FTIR-ATR spectroscopy with novel microstructured single reflection elements (mSRE) basing on silicon wafers as internal reflection elements

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Outline

- Introduction/Motivation
- Novel microstructured single reflection elements at silicon wafers for ATR-FTIR spectroscopy
- *In situ*-Investigations
  - Wet etch of thermal SiO_2 layers at Si
  - Chemical mechanical planarisation of SiO_2 layers
  - Native SiO_2 layers and surface termination at Si
  - Interactions of additives for Cu electrodeposition
  - General applications in (bio)analytical chemistry
- Conclusion / Outlook

Motivation

- Characterisation of thin-films on Si/SiO_2 substrates
- Original focus on chemical-mechanical polishing (CMP) and electrochemical deposition (ECD):
  - Wet chemical processes (e.g. with aqueous solutions)
  - Surface reactions
  - Tribochemical/physicochemical investigations

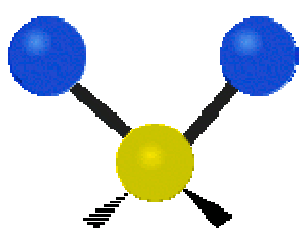
→ *In situ* measurement 

 Surface not accessible with common surface analytical methods like XPS, XRD, SIMS, LEED (mostly vacuum at interesting face)

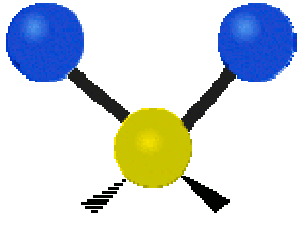
- Fourier transform infrared (FTIR) spectroscopy
  - Molecular spectroscopy (information on composition and structure)
  - Based on change in dipole moment due to molecule vibrations
  - Vacuum not necessary, but applicable at each face, if advantageous

Internal vs. external reflection technique

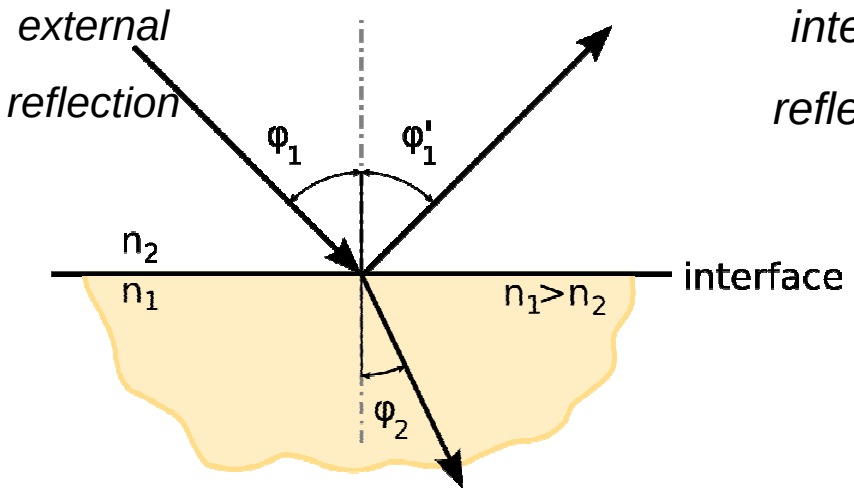
- External reflection: IR penetrates ambient and layer, IRRAS
- Internal reflection: IR penetrates substrate and is attanuated by layer, ATR
- Advantages of the ATR technique:
  - Measurement of thick or strong absorbing media
  - No interferences on thin samples/layers
  - Surface sensitivity
  - Works with polarisation
  - No direct contact needed
  - Transmission like spectra

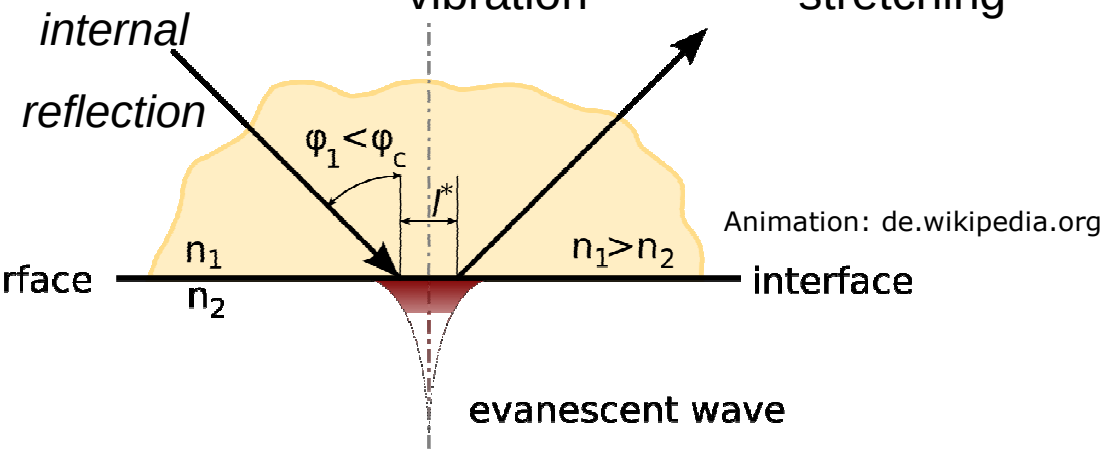


scissoring vibration



asymmetric stretching

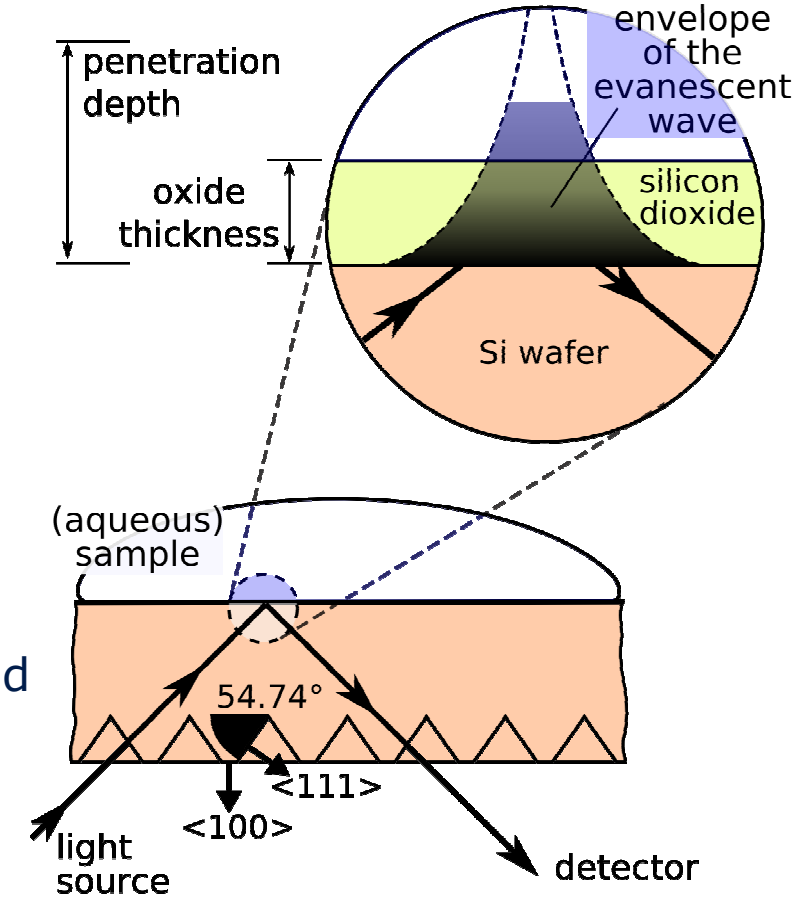




Animation: de.wikipedia.org

Microstructured SRE for ATR-FTIR

- Common Si {100} wafer
- Microstructure on the wafer backside
  - V-shaped grooves of Si(111) faces
  - common MEMS fabrication technologies (e.g. wet chemical crystal oriented etch)
- IR beam from the wafers backside, optical path can be purged or evacuated
- Attenuated total reflection (ATR) at the Si/SiO_2 or Si/ambient interface
- Penetration depth can be partially controlled
- Horizontal or vertical sample orientation
- Sample side is free accessible



H. Schumacher, U. Künzelmann, B. Vasilev, J. W. Bartha, and K. J. Eichhorn „Applications of Microstructured Silicon Wafers as Internal Reflection Elements in ATR-FTIR Spectroscopy" ***Applied Spectroscopy* 64** (9), 2010, p. 1022-1027

Multi- vs. microstructured single RE

- mSRE has a very short optical path (≈1mm) in Si (70mm with MRE)
  - ✓ No limitation due to Si lattice vibrations
  - ✓ Enhanced measurement range for Si reflection elements (entire mid and far infrared spectral range)

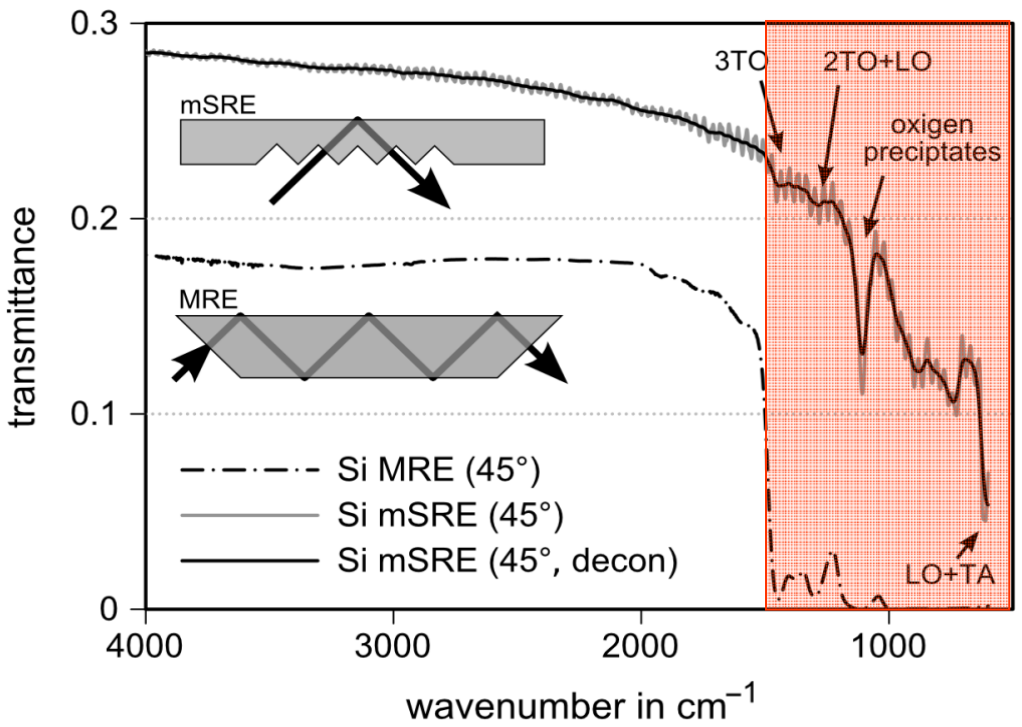
Transmission spectra of

novel Si-mSRE

and

conventional Si-MRE

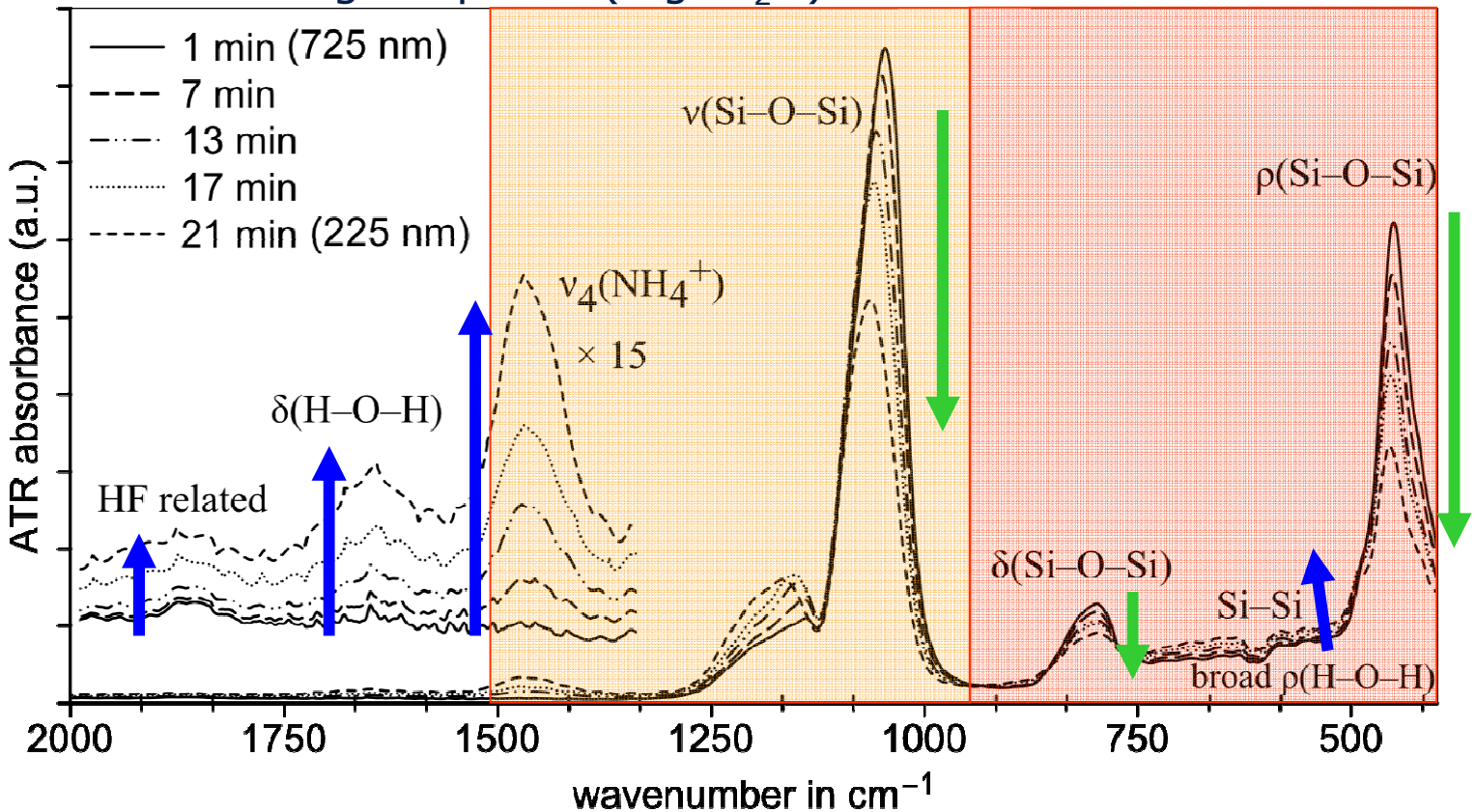
referenced to air



Wet etch of thick thermal oxide

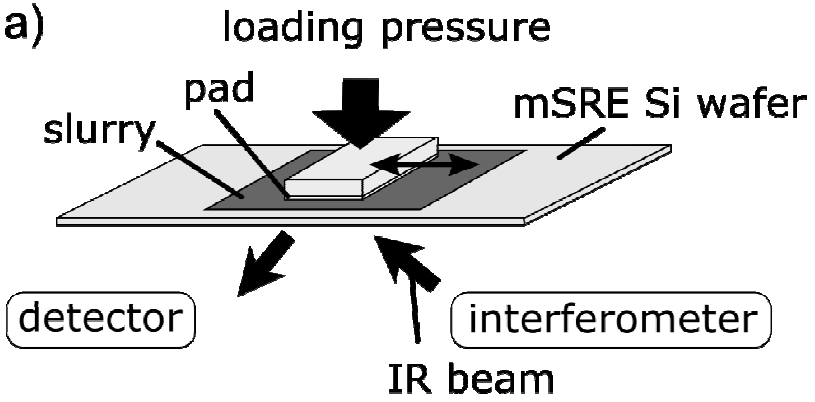
- Wet etch of SiO_2 with buffered oxide etch solution (H_2O, HF, NH_4F)
- *In situ* ATR-FTIR (DTGS detector, 4 cm^{-1}, 64 scans)
- Decrease of SiO_2 assigned peaks
- Increase of BOE assigned peaks (e.g. H_2O)

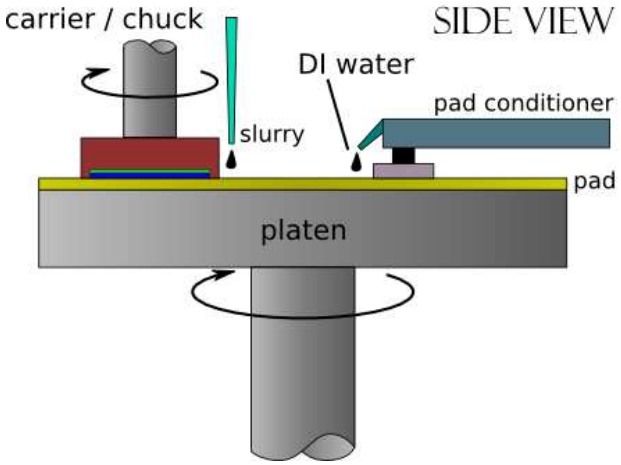
Now accessible with mSRE!

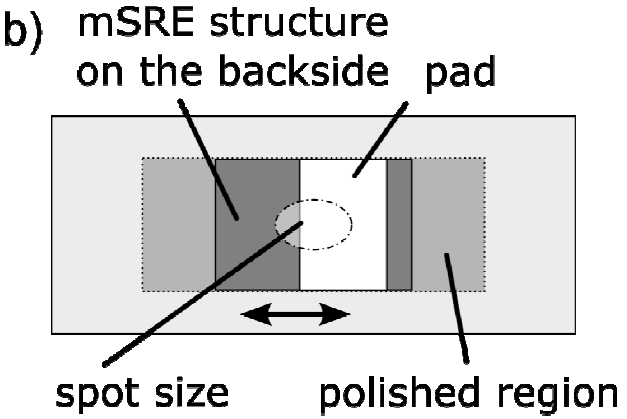


Experimental setup (CMP)

- Single reflection measurement cell
- Angle of incidence of 35° on {100} wafer backside
- Information depth ≈ 900 nm @ 1000 cm^{-1}



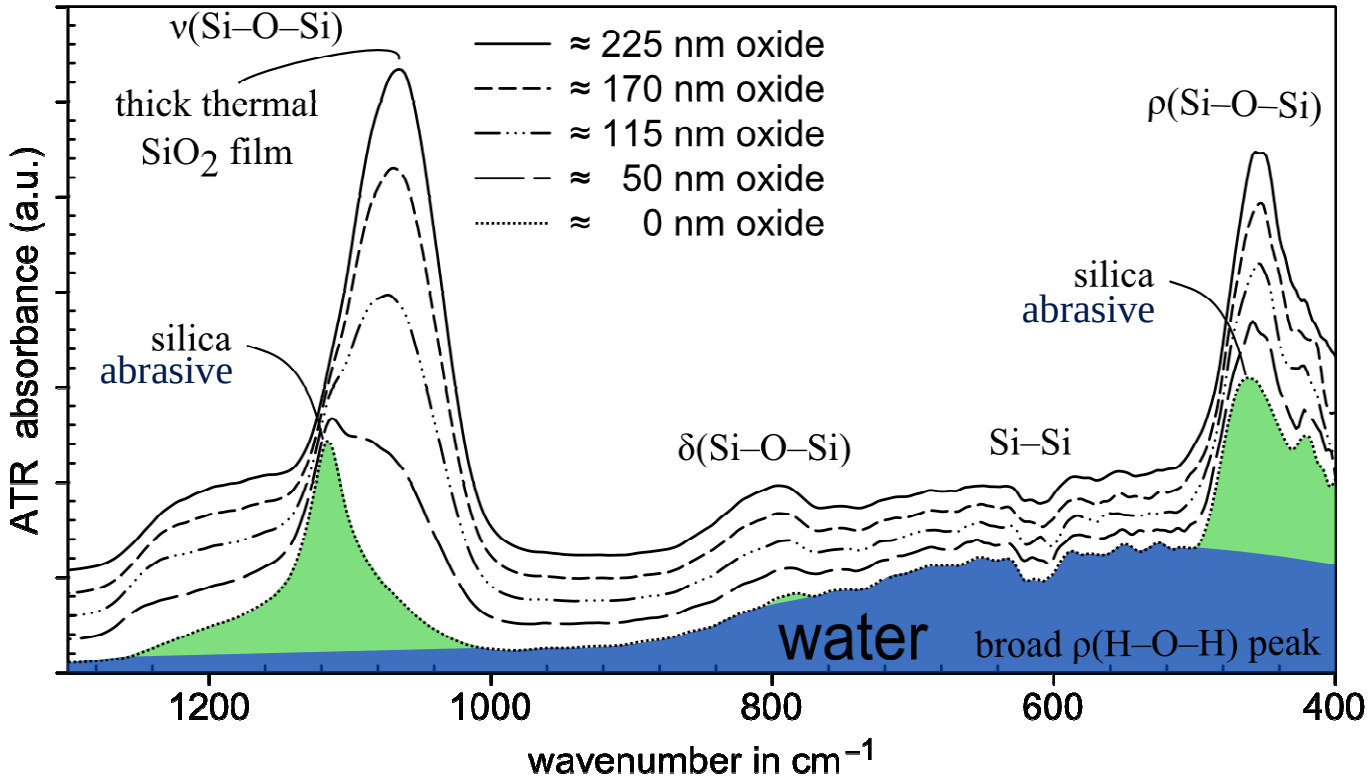




Schematic of the polishing configuration and of the simulator at the FTIR instrument

In situ measurement during CMP

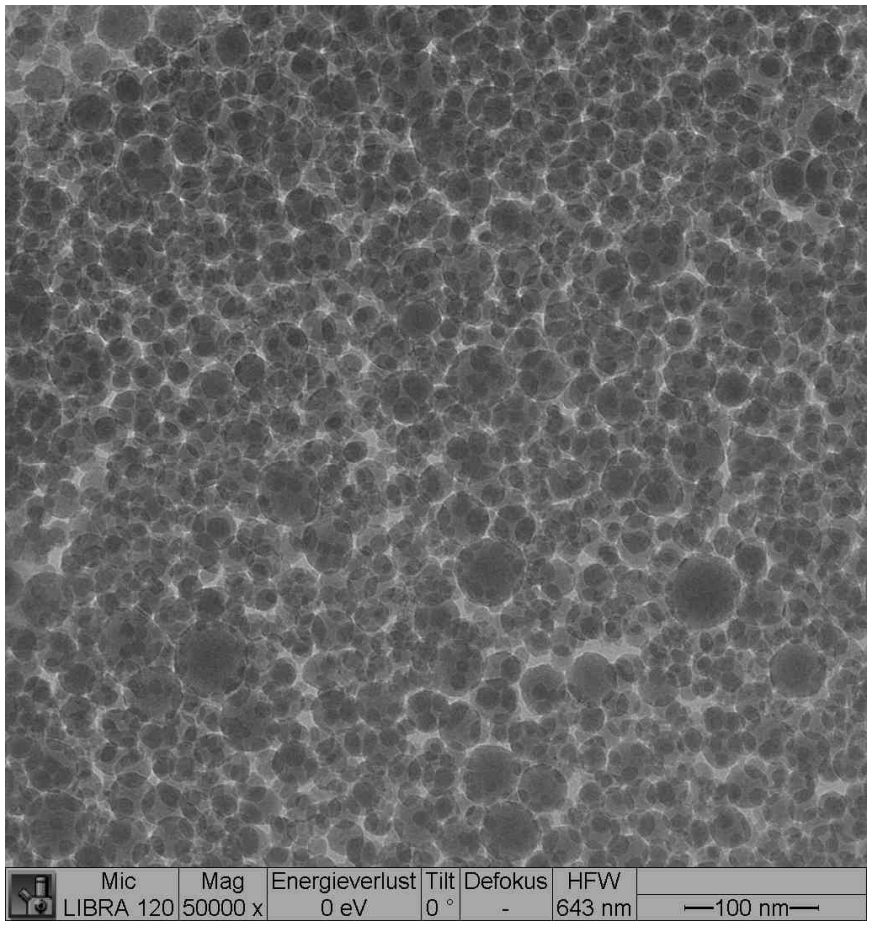
- Silica based, particle size ≈50 nm; 30 wt.% solids; pH 10; NH_4OH chemistry
- Pad: IC 1000, conditioned, linear movement
- Back pressure ≈ 11 psi
- FTIR: DTGS detector, 64 scans/spectrum, 4 cm^{-1} spectral resolution



Spectra referenced to bare mSRE

- Decreasing oxide peaks
- Increasing slurry peaks
- Peaks of colloidal silica abrasive occure

In situ measurement during CMP

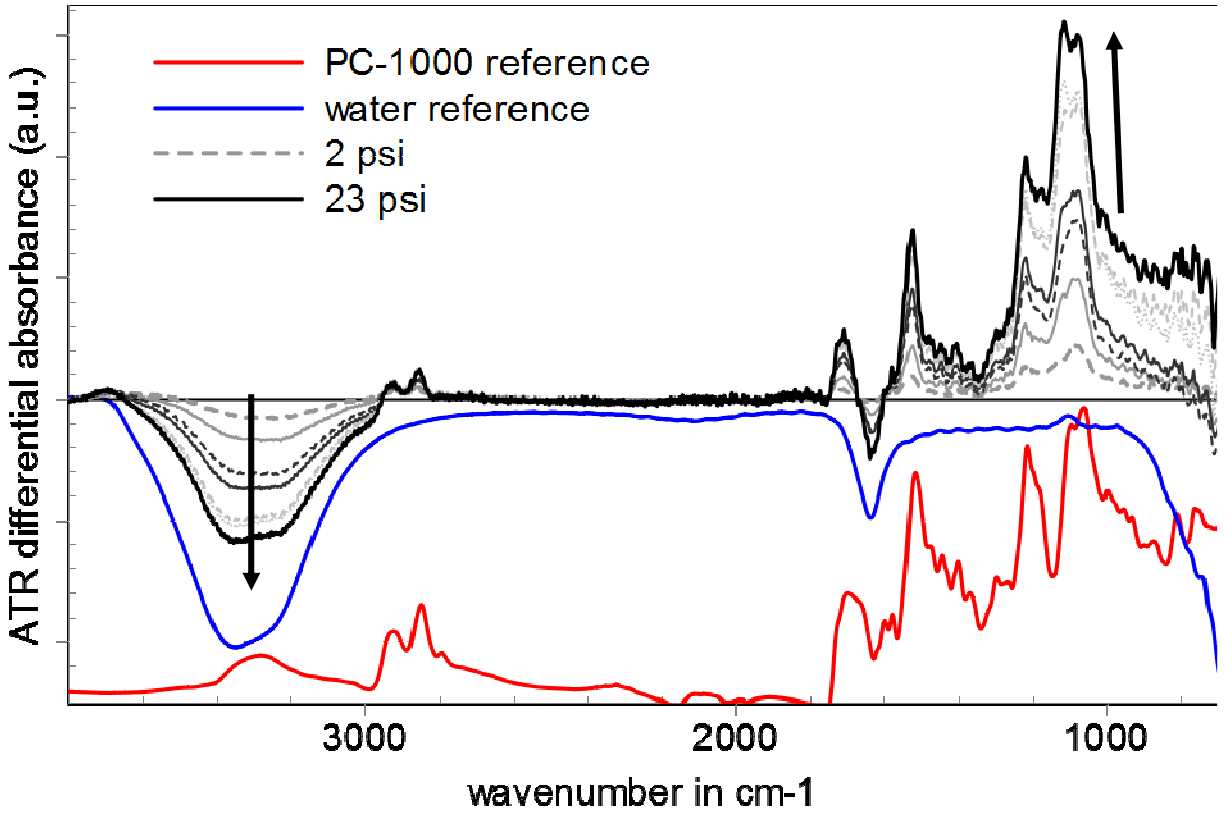


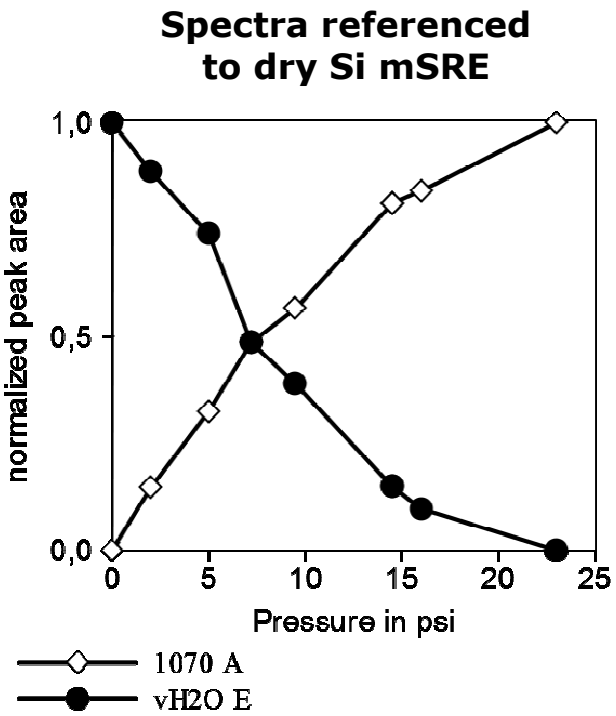
Cryo TEM Image
of nono-disperse SiO_2

by Kathrin Estel/Dr. Formanek (Leibniz IPF Dresden)

Impact of the polishing pad

- Not observed during polishing
- Observable during static measurement

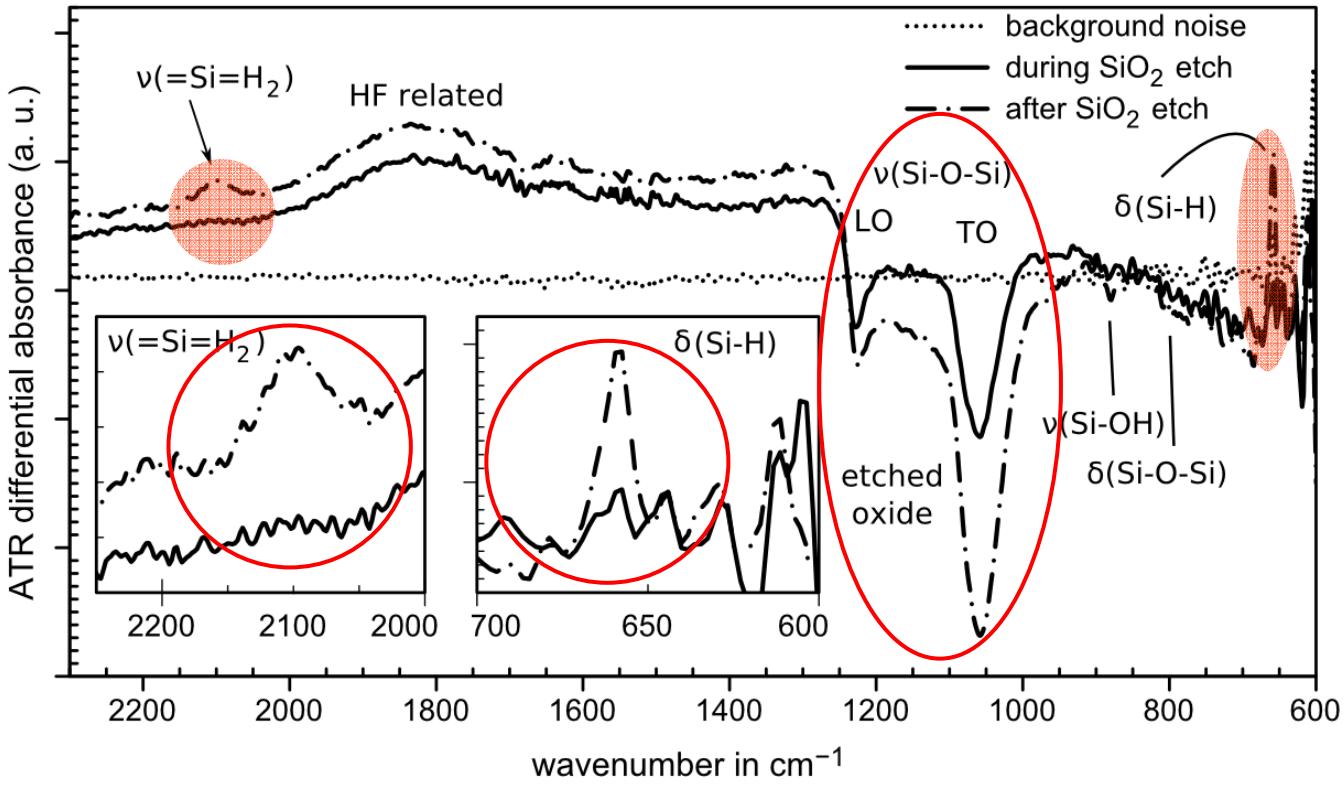




Thin layers and surface termination

- Wet chemical etch of an approx. 2 nm thin SiO_2 with diluted HF-solution
- Native oxide is removed → *negative peak*
- When reaching bulk silicon Si-H vibrations arise → *positive peak*

  → Surface termination with hydrogen (silane groups)

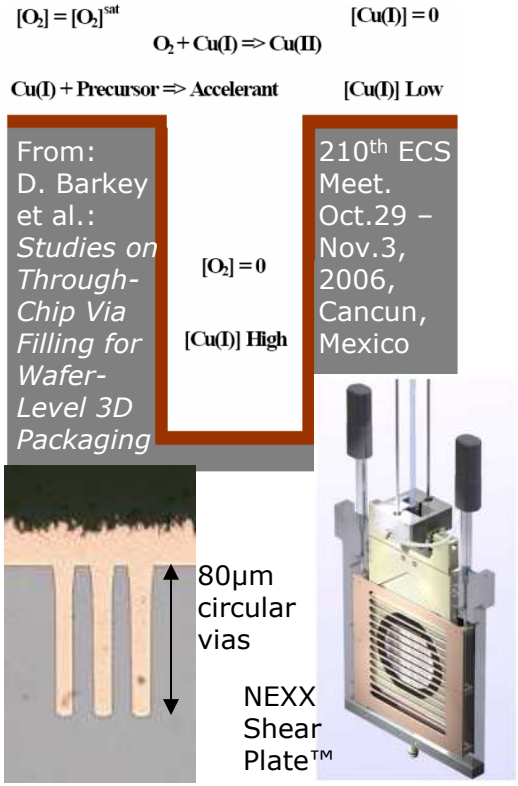


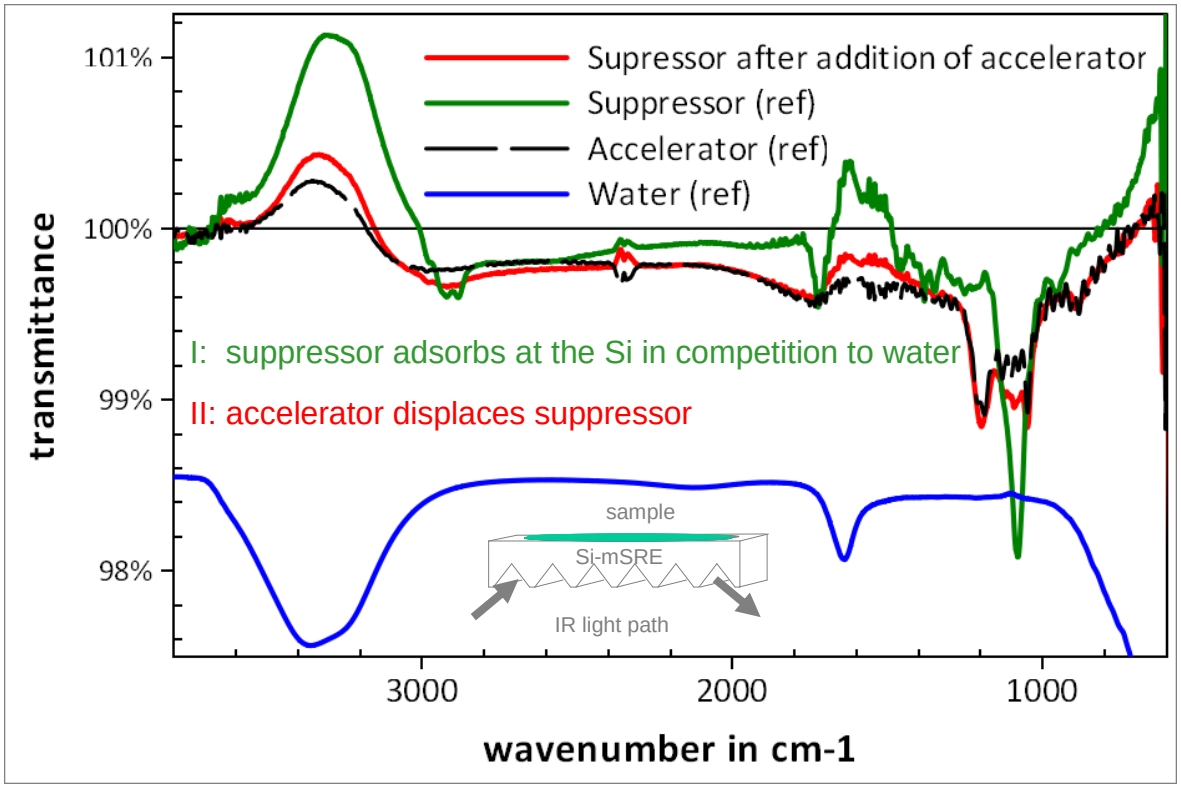
Spectra referenced to water

Schumacher et al.
Applied Spectroscopy ***64****/9 (2010), 1022*

Interaction of plating additives

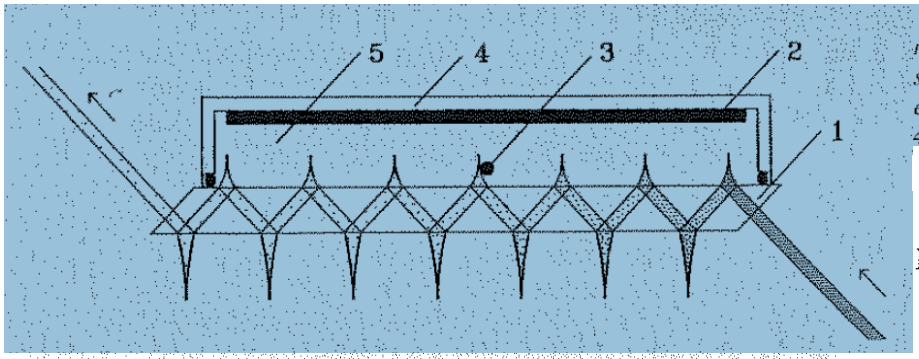
- Suppressor (e.g. *polyethylene glycol, PEG*) adsorbs at exposed areas and inhibits the Cu deposition → global polarisation
- Accelerator (e.g. *bis-(3-sulfopropyl)-disulfide, SPS*) displaces suppressor at the bottom (forming *(3-mercaptopropyl)sulfonate*) → local depolarisation



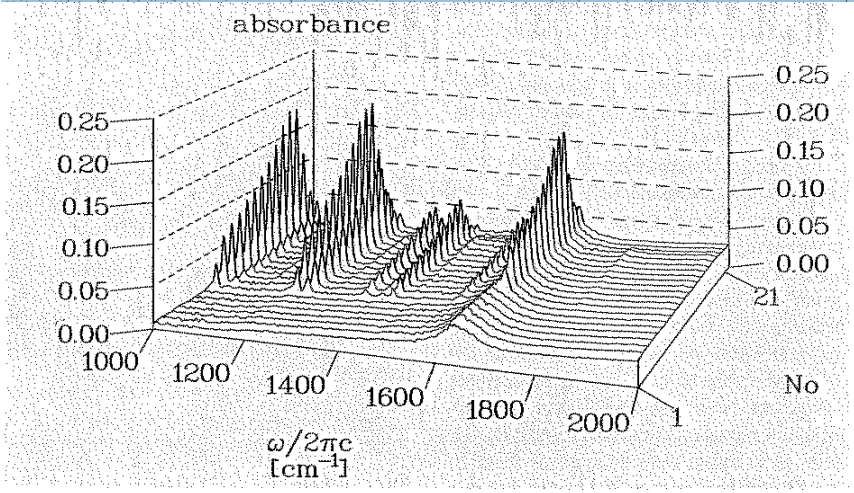


Application in spectroelectrochemisty I

In-situ-spectroelectrochemical measurements during the reduction of methylviologene



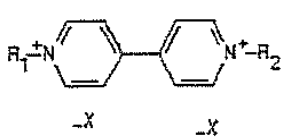
Principle of ATR spectroscopy with multiple reflections; the incident ray is totally reflected at the electrolyte-ATR element interface. Part of the light is absorbed in the small electrolyte region in the vicinity of the ATR element. Key: 1 = Germanium ATR element, 2 = Pt counter electrode, 3 = AgCl-coated Ag wire as reference electrode, 4 = PMMA main body of cell, 5 = electrolyte.



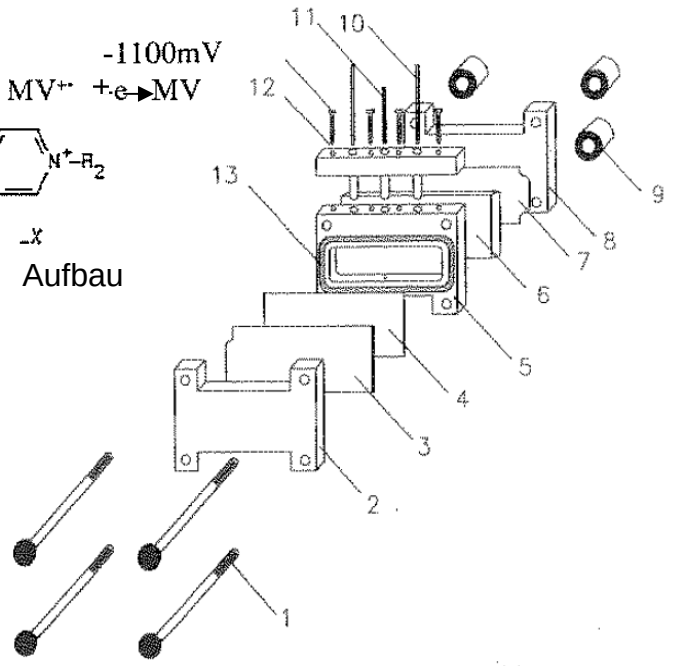
ATR spectra of a 1 mM MV^{2+} solution during the electrochemical cycle.

-700 mV -1100mV

MV^{2+} +e → $MV^{+\cdot}$ +e → MV



Aufbau

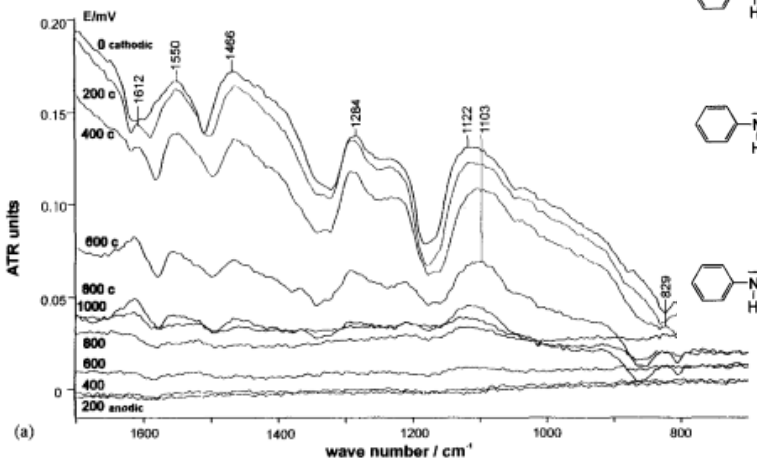


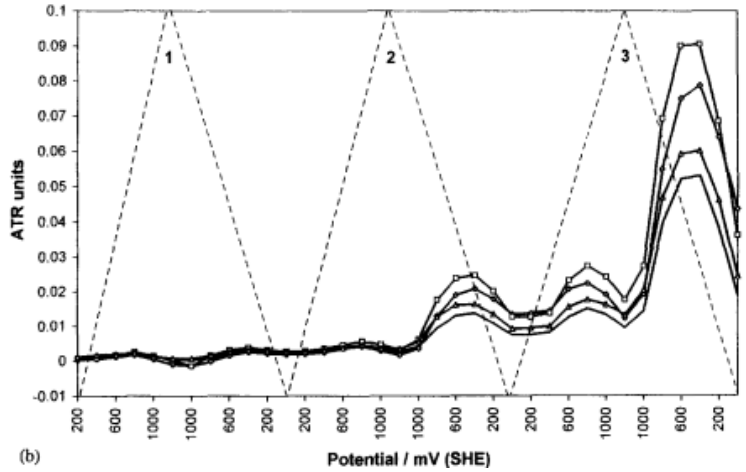
Spectroelectrochemical cell used for our measurements. Key: 1 = screw, 2 = aluminum mount, 3 = counter electrode contact strip, 4 = Pt counter electrode, 5 = PMMA main body, 6 = Ge ATR element, 7 = working electrode contact strip, 9 = nut, 10 = electrolyte inlet tube, 11 = AgCl-coated Ag wire as reference electrode.

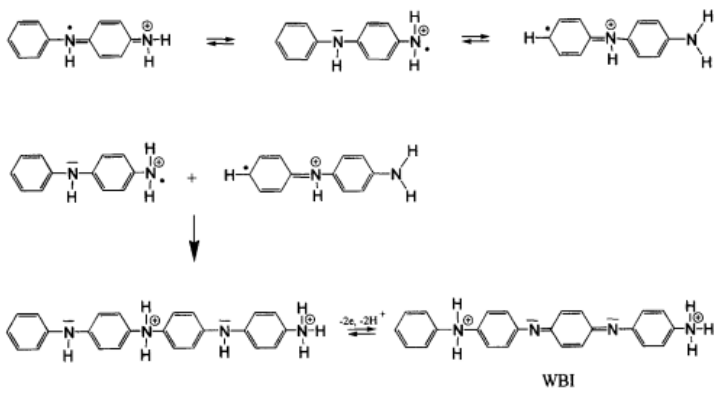
J. Sturm, U. Künzelmann, S. Bischoff, L. Dunsch: *Bruker-Report* **142** (1996), 8-11

Application in spectroelectrochemisty II

Initial states in the electropolymerization of aniline and p-aminodiphenylamine







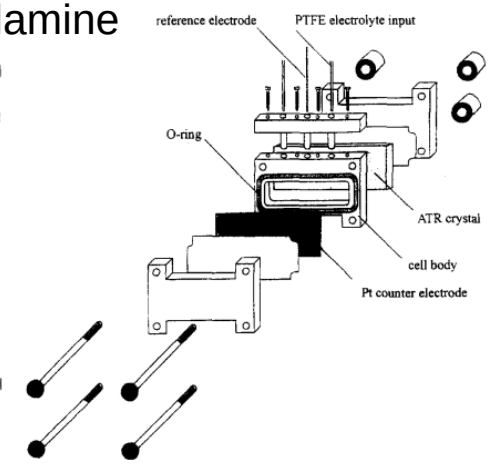


Fig. 1. Explosion scheme of the spectroelectrochemical FT-IR/ATR cell.

a) *In situ* FTIR/ATR spectra of the first cycle of the electrochemical oxidation of aniline at a gold grid/ZnSe reflection element.
Electrolyte: 0.05 M aniline/0.5 M H_2S0_4 after a pre-cycle 0 - 1.2 V (SHE);
1st cycle: 0 - 1 V (SHE), potential range: -200 to 800 mV (SHE);
scan rate:10 mV/s; reference spectrum: uncovered gold grid.

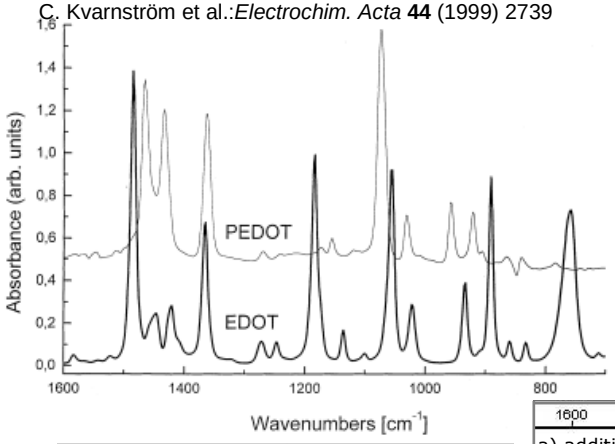
(b) *In situ* FTIR spectroscopy during the potentiodynamic formation of PANI within 1-3 cycles: ATR intensity of specific vibration modes vs. Potential. change of characteristic vibrations: ○:1485; ¯: 1260; □: 1579; ▲: 1156 cm^{-1}

A. Zimmermann, U. Künzelmannm, L. Dunsch: "Initial states in the electropolymerization of aniline and p-aminodiphenylamine as studied by in situ FT-IR and UV-Vis spectroelectrochemistry" *Synthetic Metals* **93** (1998) 17-25 .

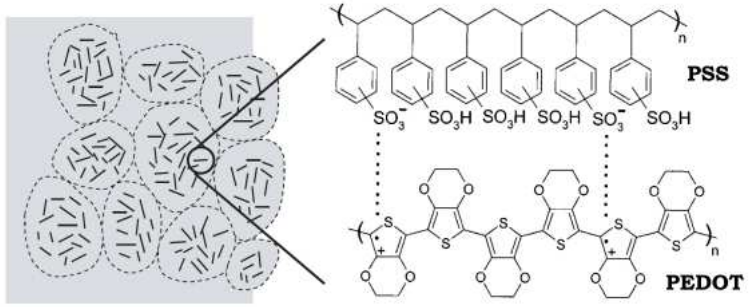
Intrinsically conductive polymers

Influence of ammonia on the structure of PEDOT/PSS composite layers

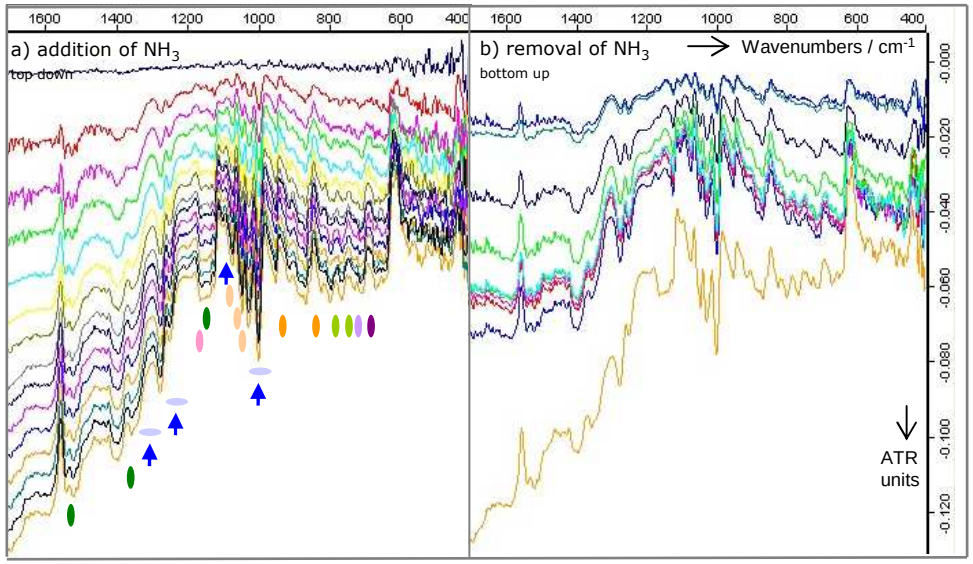
Spectra of EDOT and PEDOT (incl. band assignment) reproduced:
C. Kvarnström et al.:*Electrochim. Acta* **44** (1999) 2739

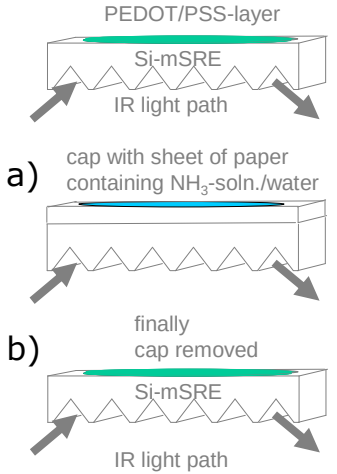


Wavenumbers (cm^{-1})	Assignments
1370	ν(C–C)$_{ring}$
1323–1290	doping-induced band
1247–1199	doping-induced band
1183	ν(C=C)$_{ring}$, ν(-COROC-)
1168	ν(C–C)$_{ring}$
1144–1128	ν(-COROC-)
1090	doping-induced band
1093–1076	ν(-COROC-)
1052–1047	ν(-COROC-)
978–1026 shift	doping-induced band
943–930	ν(C–S)$_{ring}$
830	ν(C–S)$_{ring}$
787	γ(CH)
760	γ(CH)
727	δ(C–S)
697	δ(C–S–C)$_{ring}$



reproduced: M. M de Kok et al. : *Phys. Stat. Sol. (A)* **201** (2004) 1342





a) *In situ* FTIR/ATR spectra of the structural changes of PEDOT/PSS layers by treatment with ammonia from aqueous solution.
b) Recover of the initial state by removing the ammonia source.
→ Spectral changes due to different binding states, conductivities and optical conditions.

Intrinsically conductive polymers

Influence of water on the structure of PEDOT/PSS composite layers

Spectra of EDOT and PEDOT (incl. band assignment) reproduced:
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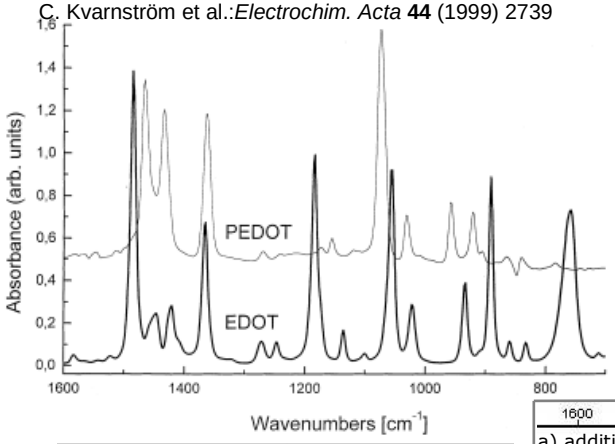

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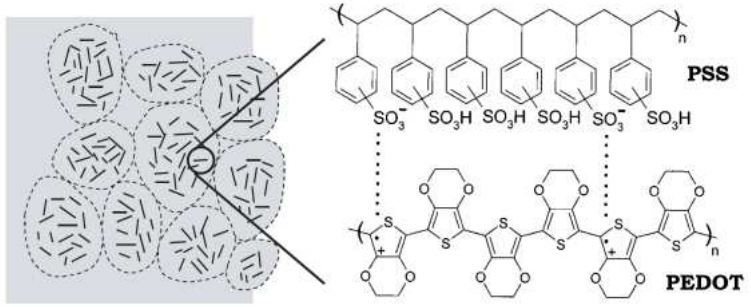

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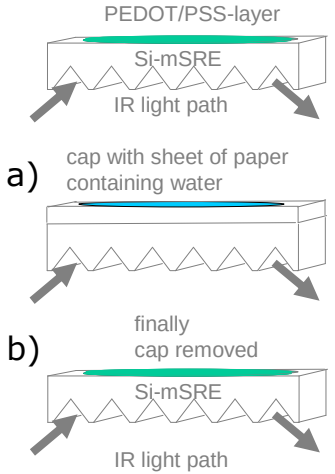
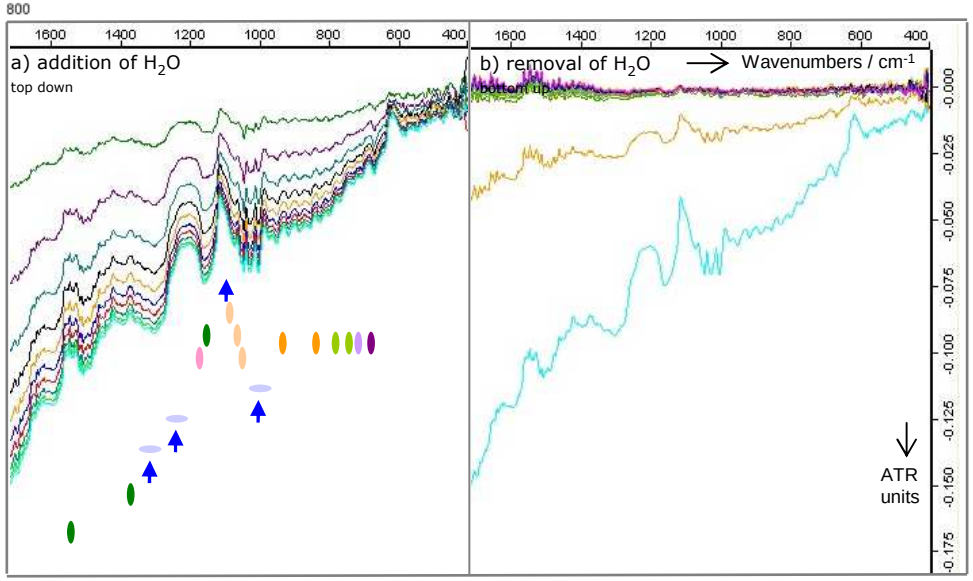
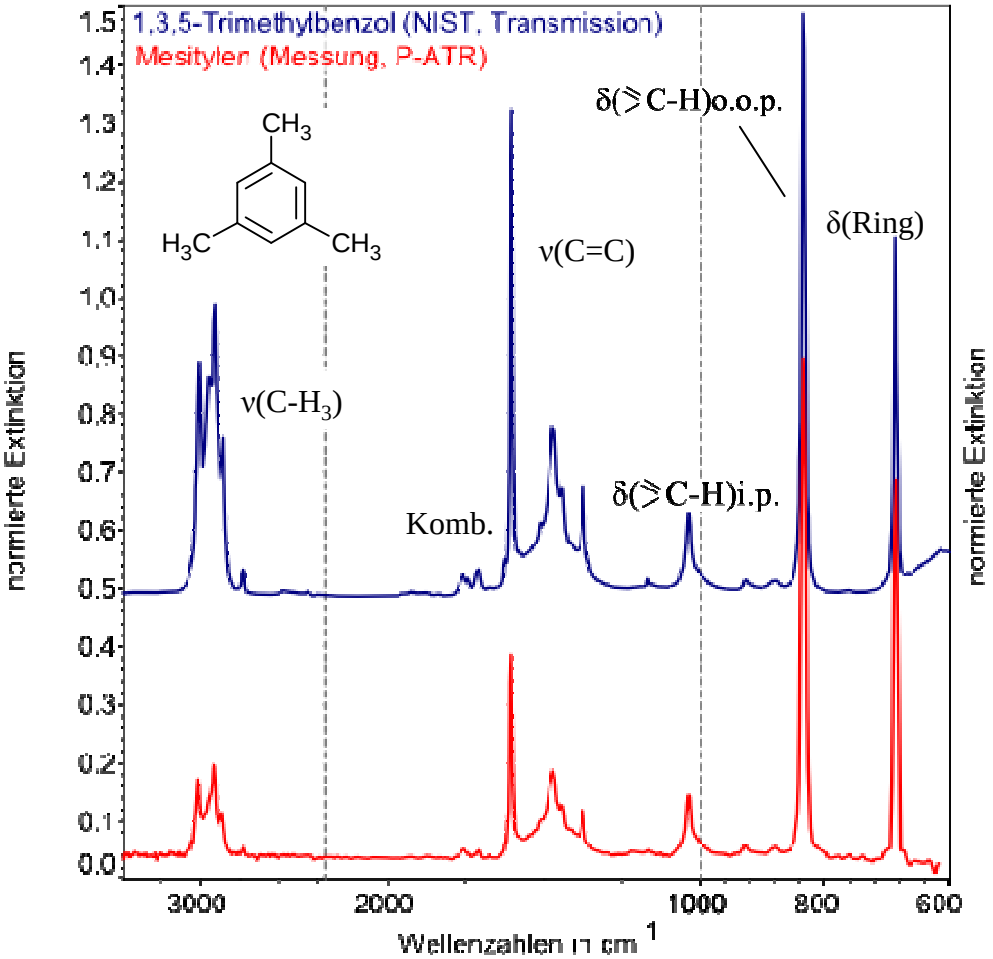




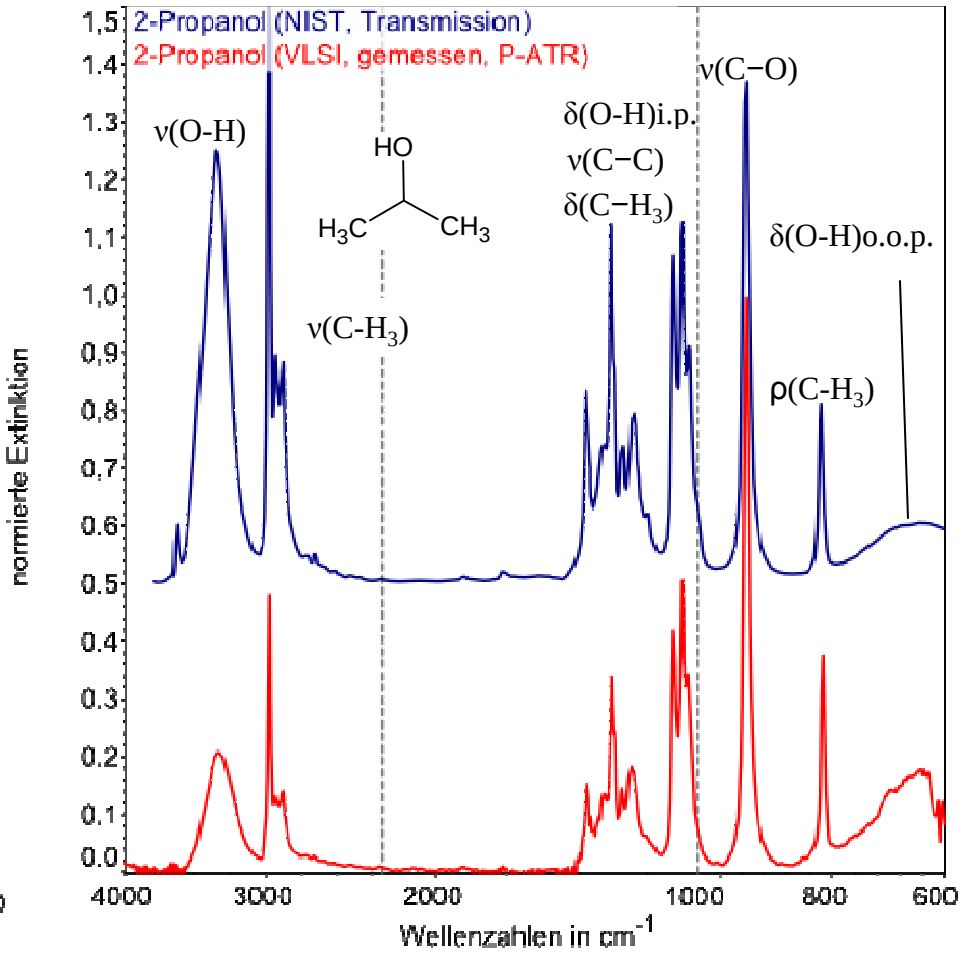
a) *In situ* FTIR/ATR spectra of the changes of PEDOT/PSS layers by treatment with water.
b) Recover of the initial state by removing the water source.
→ Spectral changes mainly in the back-ground due to different conductivities and optical conditions.

mSRE-Spectra vs. Reference Data

Mesitylen



2-Propanole



Conclusion

- Microstructured SRE for ased on backside structured Si-wafers

→ No limitations in sample size

- ATR-FTIR analysis from the wafer backside
- Enhanced usable spectral range for Si based elements

→ No limitations due silicon lattice vibrations
→ below 1500 cm^{-1}

- In situ investigations of wet chemical and *tribochemical* processes
- Detection and analysis of
  - slurry incl. abrasive and additives

  - (ultra) thin-films
  - surface allocations
  - additives for Cu electroplating
- Standard applications for FTIR measurements with cheap RE

Outlook

- Microstructured SRE applicable for investigation of polymers
- Biological samples can be measured
  → As bulk substances
  → In the encapsulated/immobilized state
- Application of barrier and/or diffusion layers provides surface selectivity
- Antibody-antigene interactions observable
- Micro-integration possible

Acknowledgement

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Thank you for your attention