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

Ulrich Künzelmann

Dresden, August 25th, 2011
Outline

► Introduction/Motivation
► Novel microstructured single reflection elements at silicon wafers for ATR-FTIR spectroscopy
► In situ-Investigations
  ● Wet etch of thermal SiO₂ layers at Si
  ● Chemical mechanical planarisation of SiO₂ layers
  ● Native SiO₂ 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/SiO₂ 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

**Motivation | Novel Technique | In situ Investigations | Conclusions**

- **External reflection:** IR penetrates ambient and layer, IRRAS
- **Internal reflection:** IR penetrates substrate and is attenuated 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

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![Diagram of external and internal reflection](image.png)

Animation: [de.wikipedia.org](http://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

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 SiO₂ with buffered oxide etch solution (H₂O, HF, NH₄F)
- In situ ATR-FTIR (DTGS detector, 4 cm⁻¹, 64 scans)
- Decrease of SiO₂ assigned peaks
- Increase of BOE assigned peaks (e.g. H₂O)

Now accessible with mSRE!
Experimental setup (CMP)

- Single reflection measurement cell
- Angle of incidence of 35° on \{100\} wafer backside
- Information depth \(\approx 900\) 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; NH₄OH chemistry
- Pad: IC 1000, conditioned, linear movement
- Back pressure ≈ 11 psi
- FTIR: DTGS detector, 64 scans/spectrum, 4 cm⁻¹ spectral resolution

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

Spectra referenced to bare mSRE
In situ measurement during CMP

Motivation | Novel Technique | In situ Investigations | Conclusions

Cryo TEM Image of nono-disperse SiO₂
by Kathrin Estel/Dr. Formanek (Leibniz IPF Dresden)
Impact of the polishing pad

- Not observed during polishing
- Observable during static measurement

Motivation | Novel Technique | In situ Investigations | Conclusions
Thin layers and surface termination

- Wet chemical etch of an approx. 2 nm thin SiO$_2$ with diluted HF-solution
- Native oxide is removed \(\rightarrow\) negative peak
- When reaching bulk silicon Si-H vibrations arise \(\rightarrow\) positive peak

\(\rightarrow\) Surface termination with hydrogen (silane groups)

Motivation | Novel Technique | **In situ Investigations** | Conclusions

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

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**Motivation**

**In situ Investigations**

**Conclusions**

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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.

Application in spectroelectrochemistry II

Initial states in the electropolymerization of aniline and p-aminodiphenylamine

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 H₂SO₄ 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

Intrinsically conductive polymers

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

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

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


Intrinsically conductive polymers
Intrinsically conductive polymers

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

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

In situ FTIR/ATR spectra of the changes of PEDOT/PSS layers by treatment with water.

Spectral changes mainly in the background due to different conductivities and optical conditions.


Motivation | Novel Technique | **In situ Investigations** | Conclusions

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PEDOT/PSS-layer

a) cap with sheet of paper containing water
b) finally cap removed


Wavenumbers / cm⁻¹

ATR units

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 background due to different conductivities and optical conditions.
mSRE-Spectra vs. Reference Data

Motivation | Novel Technique | **Standard Applications** | Conclusions

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**Mesitylen**

1,3,5-Trimethylbenzol (NIST, Transmission)
Mesityler (Messung, P-ATR)

- \(\nu(C-H)\)
- \(\delta(C-H)\)
- \(\nu(C=C)\)
- \(\delta(\text{Ring})\)
- Komb.

**2-Propanol**

2-Propanol (NIST, Transmission)
2-Propanol (VLSI, gemessen, P-ATR)

- \(\nu(O-H)\)
- \(\delta(O-H)\)
- \(\nu(C-C)\)
- \(\delta(C-H)\)
- \(\rho(C-H)\)

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nanoSeminar, Chair of “Materials Science and Nanotechnology”
TUD/Faculty Mechanical Engineering/Inst. of Material Science
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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
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Thank you for your attention