Functional Glasses:
Properties and Applications for Energy & Information
January 7, 2013
Siracusa, Sicily, Italy

Alterations of glass surfaces and functional coatings for energy conversion systems

Joachim Deubener, Gundula Helsch

TU Clausthal

outline

systems — national / EU, energy conversion, glasses, coatings

alterations — production, storage, service

tests — performance, warranty, life cycle

research for sustainable technology is founded by basic law in Germany

*"Mindful also of its responsibility toward future generations, the state shall **protect the natural foundations of life** and animals by legislation and, in accordance with law and justice, by executive and judicial action, all within the framework of the constitutional order."*

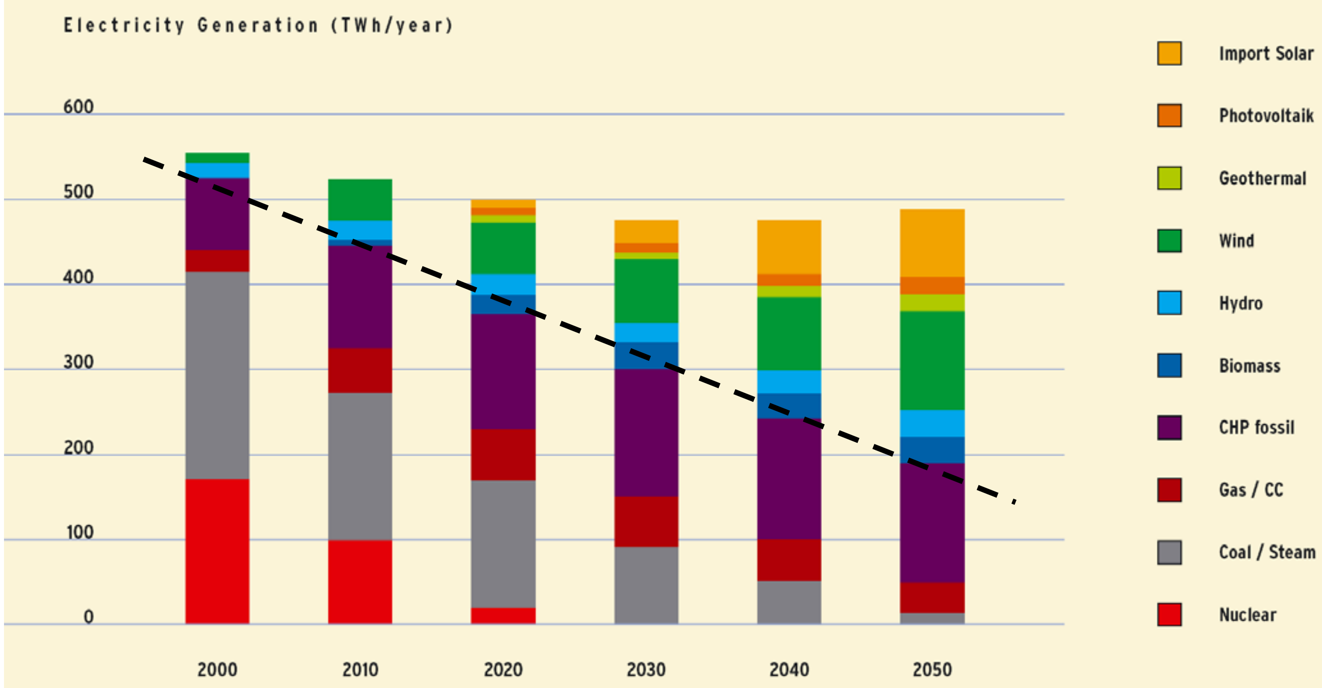
German Basic Law, Article 20a
since 2002

Germany
mission

Renewable Energy Sources Act (EEG) since 2000
by the German Federal Ministry for the Environment

EEG = Erneuerbare-Energien-Gesetz

Source: DLR



Electricity supply within a sustainable energy scenario for Germany. After 2030, renewable electricity will increasingly be employed for the generation of hydrogen for the transportation sector.

subsidies by feed-in tariffs (FIT):
every kWh that is generated from renewable energy facilities receives a fixed feed-in tariff (c/kWh) for 20 years.

hydro	7.7
wind	6.2-9.0
biomass	8.7-10.2
solar	50.6

degression 1-1.5 % / a

target

50 % renewable energy share in 2050

Renewable Energy Sources Act (EEG)

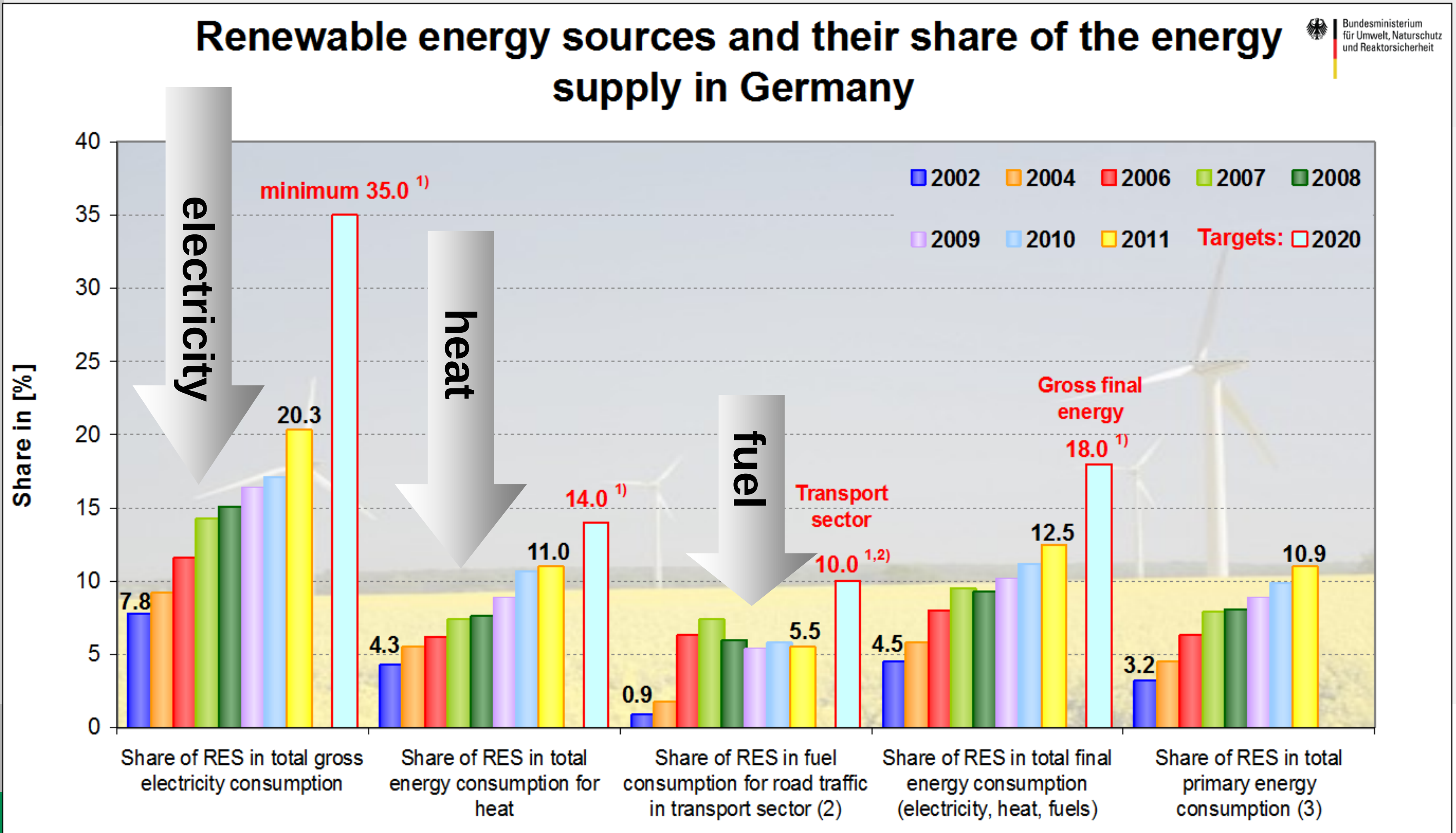
short facts

- 20.3 % of electricity,
  11.0 % of heat and
  5.5 % of fuel is generated from renewable energy (RE) sources in 2011, reducing Germany's energy imports.
- cut of 0.13 billion metric tons of CO_2 emissions only during 2010.
- renewable energy industry employs (2011) 350,000 people in Germany.
- Germany hosts several world market leaders in RE technology and Germany is today among the world's three major renewable energy economies.
- EEG serves as an archetype of similar legislation in other countries.

sources:
Federal Ministry BMU
German Energy Agency DENA
Renewable Energy Network 21, 2011

renewable energy share

evolution



1) Sources: Targets of the German Government, Renewable Energy Sources Act (EEG); Renewable Energy Sources Heat Act (EEWärmeG), EU-Directive 2009/28/EC;
2) Total consumption of engine fuels, excluding fuel in air traffic; 3) Calculated using efficiency method; source: Working Group on Energy Balances e.V. (AGEB); RES: Renewable Energy Sources;
Source: BMU-KI III 1 according to Working Group on Renewable Energy-Statistics (AGEE-Stat); image: BMU / Brigitte Hiss; as at: July 2012; all figures provisional

renewable energy share 2010-2011

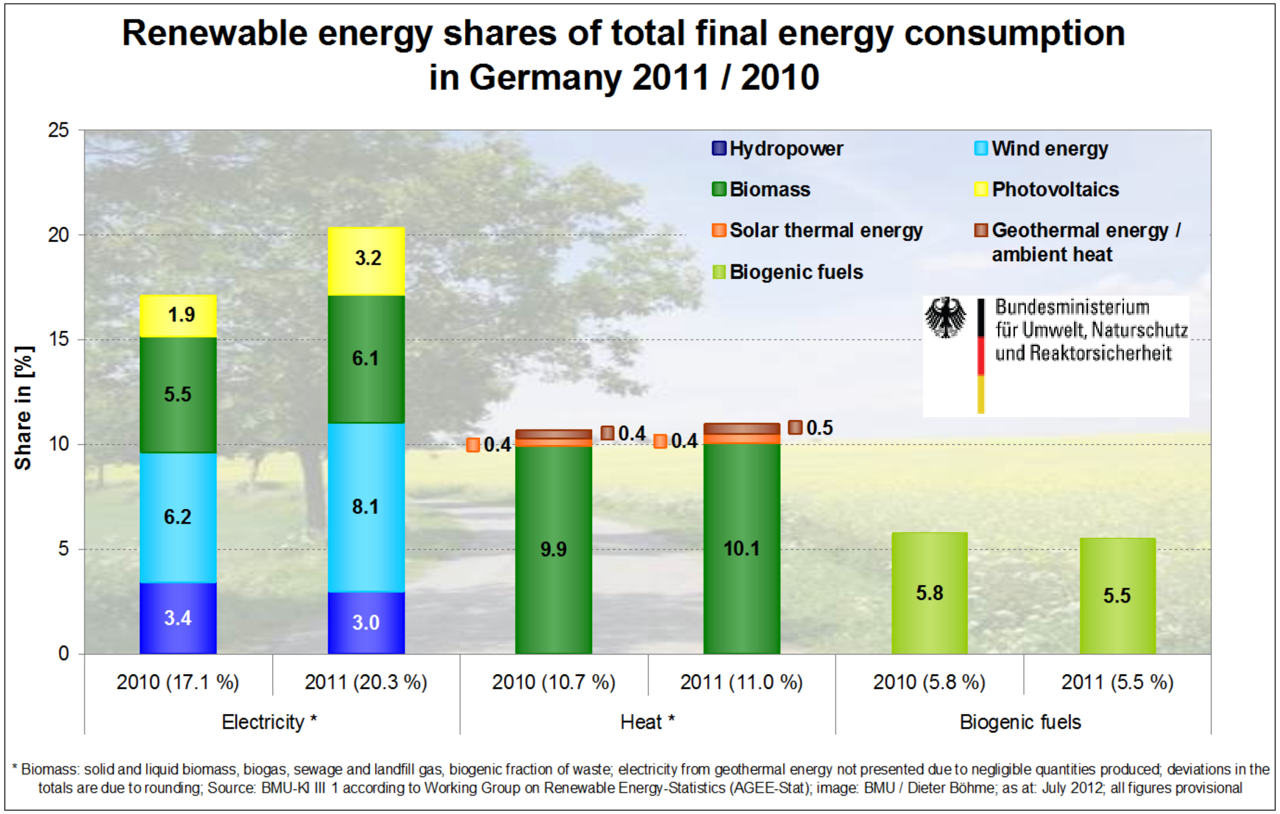
energy mix

electricity:

wind energy
> biomass
> PV
> hydro

heat:

biomass
> geothermal
> solarthermal



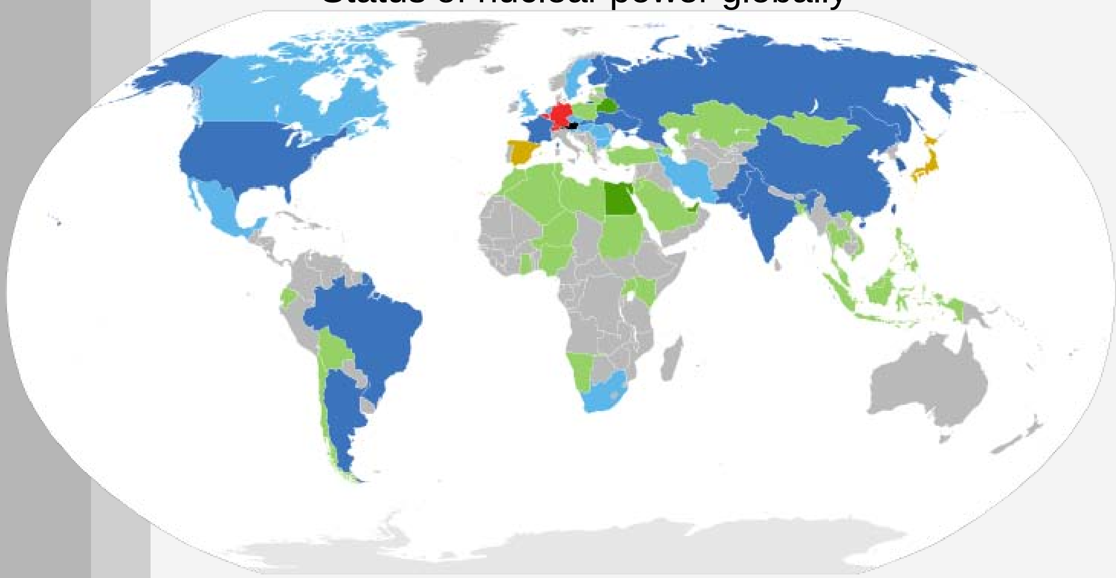
transformation of the energy system “Energiewende”

recent issues

nuclear power phase-out May 2011

after Fukushima nuclear disaster, Germany has permanently shut down 8 of its reactors and pledged to close: 1 in 2015, 1 in 2017, 1 in 2019, 3 in 2021 and the rest (3) by 2022.

Status of nuclear power globally



nuclear power proponents

- Operating reactors, building new reactor
- Operating reactors, planning new build
- No reactors, building new reactors
- No reactors, new in planning

undetermined

- Operating reactors, stable
- No reactors

nuclear power oponents

- Operating reactors, decided on phase-out
- Civil nuclear power is illegal

sources:
Ichabod Paleogene, Krzysztof Kori
Creative Commons

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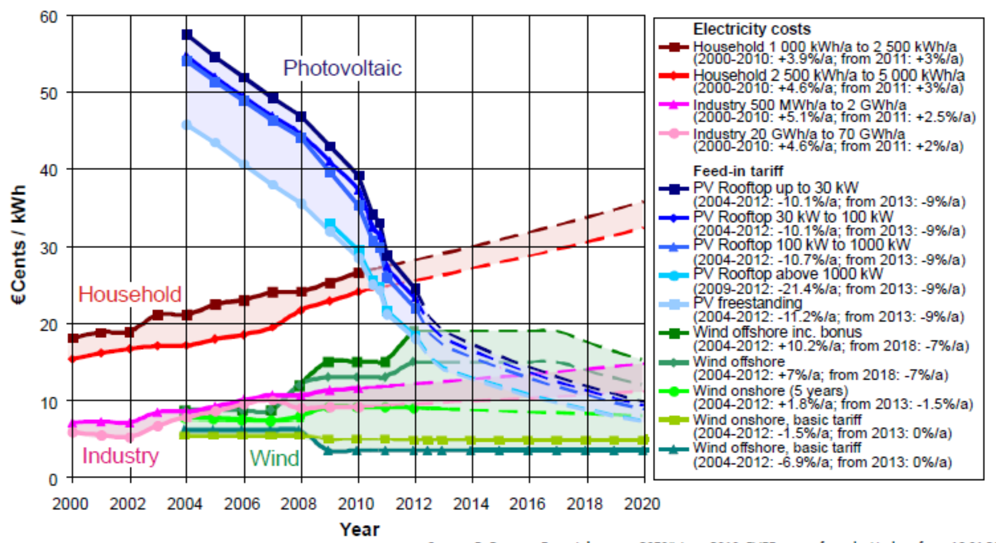
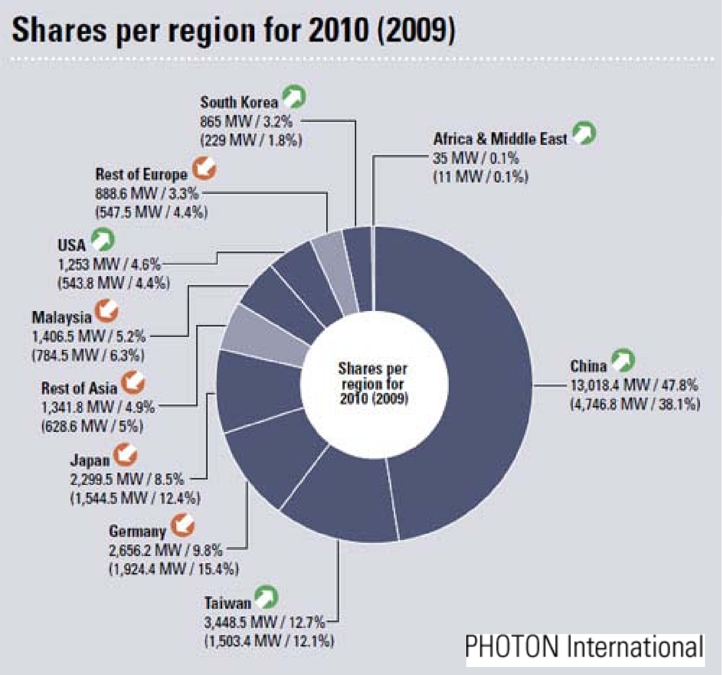
PV-amendment
April 2012

after PV prize crash (towards grid parity), Germany reduced FIT for new installed facilities by ca. 40-45 %
from 28.7 (2011) to 17.0 (2013) c/kWh (< 10kW)
from 21.6 (2011) to 11.8 (2013) c/kWh (> 1 MW)

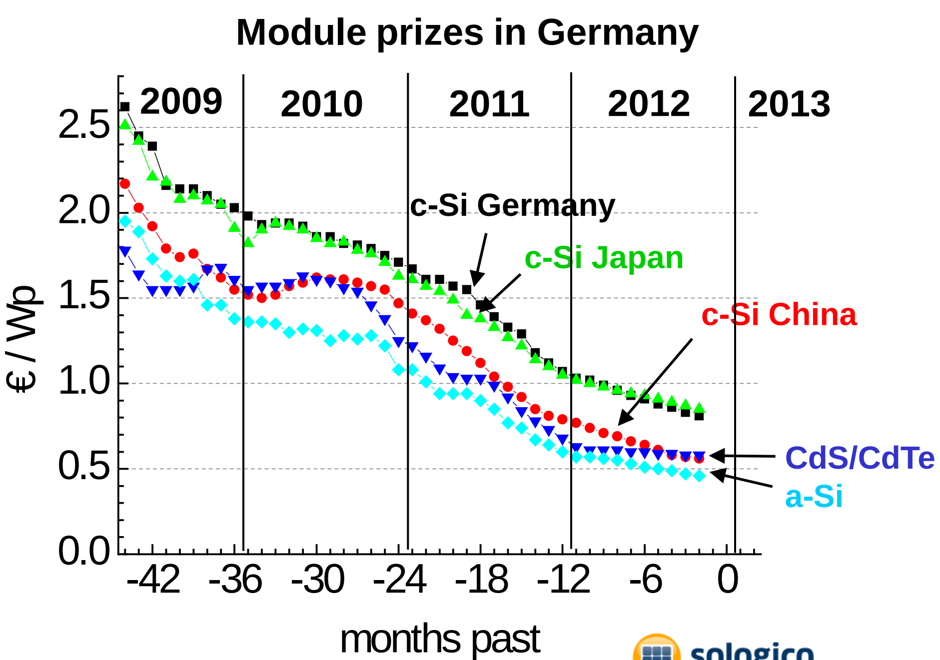


sources:
B. Burger „Energiekonzept 2050“ June 2010, FVEE,
Updated by
Fraunhofer ISE Photovoltaik Report, Dec. 12th, 2012

PV industry crisis
2011-2012



- worldwide overproduction.
- Germany had a production capacity of 3 GW/a. China alone has a production capacity of 30 GW/a
- dramatic fall in production costs.
- solar panels are becoming a commodity, and their production migrates to low cost countries, emerging countries for the most part.
- China offered huge credit lines with very low interest rates.
- market shakeout.
- most German producers went out of market (40,000 – 100,000 employees).



sources:
E. Weber (ISE), ParisTech Review, April 13th, 2012

sologico YOUR PV MARKETPLACE

transformation of the energy system “Energiewende”

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third act revision (EEG)
August 2012

after Arab spring, Germany aims to speed up the expansion of offshore wind farms and north-bond fast grid system.

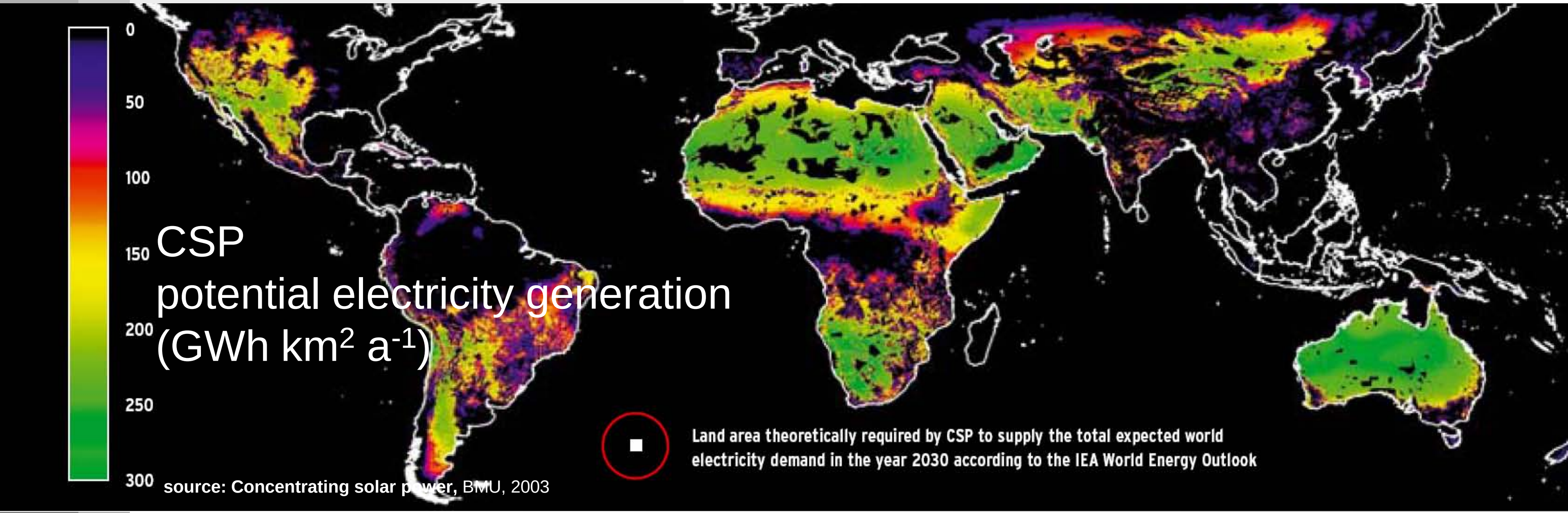
Gobal RE sources

for meeting the 10TW renewable energy challenge in 2050

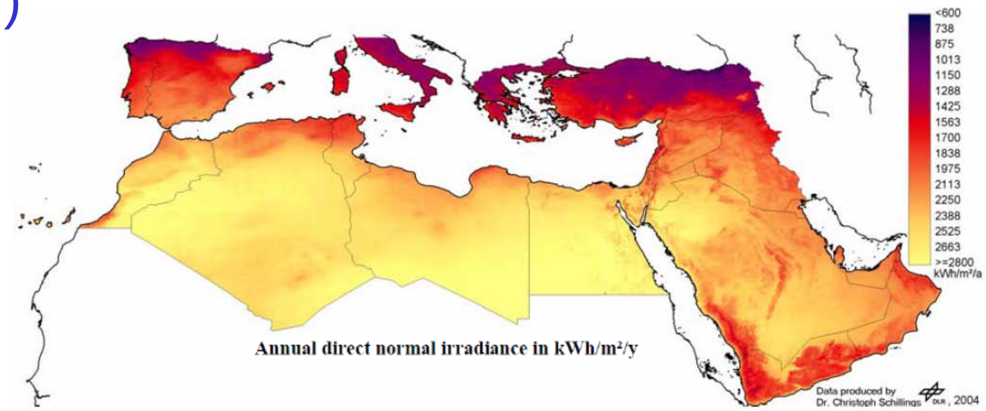
Renewable Energy Sources

- hydroelectric resource 0.5 TW
- from all tides & ocean currents 2 TW
- geothermal integrated over all the land area 12 TW
- globally extractable wind power 2-4 TW
- **solar energy striking the earth 120,000 TW !!!**

total solar irradiance
1.366 kW/m^2



concentrated solar power (CSP)
in the EU-MENA
potential 1700 TW

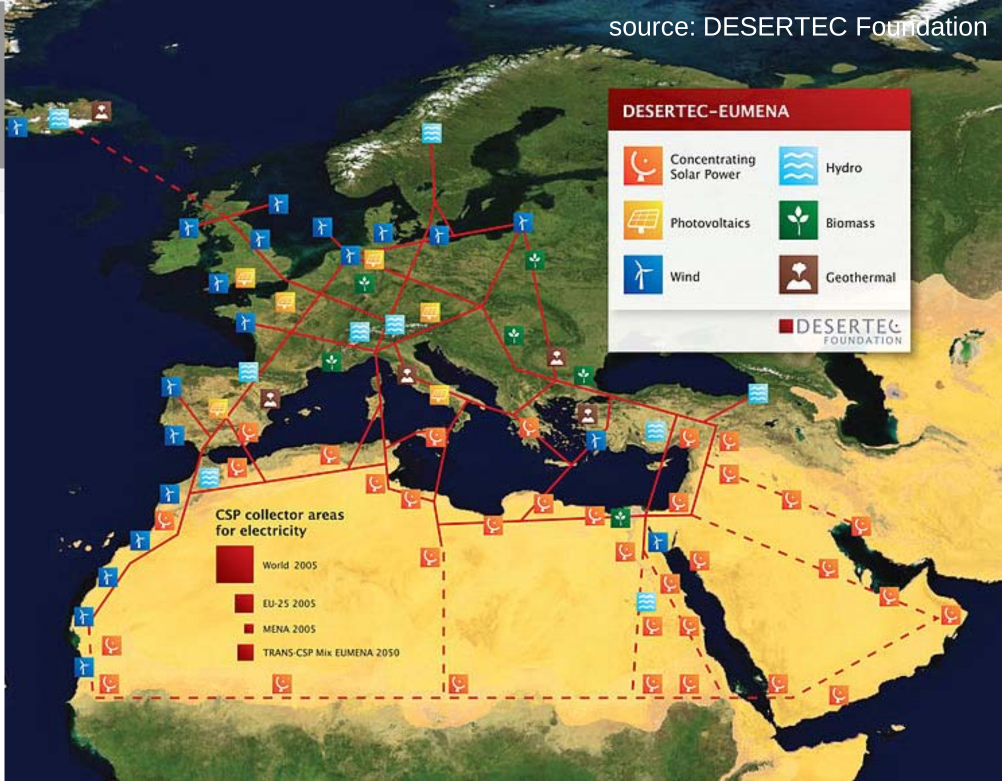


MENA = Middle East North Africa

DESERTEC Concept

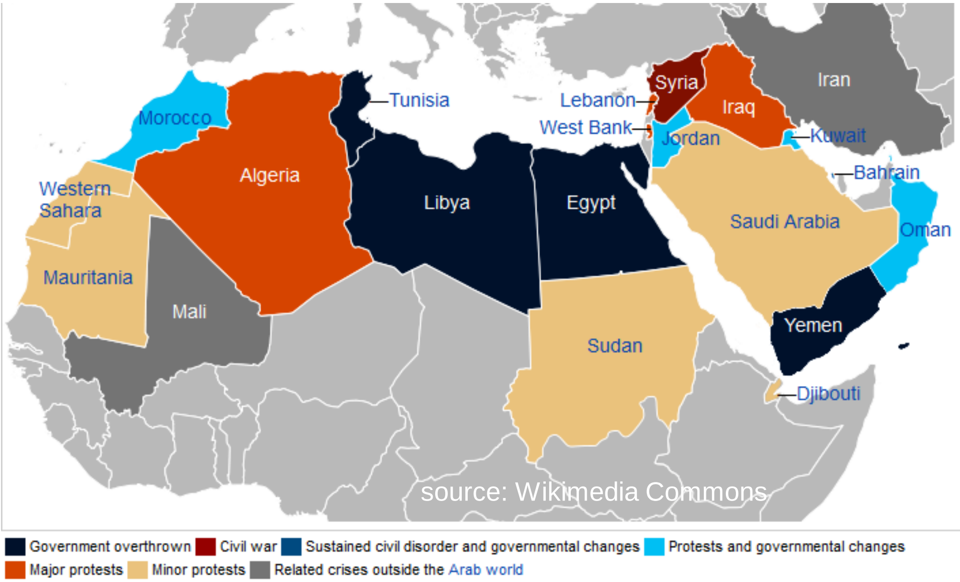
CSP in EU-MENA

- founded in 2009
- harvesting sustainable power (CSP) from MENA desert regions.
- Using energy in EU via low-loss high-voltage direct current transmission (10–15% transmission losses between the desert regions and Europe).



Obstacles

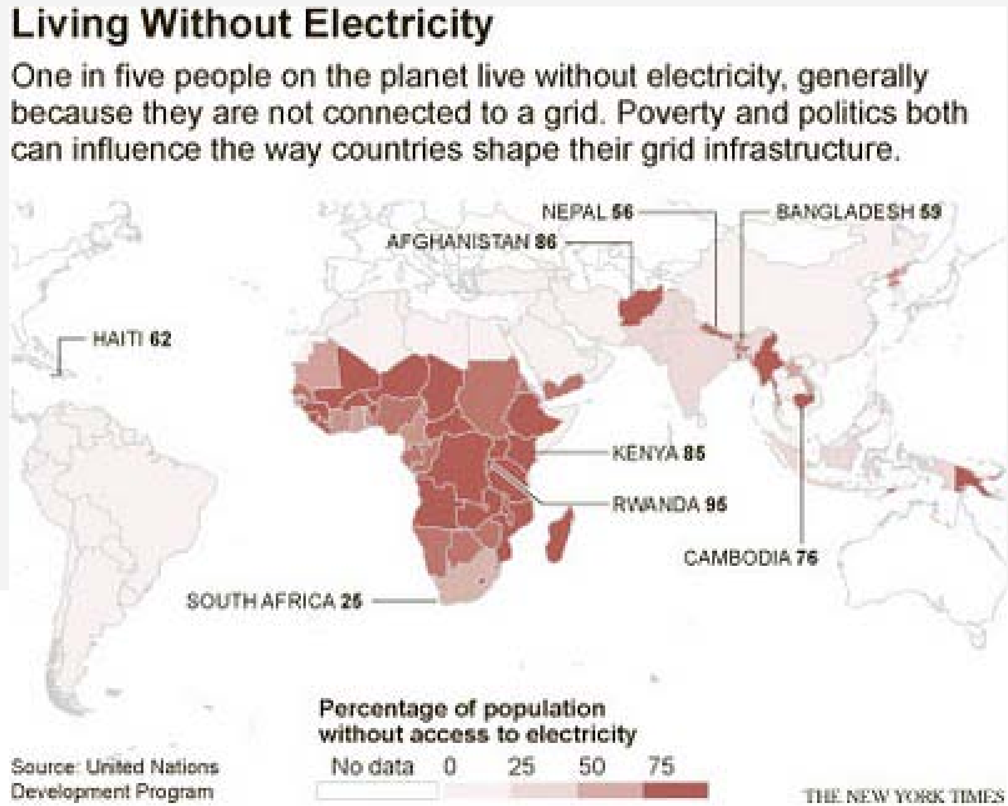
- Central plants and transmission lines target for terror attacks.
- lack of long-term policital stability in MENA region (Arab Spring since 2010).



off-grid living

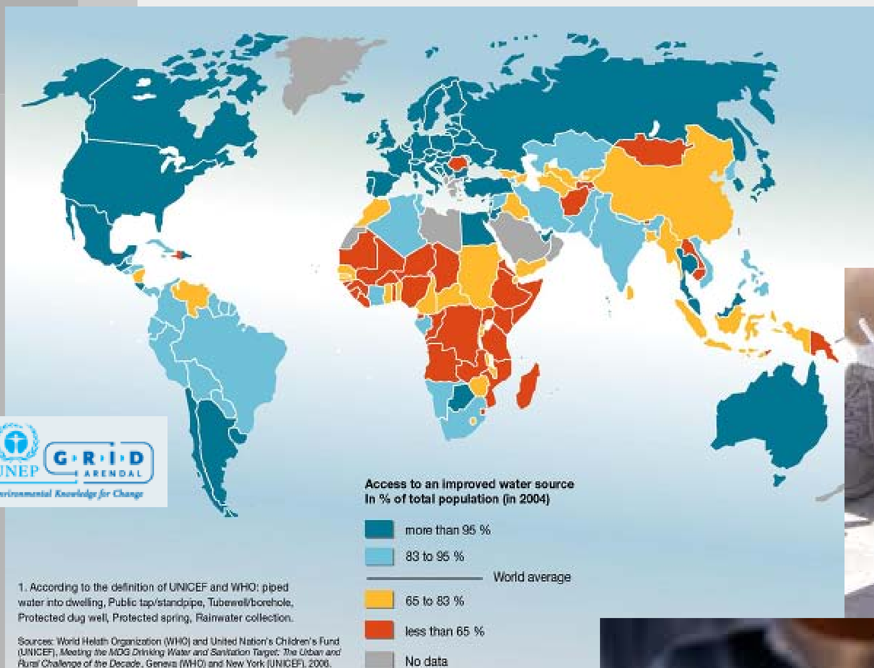
pin-and-run modules

The United Nations:
2 billion people across the globe live without electricity.
Off-grid electricity using cheap solar panels and high-efficiency LED lights is the most realistic option for many areas

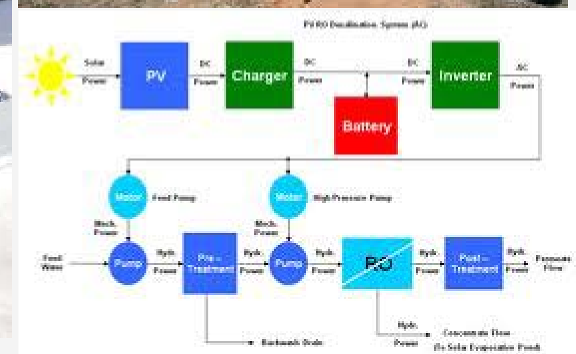


provide access to clean water
off-grid solar applications

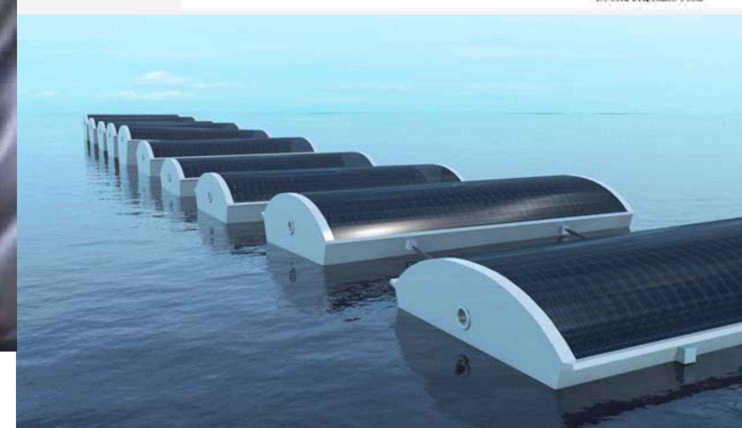
The United Nations:
1.1 billion people live without access to clean water.
That's about one in six people in the world.



Desalination



Solar Stills



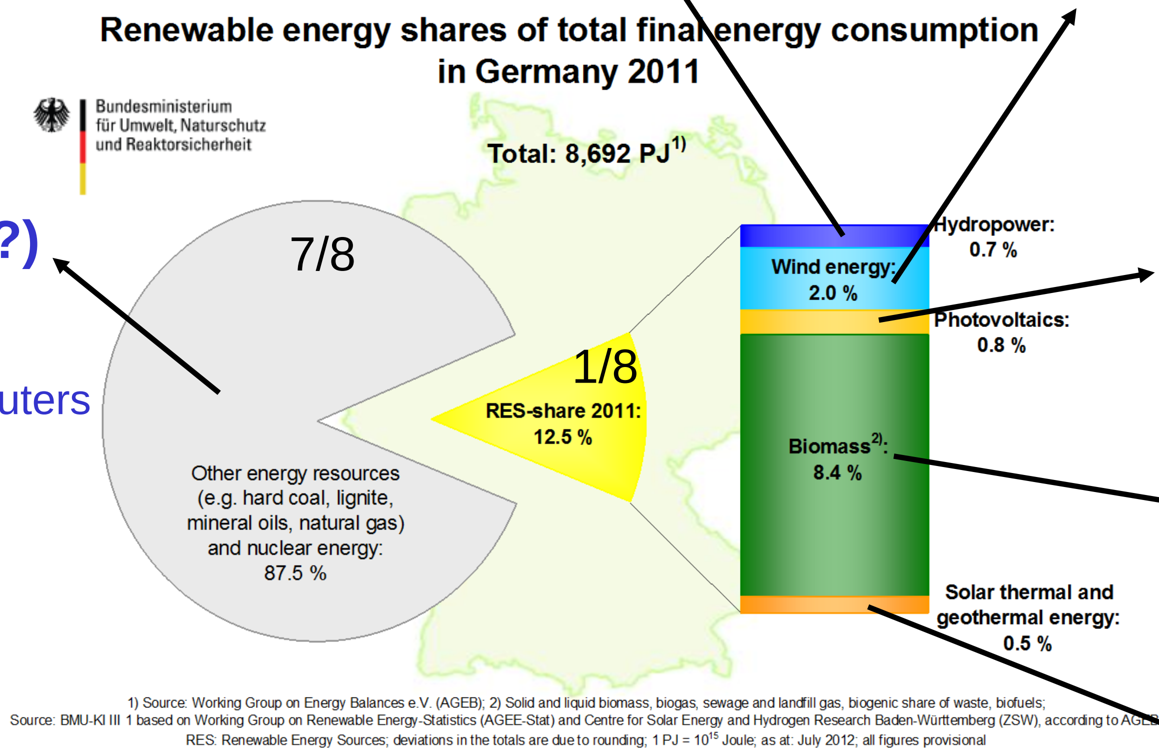
Glasses in energy applications

hydropower (?)

wind energy
glass fibre composites

PV
cover glasses
substrates
superstrates

fossil Power (?)
heat exchangers
(enamels)
seals & flow distributers
(glass-ceramics)



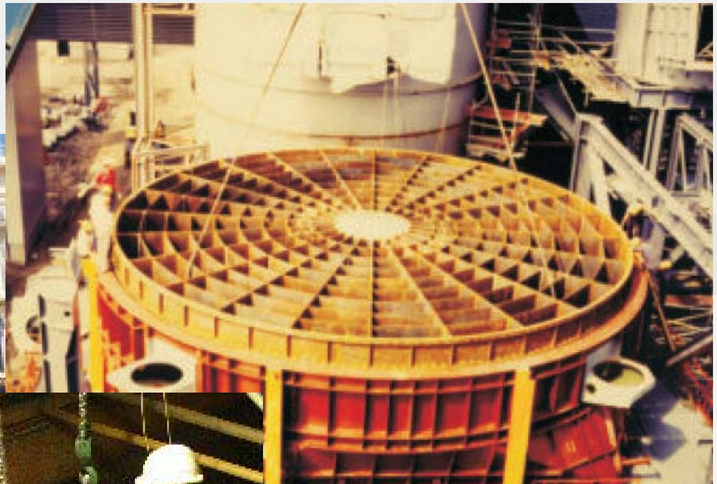
biomass (?)
tanks
(enamels)

solar thermal
cover glasses, tubes,
concentrators,
mirror substrates

lack of glass applications in several key sectors !

coal power plant

rotary air-gas and gas-gas heat exchangers



air-gas exchangers
heating up air for combustion

gas-gas exchangers
heating up flue gas after $DeSO_x$ and before $DeNO_x$

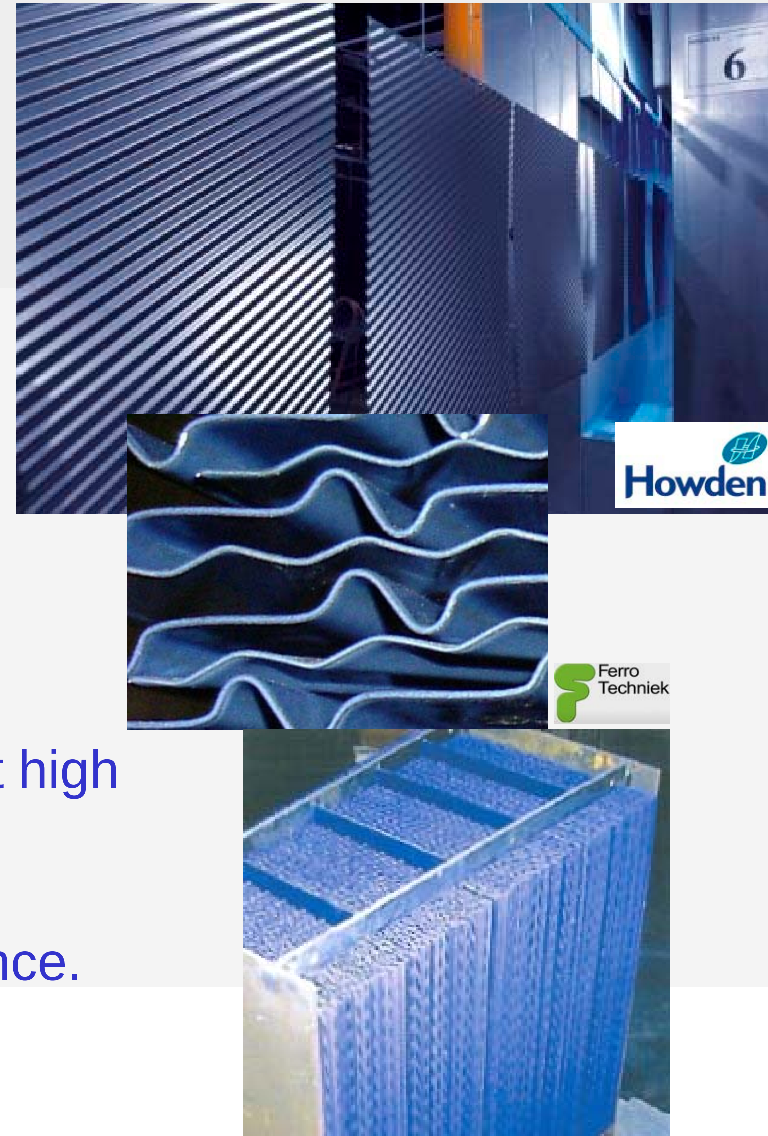
thick film coating: enamel
exchanger area ≈ 5-20 soccer fields

Glassy thick films for fossil power applications

enamelled plates

Elements for gas-gas heaters have enamel coatings of:

- no open porosity,
- high acid resistance,
- edge coverage,
- small thickness tolerance to permit high element packing pressure, and
- complex profiles to induce turbulence.



Glassy thick films for biomass/-gas applications

segmented silo

Segmented panels for silos
up to 7000 m^3

to treat:
biogas digesters
sludge

have enamel coatings of:

- no open porosity,
- high acid resistance (inside)
- high resistance to atmospheric and UV corrosion (outside)
- easy cleanability

Glasses for solar bio-fuel generation

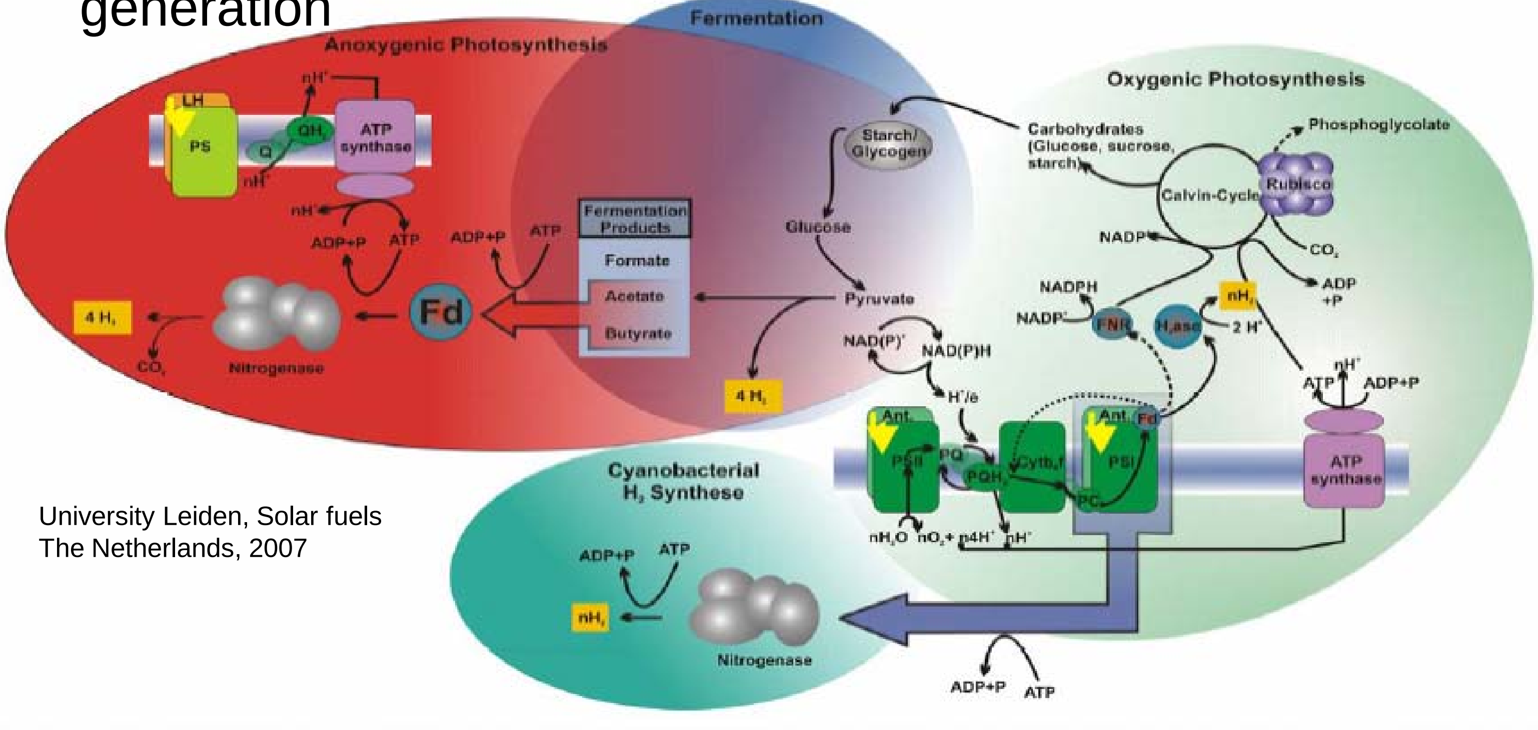
principles

applications

transparent glass reactors
vessels and pipes

University Leiden, Solar fuels
The Netherlands, 2007

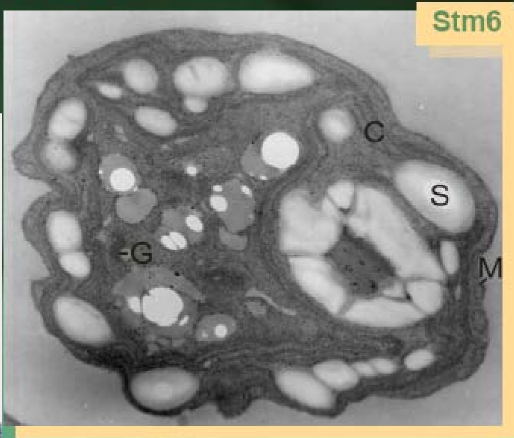
biochemistry of solar powered H_2 generation



University Leiden, Solar fuels
The Netherlands, 2007

Chlamydomonas reinhardtii (the green yeast)

- 1.6-2% PCE into H_2
- 5% medium term goal
- Fuel cell purity (>98%)
- 14 days
- Expected costs € 10/m²
- Prototyping stage 200-500 l



Provided by Uwe Kahmann

Klötze (Wolfsburg)

applications

500 km pipeline
approx. 2000 m^3
130 t algae p.a.

http://www.ssnmr.leidenuniv.nl/content_docs/cleansolarfuels.pdf

PV driving factors

cost reduction solar cell

glass costs 20 - 40%

Production issues:

- **raw materials**
- **tank operation**
- **forming**
- **cooling**
- **storage**

Glass performance:

- **solar transmittance**
- **coatability**
- **robustness**
- **weatherablity**

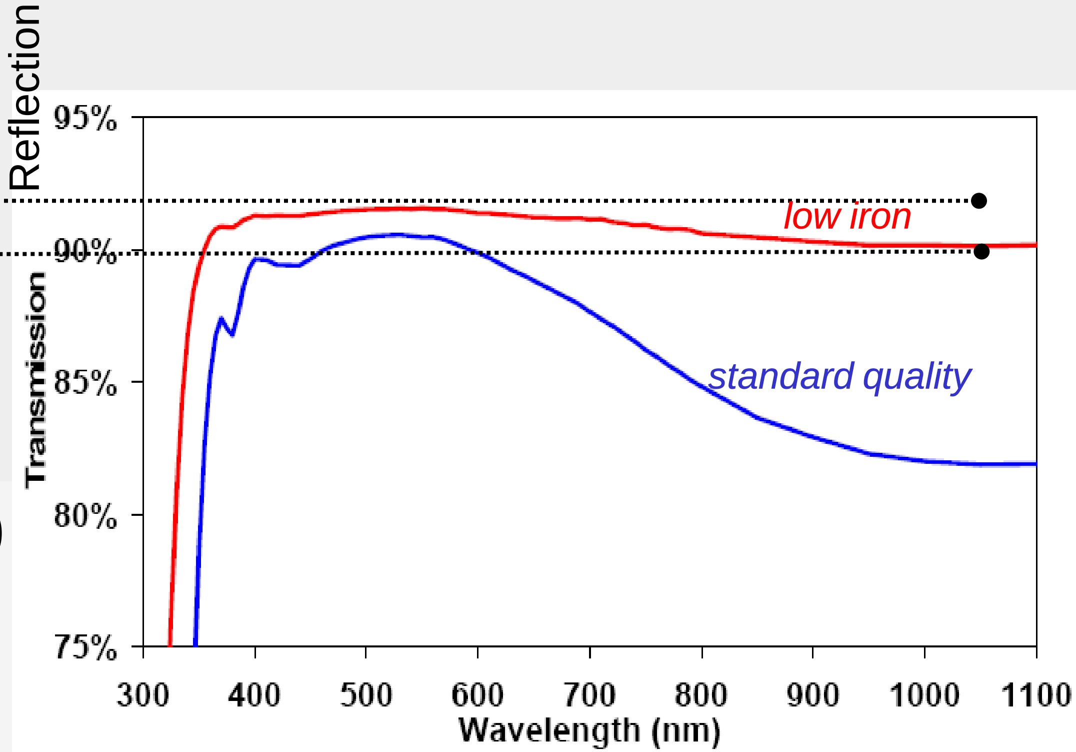
Transmittance = 100 % – (Reflectance + Absorbance)

$$R = \left(\frac{1-n}{1+n}\right)^2 \qquad \alpha = \varepsilon \times c \times d$$

solar glass = AR-coated + low iron + thin glass

Front glass

92 %
Absorption
90 %



Status:

d ≈ 3 mm
floated, rolled (patterned)
soda-lime-silica glass
toughened (thermal)
Fe < 100 ppmw
AR-coated

R&D:

improve failure resistance
→ thinner glass

improve flat glass processing
→ integration of coating (TCO, AR , ion strengthening and alkali-barrier coatings) into production (in/on–line)

solar cover gl

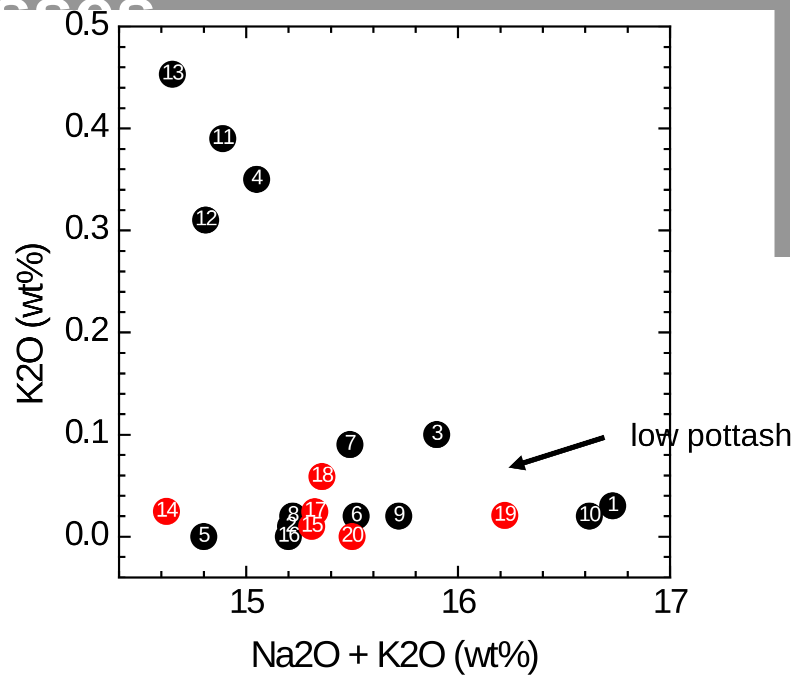
soda-lime-silica
(PV, domestic water

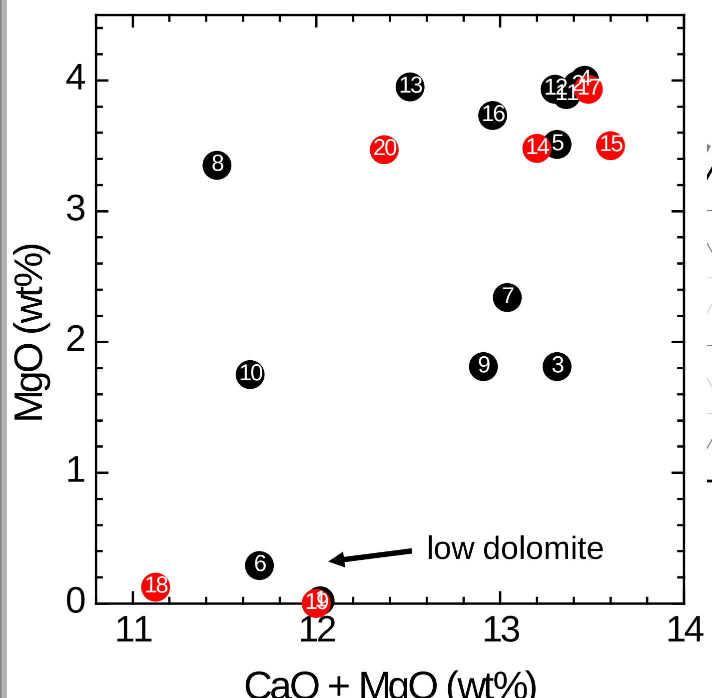
composition by LA-ICP-MS

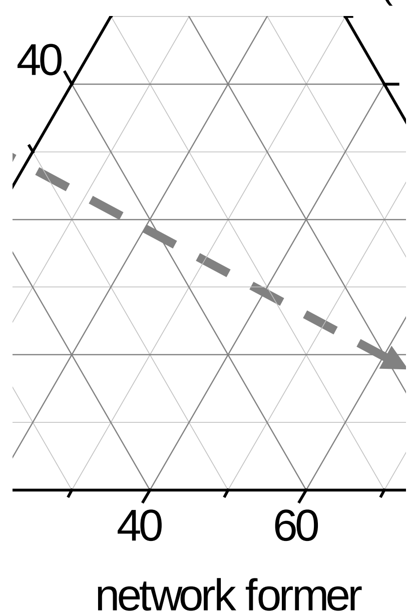
- ● **14 floated**
- ● **6 rolled** (slightly r

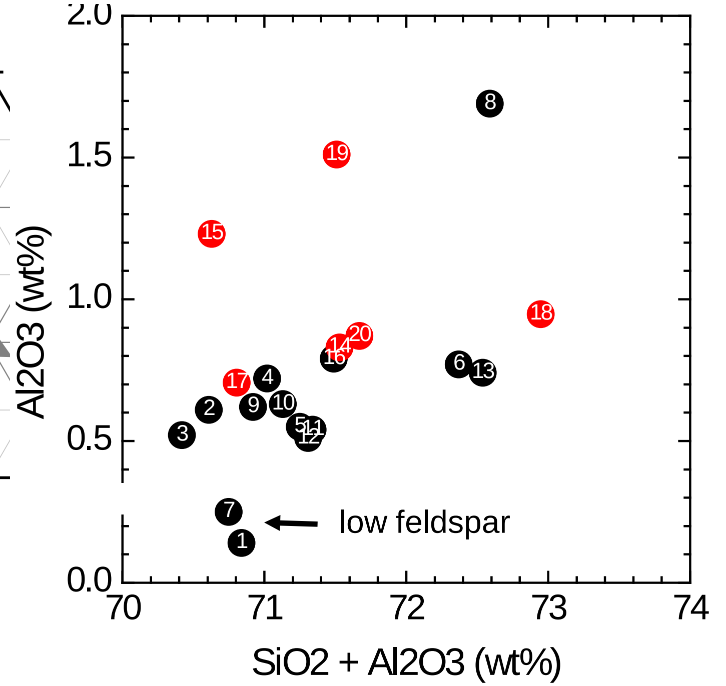
soda-lime-silic glasses

72 - 15.5 – 12.!





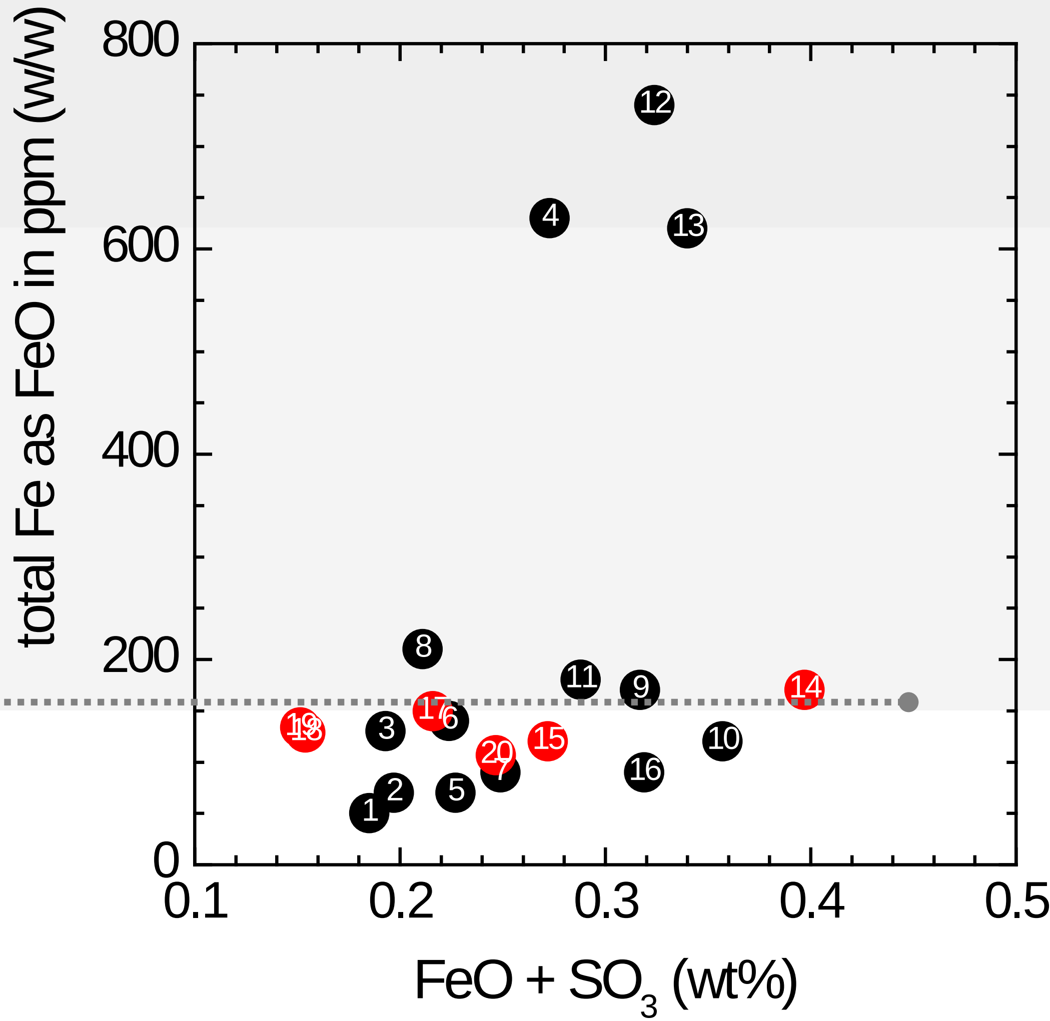




minor components and traces (iron conc.)

total iron by
LA-ICP-MS

solar glass limit
Fe = 100 ppm (w/w)



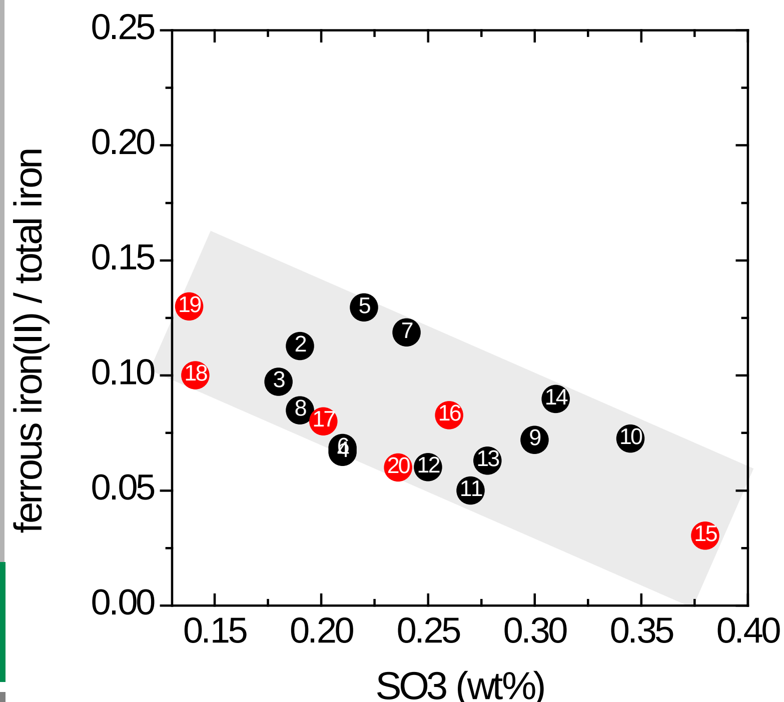
iron speciation and redox

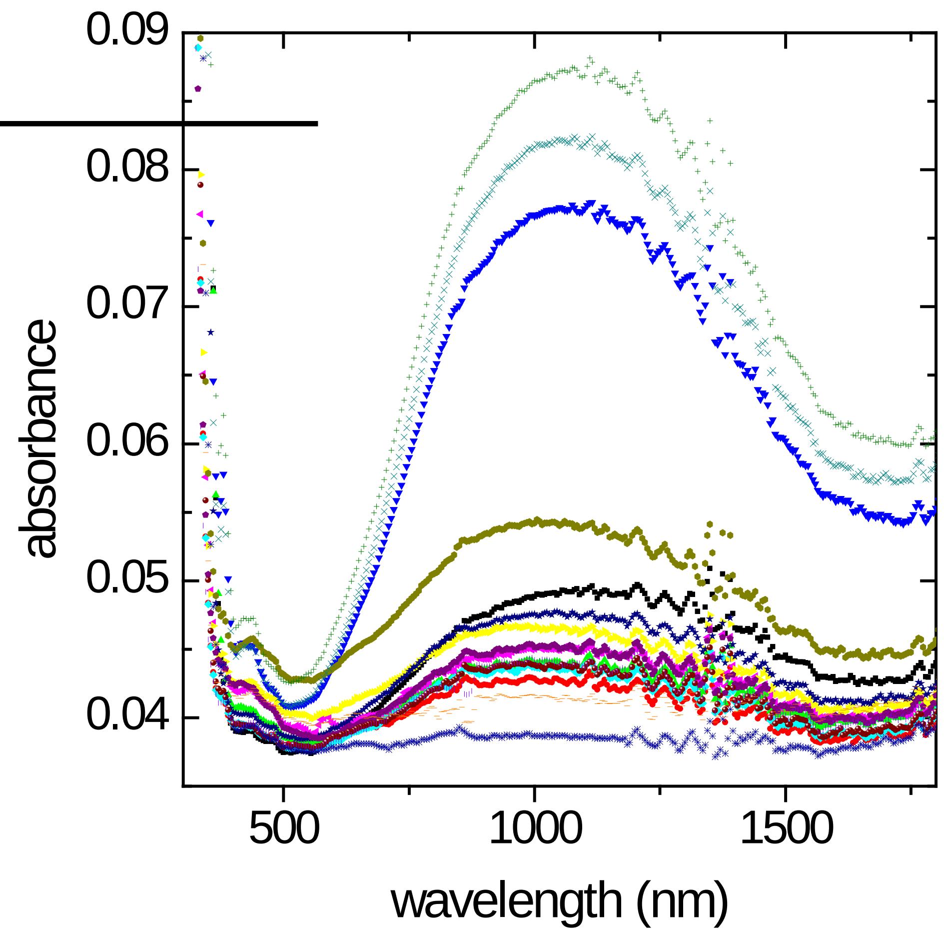
ferrous iron(II) by **NIR-Photospectrometry**

using ε = 53.8 l mol^{-1} cm^{-1}

Ades (1990), Traverse (1992)

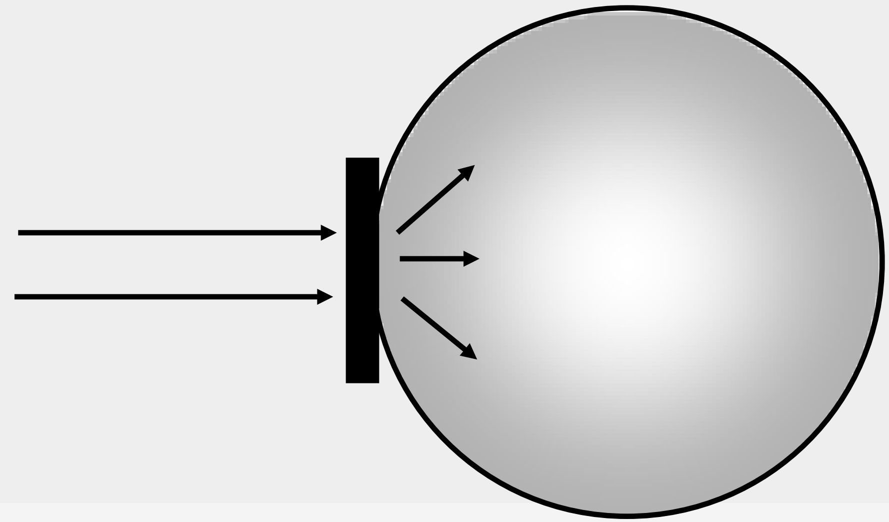
LA-ICP-MS → $\frac{[Fe^{2+}]}{[Fe_{total}]}$ ← NIR





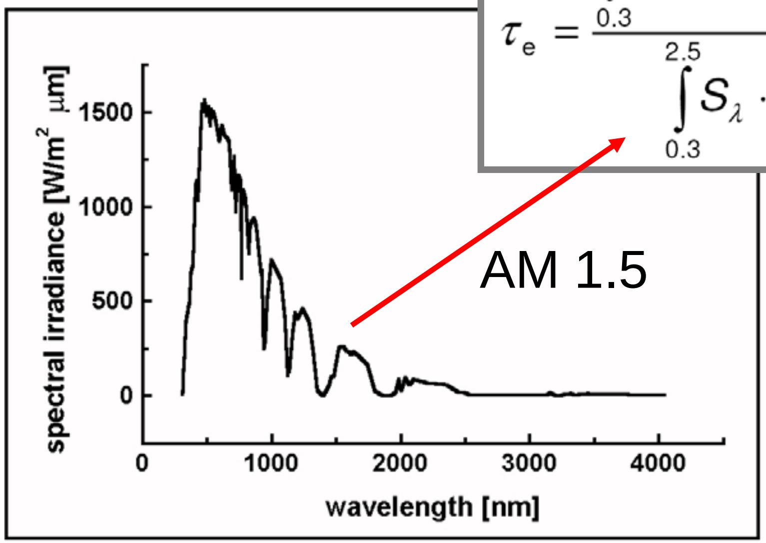
solar transmittance

EN 410



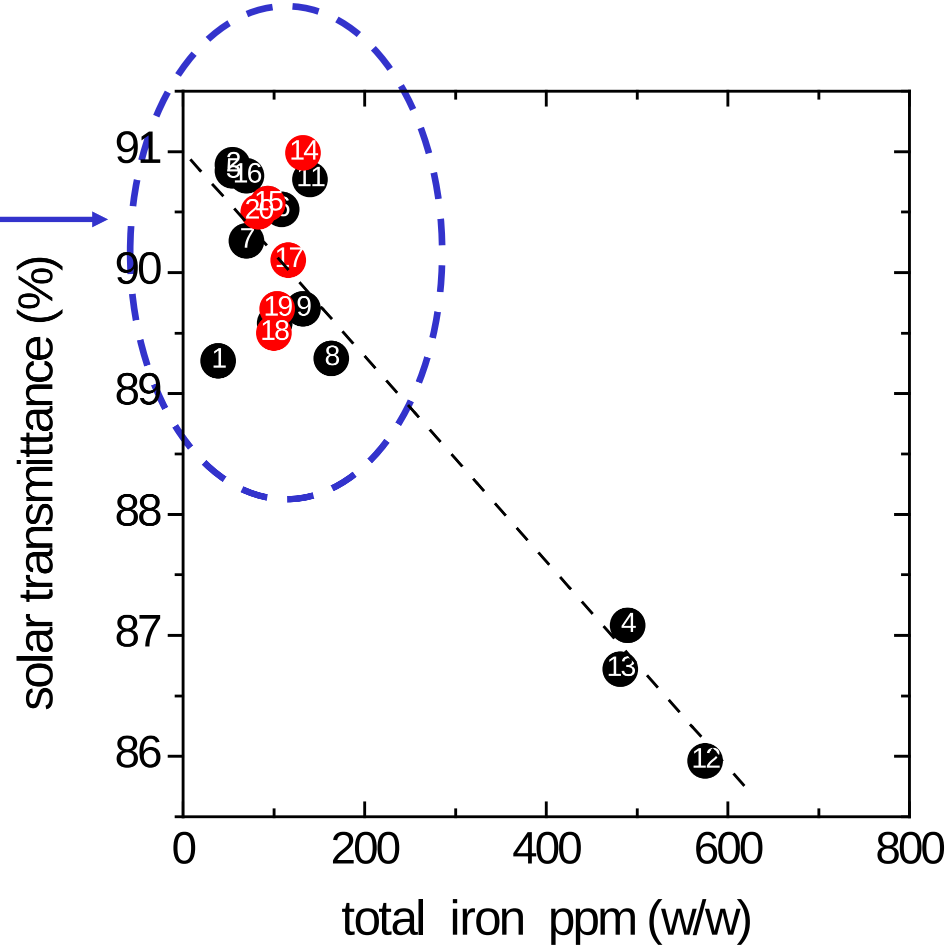
- integrating sphere
- 300 < λ > 2500 nm
- normalized by AM 1.5

$$\tau_e = \frac{\int_{0.3}^{2.5} T_{gh}(\lambda) \cdot S_\lambda \cdot d\lambda}{\int_{0.3}^{2.5} S_\lambda \cdot d\lambda}$$

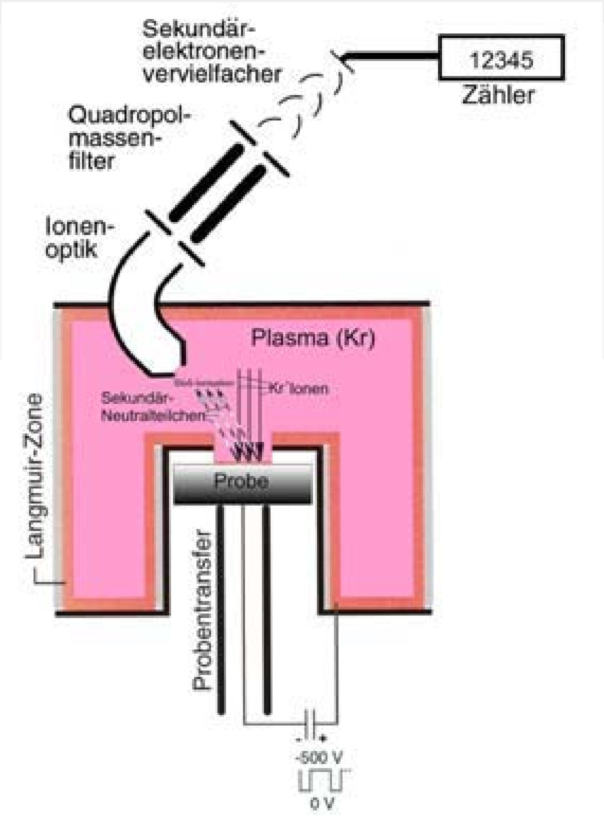


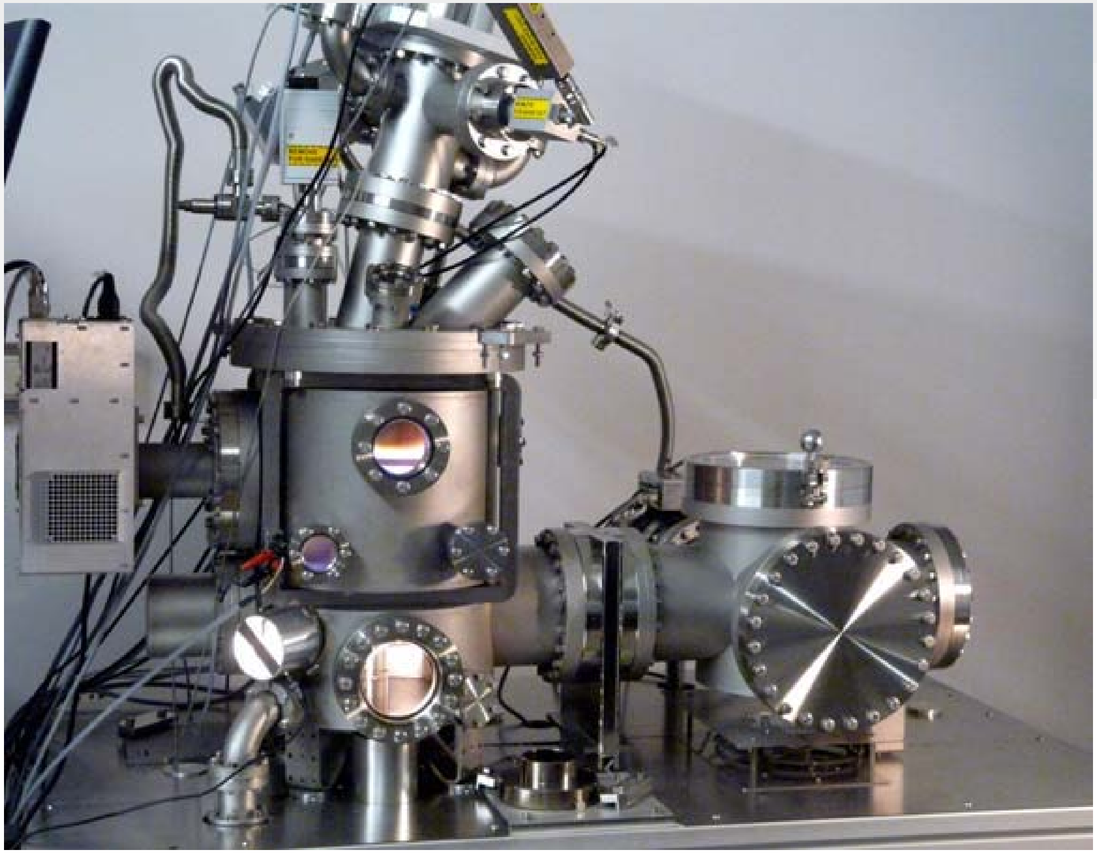
solar transmittance vs. iron conc.

solar transmittance independent of floating/rolling process



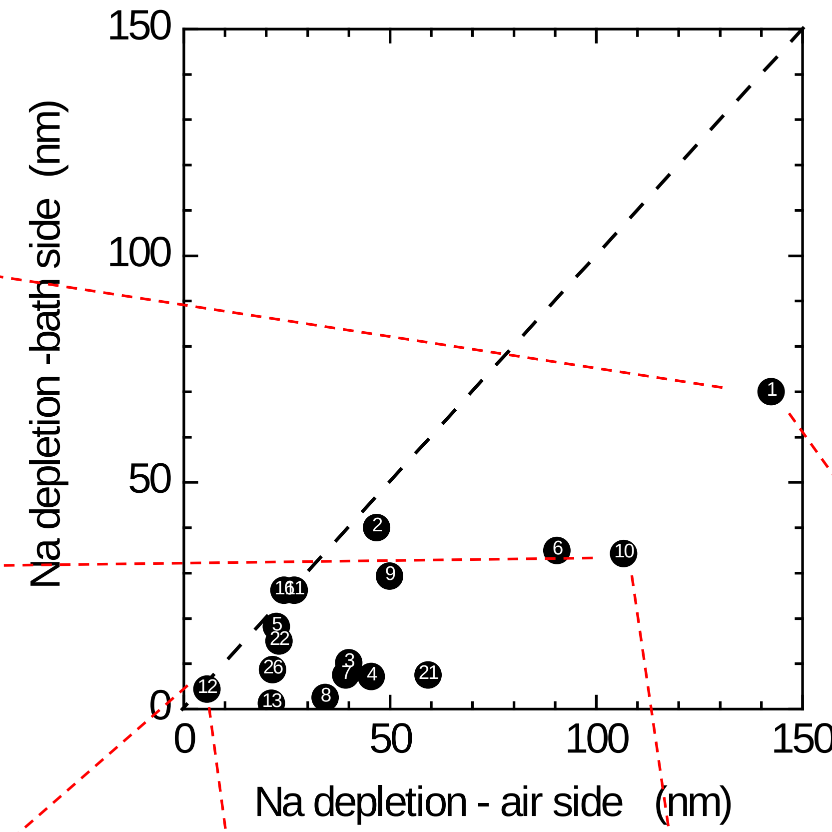
Near surface chemistry (depth profiling)
by
Secondary Neutral Mass Spectrometry (SNMS)
INA-X, Specs-Germany

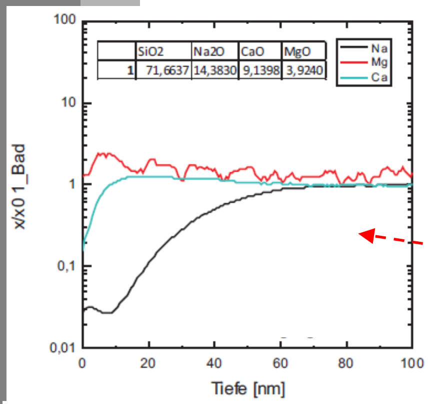


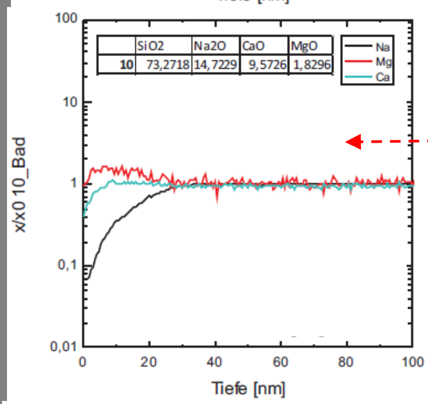


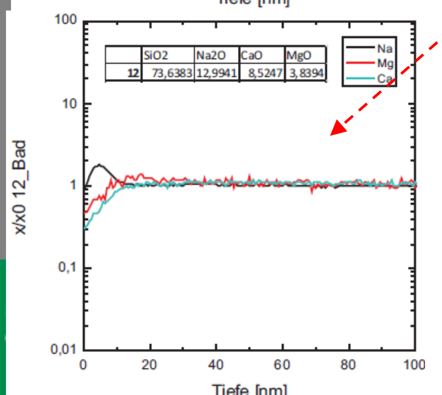
solar glass surface chemistry (float)

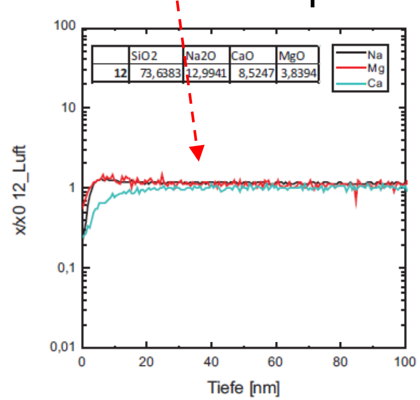
as recieved

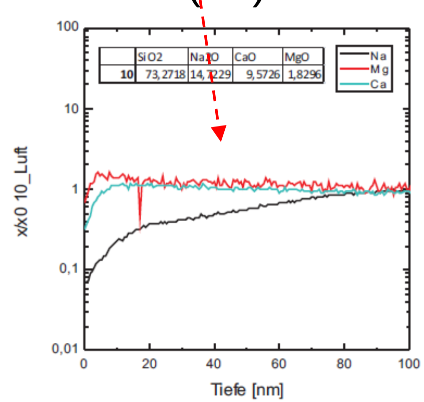


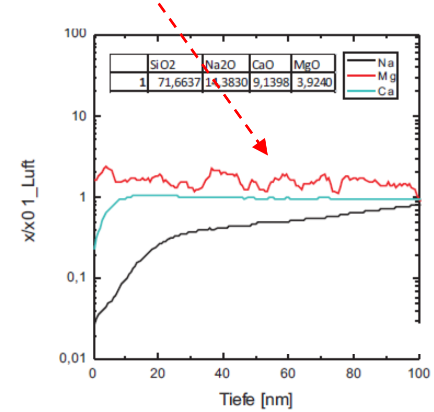










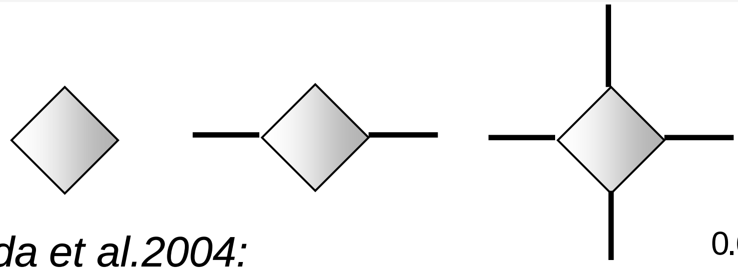


surface concentration by SNMS

sodium depletion air side > bath side

alterations due to different storage condition *(t, T, RH, etc.)*

crack initation on sharp loading

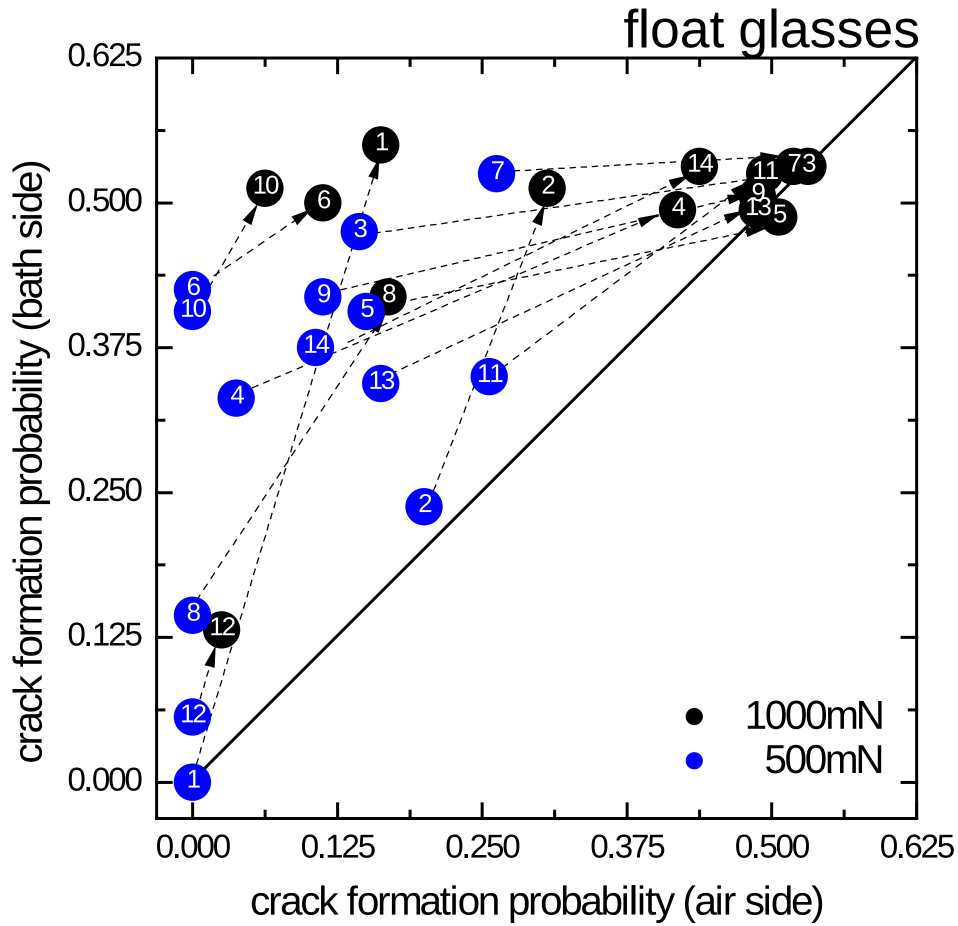


Yoshida et al.2004:

$$\text{crack formation probability} = \frac{\#\ \text{radial cracks}}{\#\ \text{corners}}$$

crack formation: bath > air

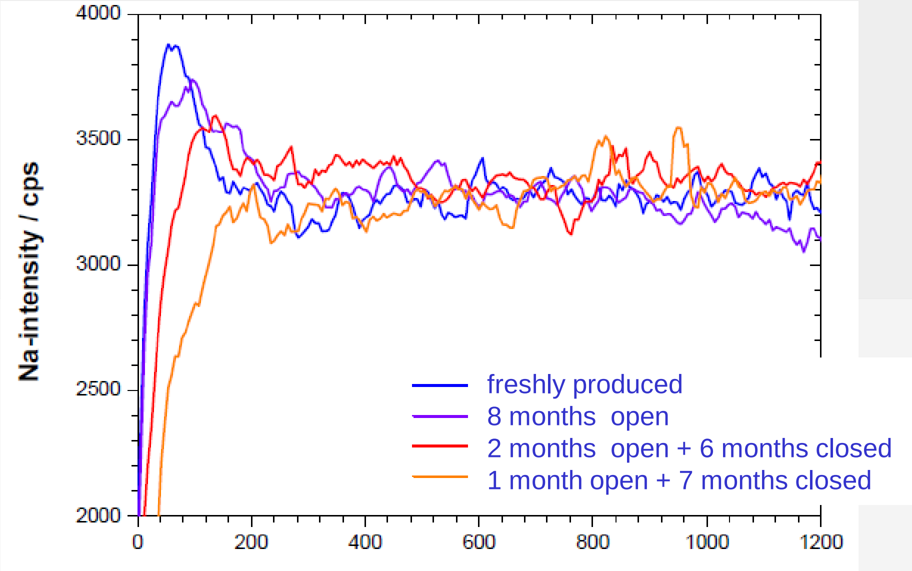
crack initiation load: air > bath



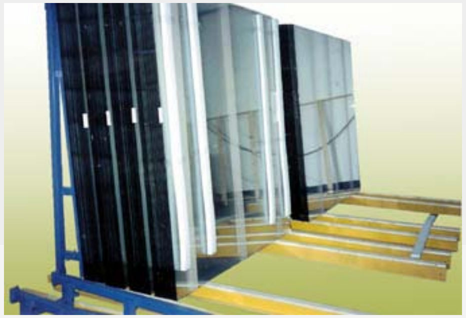
surfaces alteration (float glass)

storage conditions

source: AiF Nr. 15837 BG

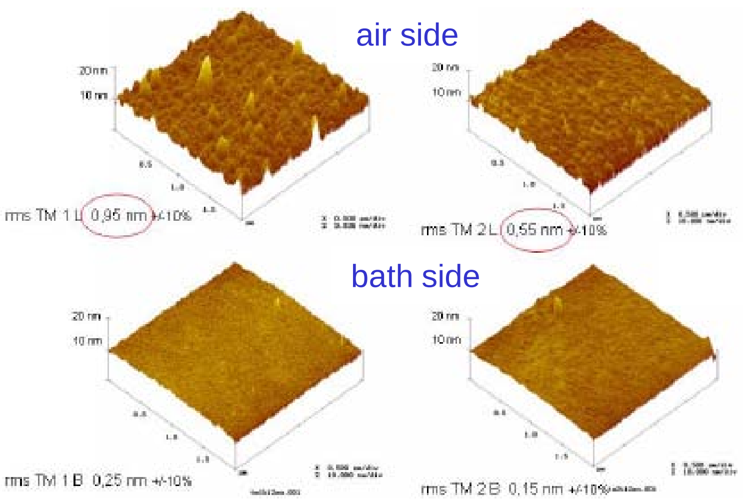


sputter rate ca. 0.2 nm/ s



stack + separation powder
"open" = packing-free
"closed" = packed

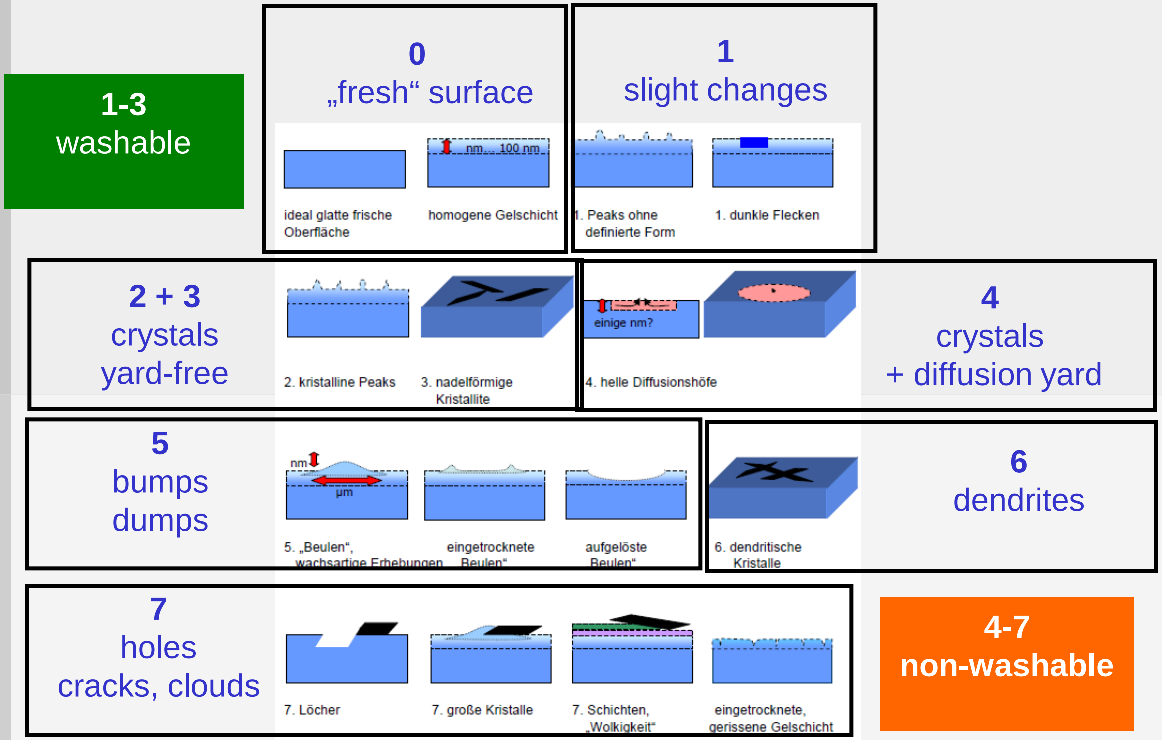
after 12 months open



PMMA PMMA + acid buffer

alterations
air side > bath side
closed > open
pH uncontrolled > pH controlled

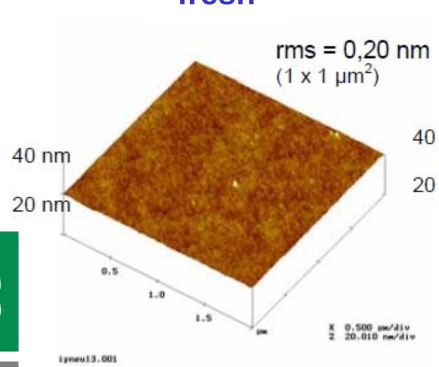
source: AiF Nr. 15837 BG



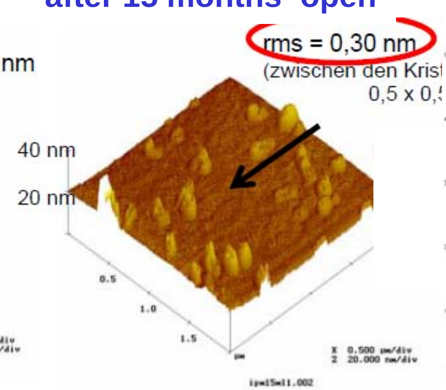
classification of
surficial alterations
(storage)
by E. Rädlein (TU Ilmenau)

irrreversible alterations
= non-washable

air side
fresh

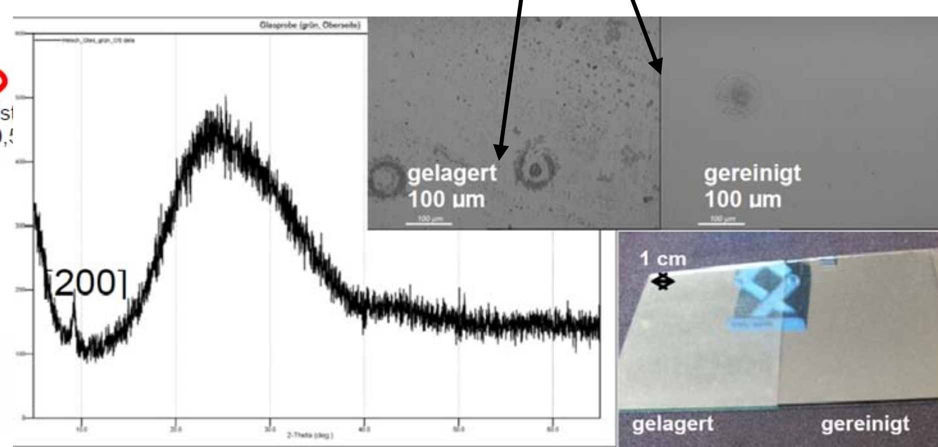


air side
after 15 months open



air side, after 15 years open

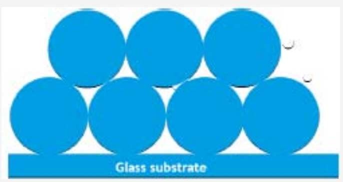
type 4
crystals
+ diffusion yard



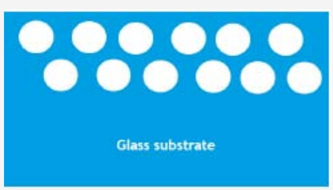
AR coating market

sol-gel improvements

solid silica particles
open porosity

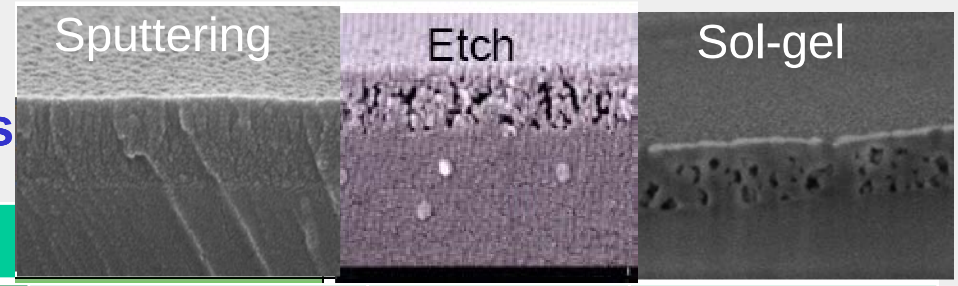


core-shell particles
(hollow sphere)
internal porosity

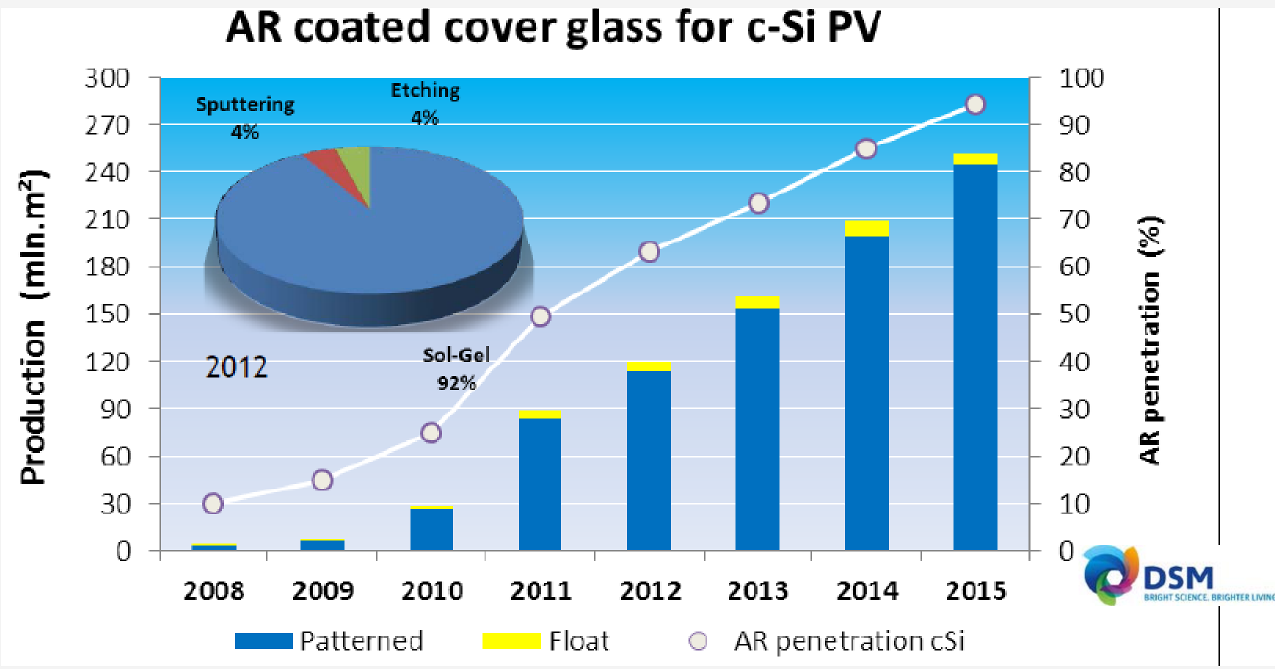


DSM ARC (KhepriCoat®)

competitive technologies



	Sputtering	Etch	Sol-gel
process limitations	**vacuum, multiple deposition**	**acids, process control**	**high temperature cure**



AR coating tests

reliability and durability tests

Mechanical Durability			Environmental Durability	
Coating Robustness	Standard	Test	Coating Resistance to:	Standard
Adhesion	ASTM D3359	Crosshatch Tape Test	Damp Heat	IEC 61215
Abrasion Resistance	EN 1096-2	Felt Rub Test	UV Exposure	IEC 61215
	ISO 9211-3	Blown Dust	Thermal Cycling	IEC 61215
			Humidity Freeze	IEC 61215
			Acid Rain	EN 1096-2
			Condensation	EN 1096-2
			Salt Mist	ISO 9211-3
			Outdoor exposure (IWI and rooftop)	-

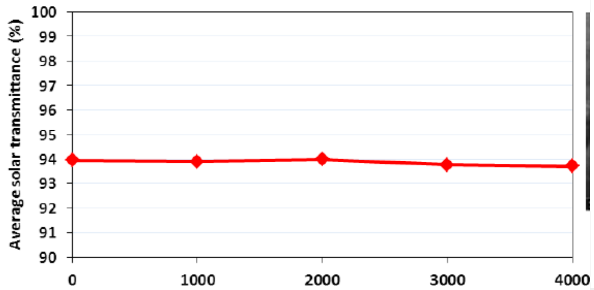
test are made to be passed ...

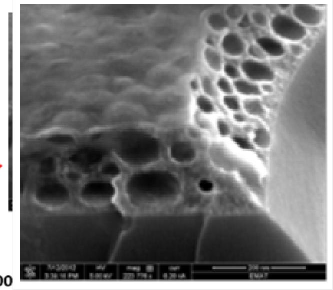
Durability:

Long-term performance through unique **closed pore** nanostructure.

The advantage of the closed and smooth surface is the sharply reduced risk of hydrolysis –that means no water molecule penetration into the surface.

Interfloat corporation





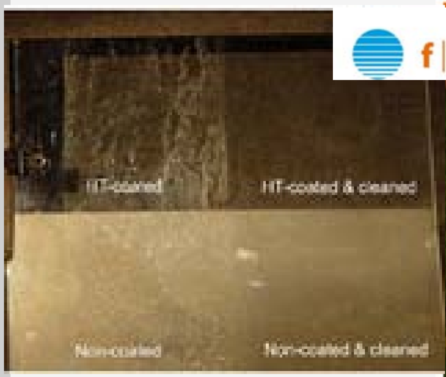
Proven durability in the laboratory and in-situ on life-sized modules:

Test	Description	ΔT [%]
Abrasion resistance (EN 1096-2)	Felt rubbing	– 0,33 %
Immersion test	Immersion in 85ºC water for 100 hours	+ 0,22 %
Immersion test saline	Immersion in 35ºC salt solution (50 g NaCl per liter) for 100 hours	+ 0,05 %
Immersion test	Acid immersion in 35ºC acid solution (0,1 M H_2SO_4) for 100 hours	+ 0,05 %
Vapor test	Exposure to water vapor	– 0,21 %
Damp-heat test (IEC 61215)	Exposure to 85ºC, 85% humidity for 1000 hours	– 0,53 %
Thermal cycling test (IEC 61215)	200 cycles from -40ºC to 85ºC	– 0,12 %
Humidity-freeze test (IEC 61215)	10 cycles from 85ºC, 85% humidity to -40ºC	– 0,50 %

CENTROSOLAR GLAS

Our antireflective glass CENTROSOL HiT has undergone a number of qualification tests to determine its utility and resistance to ageing under realistic conditions.

1 Damp heat steady state test of AR glasses in conformity with IEC 61215
Constant 85°C, 85% rh, 1,000 hours
2 Damp heat steady state test of AR PV modules acc. to IEC 61215
Constant 85°C, 85% rh, 1,000 hours
3 Condensation water climate test of AR glasses acc. to DIN 50017 / EN 1096-2
Constant 40°C, 100% rh, 480 hours
4 Condensation water climate test in a saturated Sulfur dioxide atmosphere of AR glasses acc. to DIN 50018 / EN 1096-2
Cycles: 40°C, 100 rh, 8 hours + 18-28°C, 75% rh, 16 hours, 5 ppm SO_2, 23 cycles
5 Thermal cycling testing of AR glasses in conformity with IEC 1215
Cycles: –18°C/-80°C, 56 cycles
6 Thermal cycling testing of AR PV modules acc. to IEC 1215
Cycles: -40°C/+85°C, 200 cycles
7 Salt spray test of AR glasses acc. DIN 50021
8 Outdoor exposure tests at ISE Freiburg as part of IEA Task 27 (testing of different materials)
8 Outdoor exposure tests, exposure racks in Fürth, Furth, Gernsheim, Freiburg
9 Hail impact testing of AR glasses acc. to IEC 1215
10 Frost test
-20°C, 8 weeks, with ice formation
11 Boiling test
10 min. boiling in demineralized water at 100°C
12 Abrasion test acc. to EN 1096-2 (Crockmeter Test)
Mechanical rubbing with felt fingers, weight 400 g, 1,000 cycles



f | solar

AGC SOLAR

SPARC COATING

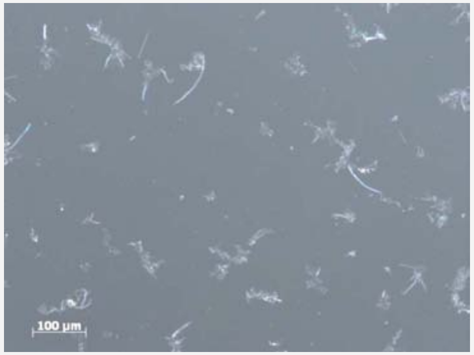
SOLAR PLUS ANTI-REFLECTIVE COATING (SPARC)

DURABILITY TESTS*

Damped heat	Passed	IEC 61215
Thermal cycle	Passed	IEC 61215
Climatic SO2	Passed	EN1096-2 (DIN 50018)
Salt spray	Passed	EN1096-2 (DIN 50021)
Mechanical resistance	Passed	EN 1096-2

heat-damp test
effect of “storage history“ on coating with single porous SiO_2 layer (sol-gel)

• Own measurements showed that float glasses with increased “storage history” had problems to withstand heat-damp test on the air-side but were intact on bath-side with crystals (washable).



196 h 85% RH, 85 °C

• Borosilicate glass tubes showed only slight changes with “storage history“ on heat-damp testing. AR-coat intact on both sides

196 h 85% RH, 85 °C

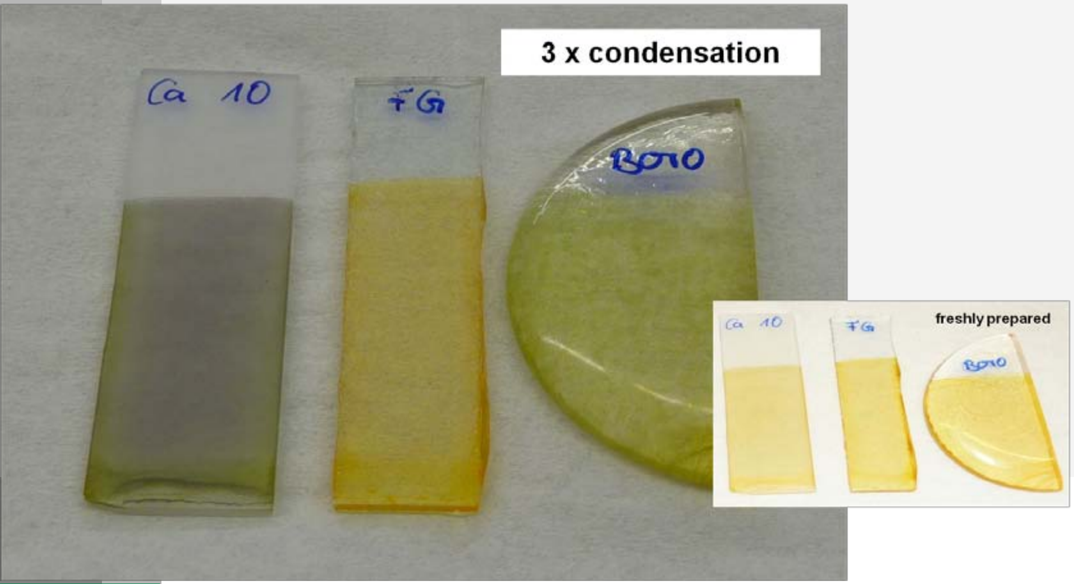
coatability depend on
degree of surface alteration (“storage history”)
→ minimize storage
→ seal fresh surface

ultra-thin cabon coating - Lee, Rajagopalan & Pantano, 356 JNCS (2010) 236

source: AiF Nr. 15837 BG

... at least monitor quality
glass corrosion sensors

- **Application:**
  sensor plate at glass stack monitors environmetal condition by colour changes and gives references for the coatability

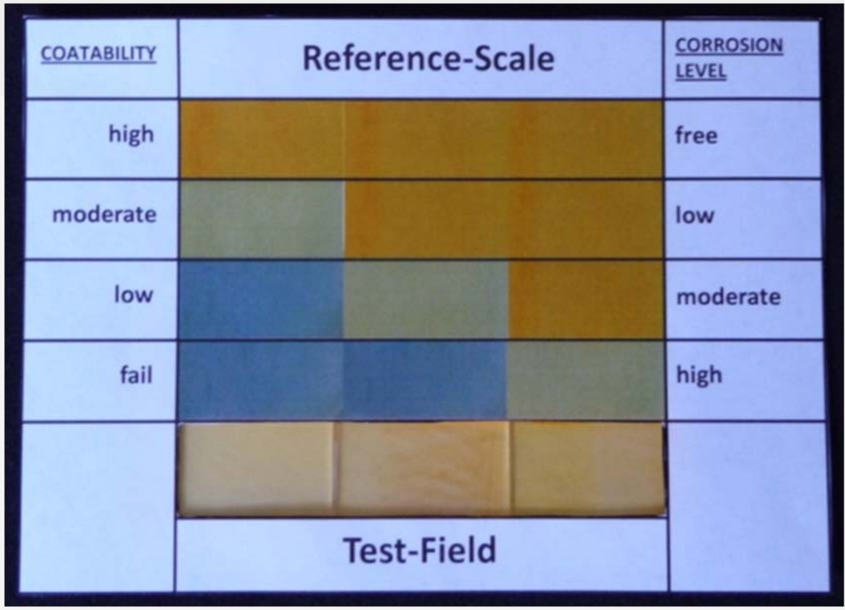


source: patent application
DE 102009050714 A1

Innovation

detection of glass corrosion by sensor plates

- ➢ glass segments with different corrosion sensibility
- ➢ pH-indicators of different transition ranges.



Benefits

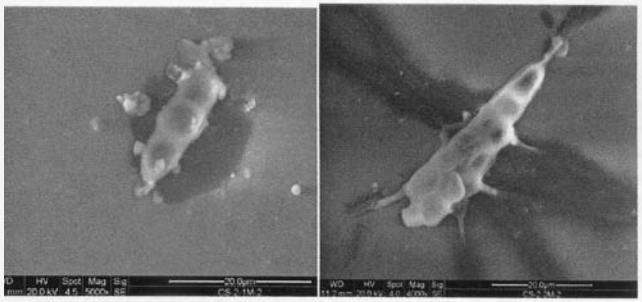
- ➢ Recognizing of corrosive environmental influences to the glass during transport and storage.
- ➢ Sorting-out of damaged glass to assure quality previously.
- ➢ Economical advantages due to avoiding consequential losses and complaints.

biofouling

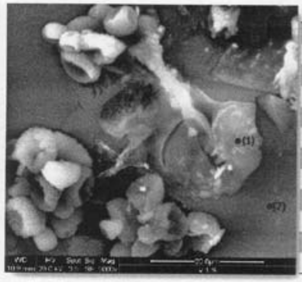
AR coatings for PV, domestic water heating

Alterations of nanoporous AR coatings due to aggregates of microorganisms and formation of biofilms

microbe fouling
on porous silica AR coat
after outdoor exposure tests
4 months (ESEM images)



source: FORGLAS, Report 2012



Elemente	(1) Organik	(2) Glas
C	50,89	5,01
O	38,33	61,96
Na	1,90	6,64
Mg	0,17	0,47
Al	0,38	0,30
Si	6,70	22,60
P	0,11	
S	0,12	
K	0,08	
Ca	0,85	3,02
Ti	0,20	
Fe	0,29	

Angaben in Atomprozent

adding of biocides

→ **Ag, Pd, Cu, ... (nano particles)**

adding of antimicrobial activity

→ **increasing hydrophobicity**

→ **photocatalytic oxidation (PCO)**

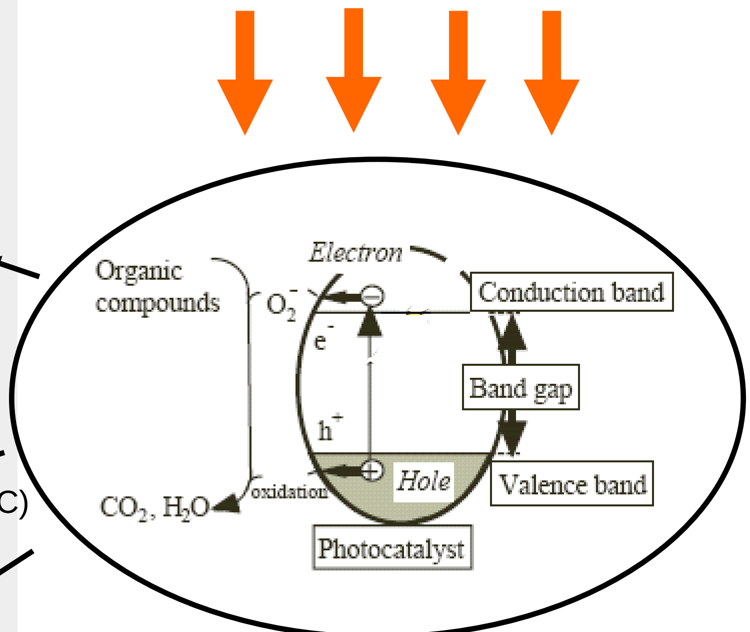
solar photocatalysis

potentials

photocatalytic oxidation (PCO)

$h\nu > \Delta E_g$

photoinduced hydrophilicity (PIH)



water purification
anti -bacterial

air purification
volatile organic compounds (VOC)
urban pollutants (NO_x)

solar fuel
hydrogen generation

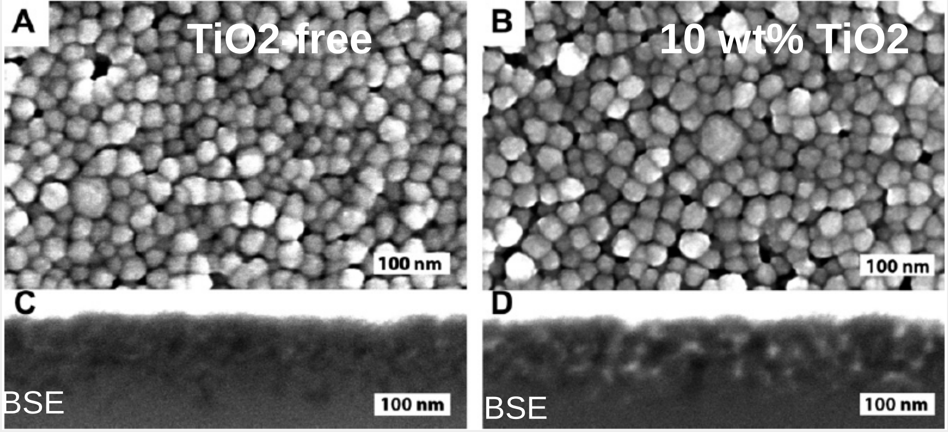
easy-to-clean
Pilkington Glass (ActivTM)
St-Gobain (BiocleanTM)
PPG (SunCleanTM)

anti-fog

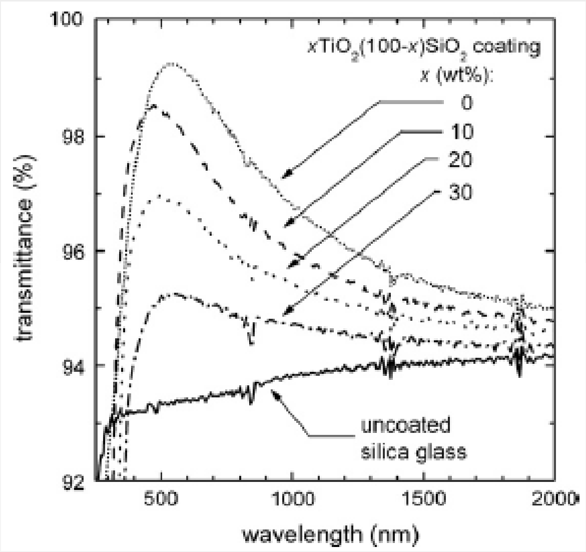
oxide	E_g(eV)
NiO	0.93
CuO	1.7
CdO	2.1
Fe_2O_3	2.2
TiO_2	3.0
ZnO	3.2

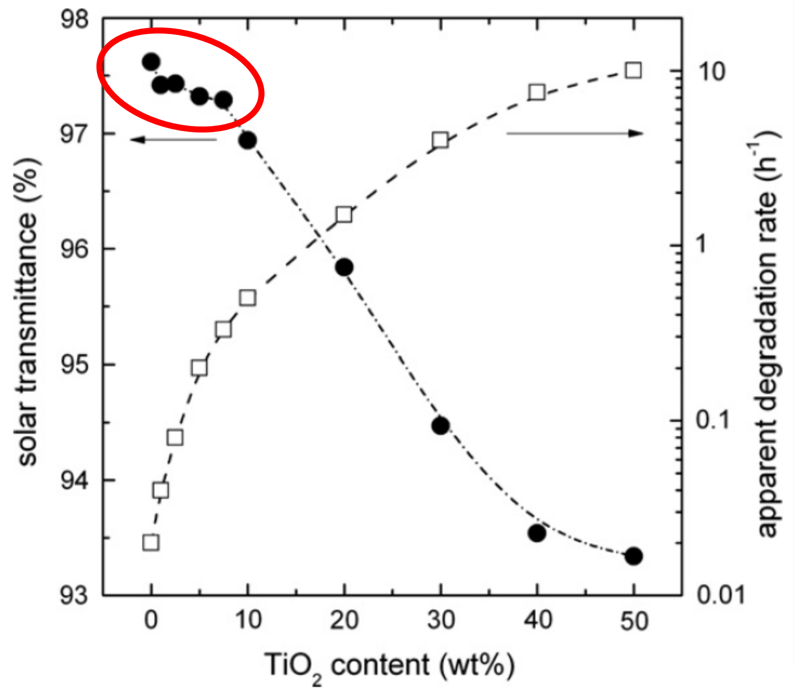
AR-coat with PCO

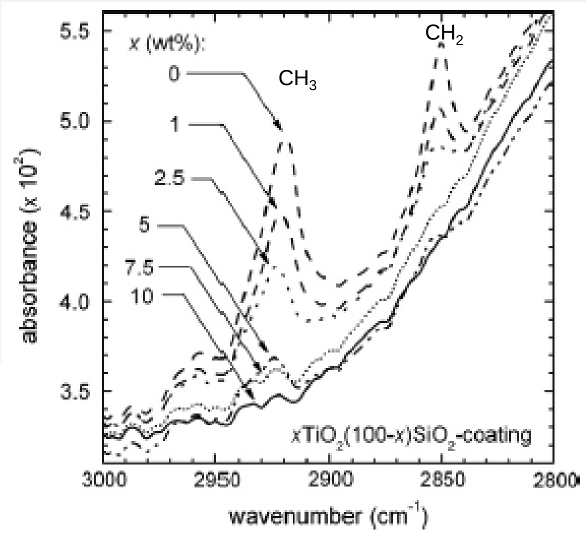
anti-fouling



anatase stable despite curing > 500°C



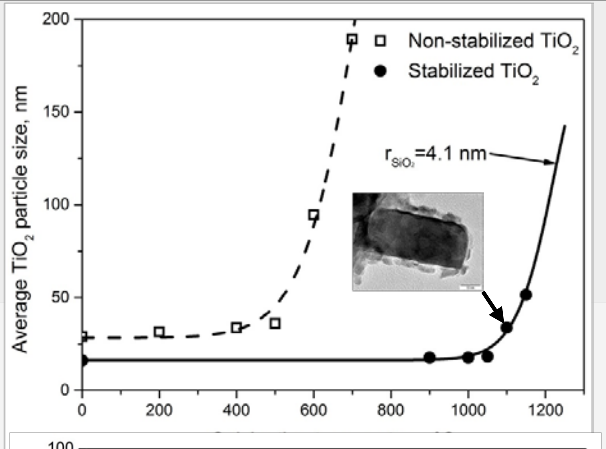


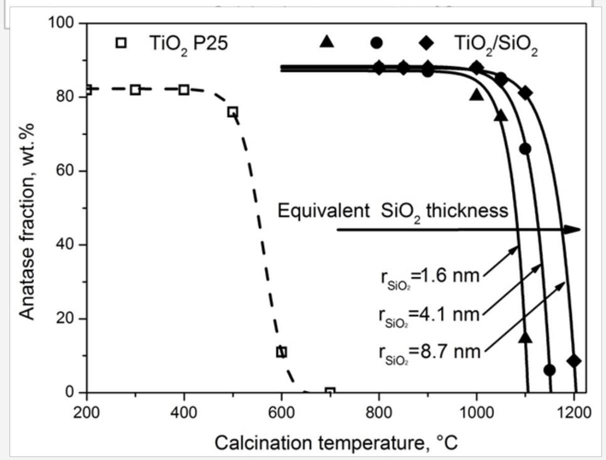


G. Helsch et al., Solar Energy 96 (2012) 831

outdore exposure started

AR-coat with PCO
HT-stability

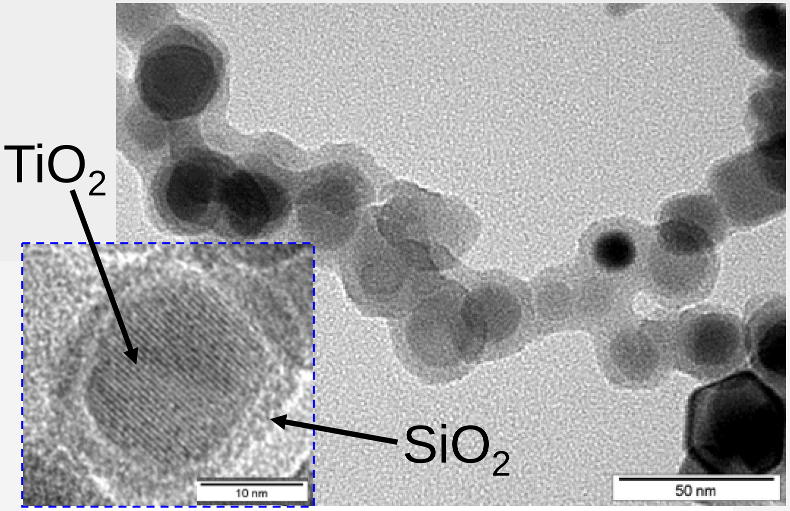


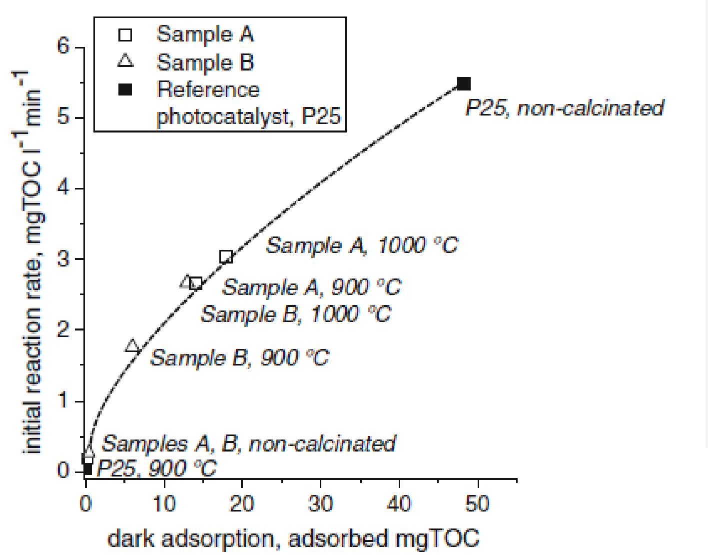


Qi et al., in Handbook of functional Nanomaterials" (2013) in prep.

HT-stable anatase (1000°C) by interface passivation particle growth is retarded

sols of core-shell nano-particles





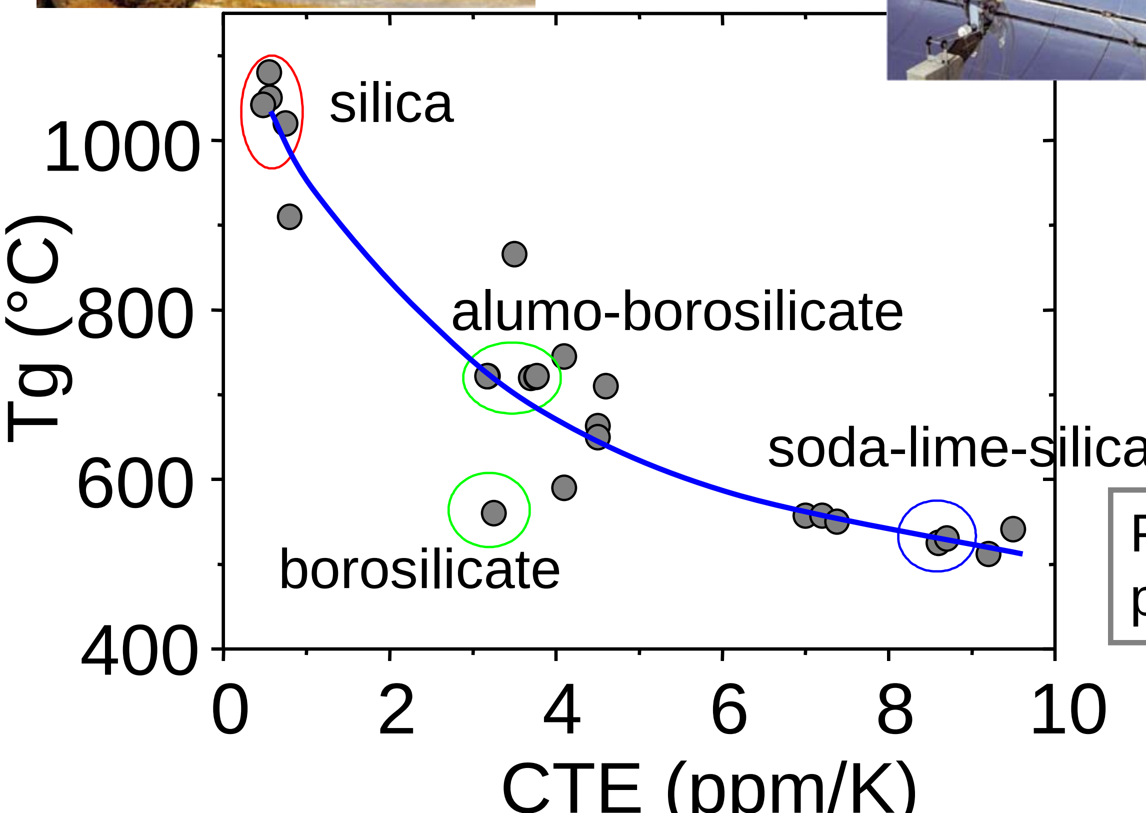
Qi et al., J. Nanopart. Res.13 (2011) 1325

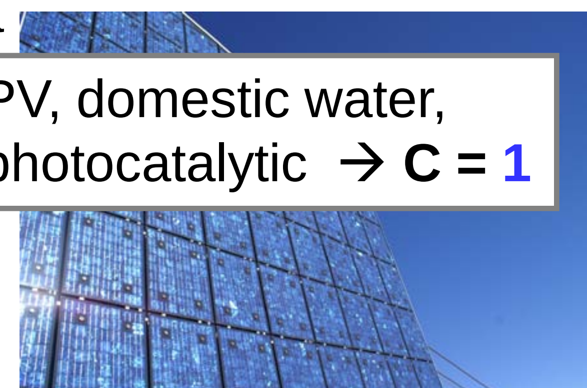
glasses for solar energy conversion systems

geometric concentration factor C

tower → **C >** **1000**

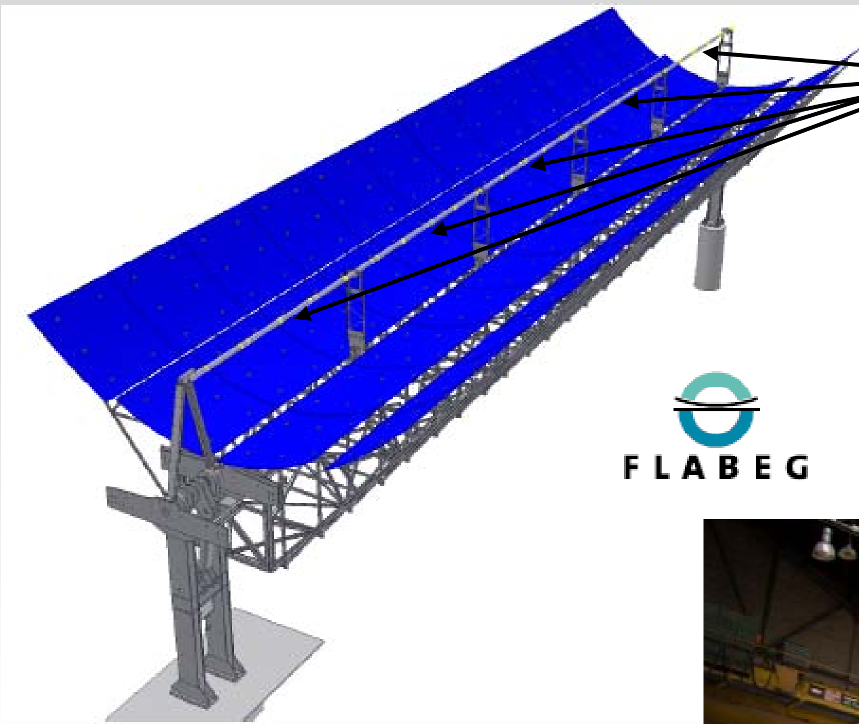
trough → **C <** **100**





PV, domestic water, photocatalytic → **C =** **1**

AR coatings for trough receiver tubes
borosilicate glasses



connected receiver tubes
each 4 m length

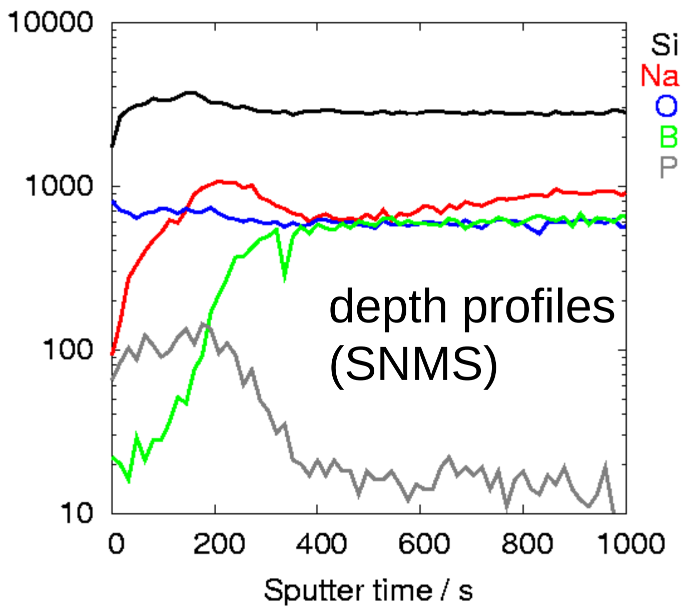
operating temperature ca. 400°C

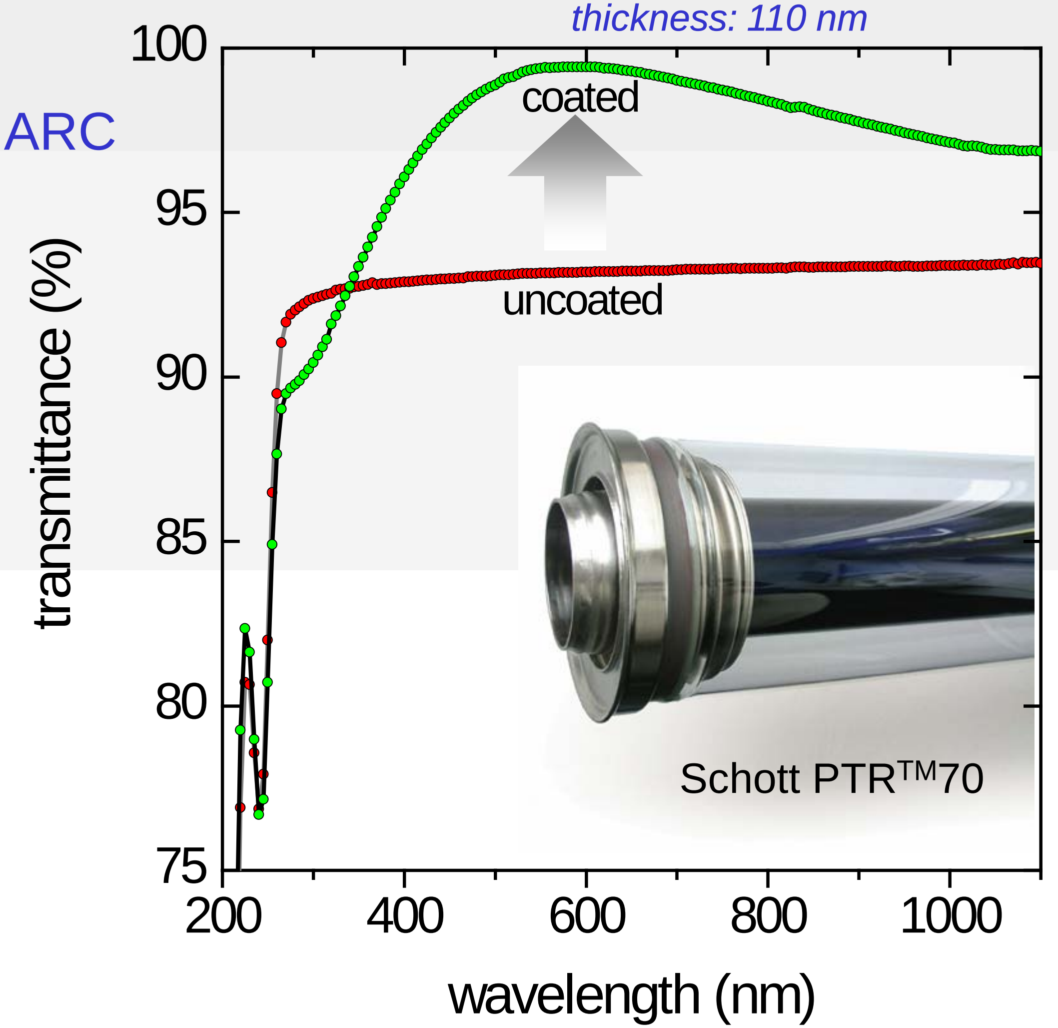
source:
Flabeg,
Glas und Solar, Otti 2012

AR coating
on borosilicate glass tubes

minimizing alterations due to mechanical impacts:
goal:
higlhy adhesive
long-term abrasion resistant ARC

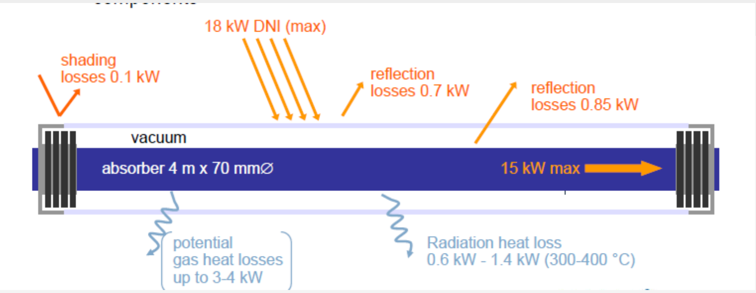
was achieved inter alia by chemical modifcations





Krzyzak,M. et al.
German pat., 2003, DE 102099949 A1
Chinese pat. , 2007 CN CN 1319889C

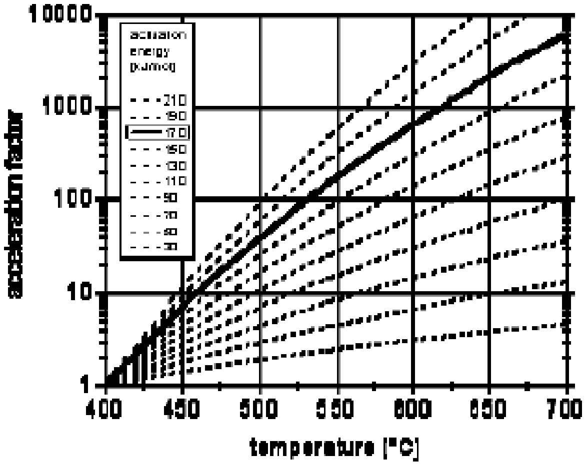
Accelerated aging tests
projection of lifetime performance



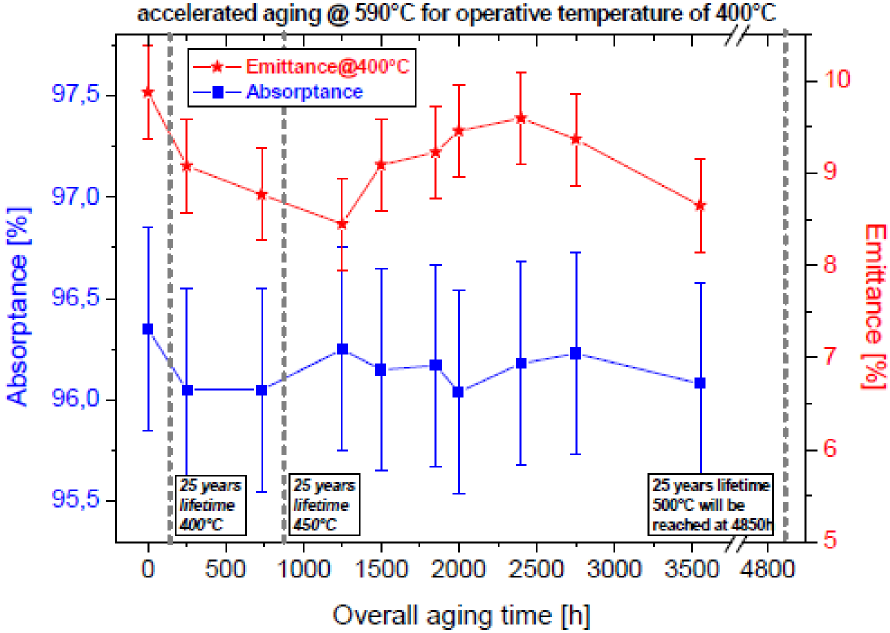
170 kJ/mol

Minimum aging time [h]	Aging temperature [°C]
1050	510
643	525
295	550
93	590
16	660
6	700
2	750

calculated acceleration factors vs. aging test temperature
for different aging mechanisms, i.e. activation energies,
(operating temperature 400°C)



source: M. Arntzen
in : Glas und Solar, Otti 2012

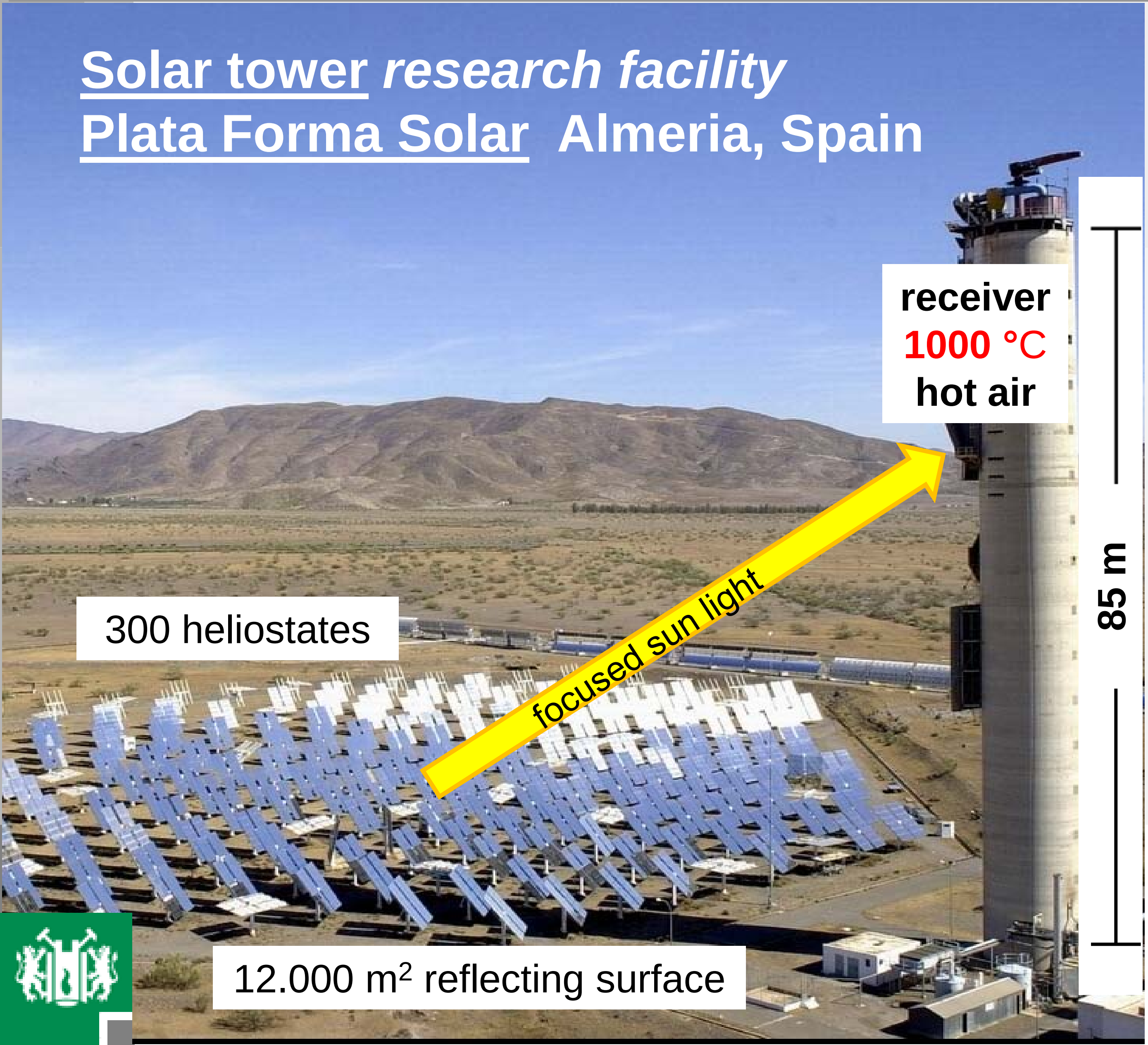


- Length of test necessary for 550 °C working temperature during 25 years:
  - ~ 1000 days at 590 °C
  - ~ 170 days at 660 °C (maximum test temperature)

© SCHOTT Solar CSP GmbH

Thermal alterations of AR

on silica glass windows for volume pressure receivers



1m²
receiver
window
silica glass

AR coated transparent cover glass

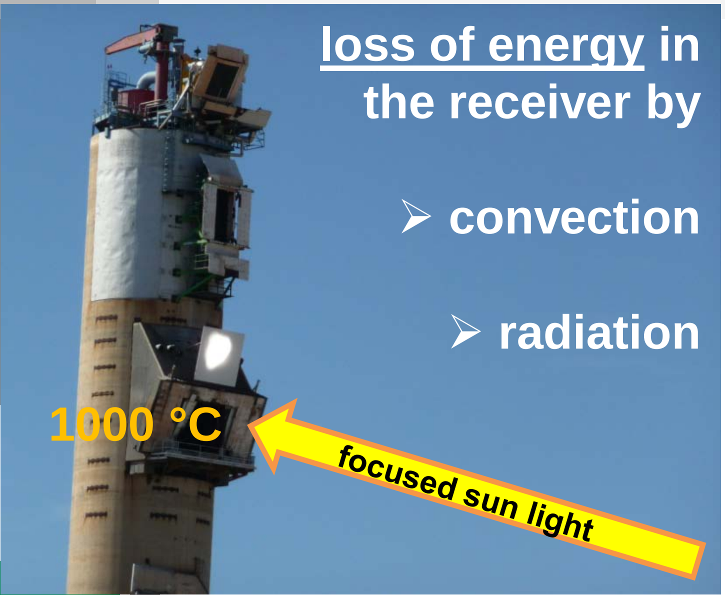
ARTRANS 2007-2009 (DLR)

thermal calculations
4% efficiency gain

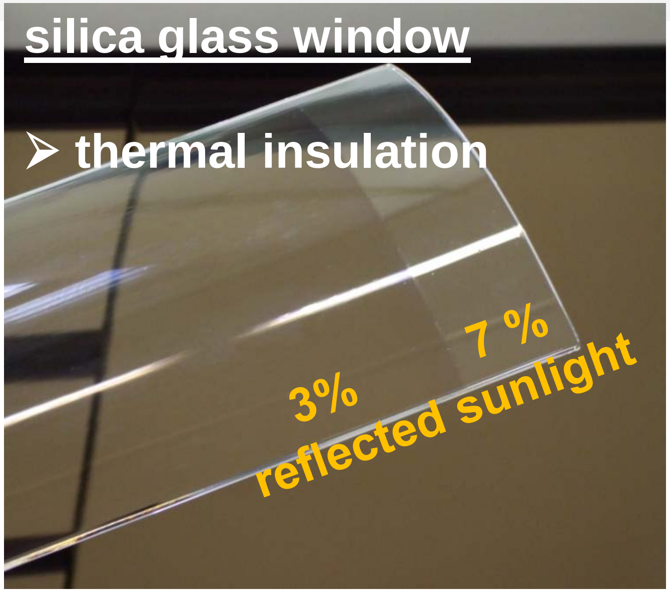
window design
(stacked tube segments)

coating
SiO_2 containing porous layer
(1.2 m x 1.2 m)

assembling and test run
(2010)

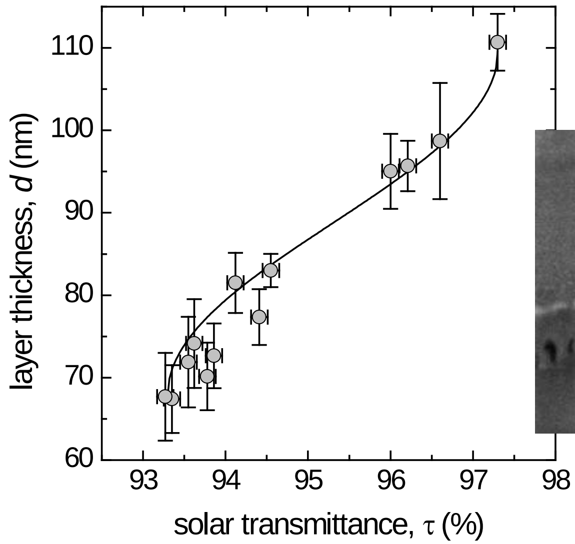


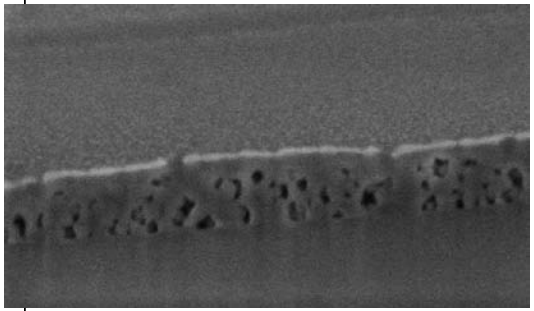
Antireflective coating for compensation of reflective losses

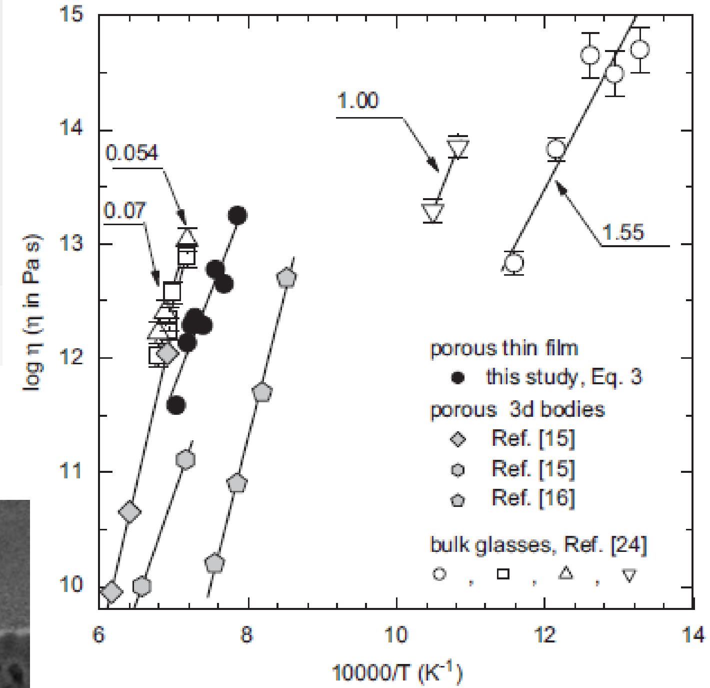


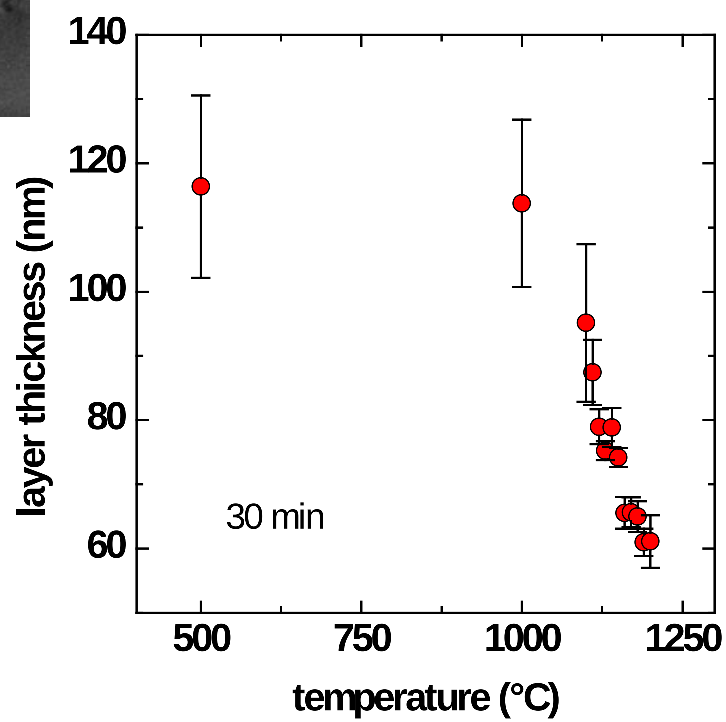
Thermal alterations of AR coating
on silica glass windows for volume pressure receivers

Helsch et al., Solar Energy Mat. Solar Cells 94 (2010) 2191









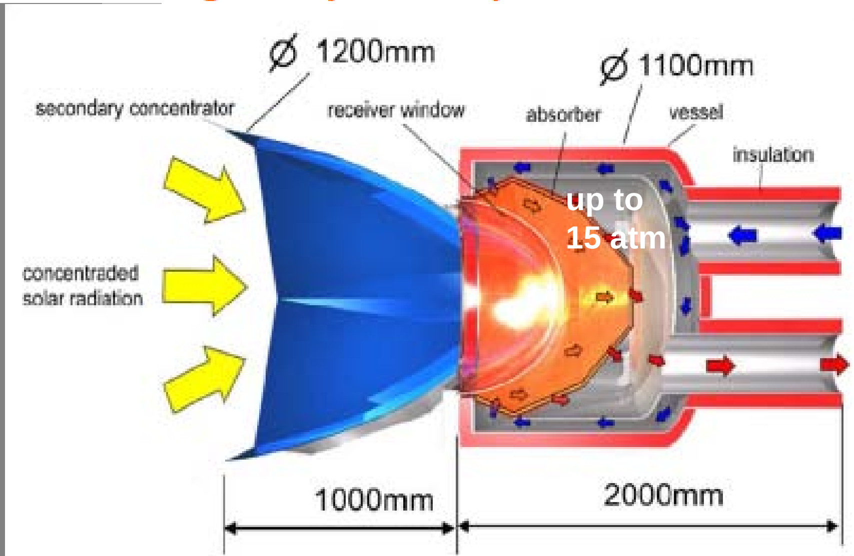
- **solar transmittance as a quantitative measure of the densification process**

- **viscosity based mechanism of densification** in agreement with 3D-shrinkage of porous SiO2 soots & powder compacts (Scherer 1976, Sacks & Tseng 1984)

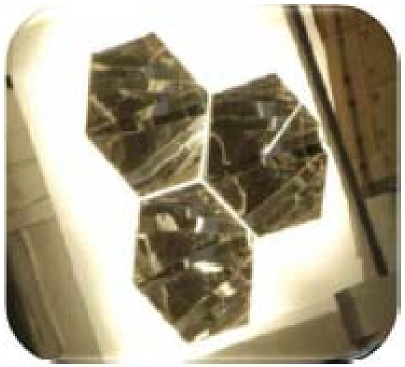
Soltrac II – alliance (DLR, Heraeus, Abengoa ,TUC)

2012-2014

Soltrec - high temperature pressurized volumetric air receiver



- Raise receiver outlet temperature up to **1000°C** for air receivers
- High receiver efficiency
- Low pressure drop
- Highly modular and scalable to any power plant size
- Commercialization



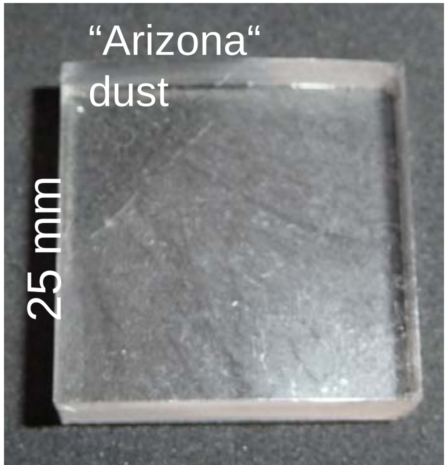
source: **Roman Korzynietz*, Reiner Buck[1], Ralf Uhlig[1]**

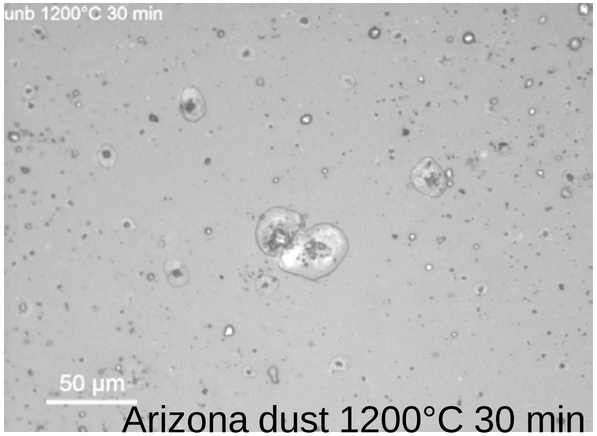
*Abengoa Solar NT, Rambla del Obispo Orberá 11, 1ª planta, 04001 Almería, Spain

[1] Deutsches Zentrum für Luft- und Raumfahrt e.V., Pfaffenwaldring 38-40, 70569 Stuttgart

14. Kölner Sonnenkolloquium

thermal alterations of AR coated and uncoated silica window (TUC)





Arizona dust 1200°C 30 min