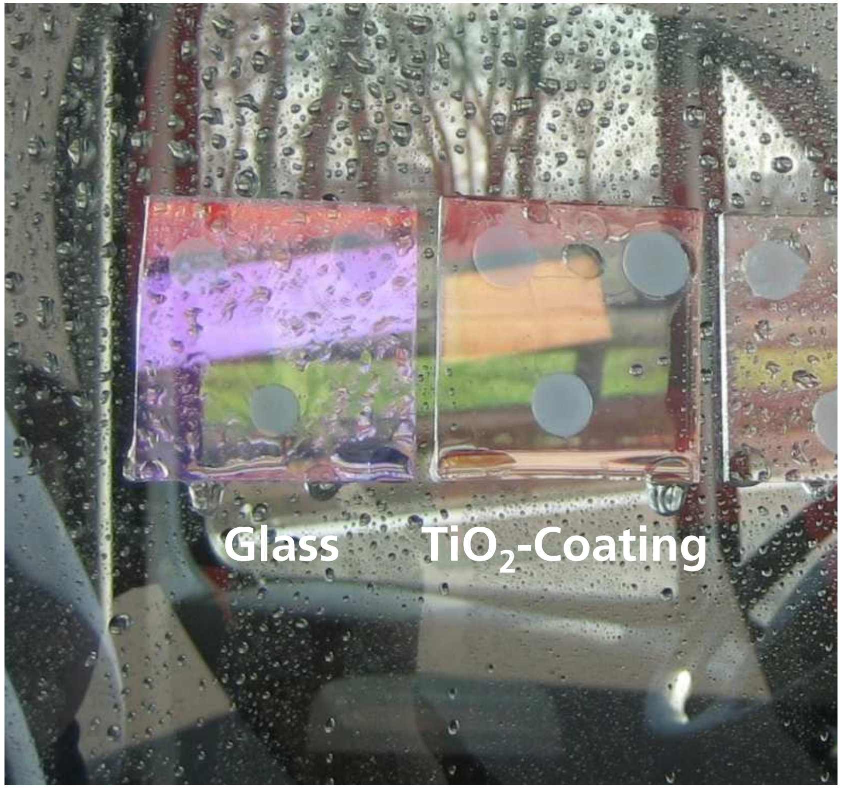
Olive oil

≈ 3 years

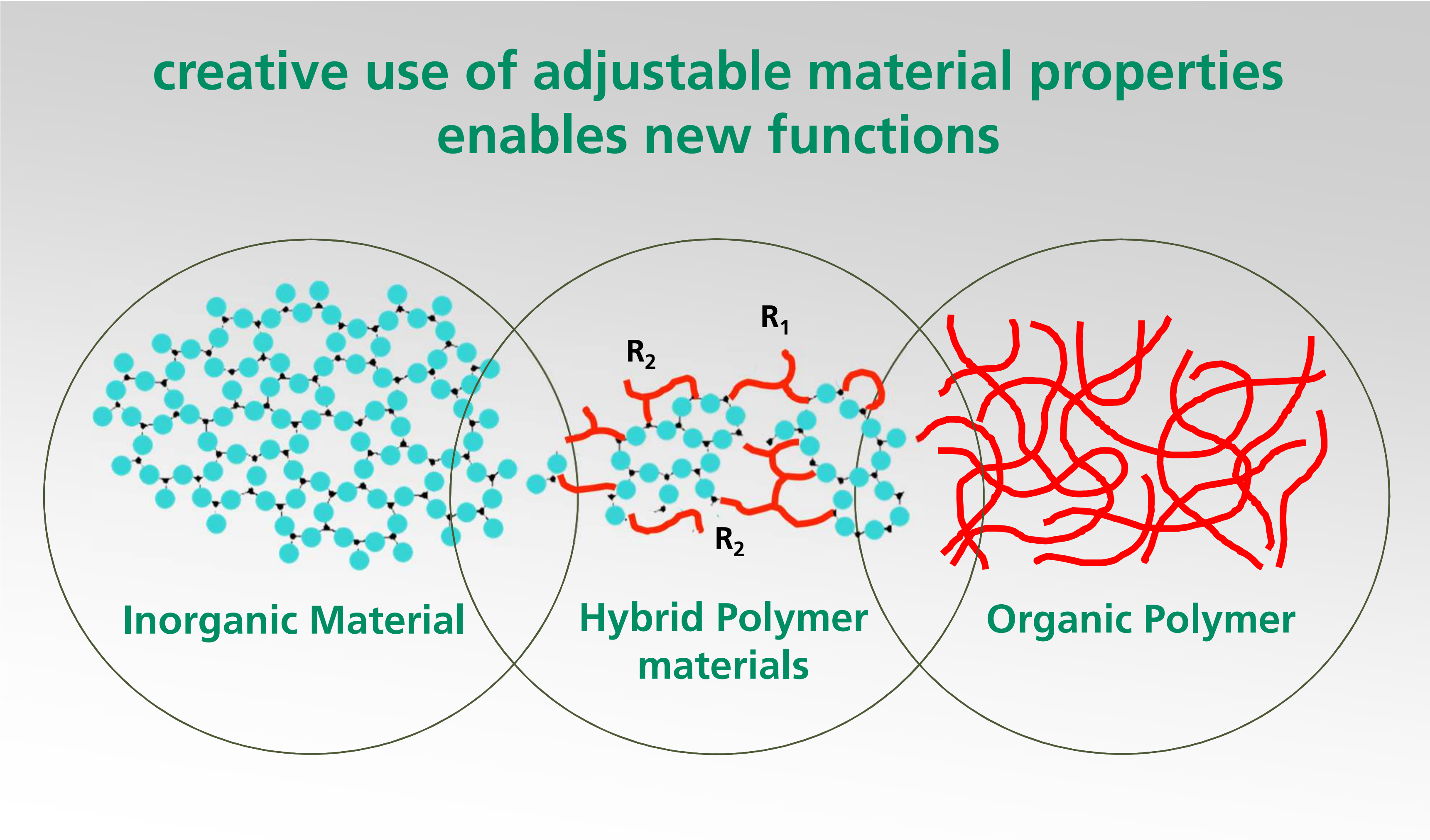
3 m distance from window

5 µW/cm²

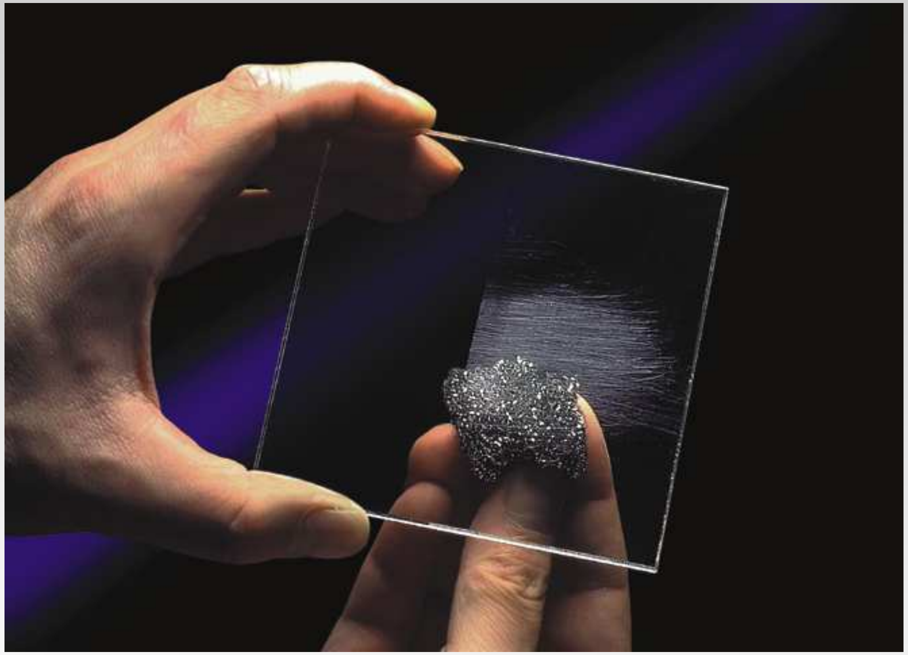
Degradation of Finger Prints and Superhydrophilicity



Hybrid Polymer Chemistry at Fraunhofer ISC



Scratch Resistant Coatings / Thermal and UV-Curing

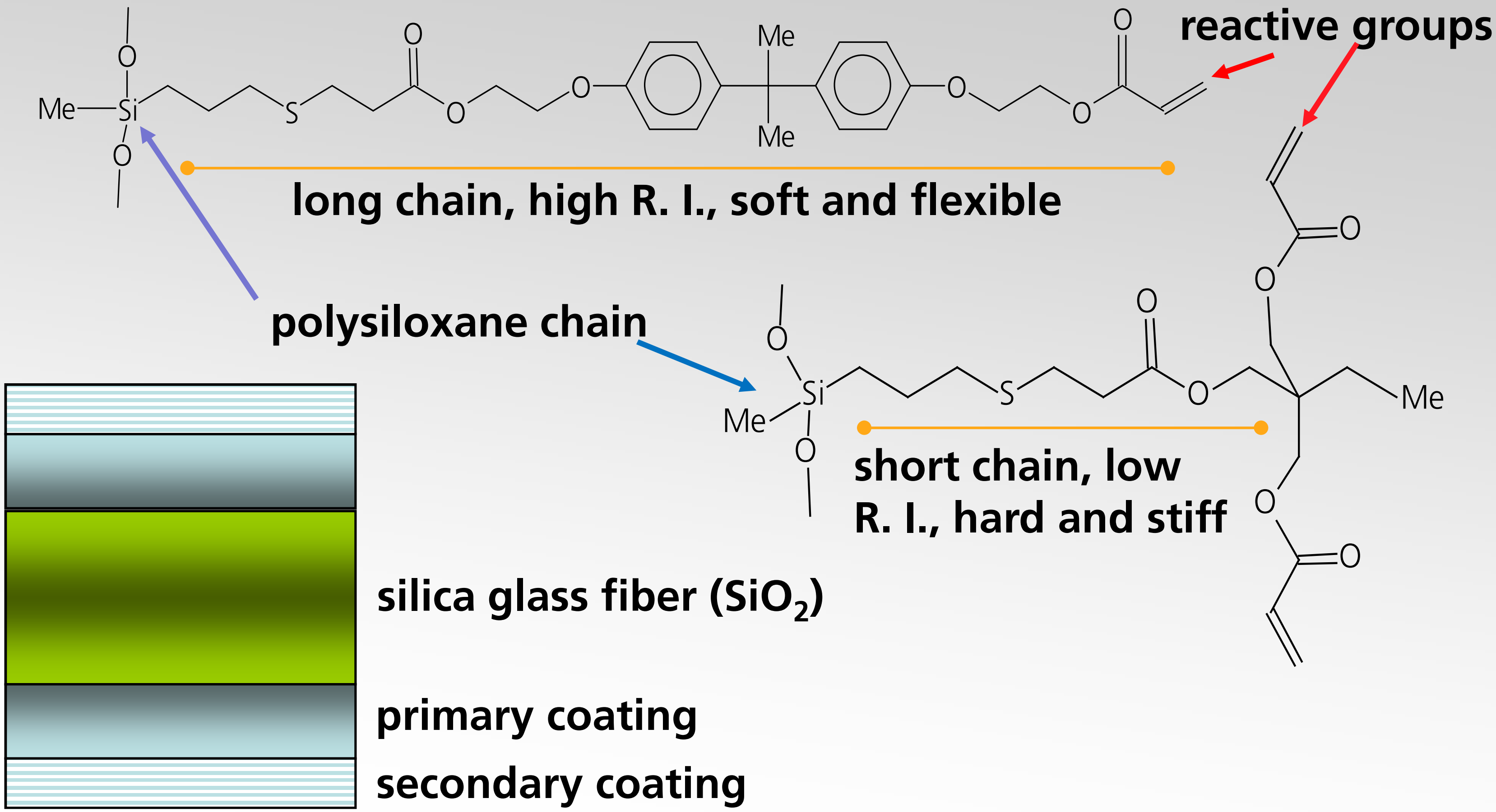


Steel wool performance test

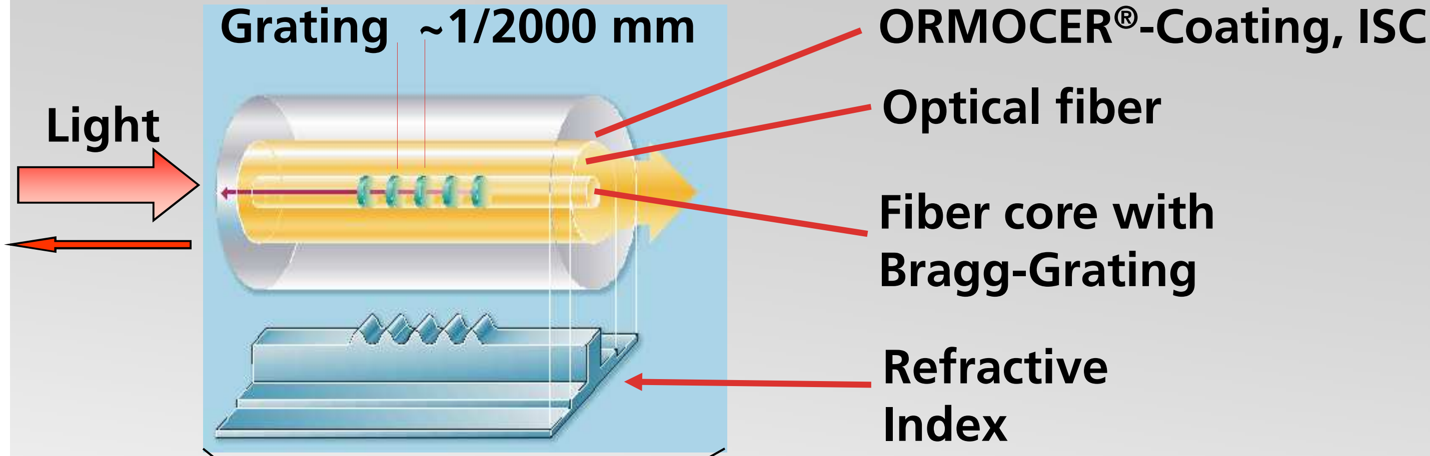
PMMA-Lenses

Glass Fiber Coatings – Ultrafast Curing Processes

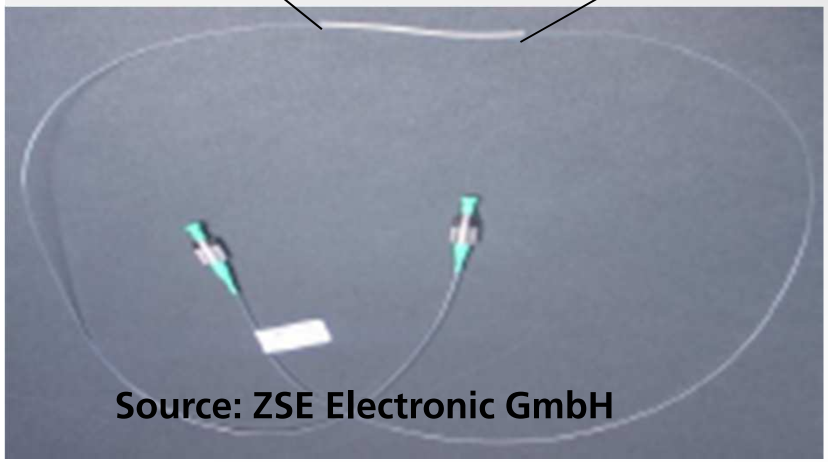
UV-exposure / few seconds



New Protective Hybrid Coating for Optical Strain Sensors



Source: IPHT Jena



Source: ZSE Electronic GmbH

Optical strain sensor

Measuring strain by wavelength specific Bragg reflectivity

Mounting directly on the surface of the device by adhesive bonding

Commercial Product: Fiber-Bragg-Grating Sensors

Construction and Infrastructure Monitoring (Earth Quake Warning)

Engine Monitoring in Automotive Technolgoy

Source: FBGS Technologies, Jena

Structural Health Monitoring of Wind Turbines

Temperature Sensors for medical Devices

Multifunctional Coatings for Textile Fibers

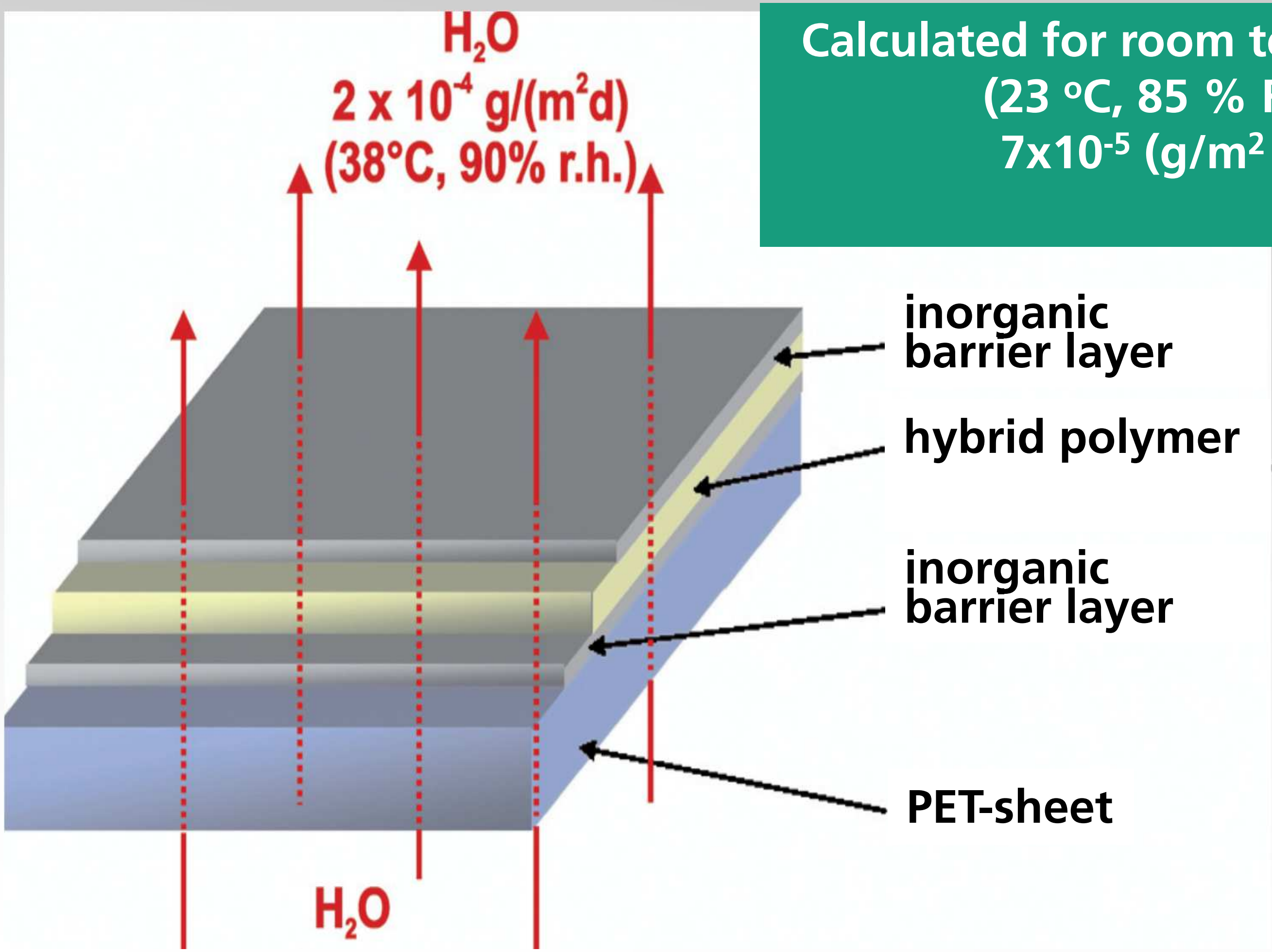
antimicrobial

flame retardand

hydrophobic

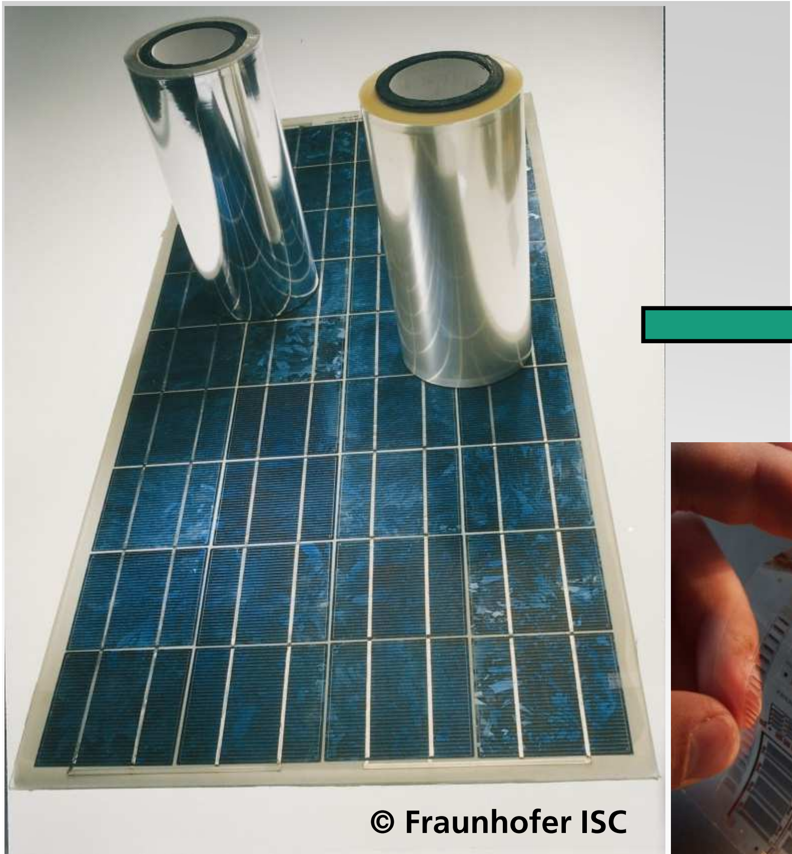
oleophobic

Recent Results from R2R Processing

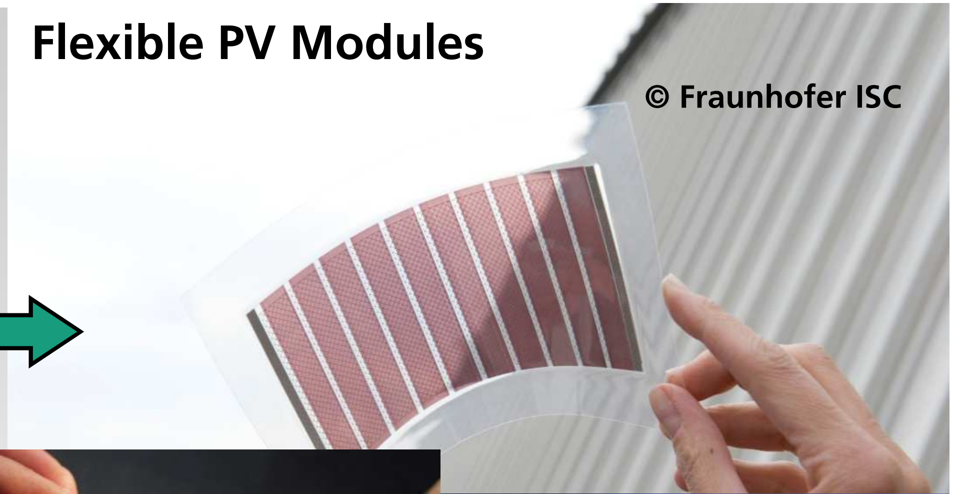


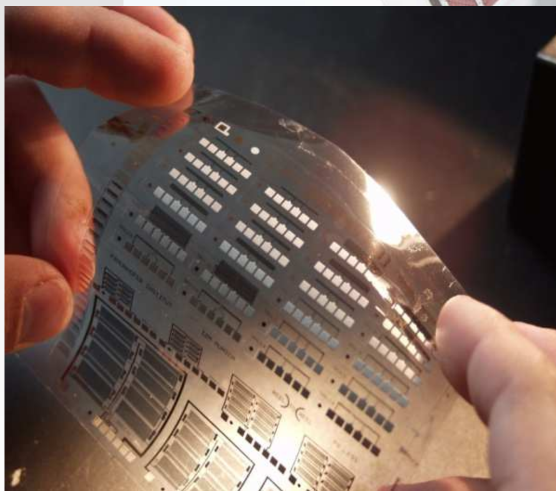
Calculated for room temperature
(23 °C, 85 % RH)
7×10^{-5} (g/m² d)

Barrier Sheets for Organic Photovoltaics and LEDs



Flexible PV Modules





Producer: Amcor Flexibles, Konstanz (DE)

Scavenger- and –Indicator Coatings for Food Packaging

- Development of hybrid coating systems (ORMOCERs) for plastic films
- Active, oxygen binding coating integrated in food packaging materials
- Indicator doped layers monitor oxygen uptake through discoloration
- Improvement of durability of foodstuff and control function for consumers
- In combination with passive barrier films suitable for technical areas requiring ultra high barrier functions

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Decorative Coatings for Crystal Glass

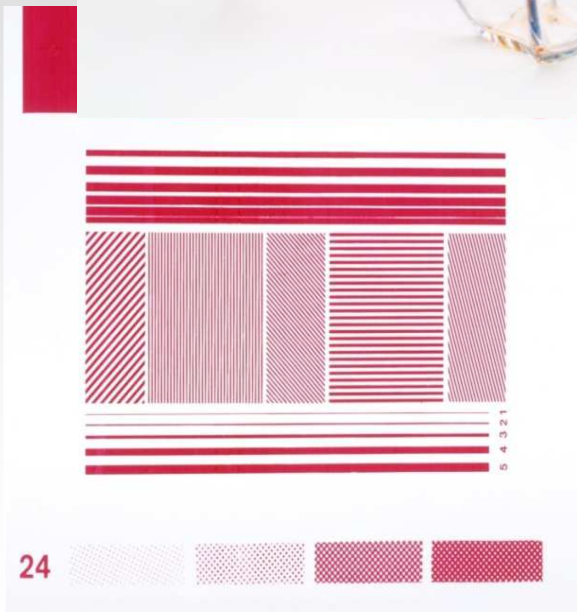
Simple application and outstanding properties

Spraying technique for complex shapes

Excellent adhesion and abrasion resistance

High colour intensity and variability

Glass-like appearance and touch

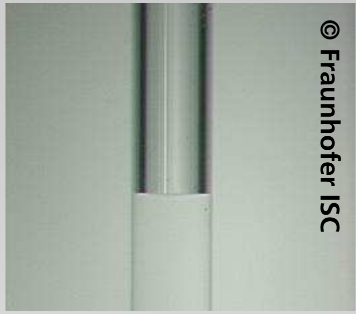


Low Surface Free Energy for Glass Containers

Quelle: www.zwieselkristallglas-shop.com

Hybrid coatings generate ultrahydro-phobic glass surfaces

Wettable surface



Non-wettable surface

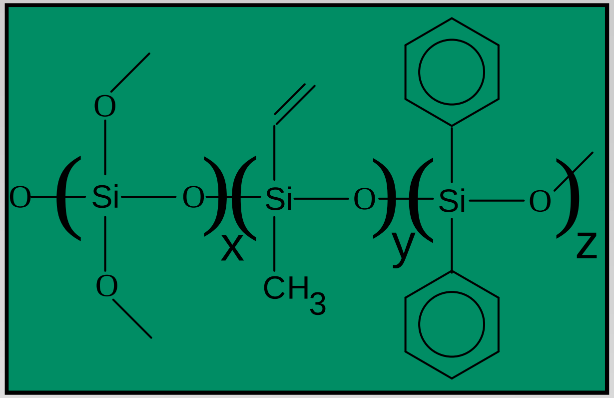
New thermometers without mercury through non-wettable glass capillary

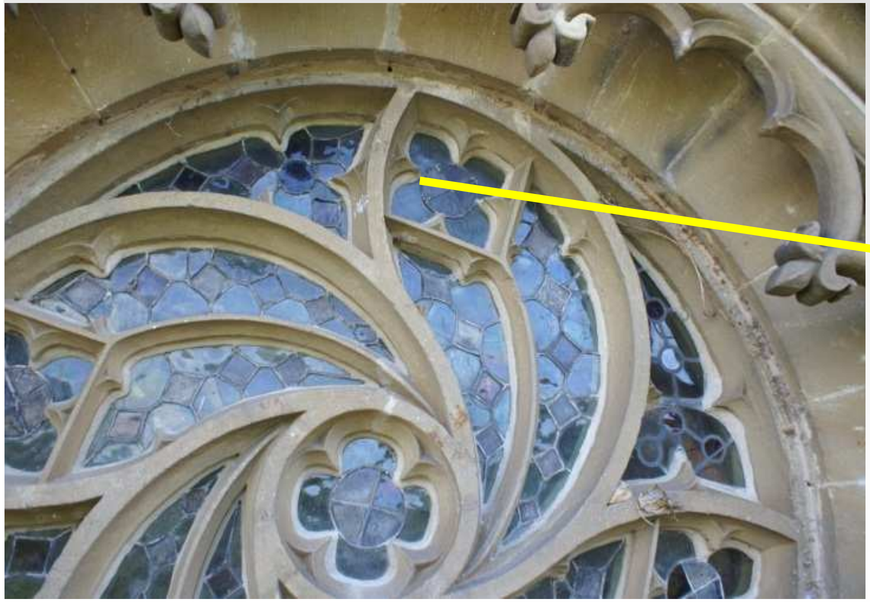
Protective Hybrid Coating for Historical Glasses

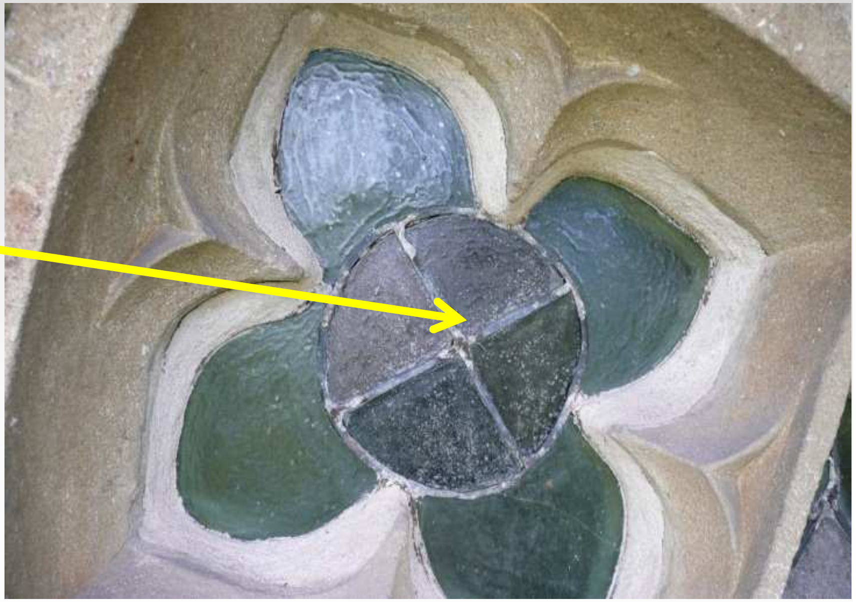
Herrgottskirche Creglingen (DE) – Outside view (2010)

Application of Protective Coating for Historical Glasses

Coated with hybrid material in 1988
Spectroscopic investigation in 2010







Raman Microscopy – Excitation in the Vis-/NIR-range

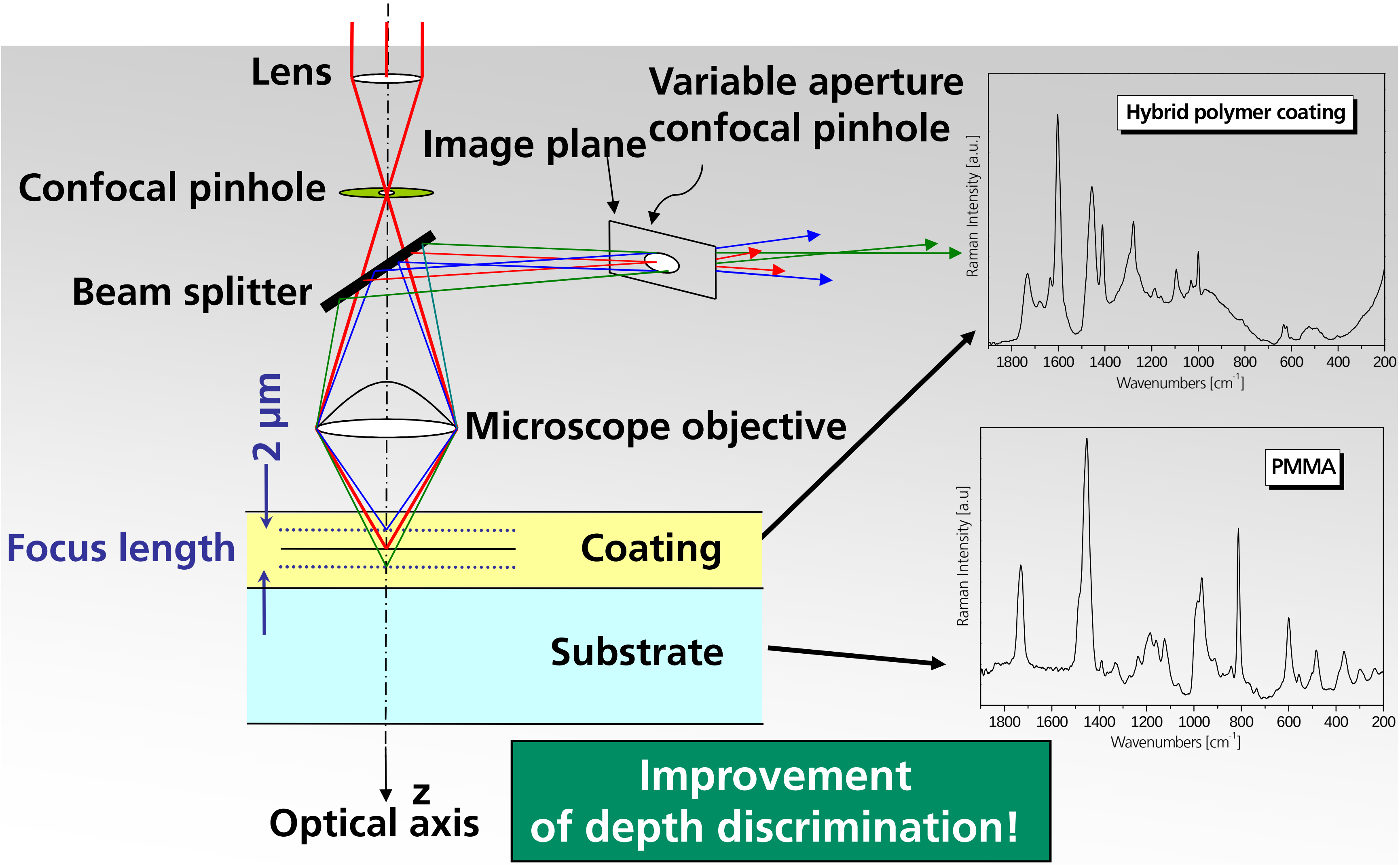
488 nm (Ar^+)

514 nm (Ar^+)

633 nm (He-Ne)

785 nm (Diode)

Principle of Confocal Micro-Raman-Spectroscopy



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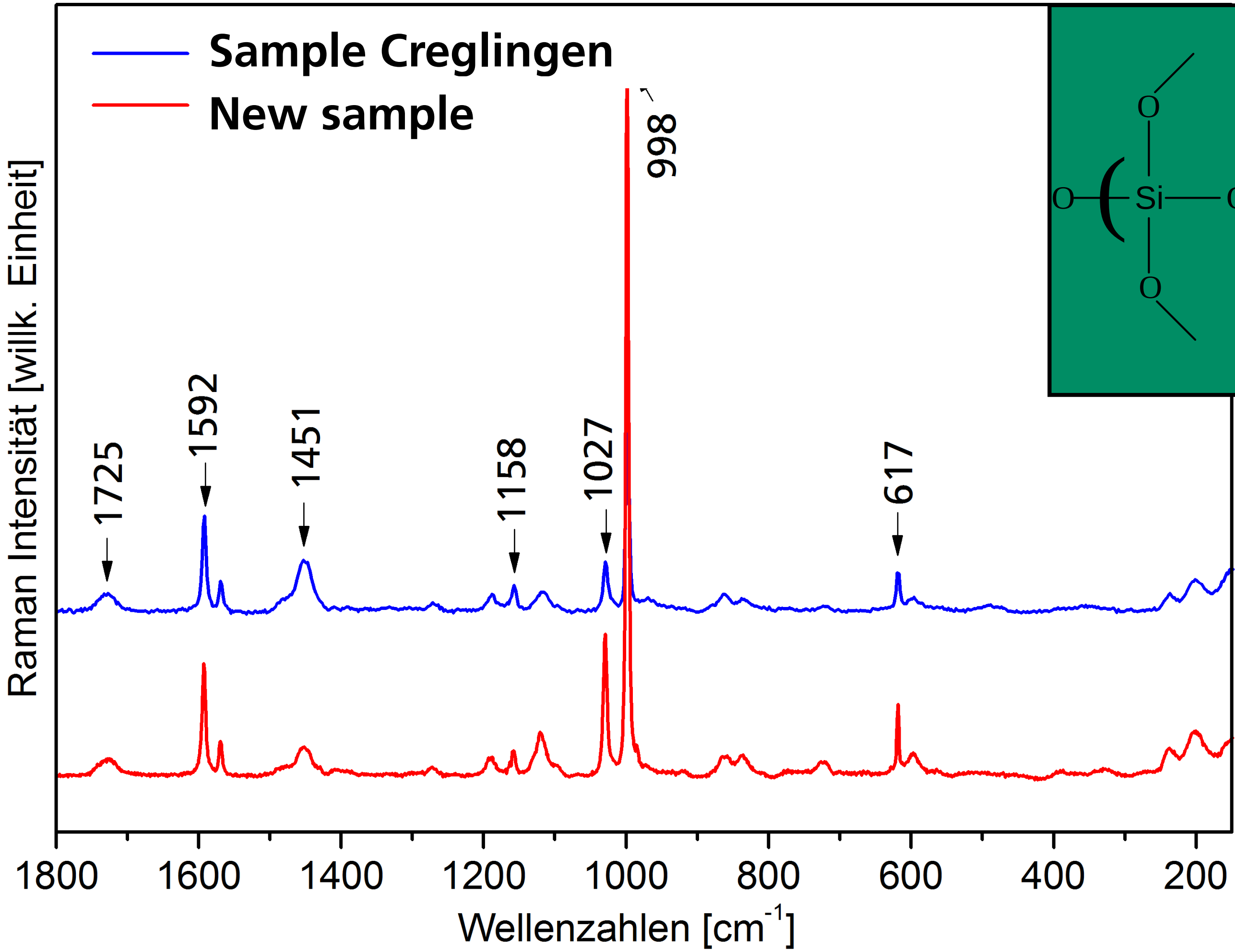
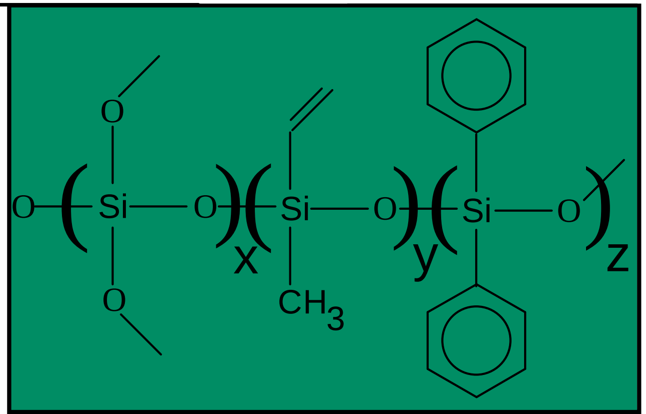
Micro-Raman-Spectrum of the ORMOCER®-Coating





After 22 years!

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Calculation of the Costs of a Hybrid Polymer Coating

Assumptions:

Dry film thickness	5 µm → ca. 40 % of the wet film thickness
Wet film thickness:	12,5 µm
Yield:	20 to 100 % (depending on the coating method)
Consumption per m^2:	12,5 to 62,5 ml
Coated area (1 Liter):	16 to 80 m^2

Typical Coating Formulation

Volume [l]	Cost [€]	Cost/Liter [€/l]
1	600	600
2	700	350
5	750	150
10	900	90
20	1300	65
50	2500	50
100	4000	40

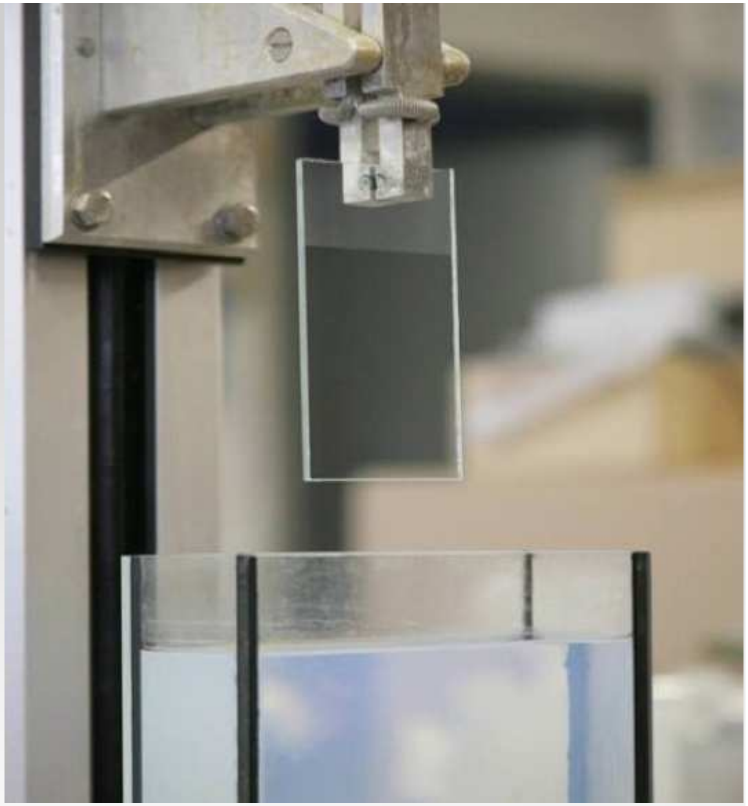
Typical Coating Techniques

- Worst case
  - Spraying of small parts (80 % overspray)
  - Low volume application (high cost/l)
  - ➢ 21,90 €/m²
- Best case
  - Dip coating procedure (ca. 100 % yield)
  - High volume application (low cost/l)
  - ➢ 0,50 €/m²

Typical Coating Techniques

- Case 3
  - Spraying of small parts (80 % overspray)
  - High volume application (low cost/l)
  - ➢ **<u>2,50 €/m²</u>**

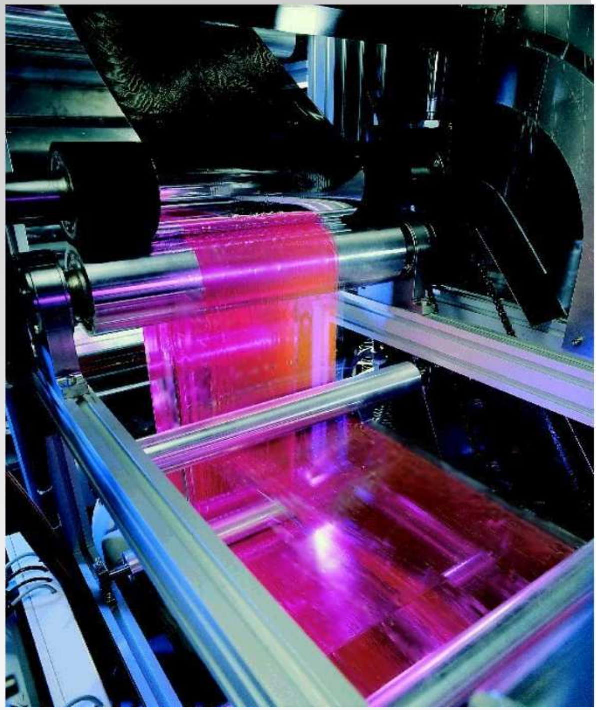
- Case 4
  - Dip coating (ca. 100 % yield)
  - Small volume application (high cost/l)
  - ➢ **<u>4,40 €/m²</u>**



R2R Production of Ultrabarrier Foils (UBF)

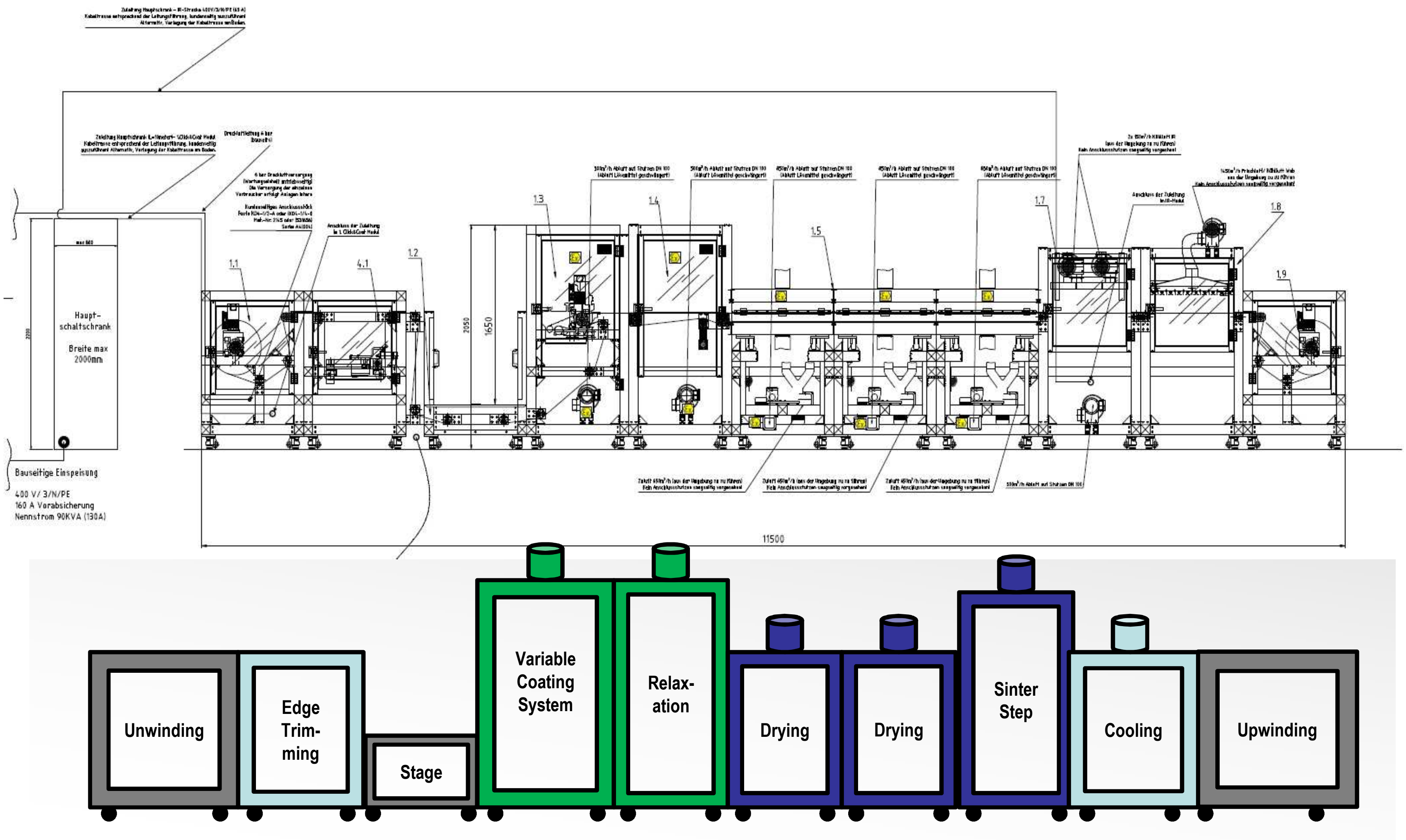
Application of very thin hybrid films (< 100 nm)

Fraunhofer IVV



Schematic view of closed R2R coating machine (dust-free application)

Schematic of R2R Coating Equipment



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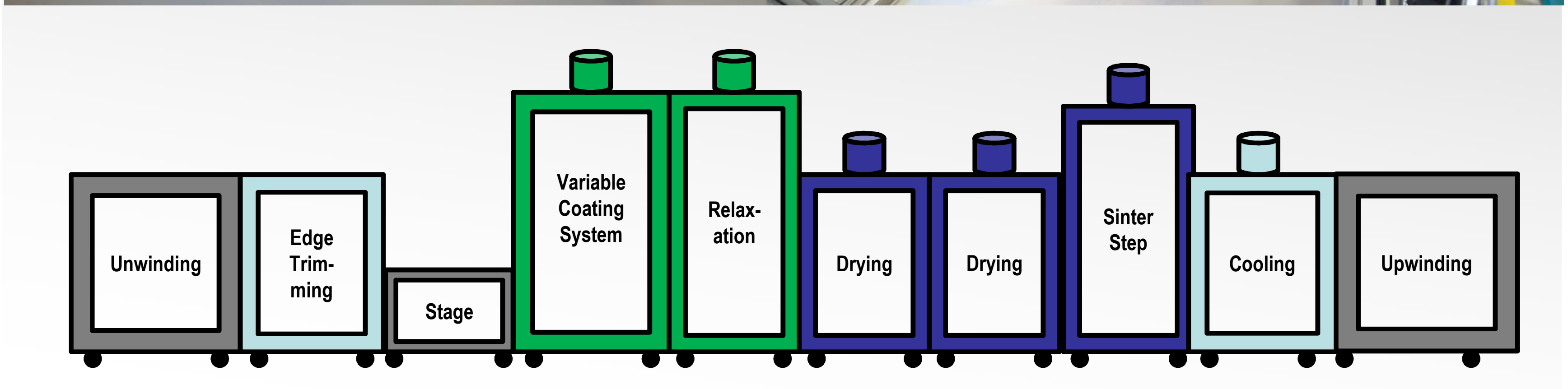
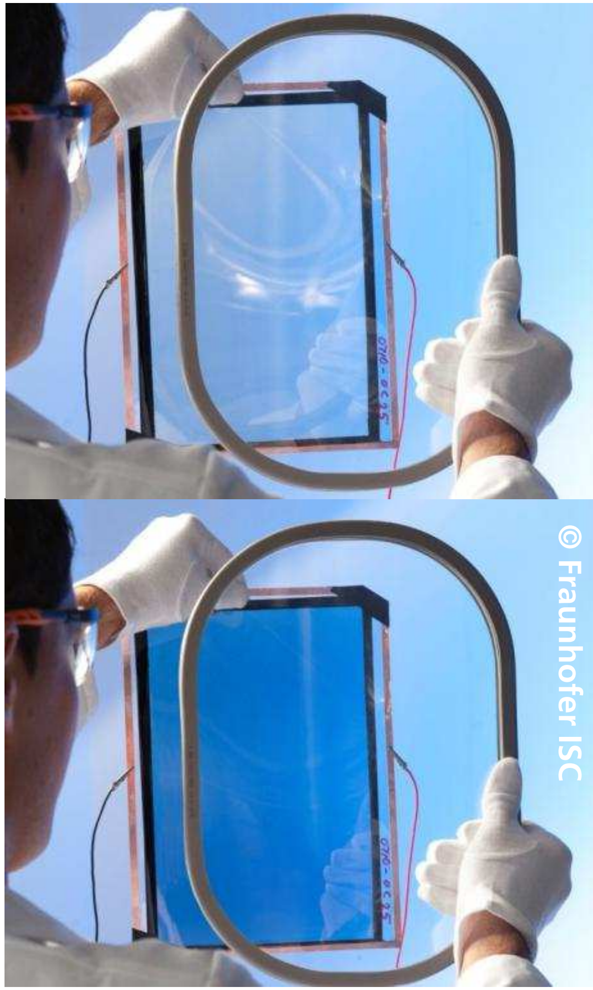
Realized Configuration of R2R Coating Machine



EU-Project INNOSHADE – Electrochromic plastic glazing based on PEDOT-derivatives

Benefits

- Large-scale, cost-effective, light impact-resistant ECD technology – compatible with plastic substrates
- Short reaction time even with more expensive components at low energy consumption
- Modular production process enables high performance in production and assembly lines, e.g. in roll-to-toll process
- High stability despite varying strain



Manufacture of Multilayer Systems via R2R processing

Electrochromic thin films

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Thank you for your attention!

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