Hydrophobicity Patterning of Gas Diffusion Media for Polymer Electrolyte Fuel Cells

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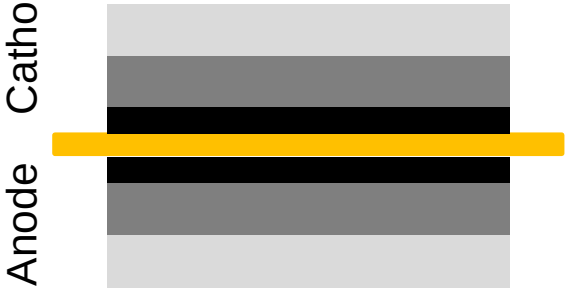
Outline

Water Management and the Role of the GDL
Analytic tools
Heterogenous Modifications
Methods of Irradiation

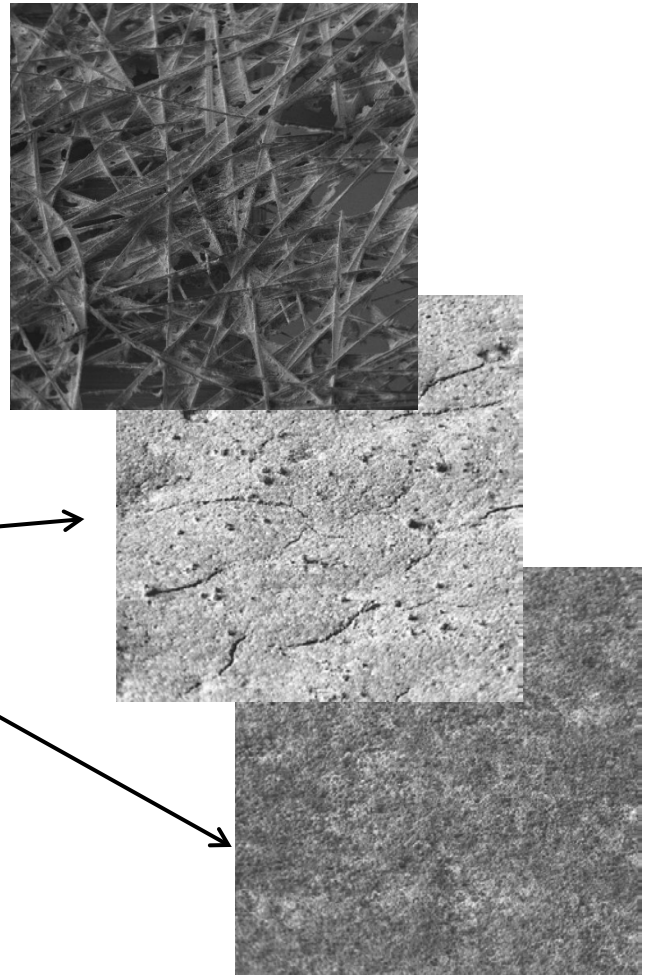
- Mechanical stressing/damaging
- X-ray
- Ion beam modification
- Chemical modification
- Laser
- …

Feasibility

Polymer Electrolyte Fuel Cells



Carbon fiber paper
Microporous layer
Reaction layer
Membrane
Reaction layer
Microporous layer
Carbon fiber paper



SEM: 3x3 mm

Water Management and the Role of the GDL

Concurrent requirements need a fine balance of hydrophobicity

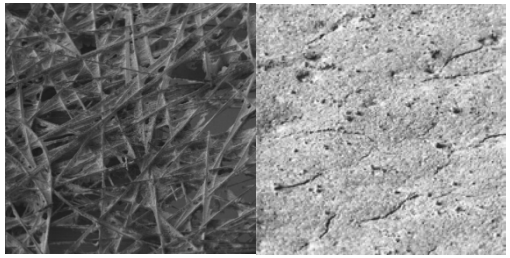
condensing droplets

excess product water

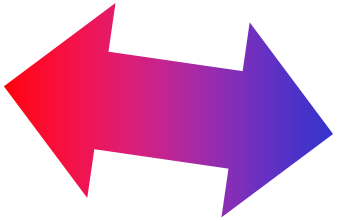
Gas diffusion media:
ideally dry
free pores
high gas diffusivity
high cell performance

complete flooding

blocked reactant pathways



GDL backing MPL



charge transporter depletion

current limitation

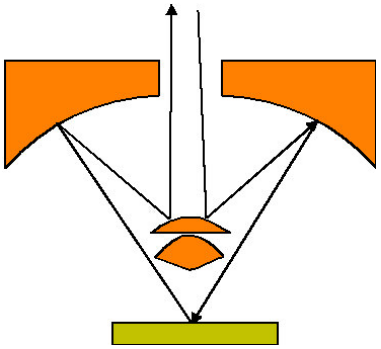
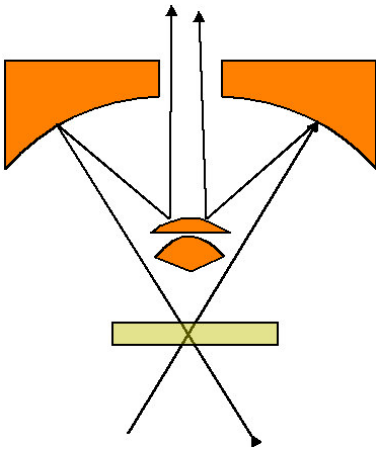
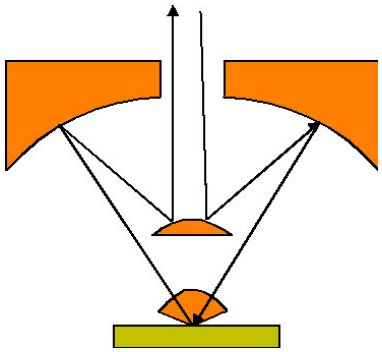
Membranes:
ideally humid
high proton mobility
high current densities possible
high cell performance

cracks

irreversible cell breakdown

Simulation: Laterally heterogeneous hydrophobicity is advantageous

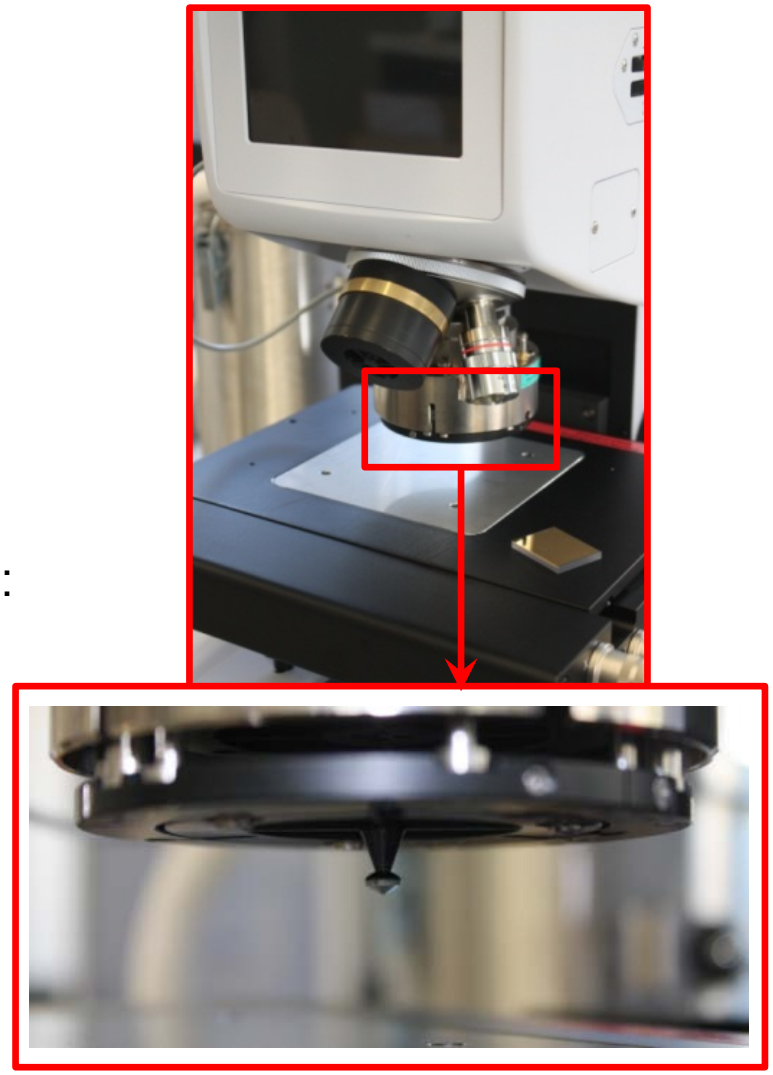
Infrared Spectro*micro*scopy

Reflection	Transmission	Attenuated total reflection (ATR):
		
weak signal on dark samples	Bulk information, transparent samples, e.g. membranes	~5 µm surface information, sample contact – damage possible

Infrared Spectro*micro*scopy

- Single HgCdTe (MCT) detector:
Lateral resolution ~30 µm
XY stage → large scale mapping

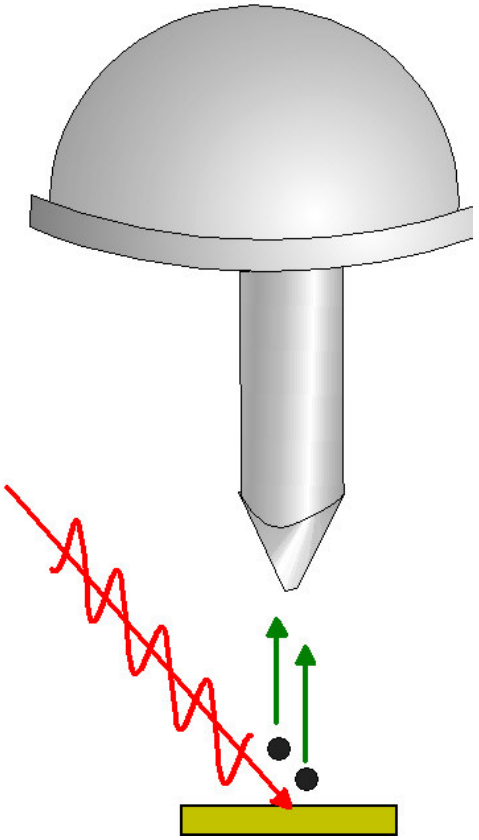
- Imaging focal plane array (FPA) detector:
Lateral resolution ~1 µm
→ small scale mapping



IR microscope with
Ge ATR-Crystal

X-Ray Photoemission Spectroscopy

- Excitation of core level electrons with x-rays (~1-1.5 keV)
- Emission core level electrons
- Analysis of excess energy
- Detection of elements
- Detection of chemical state
- Surface sensitivity <10 nm
- Ultra high vacuum necessary
- X-Ray damage possible



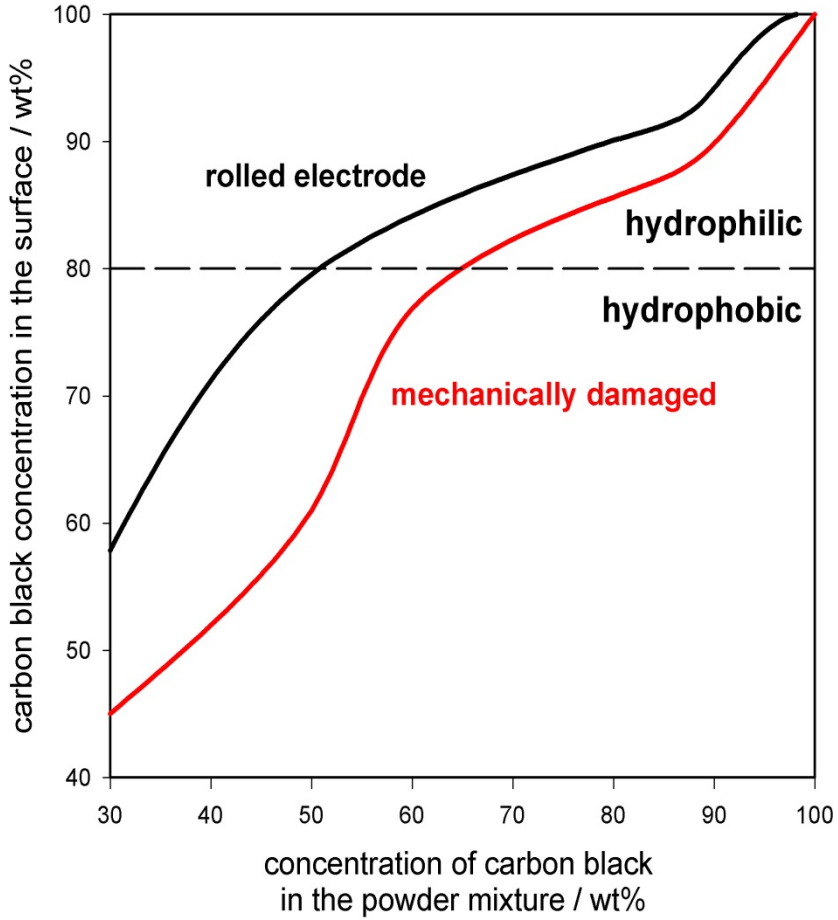
Carbon black content [wt%]	Wetting behavior of non-stressed surface	Wetting behavior of mechanically stressed surface
30	Hydrophobic	Hydrophobic
40	Wetted by liquid water, not by water vapor	Hydrophobic
50	Wetted by liquid water, not by water vapor	Hydrophobic
60	Wetted by liquid water, not by water vapor	Hydrophobic
70	Hydrophilic	Hydrophilic
80	Hydrophilic	Hydrophilic
90	Hydrophilic	Hydrophilic
100	Hydrophilic	Hydrophilic

-Correlation between PTFE-concentration in the surface determined by XPS and the hydrophilic/hydrophobic character

-carbon concentration at the surface of electrodes prepared from different mixtures of carbon black and PTFE

-➢ hydrophilic surface at carbon black concentrations above 80 wt%

-➢ hydrophobic surface at PTFE concentrations above 20 wt%



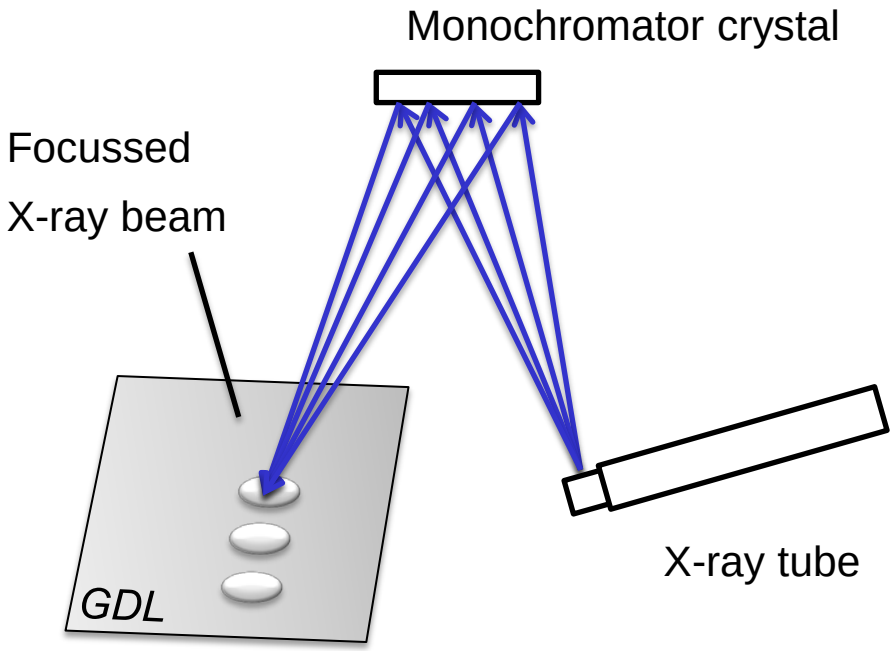
- distribution of PTFE ist important
- preparation process influences the PTFE distribution
- XPS measurements allow to assess the hydrophilic/hydrophobic character

X-ray irradiation

- Spot patterning
- Decomposition of PTFE: breaking of the C-F bond
- Reduced PTFE – C ratio

→ Reduced hydrophobicity

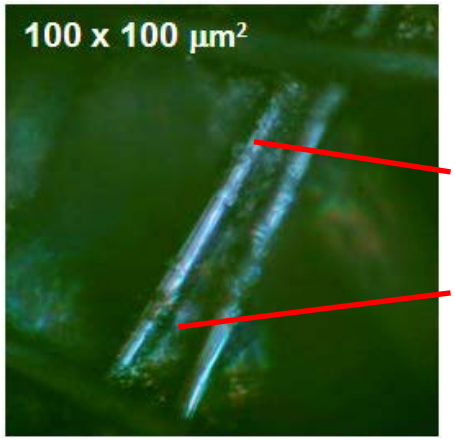
- Backing and microporous layer



(Al Kα, 1486,7 eV, 400 W, spot size ~0.8 mm)

Schulze et al., *XPS analysis of PTFE decomposition due to ionizing radiation*, Fresenius J Anal Chem 353 (1995) 778

X-ray irradiation

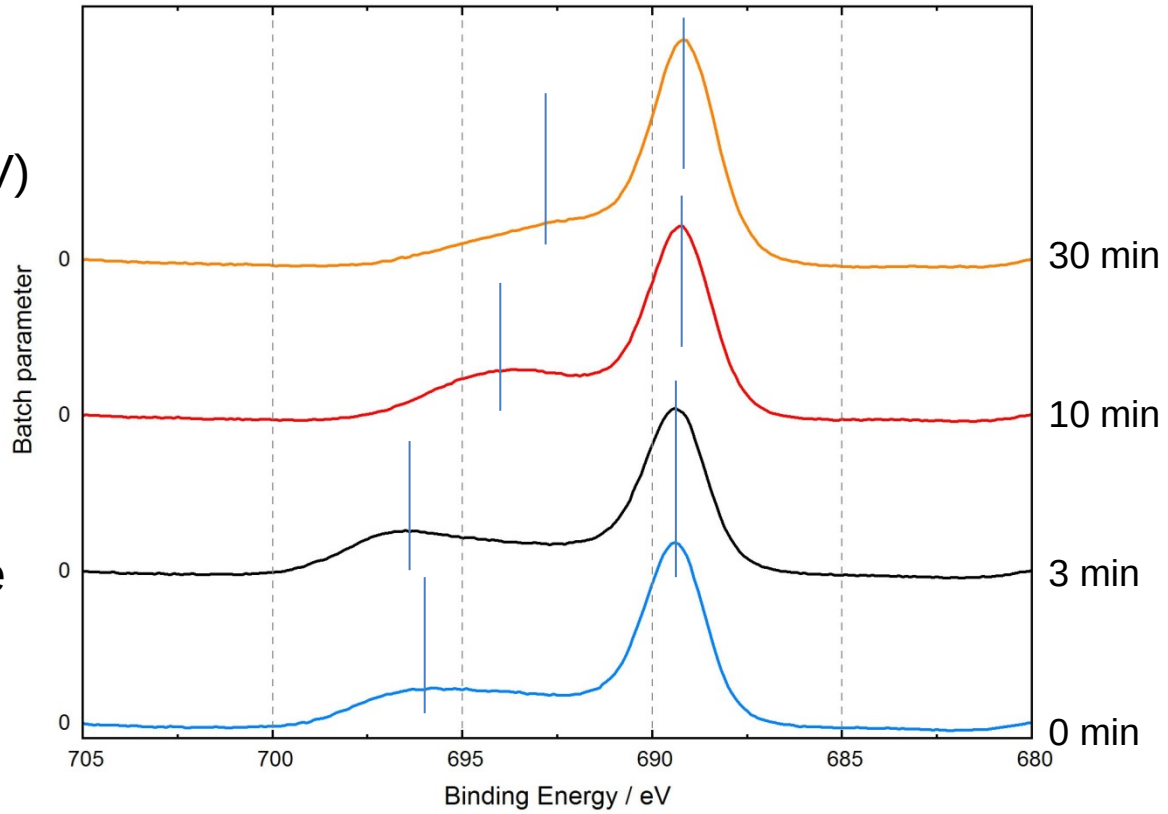


Small spot XPS analysis (GDL backing)

Fluorine 1s signal:
- Main signal (689 eV) slightly shifted

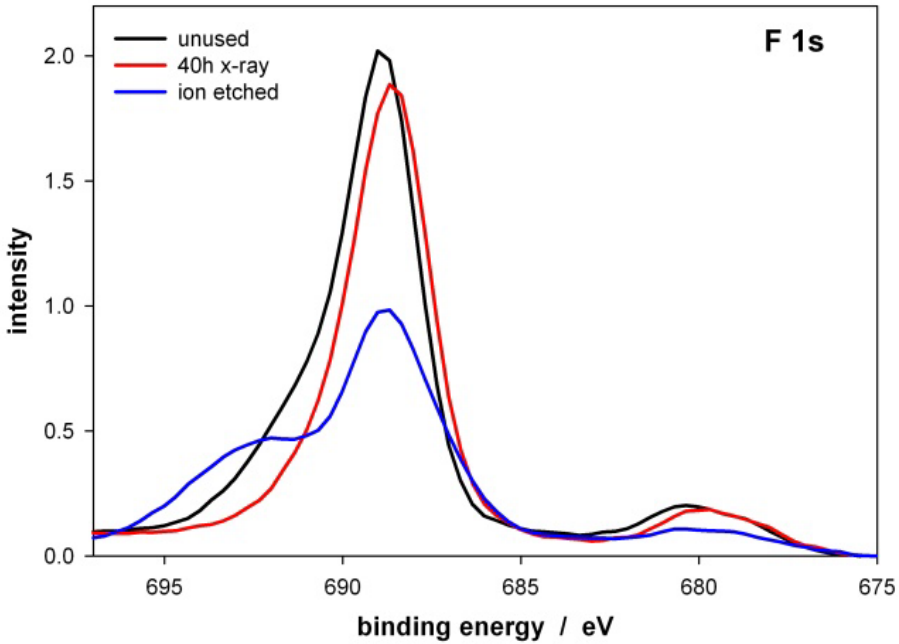
- Bysignal (696 eV): Charging reduced

Modification possible and scalable

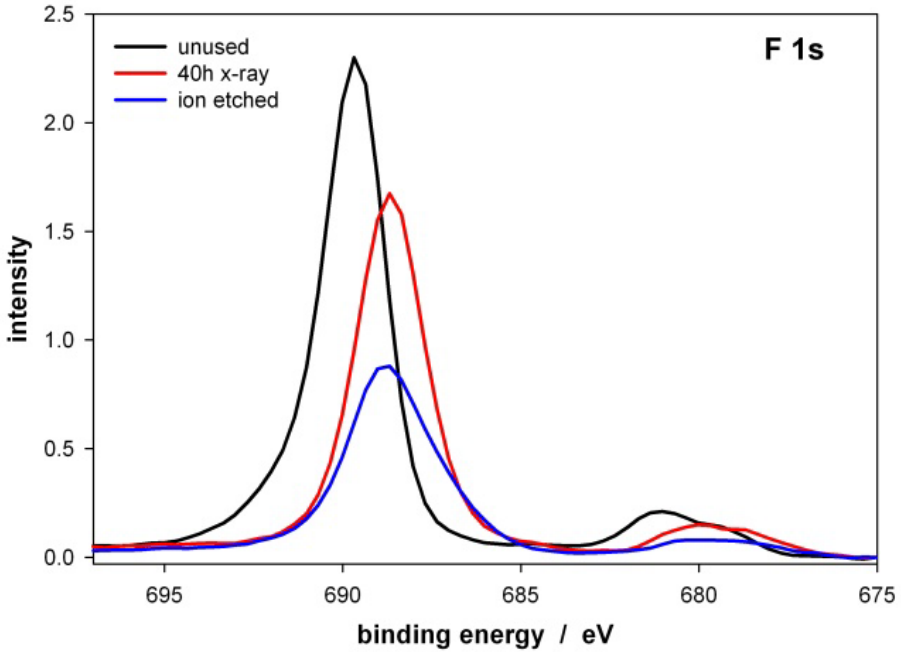


XP spectra F1s after exposure to ionizating radiation

GDL



MPL



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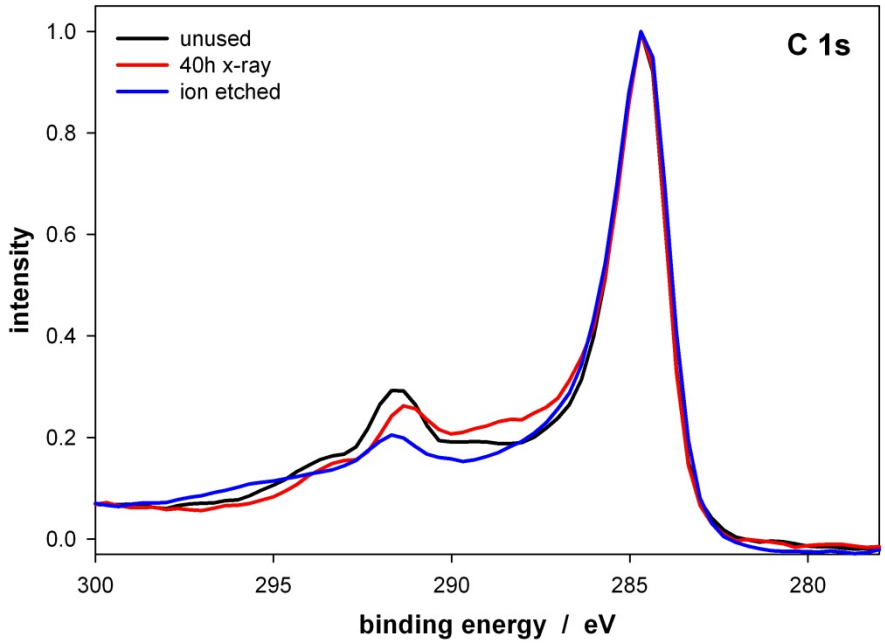

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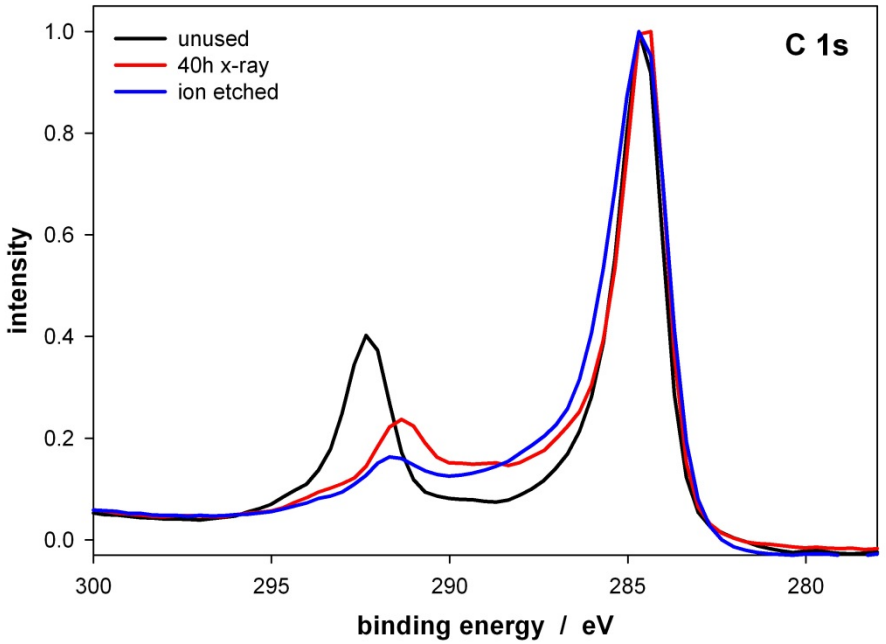
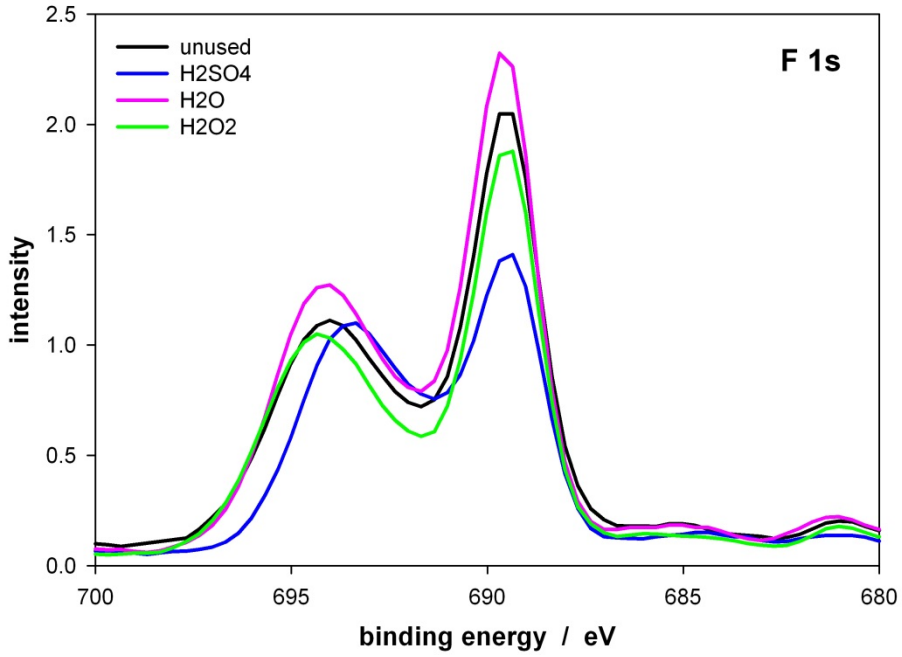
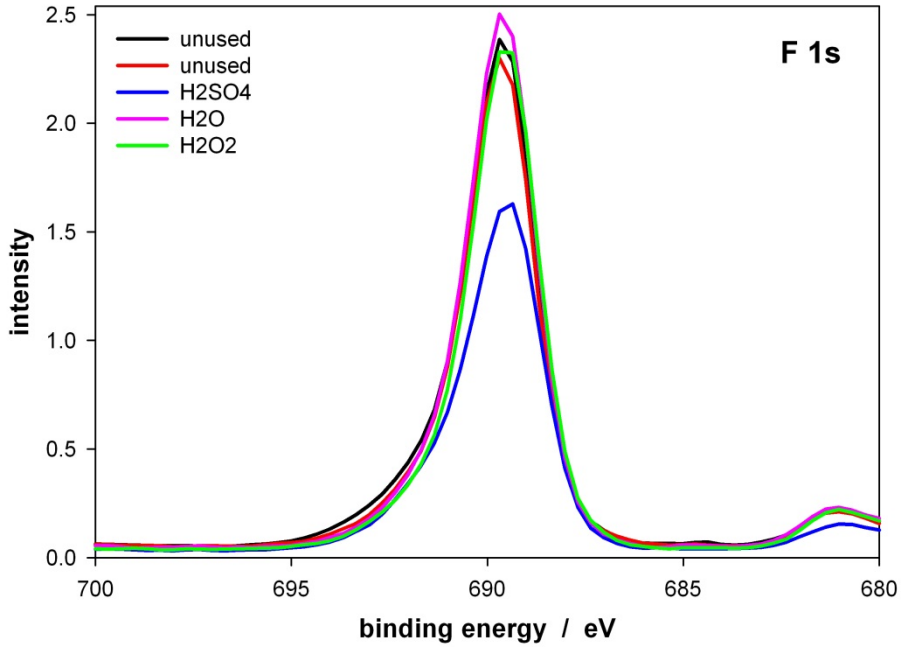


XP spectra F1s after chemical modification

GDL

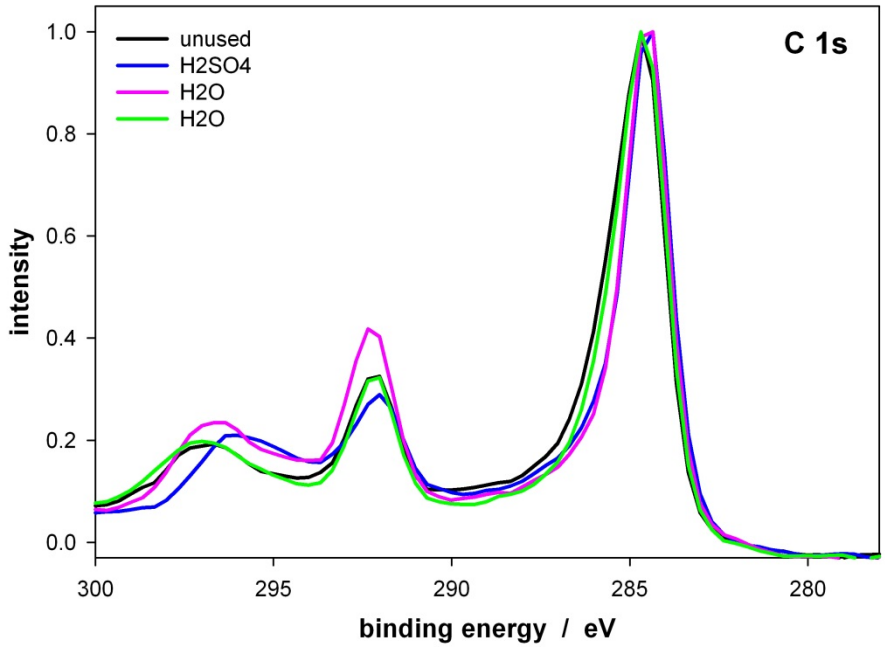


MPL



XP spectra C1s after chemical modification

GDL



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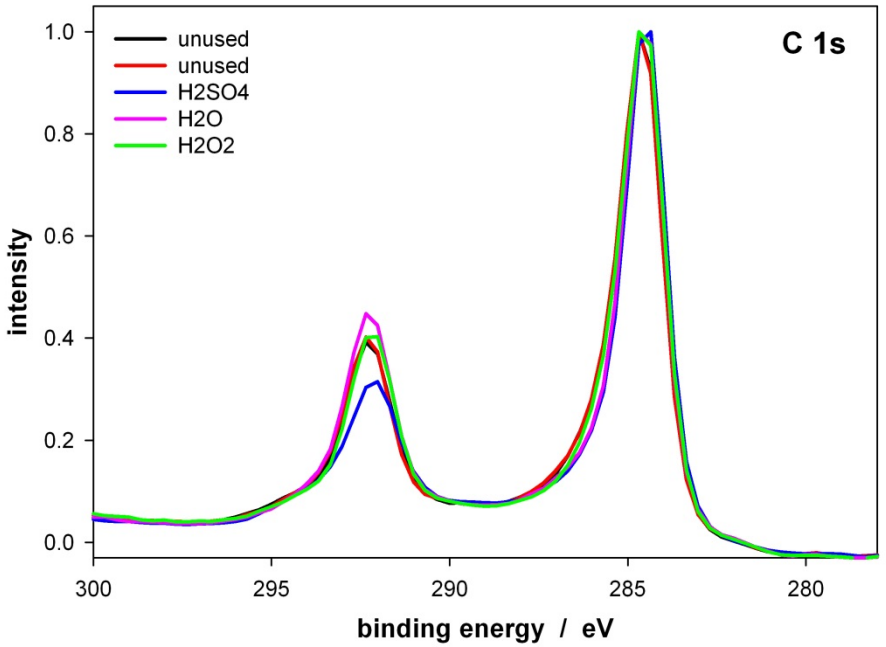
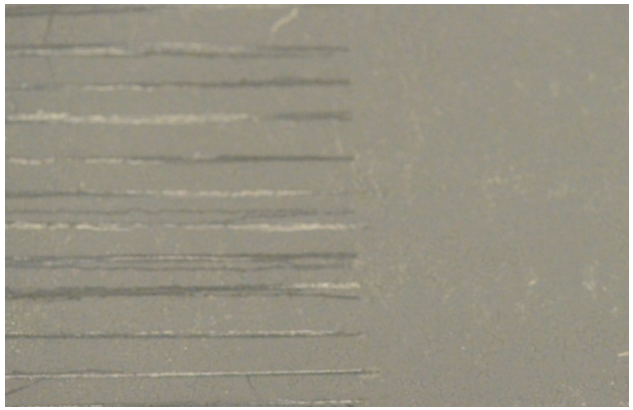
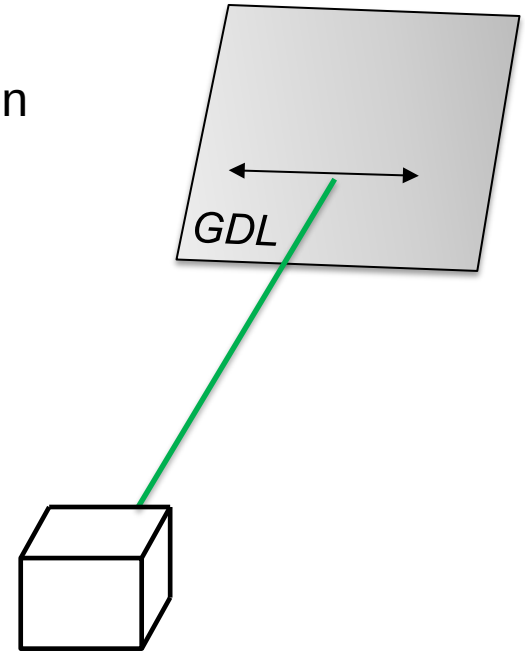


Laser irradiation

- Line patterning
- Thermal load
- Quick burning of MPL material → trenches
- Weak impact on GDL backing – heat dissipation



Partially laser irradiated MPL

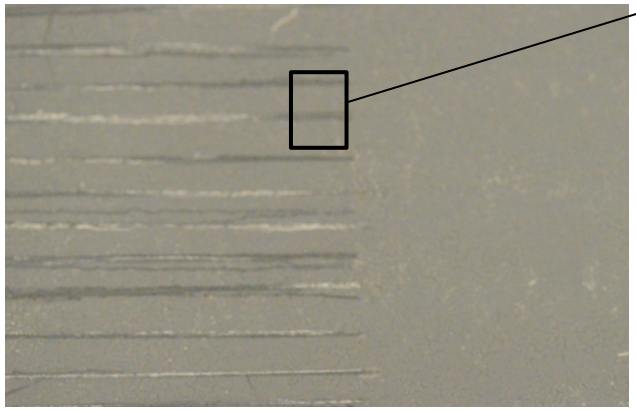


(532 nm, 400 mW)

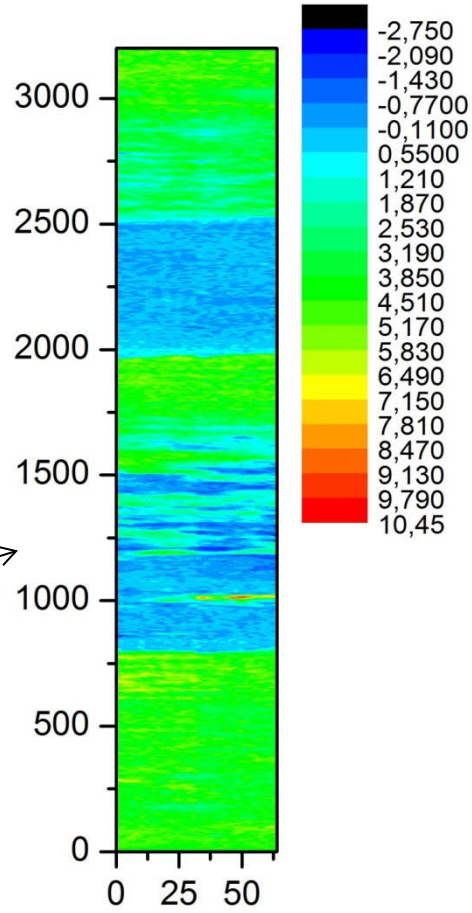
Laser Irradiation

MPL: Imaging IR absorption analysis

Intensity of C-F stretch vibrations missing inside trenches → no PTFE



Partially laser irradiated MPL

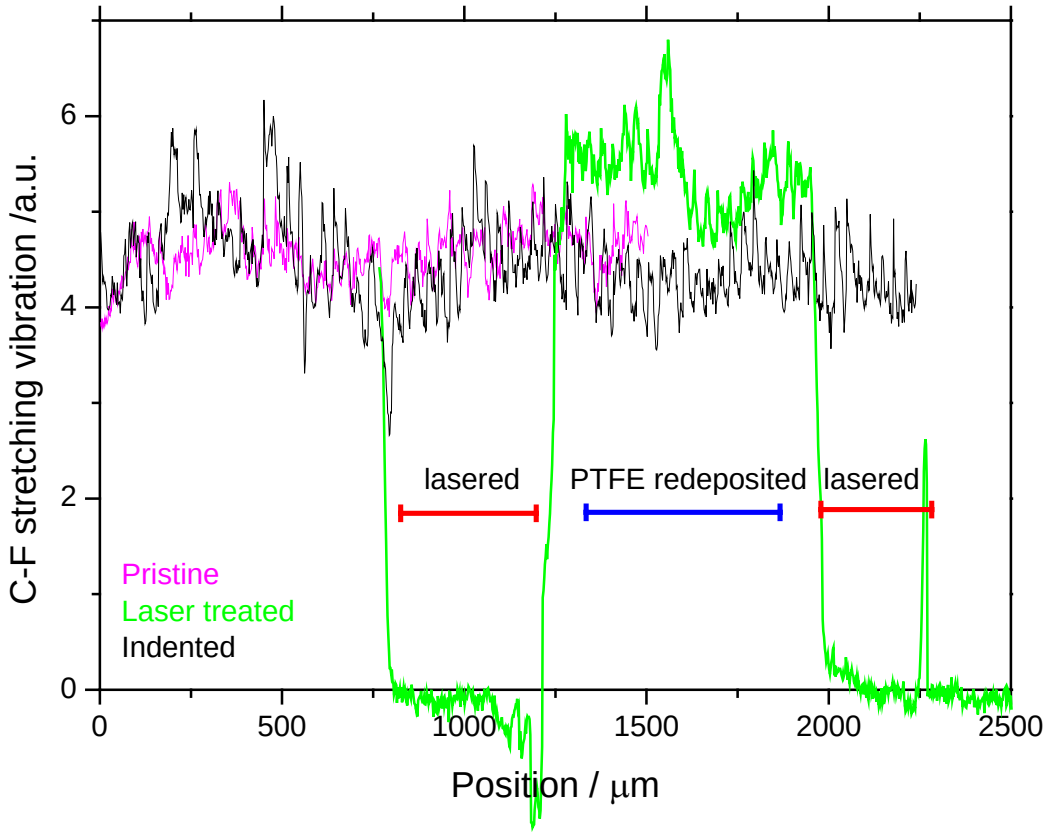


ATR-FTIR mapping of C-F stretch vibration

Laser irradiation

MPL IR absorption analysis

Line profiles:
-Zero PTFE in trenches
-Increased PTFE between trenches → redeposition
-No chemical change on mechanical indenting

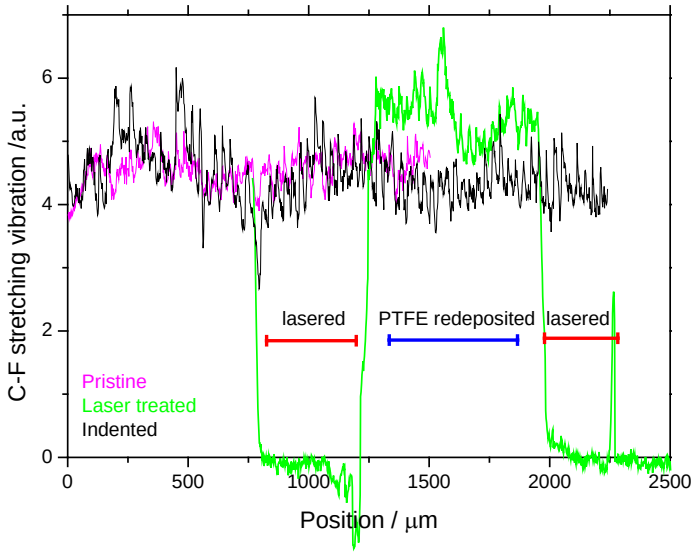


Line profiles from ATR-FTIR data (C-F stretch vibration)

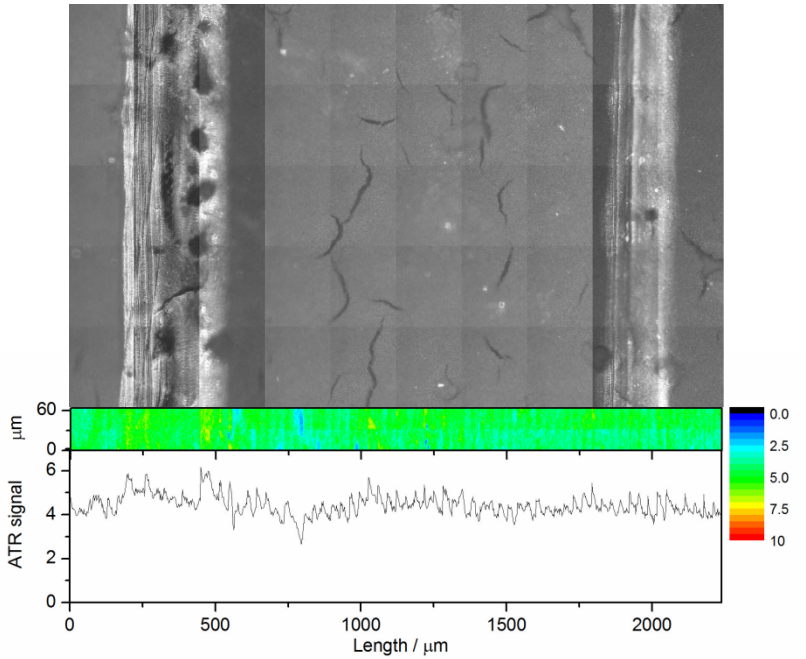
Mechanical indenting

MPL indented with spine of scalpel
→width similar to laser trenches

No chemical influence



Line profiles from ATR-FTIR data (C-F stretch vibration)



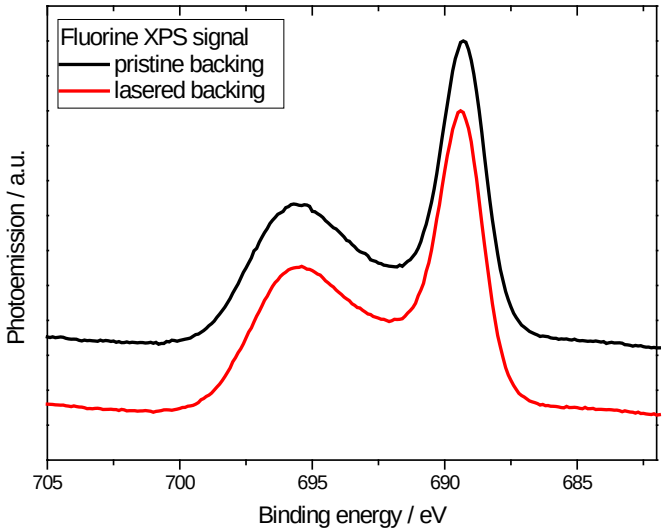
ATR-FTIR mapping of C-F stretch vibration

Laser irradiation

GDL backing

No impact visible by eye

Small spot XPS analysis:
Fluorine 1s signal does not
Reveal PTFE decomposition



→ GDL unchanged with 532 nm / 400 mW within >10 min spot irradiation

Applicability and Feasibility

Method	X-rays	Laser	Ion beam
Mechanism	Breaking of chemical bonds in PTFE	Thermal decomposition	Atomic scale decomposition
Effectivity	medium	MPL: very high Backing: very low	high
Lab scale time demand	high	low	high
Lab scale effort	high	low	high
Production scale time demand	Reasonable: batch processing with masks	low	high
Production scale effort	Low to reasonable: possibly ambient pressure irradiation	low: easy automisation	high
Feasibility	Reasonable	MPL: OK Backing: difficult	?

Acknowledgements

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Thank you for your attention!