OTPIP XXVIII

From a ToF-SIMS study on glass corrosion to self-healing surfaces

René Feder, Christian Thieme

Fraunhofer IMWS

Weinbergcampus in Halle/Saale

WEINBERG CAMPUS TECHNOLOGIEPARK 25 JAHRE

1992/2016
Foundation

330
Employees

Halle
(Main-)Site

IMWS/CAM
(Center for Applied Microstructure Diagnostics)

Fraunhofer IMWS

Fraunhofer IMWS

Who we are

1 We address the smallest dimension - with microstructure-based diagnostics and technology development for innovative materials, components and systems.

2 We develop solutions for functionality, reliability, safety, durability, sustainability and accelerated development of materials.

3 We increase the material efficiency and cost-effectiveness of materials and systems, thus helping to conserve resources.

Materials Insights

From the microstructural material and component characteristics, statements can be made about the properties in the application case.

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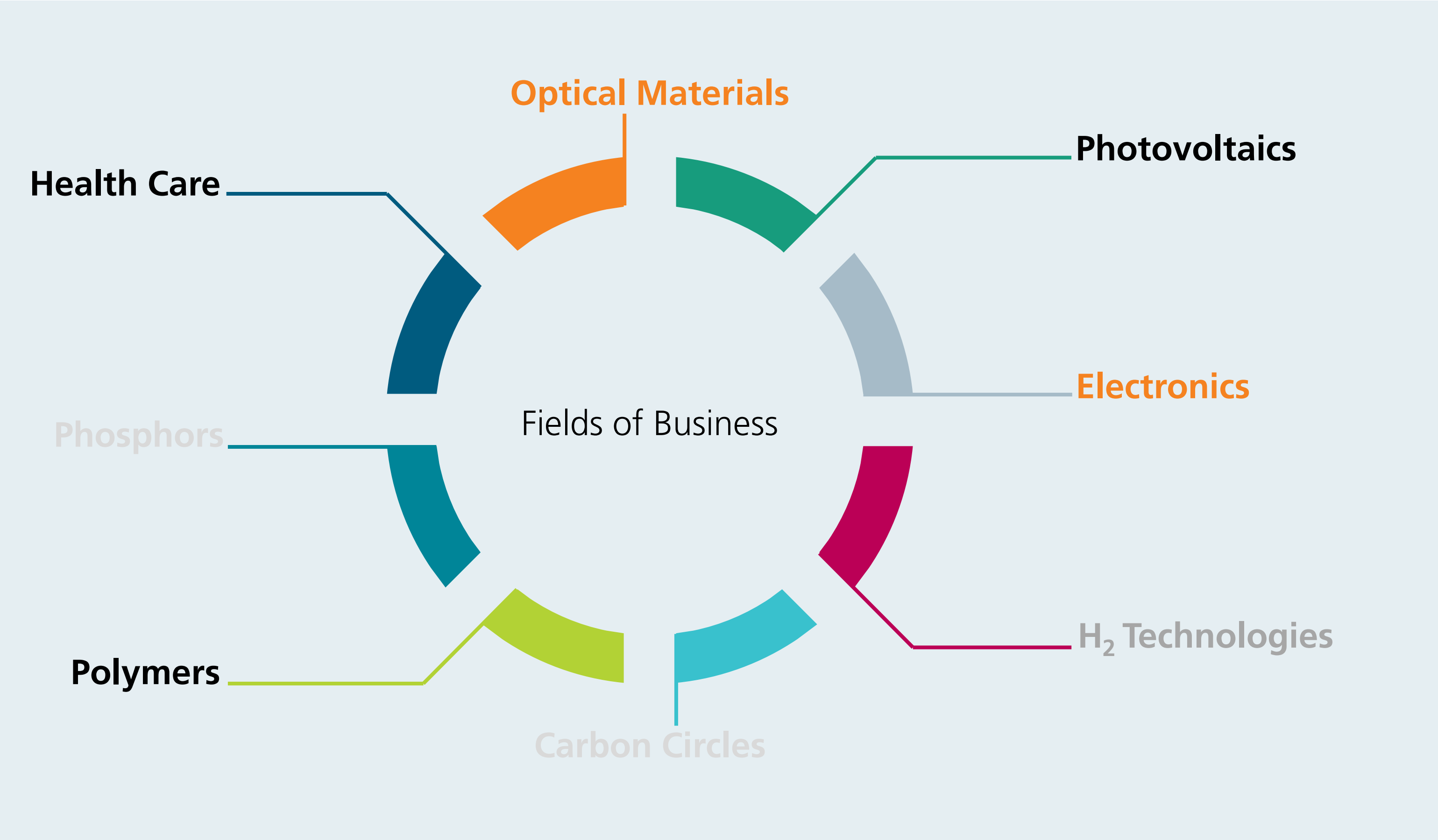
Methodically Oriented Portfolio Institute for Microstructure Diagnostics & Microstructure Design



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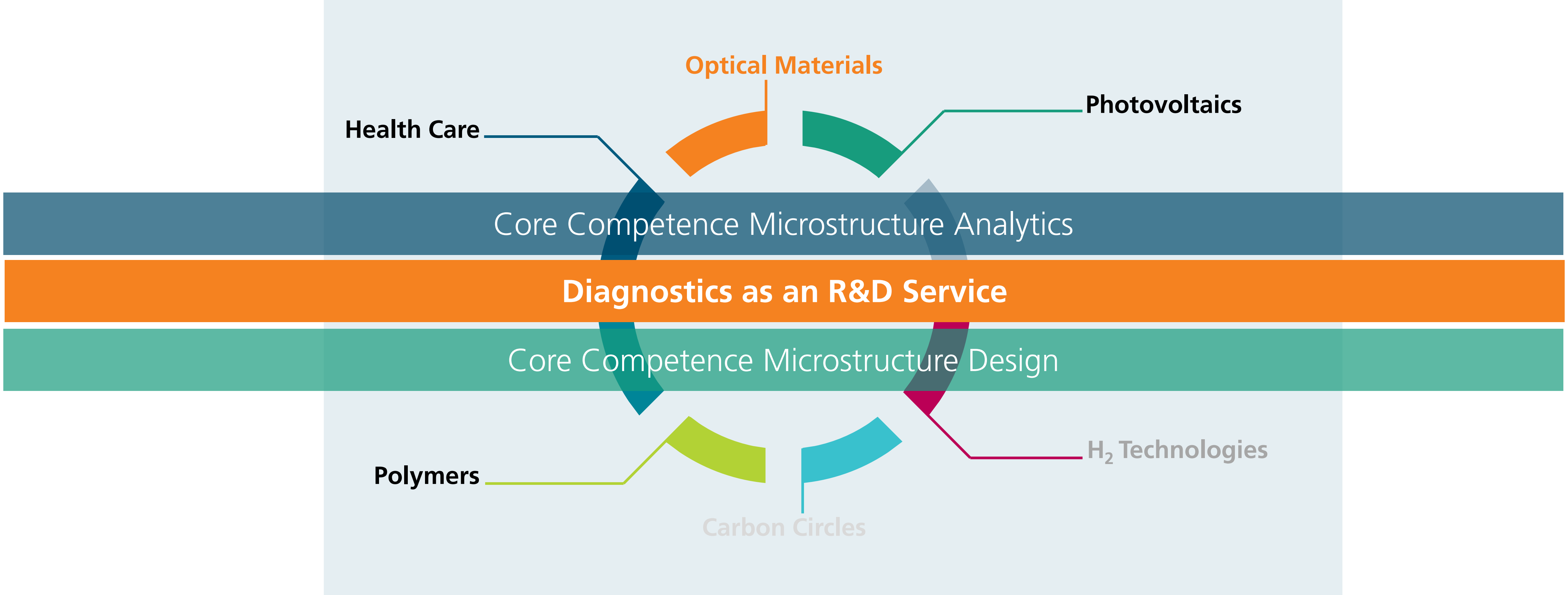


Business Unit «Optical Materials and Technologies»

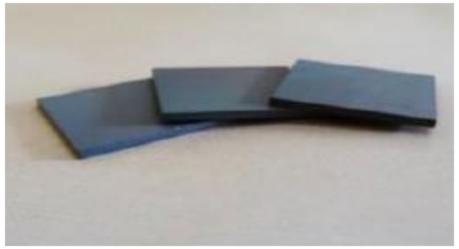
Service Offering Consists of Three Pillars

Analytics

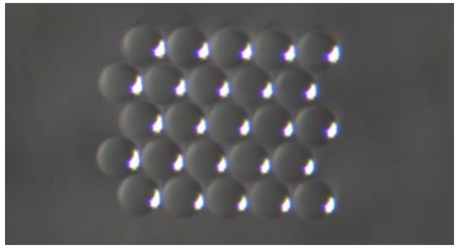
1 **Microstructure diagnostics, on industry demand**
Including sample prep for optical materials (substrates, thin films, pigments)

Technology Development

2 **Microstructure-based Materials Development**
Glasses [seals, etc.] & glass ceramics



3 **Microstructure-based Optimization of Micromachining**
using Lasers & ion beams



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Corrosion Studies

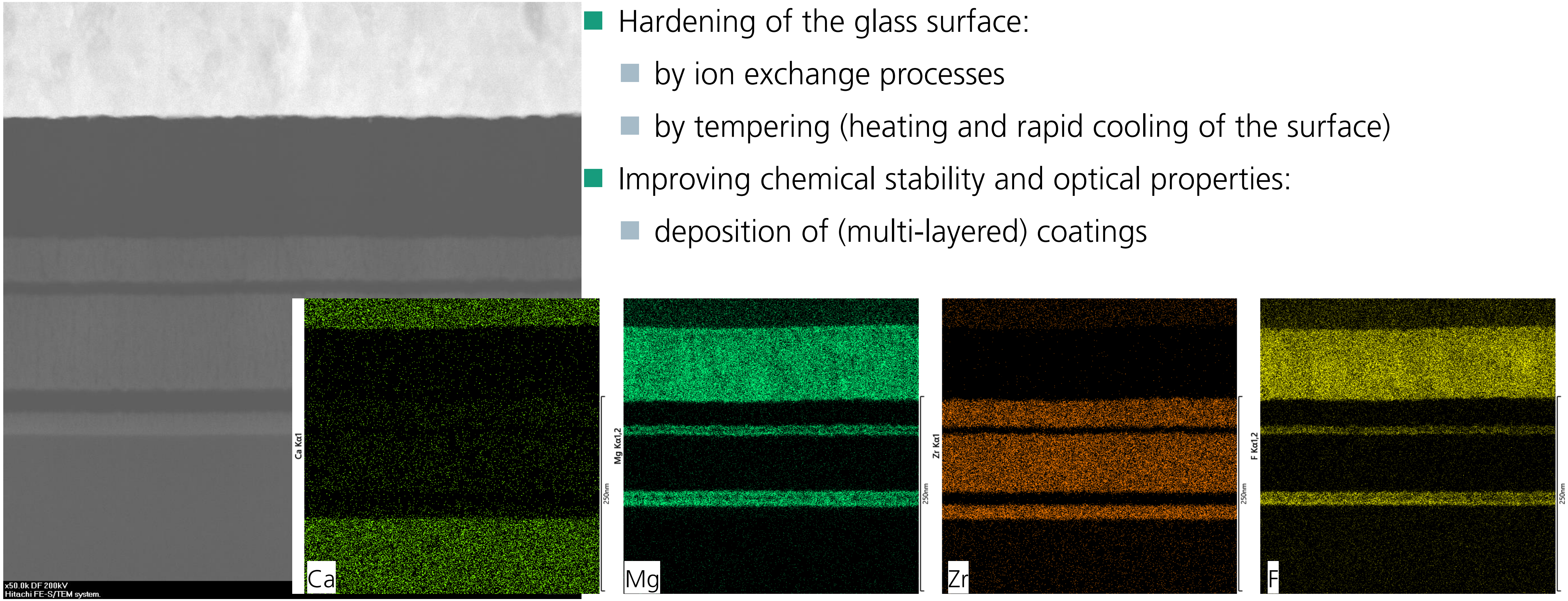
Glass as a Material

- Earliest traces of glass made by humans: > 5000 years
- Optical properties in visible range
- Great stability over time, but sensitive to stress
- Glass corrosion: depending on environmental conditions
- Industrial approach to increase durability:
  - increased hardness, especially for edges and corners
  - chemical resistance

Corrosion Studies

Glass Surface Functionalization

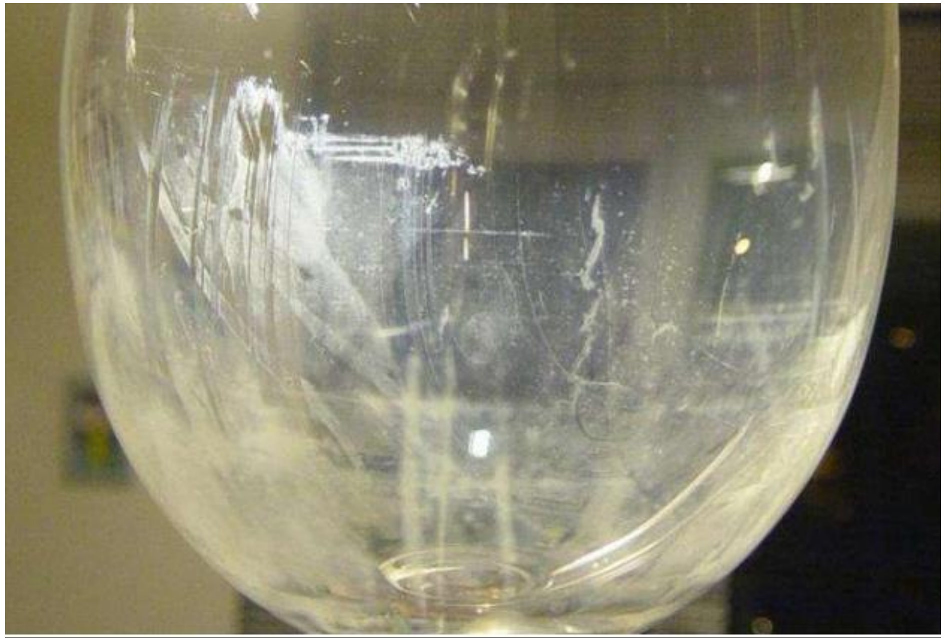
- Hardening of the glass surface:
  - by ion exchange processes
  - by tempering (heating and rapid cooling of the surface)
- Improving chemical stability and optical properties:
  - deposition of (multi-layered) coatings

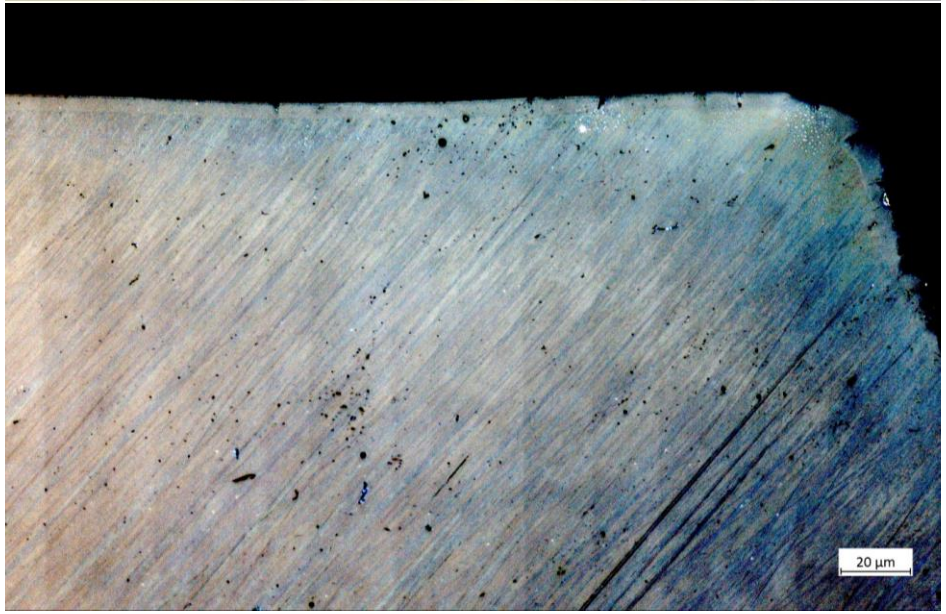


Corrosion Studies

Glass Corrosion

- General knowledge: corrosion processes of inorganic glasses are well understood.
- Ion exchange processes at the glass surface lead to the formation of a gel-like layer, influencing the mechanical and optical properties of the glass.
- Processes are accelerated in combination with water or humidity in the environment.
- The glass stoichiometry influences the corrosion behavior
- But: most of this knowledge is phenomenological.
- The microstructural mechanisms are an actual research topic, and the improvements in surface and microstructural analysis promise further insights.





How it Started

ToF-SIMS Corrosion Studies

85 SiO_2 - 15 Rb_2O glass made at 1600 °C

- Innovent and Fraunhofer IMWS wanted to improve the general knowledge about glass corrosion, in order to mitigate the process.
- Theoretical work at Innovent (Dr. Detlef Stock) indicated that superficial redistribution of elements/bonds might be key.
- IMWS suggested to have a look into the surface-near composition of a glass using time-of-flight SIMS.
- Due to its omnipresence on surfaces and very high mobility of sodium, it was decided to have a look at a quasi-binary, alkali silicate model glass
  x SiO_2 / (100-x) Rb_2O (x=90, 85, and 80, mol%).
- A “thirsty glass” was produced by bubbling with dried Ar.
- ToF-SIMS proved CO_2- and water uptake by the *x SiO_2 / (100-x) Rb_2O* glasses.

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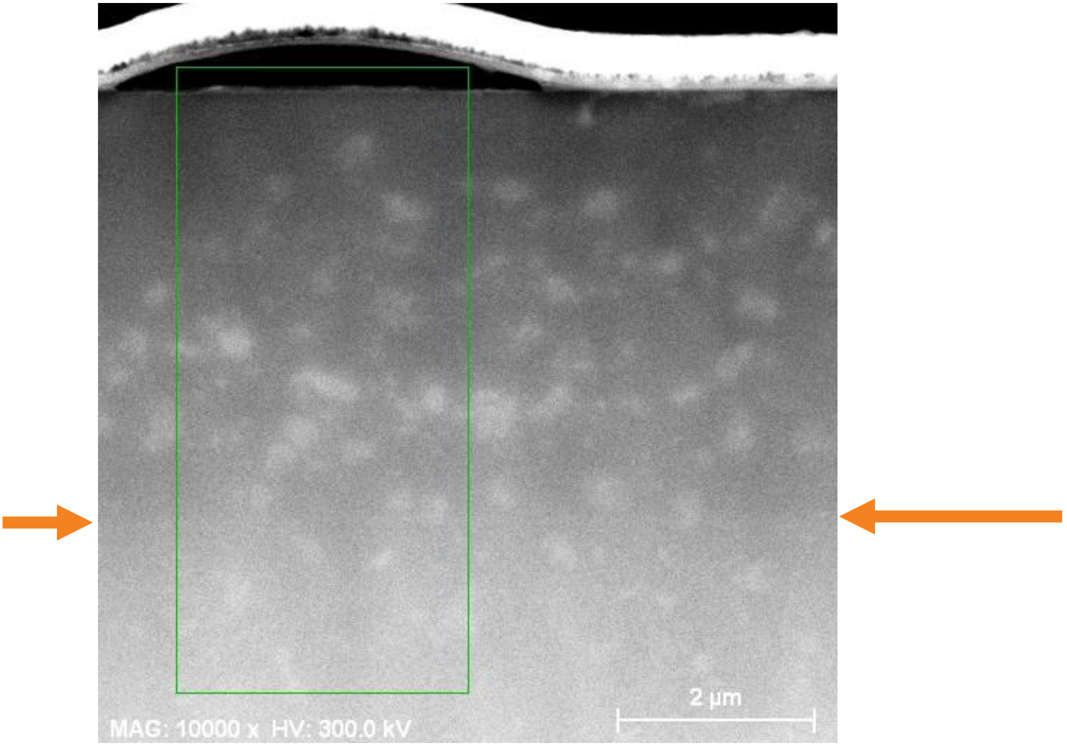
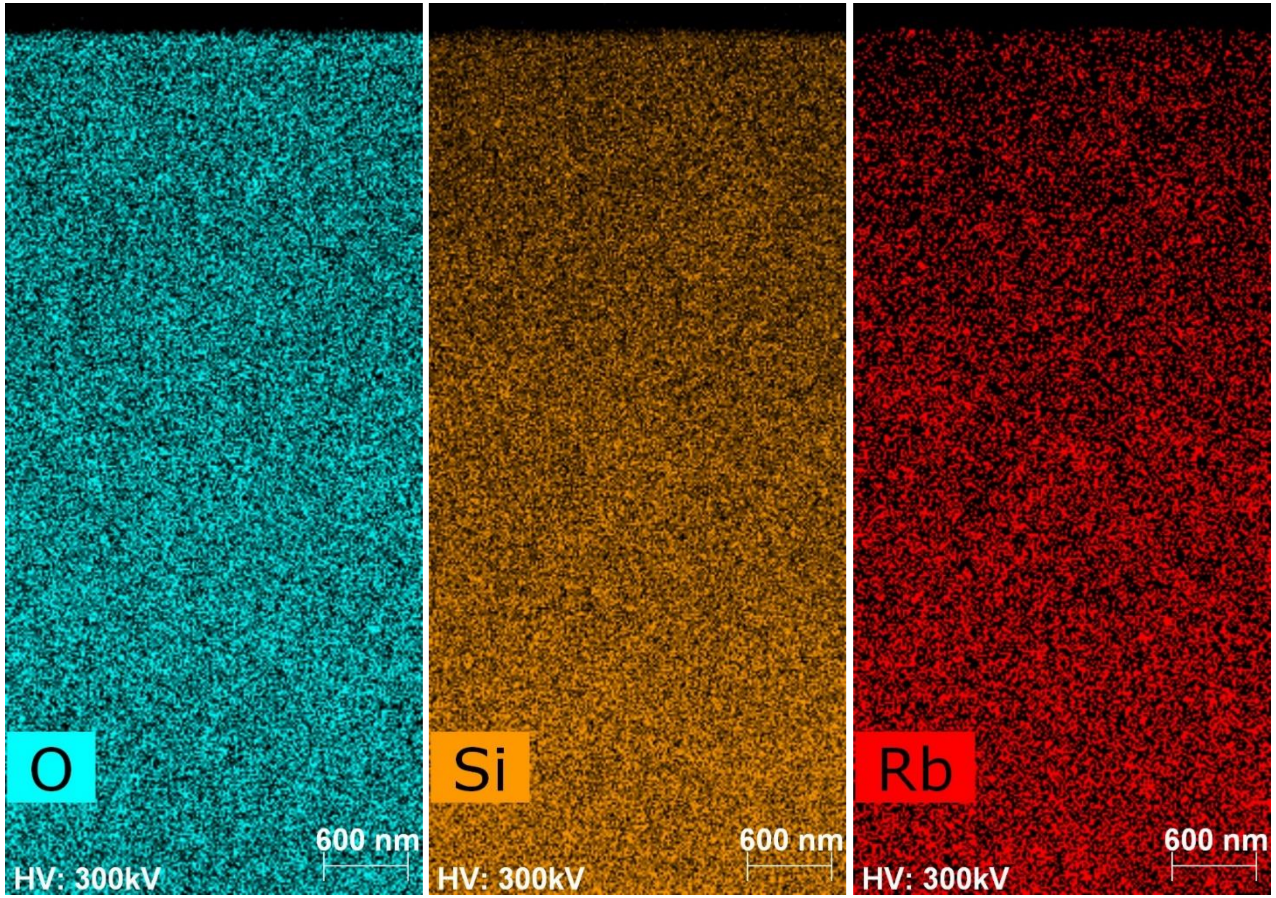
How it Started

STEM-EDX Corrosion Studies

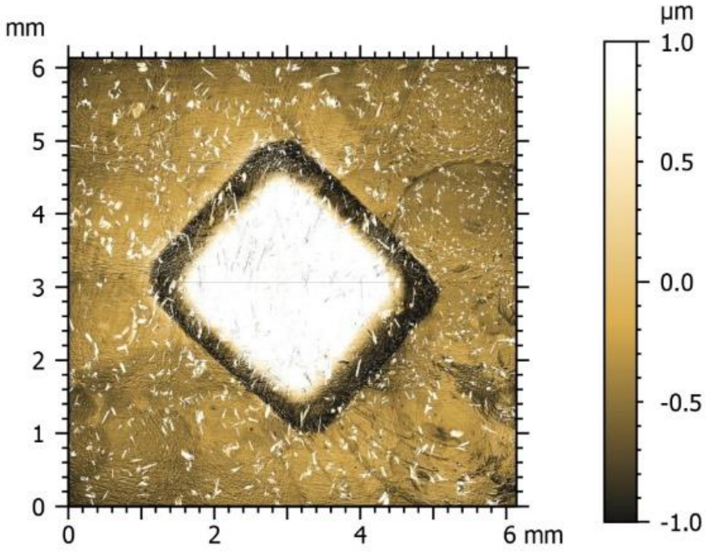


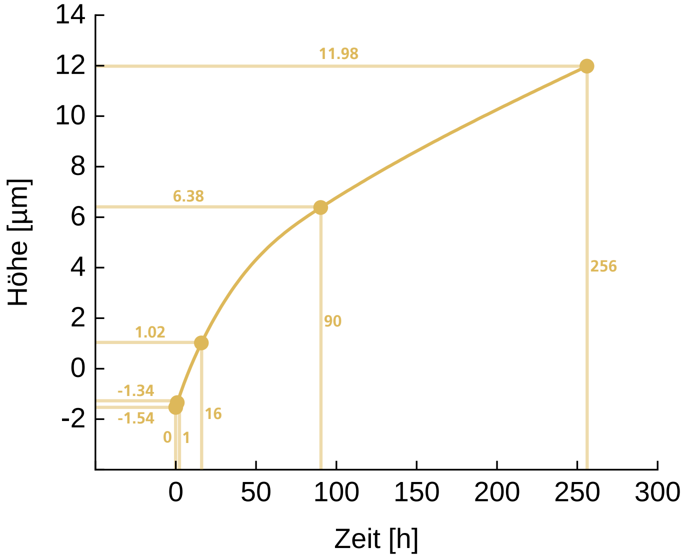


- TEM cross section also revealed some interface a few microns below the surface.

How it Started

White Light Interferometry





- Wight light interferometry was used to measure the depth of the ToF-SIMS crater (crater depth vs. sputter time)
- The crater did not have a depth, but a *height* -> problem of different refractive indices?
- Mechanical profilometry and WLI after metal coating of the surface proved the effect.

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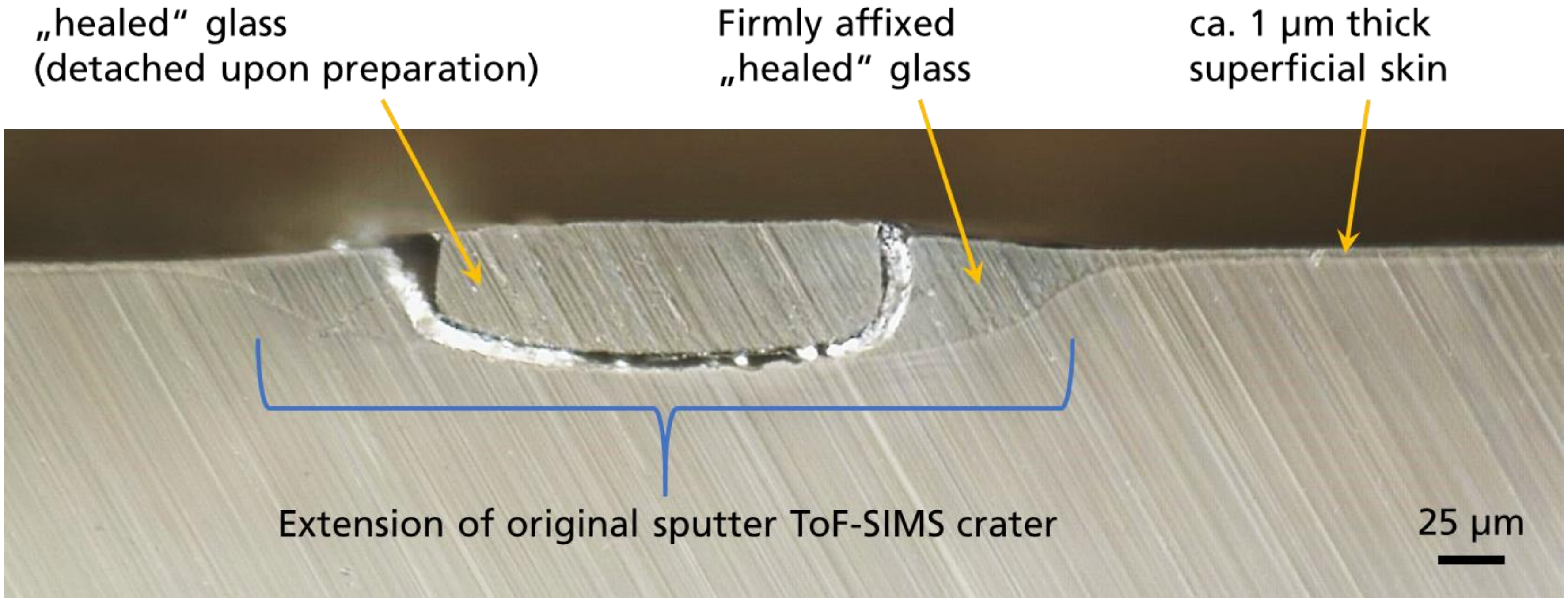
How it started

Cross section



- Optical cross section of the surface skin and the recovered volume of a superficially harmed (ToF-SIMS depth profiling down to a depth of ca. 3 µm) *80* SiO_2 */ 20* Rb_2O glass

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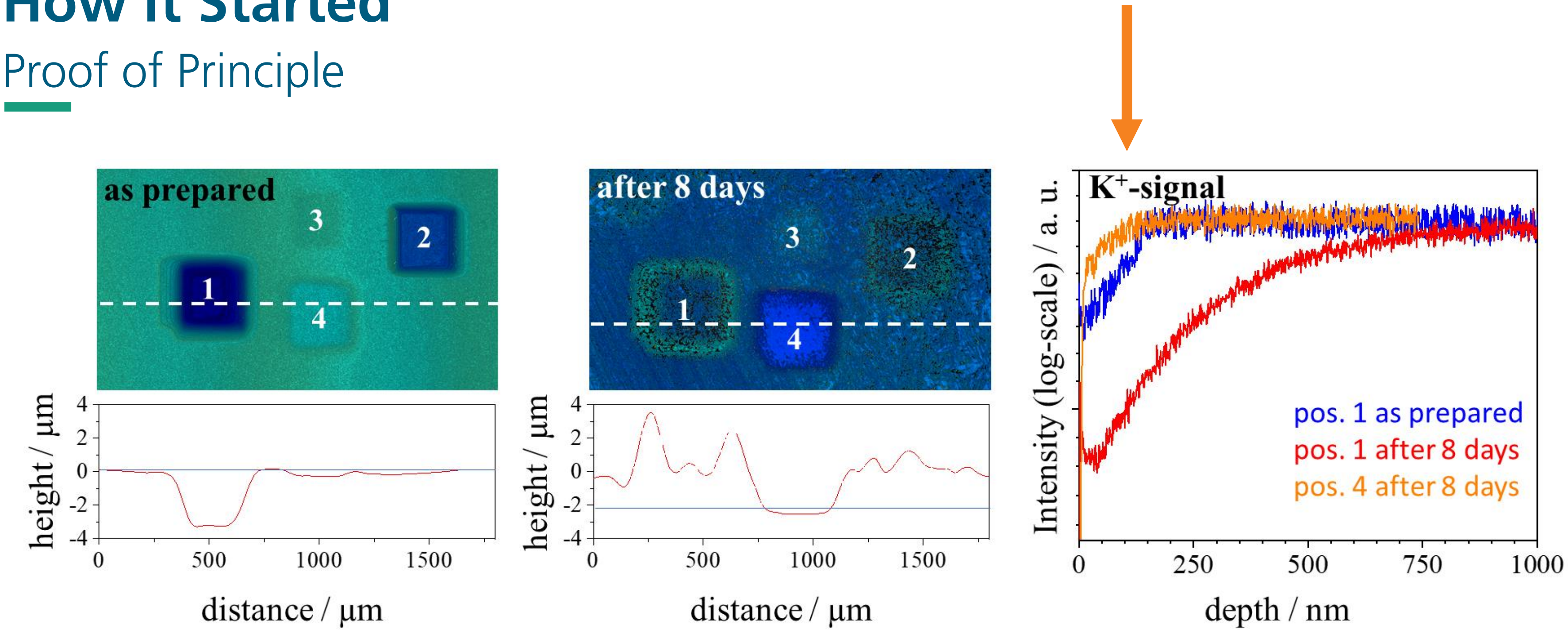
How it Started

Self Healing Glass Surface – possible explanation

- Rubidium silicate glasses are known to be highly hygroscopic.
- Therefore, contact with humidity was controlled in many ways:
  - Dry (bubbling with dried Argon) and standard melting of glass
  - Preparation of surfaces and cross-sections w and w/o water
  - Storage in exicators
- IR spectroscopy is a tool to measure the water content in glass.
- Glasses that are molten dry have the tendency to take up water afterwards.
- Upon this water uptake, the glass forms a skin that acts as a barrier against continued water uptake.
- Injuring this skin brings buried glass (that did not take up water so far) in contact with water vapor, resulting in self healing.
- **The effect is particularly pronounced for SiO_2 – Rb_2O glasses, but likely to occur in other alkali silicate glasses (in a lesser amount) as well.**

How it Started

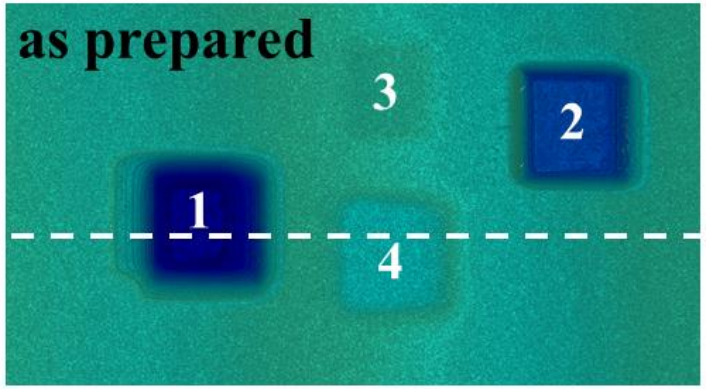
Proof of Principle

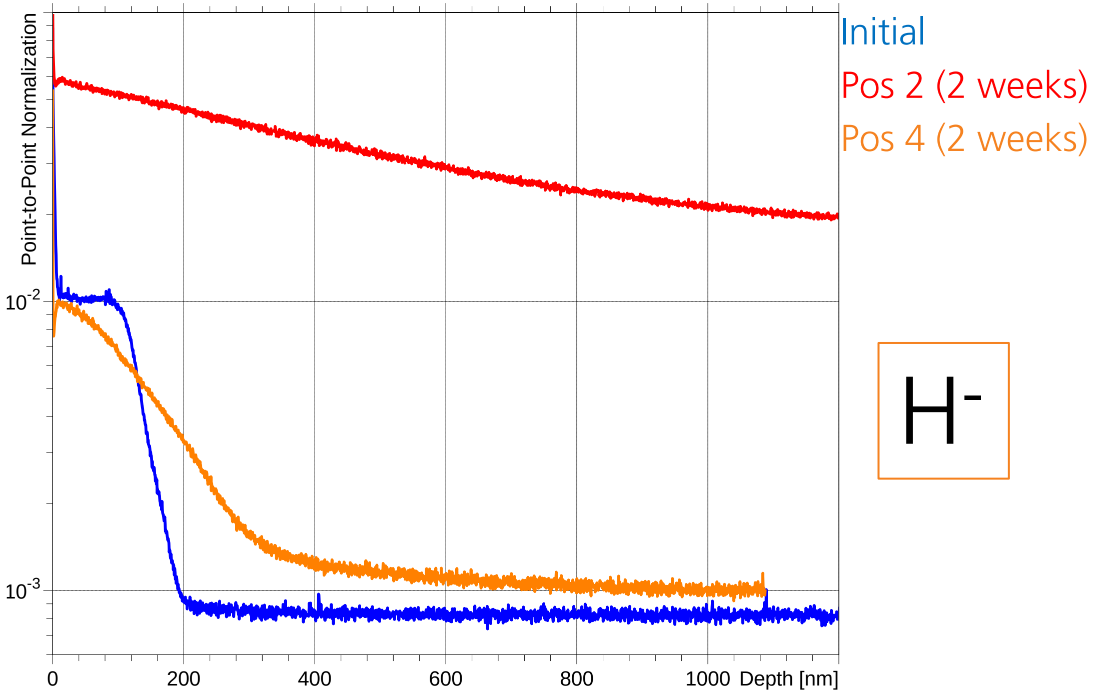


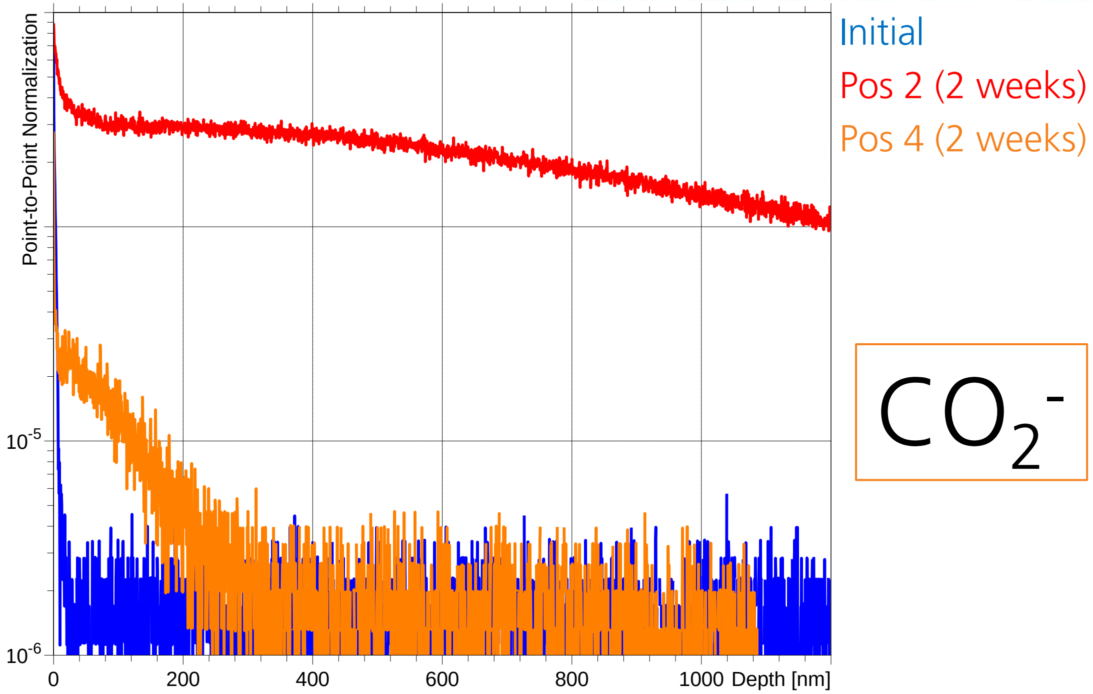
pos.	sputtering ions	depth (as prepared)
1	O^{2+}	3070 nm
2	Cs^{+}	1613 nm
3	Cs^{+}	36 nm
4	O^{2+}	139 nm

- Not just dry-molten 80 SiO_2 – 20 Rb_2O glass is prone to superficial changes after hurting the glass skin.
- Also less “exotic“ glass compositions, like 75 SiO_2 / 25 K_2O glass, show self-healing (crater 1&2).
- At depth profiling position 4, oxygen ions were used to sputter a ca. 140 nm deep excavation. The depth of the excavation exactly corresponds to the thickness of the glass skin after gentle corrosion.
- Within 8 days, this sputter crater did not show degradation nor healing (K depletion, water take-up etc.).

How it Started
Proof of Principle







- Initial depth profiling of craters #2 & #4 compared to signal after 2 weeks: complete removal of surface layer leads to a pronounced water and CO2 uptake.

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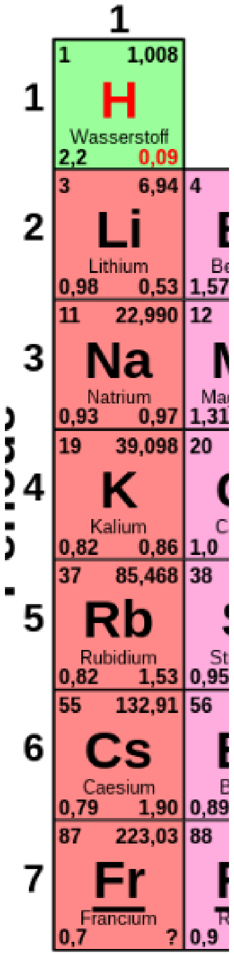
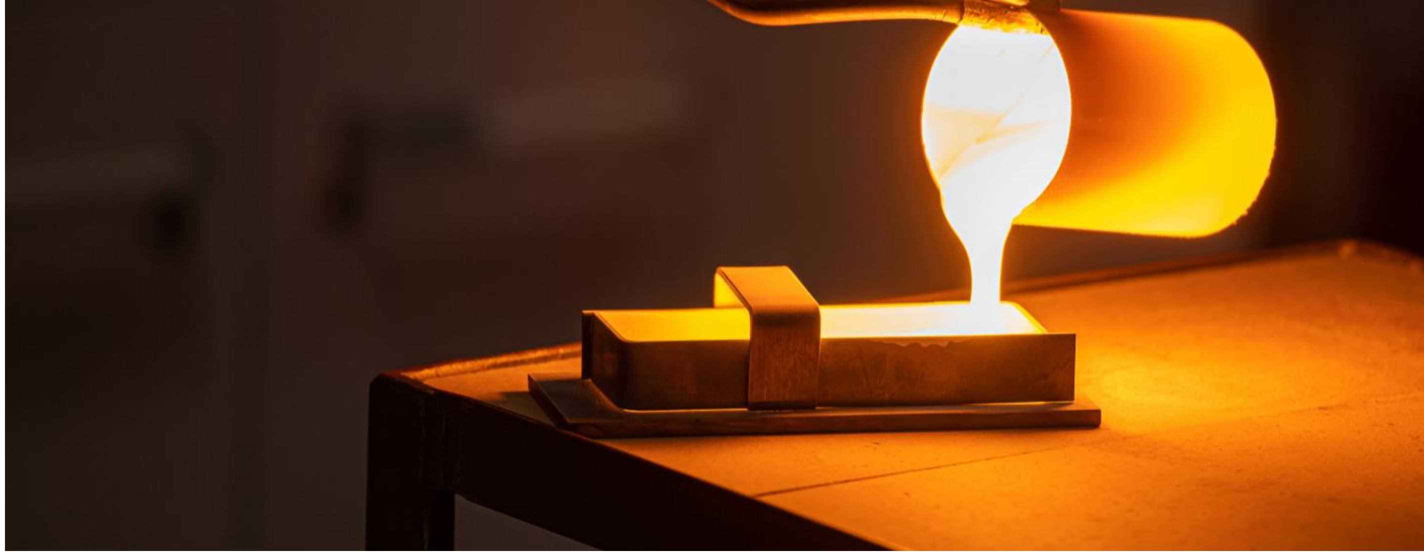
And Now?

Variation of Material Systems





- The properties of a glass are dominated by the stoichiometry of its oxide components. However, even at temperatures above 1000 °C, water is incorporated into the structure (OH-), typically between 300 ppm and 400 ppm.
- “Thirsty” glasses can be produced by bubbling (<10 ppm) with dried Ar.
- As Rb_2O-SiO_2 is quite exotic, other alkali-containing glasses have to be tested (Na, K).
- Variation of Rb_2O (or Na, K) content and water content.
- Necessary: characterization of produced glasses (DSC, IR…).

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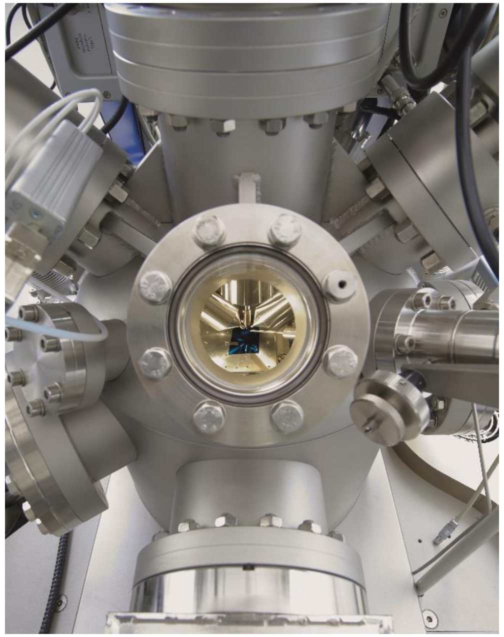
And Now?
Variation of Damage



- Ion species (O, Cs, Ar, Ga, Xe, Kr), energy and sputter depth.
- Laser damage (ablation or local melting).
- mechanical scratching or tribological testing.

- **Mechanism of the formation of new material to form a flat (healing) or convex (structuring) surface?**

Summary

- A very "thirsty" hygroscopic glass was produced at IMWS (Rb_2O-SiO_2), showing an unknown and unexplained behavior after the surface was "damaged" by ToF-SIMS depth profiling.
- The crater with a depth of a few µm "healed" itself in just a few days.
- The effect could be reproduced using Ar (ToF-SIMS) and Xe (plasma FIB) ions.
- A local removal of material leads to the formation or growth of new glass at the surface, not limited by the initial surface.
- Microstructural analysis (STEM-EDX) do not show measurable differences in the glass stoichiometry of the healed area, compared to undamaged regions.
- The stress induced by preparation and analysis of the samples did not show significant differences between the new grown glass and the bulk material, indicating comparable durability.
- The effect could successfully be translated to another hygroscopic alkali glass system (K_2O-SiO_2).

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Outlook

- FhG-internal Discover project @IMWS.
- The effect is particularly pronounced for SiO_2 – Rb_2O glasses, but likely to occur in other alkali silicate glasses (in a lesser amount) and in SiO_2-Rb_2O glasses with lower R_2O-content as well.
- Changing the stoichiometry influences the growth of the healed surface. Thus, healing of scratches without "overgrowing" should be possible (smarter self healing).
- Optically active structures can be thought of by defined injury of a suitable glass. Upscaling?
- Role of CO_2 to be clarified.
- SiO_2 – Rb_2O glass coating might be an unconventional way to protect arbitrary glass surfaces from breaking (instead of imposing strain by ion exchange).

Contact

Dr. René Feder
Microstructure of Optical Materials
Tel. +49 345 5589-274
Fax +49 3455589-101
rene.feder@imws.fraunhofer.de

Fraunhofer IMWS
Heideallee 19
06120 Halle (Saale)
www.imws.fraunhofer.de

Equipment

Microstructure Diagnostics

Preparation

Grinding
Polishing
Embedding
Sawing
Laser machining
Coating

SEM (4x)
SEM/FIB (7x)

EDXS
WDXS
EBSD
EBAC & EBIC
Ga^{+}- & Xe^{+}-FIB
Nano probing

S/TEM (3x)

EDXS (0,8 & 2 sr)
EELS
Nano diffraction
aberration corrected
60 – 300 kV
„single e^{-} detection“

ToF-SIMS (2x)

Depth profiling
Gas cluster ion source
Cryo- & heating option
Polymer analytics

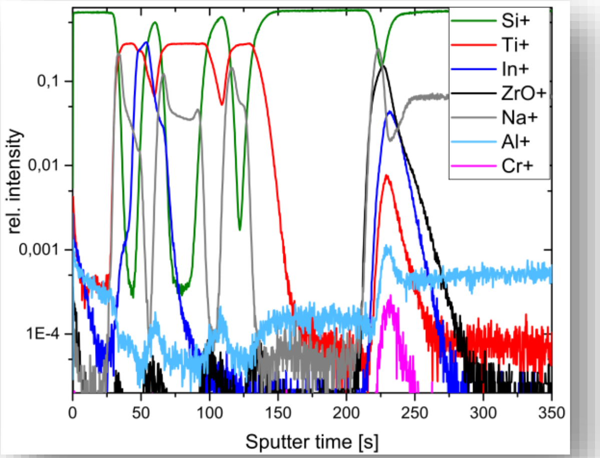
XPS

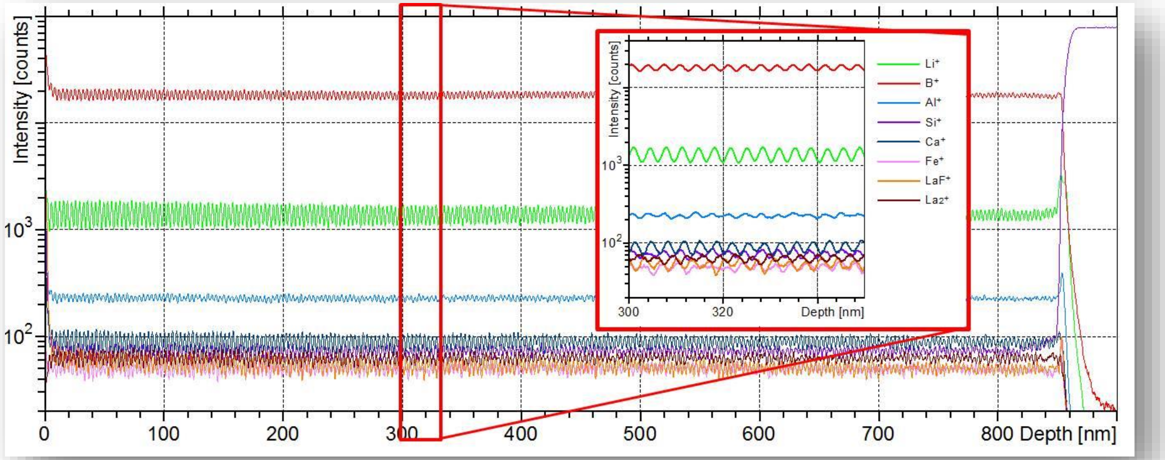
Chemical composition
Bonding stages

Optical Coatings

Typical Failures and Analysis Techniques: ToF-SIMS

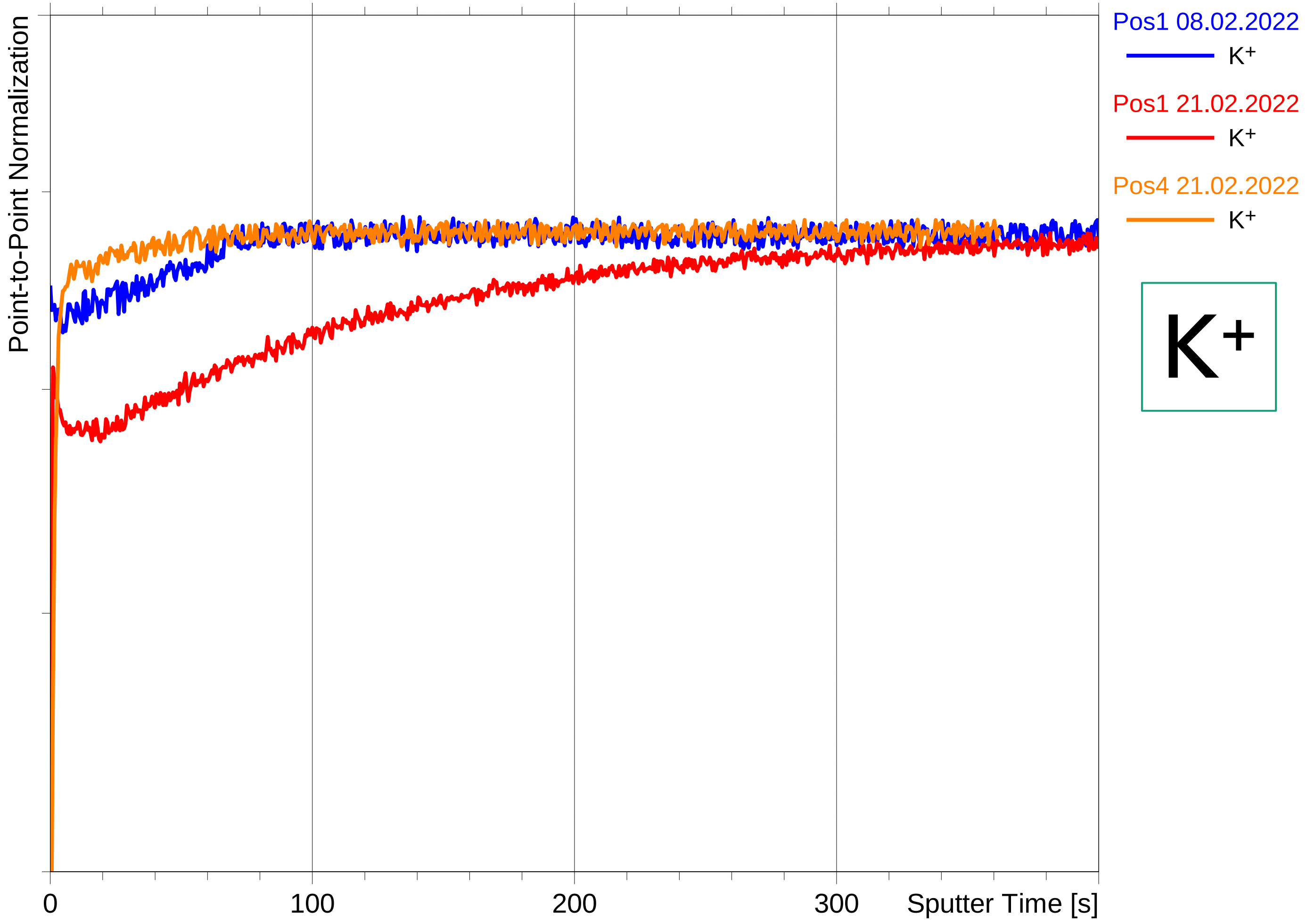
- Time-of-flight secondary ion mass spectrometry: elemental and molecular composition of a surface with detection sensitivity in ppm-ppb region.
- Depth profiling via combination with different sputtering ion beams.
- Lateral resolution < 100 nm, depth resolution ~ nm.
- Detection of (interface) contaminations, interdiffusion and spurious elements.
- GCIB (organics) and cryo options available.



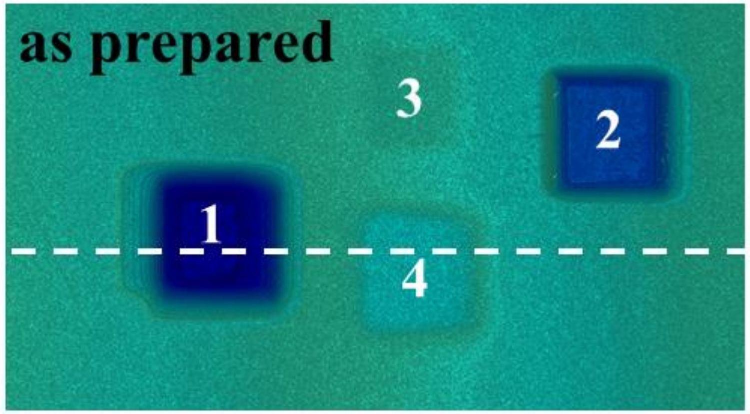


Depth Profiling, 0 – 400 s (≈ 820 nm)

Pos. 1 (pristine) = Reference vs. Pos. 1 (13 days later) vs. Pos. 4 (flat excavation, 13 days later)



- Alle signals shown here and herafter are normalised to the total intensity.



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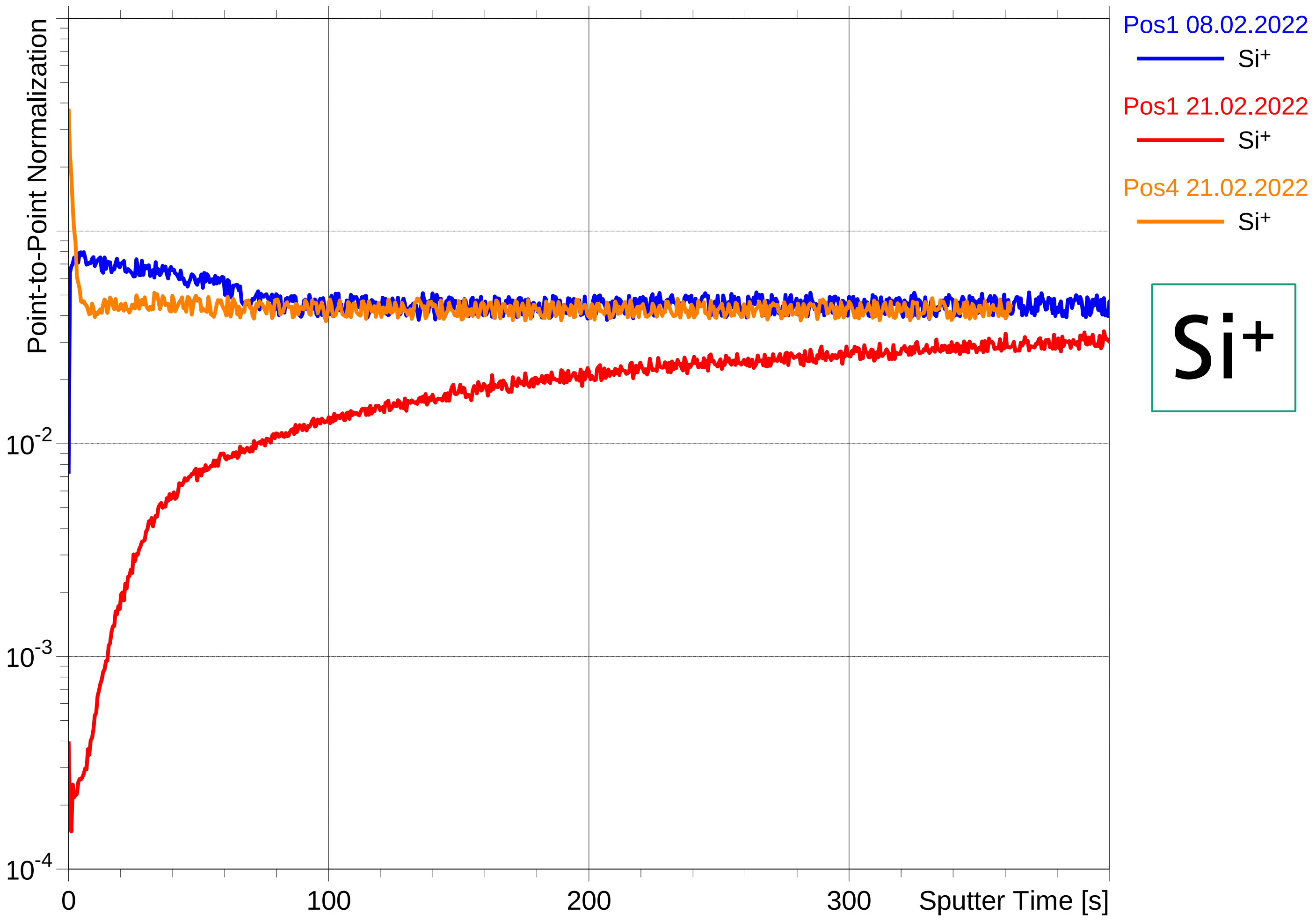
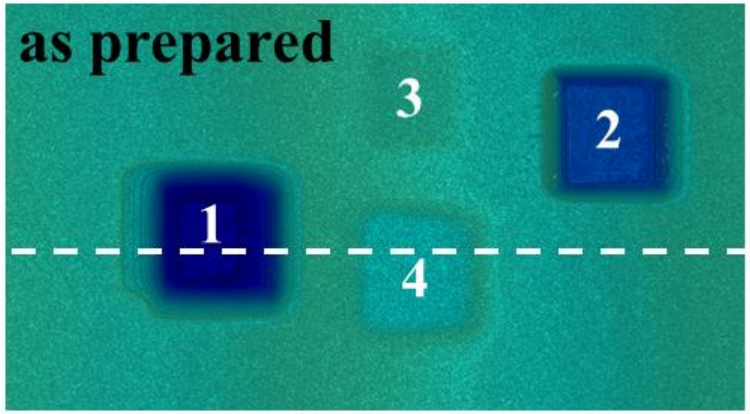
Depth Profiling, 0 – 400 s (≈ 820 nm)

Pos. 1 (pristine) = Reference vs. Pos. 1 (13 days later) vs. Pos. 4 (flat excavation, 13 days later)



- Superficially, the smooth surface of position 4 features the highest silicon intensity.
- The latter steeply drops within the first ~ 20 nm below the surface in a constant level



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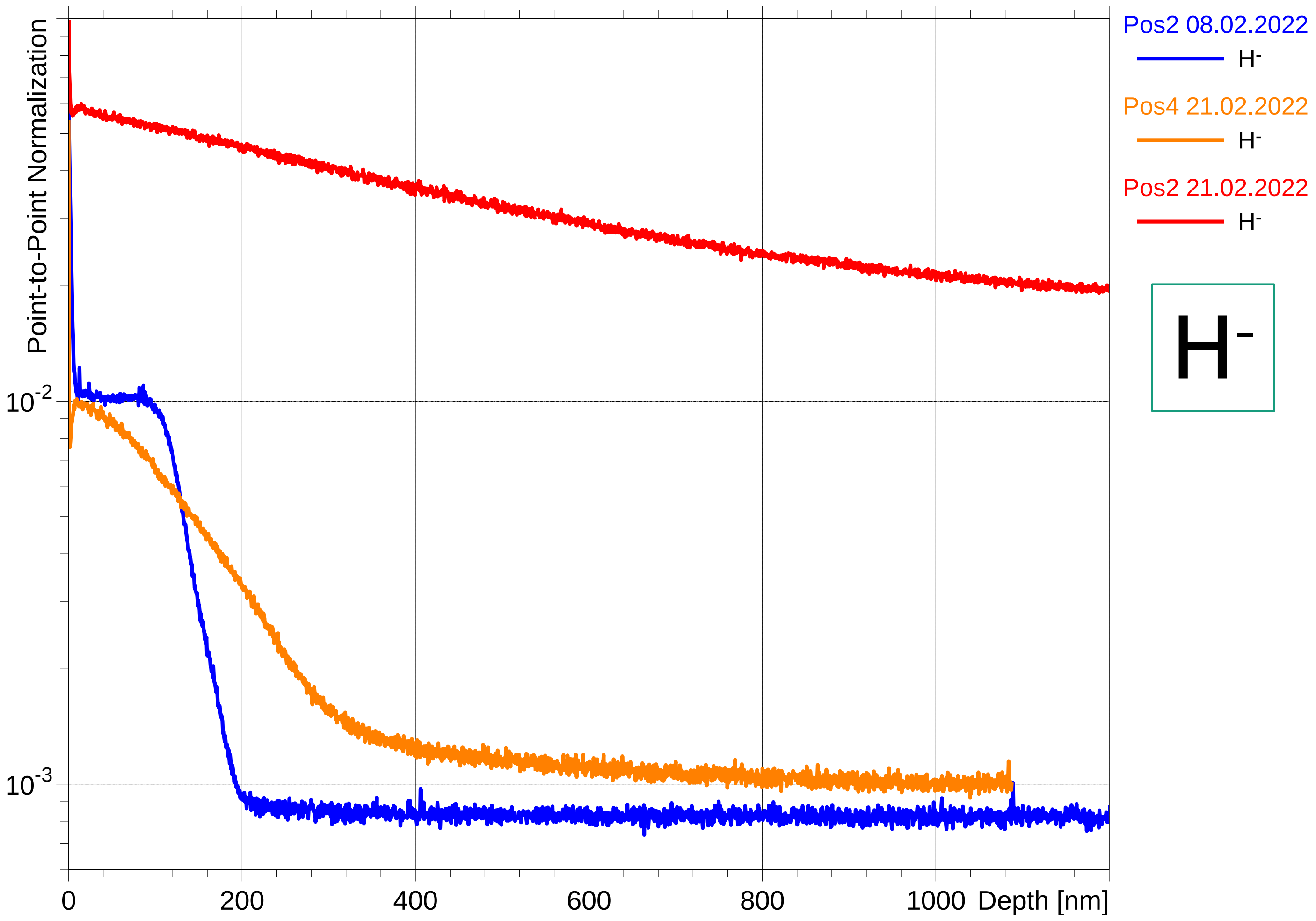
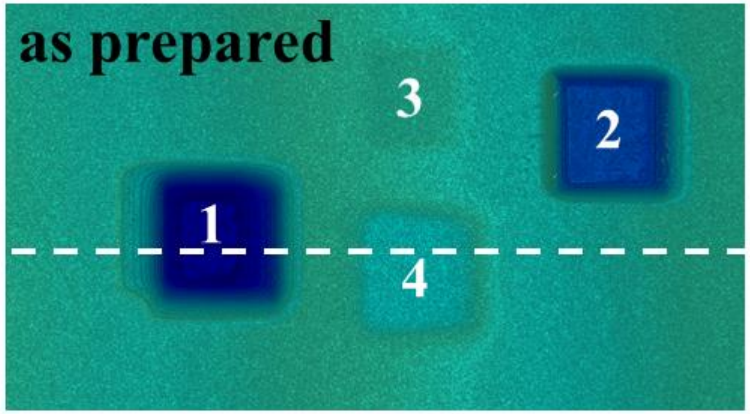
Depth Profiling, 0 – 1200 nm

Pos. 2 (pristine) = Reference vs. Pos. 2 (13 days later) vs. Pos. 4 (flat excavation, 13 days later)



- In the pristine surface, the H signal is enriched within the topmost 10 nm, goes into a plateau going 150 to 200 nm below the surface and approaches than a one order of magnitude lower bulk level
- After ageing, the freshly formed surface features a much increase H content



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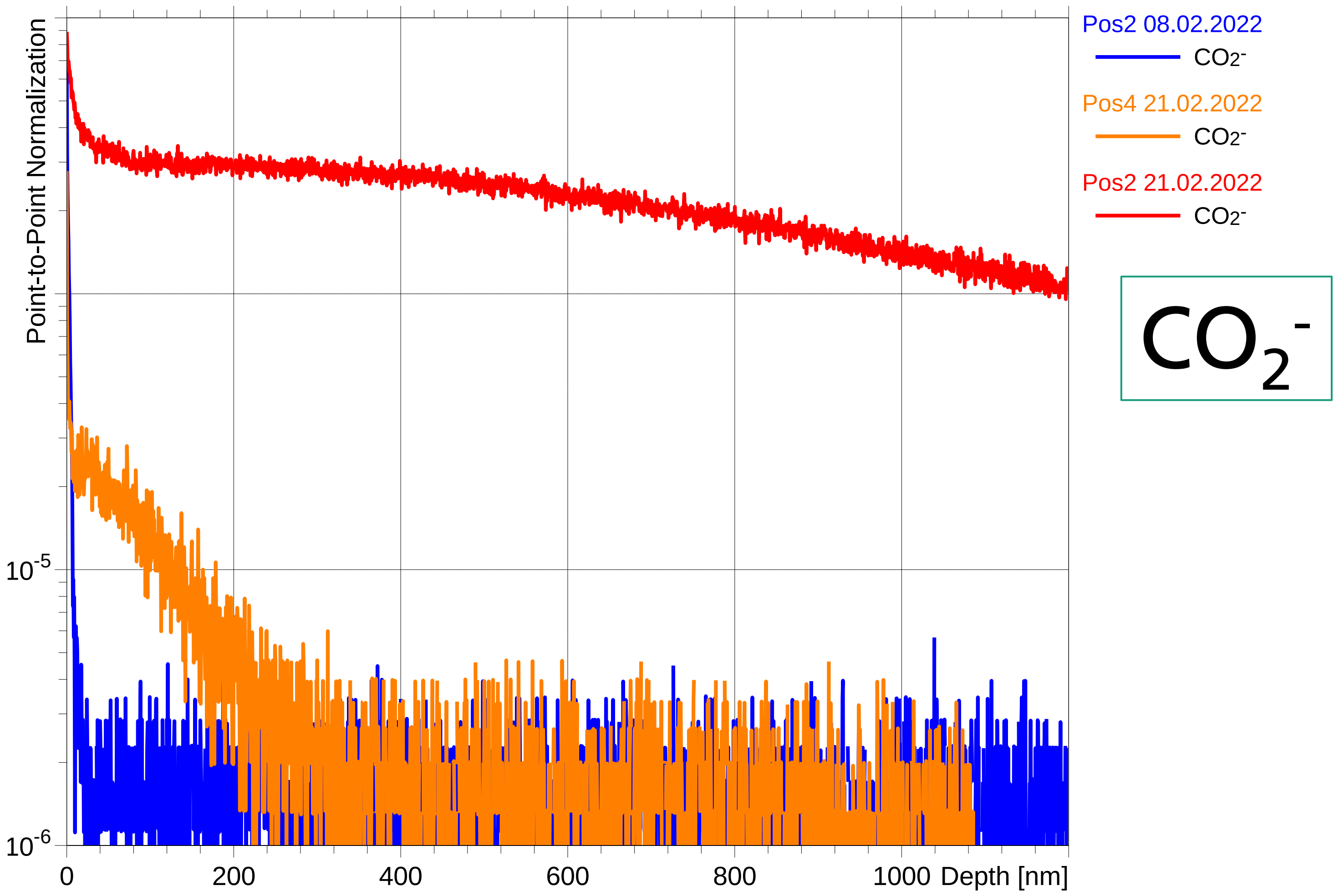
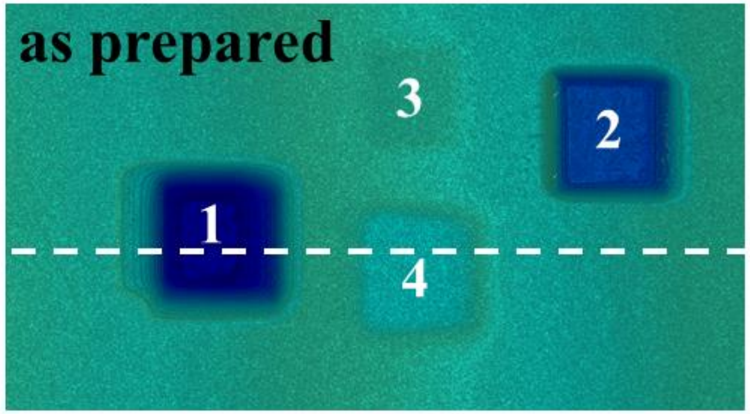
Depth Profiling, 0 – 1200 nm

Pos. 2 (pristine) = Reference vs. Pos. 2 (13 days later) vs. Pos. 4 (flat excavation, 13 days later)



- Incorporation of CO_2 after removal of 1,6 µm by Cs^+ sputtering
- Much reduced CO_2 incorporation after 140 nm O^{2+} sputtering.



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