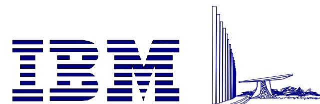
EDP-OCP Measurement Technique

H.F. Okorn-Schmidt

IBM T.J. Watson Research Center

Yorktown Heights, NY 10598

ERC TeleSeminar-October 26th, 2000



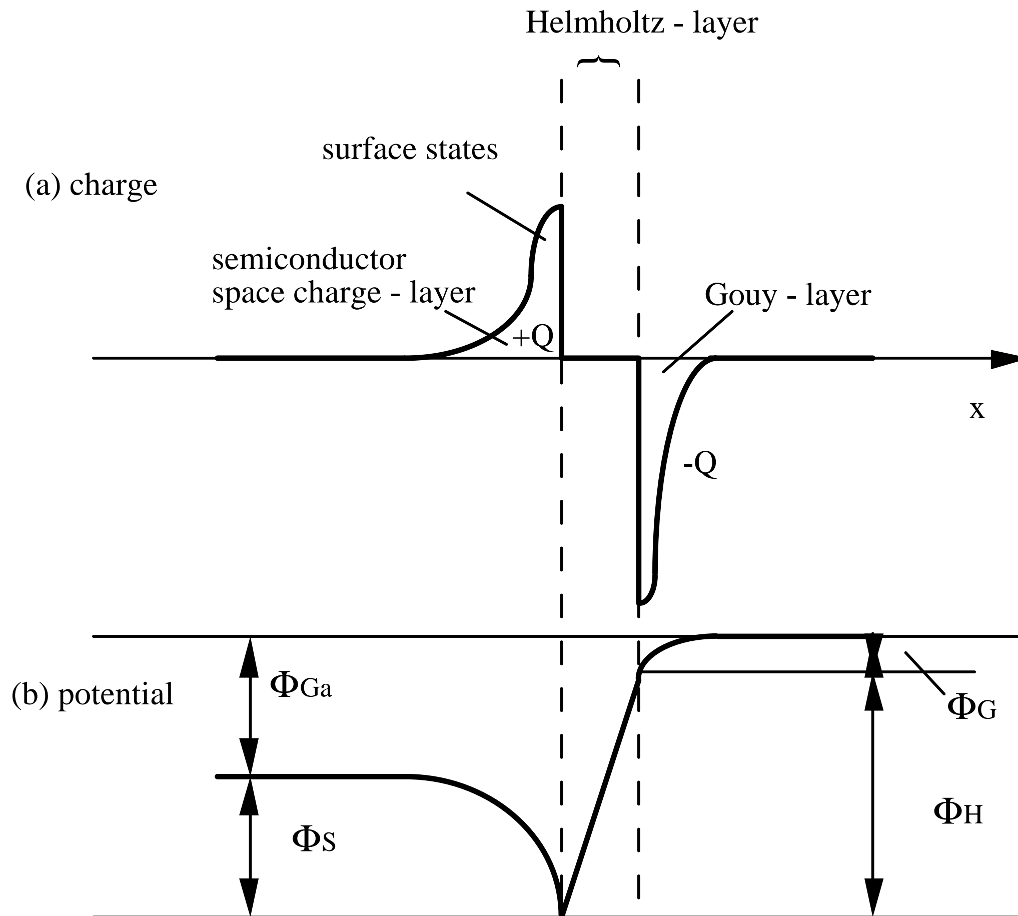
Acknowledgements

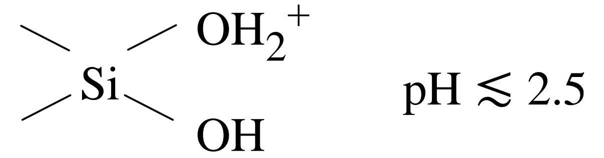
- IBM (OCP work since 1996)
  - David Rath
  - Henry Grabarz
  - Evgeni Gusev, Douglas Buchanan, Eduard Cartier, Michael Gribelyuk, Chris D'Emic, Matt Copel and Richard Murphy
- IMEC (OCP work 1992-1996)
  - UCP Group of Marc Heyns
    - Ivo Teerlinck, Serge Biesemans, Wolfgang Storm, Hugo Bender
- Siemens (OCP work 1989 - 1991)
  - Michael Huettinger, Ernst Demm, Bernd O. Kolbesen

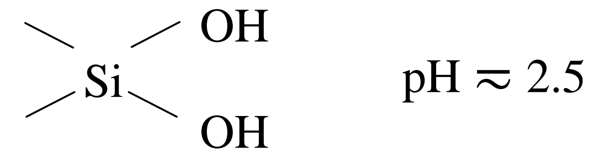
Outline

- Introduction to OCP and EDP-OCP (V_{OC})
- OCP in Oxidizing Environment
  - Oxidation Model
- OCP in Etching Environments (EDP-OCP)
  - in HF
    - chemical oxides
    - thermal oxides
    - dielectric stacks
  - in aqueous NH_3
- OCP in SC1 (simultaneous oxidation and etching process)

Introduction







Surface Charge = f (pH, surface species)

History of EDP-OCP

- 1989 - 1991 work on OCP measurements for optimizing silicide etchants (at Siemens Research, Munich)

Fig. 3 shows the variation of the corrosion potential of $MoSi_2$ in a 0,6 mol/l $K_3Fe(CN)_6$ solution for several KOH concentrations with time. The curves 3, 4 and 5 demonstrate a good and quick removal of $MoSi_2$ from its underlayer poly-Si. The initial potential is the corrosion potential of $MoSi_2$, which is a mixed potential /3/, and after a rapid increase the passivation potential of poly-Si respectively (100)-Si occurs. This enables the determination of etch rates of thin layers. A comparison between curves 3 and 5 shows that a higher KOH concentration leads to a more rapid removal of $MoSi_2$, but SEM investigations indicate that a higher KOH concentration lowers the selectivity to poly-Si.

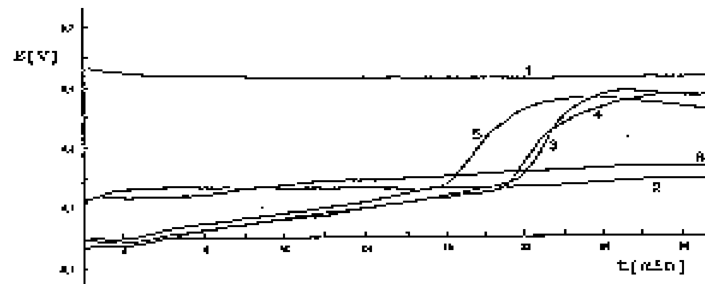


Figure 3.
Variation of the corrosion potential (vs. S.H.E) of a thin (300 nm) $MoSi_2$ layer on (100)-Si in a 0,6 mol/l $K_3Fe(CN)_6$ solution at various KOH concentrations and temperatures with time.

- 1992 - 1996 work on semiconductor oxidation and H-passivation kinetics at IMEC - much of the fundamental work

- since 1996 work on mostly EDP-OCP of thermal oxides, nitrides and alternative dielctrics (high-k and stacks) and DI/O_3 chemistries

How new is this technique ?

- Rest Potential measurements (OCP) have been and are very common in metal electrochemistry
- On Semiconductors only one significant literature before 1990:

  H. Gerischer and M. Luebke, Ber. Bunsenges. Phys. Chem. 92 (1988) 573.

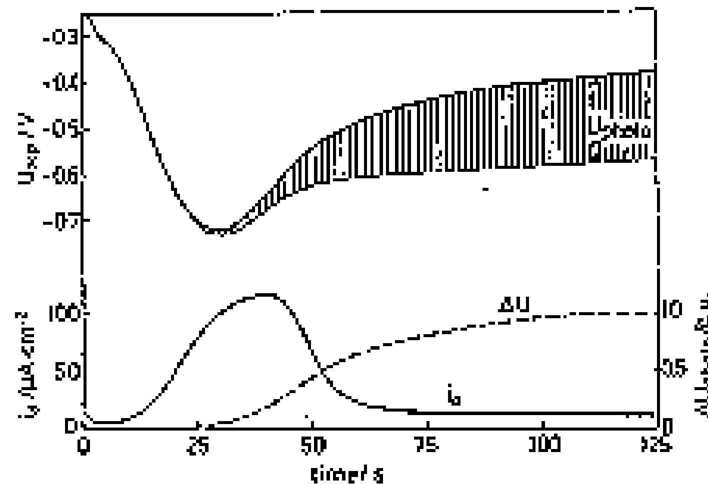
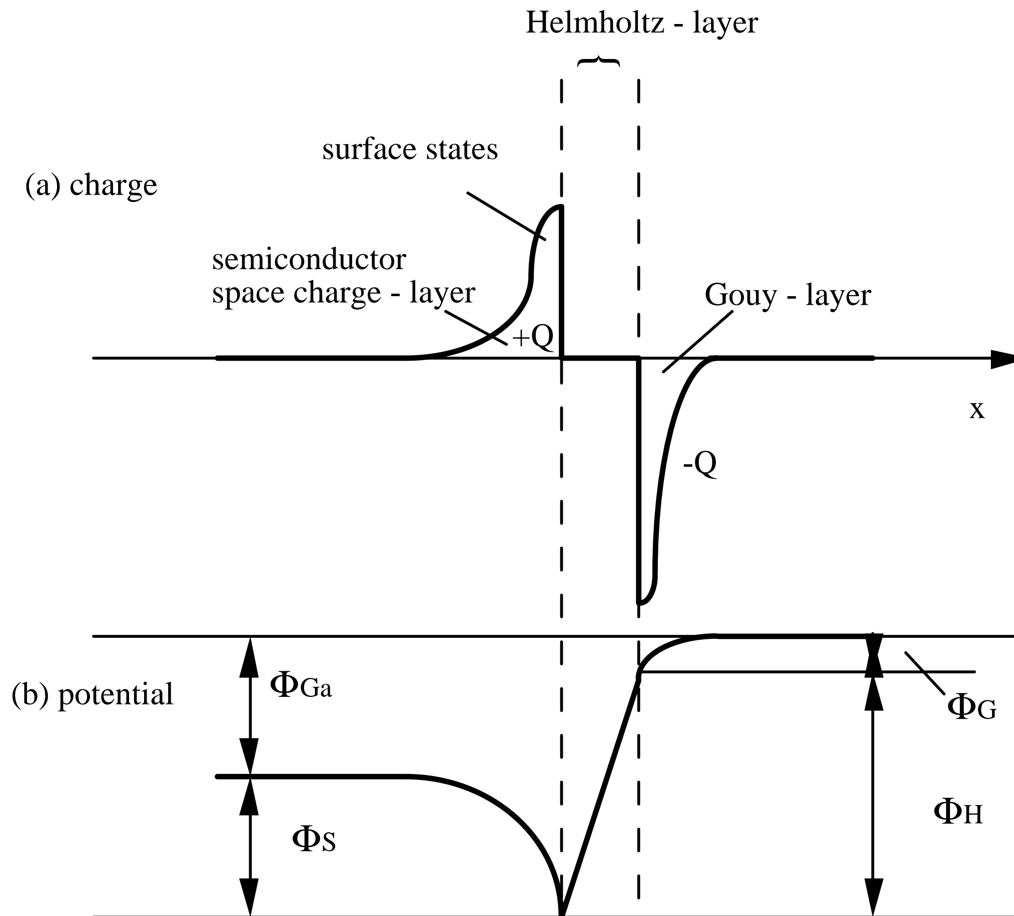


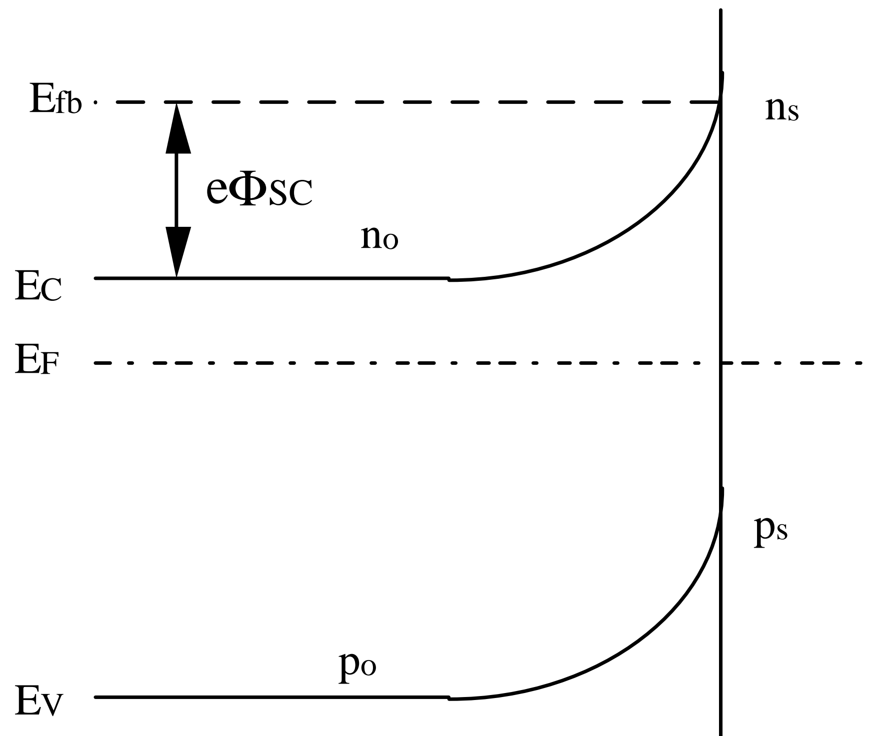
Fig. 14
The photopotential determined by short light pulses at open circuit of an n-type Si electrode during the dissolution of the oxide after switching off the illumination and the respective current in the dark.
0.13 M NH_4F solution, pH = 4

Introduction

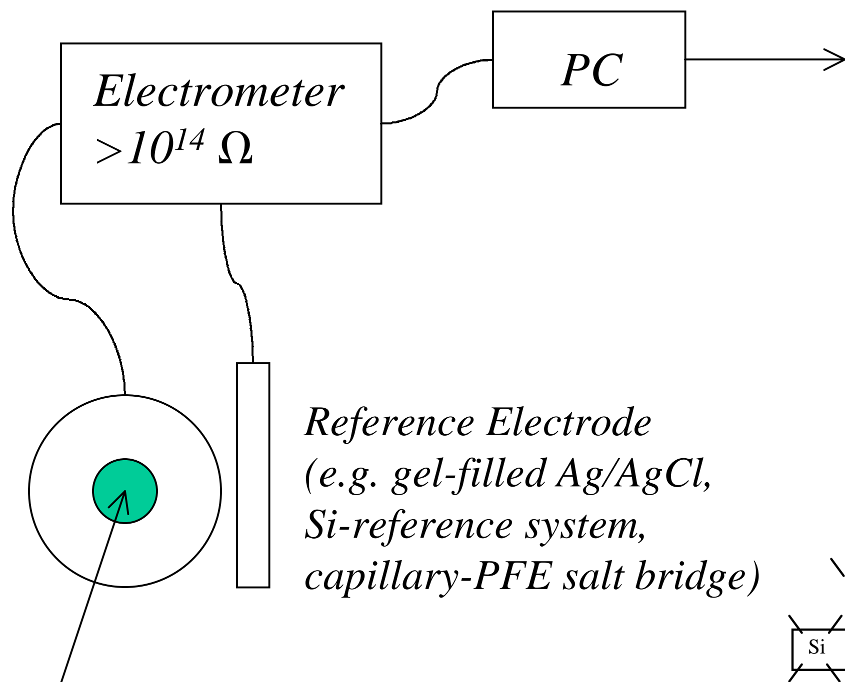


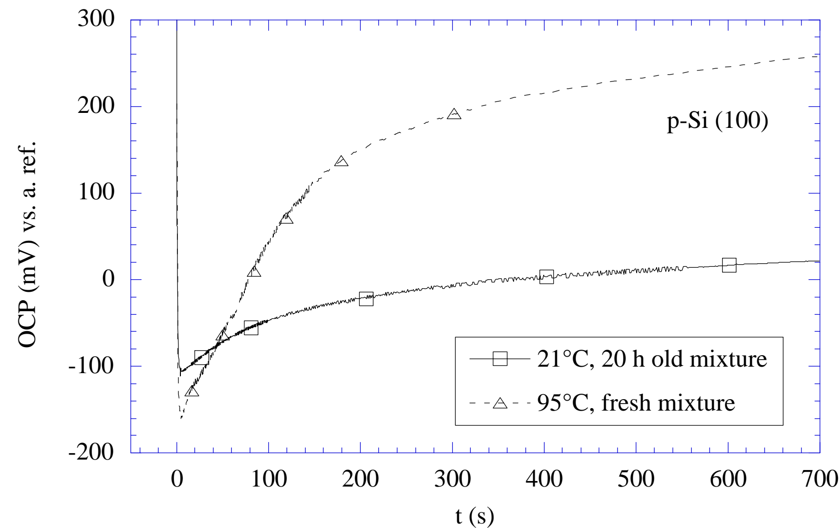
Introduction

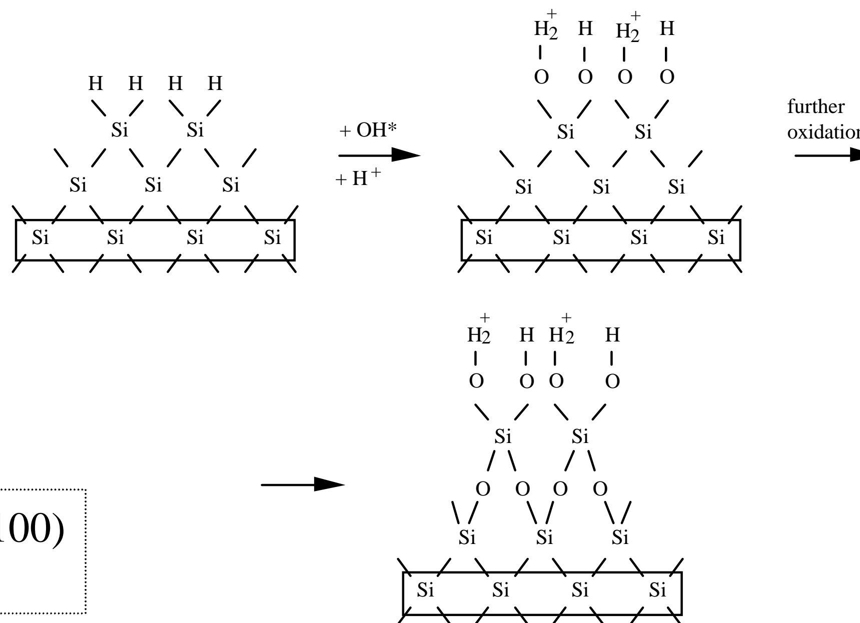
Energy band model for an n-type semiconductor.



Experimental Set-Up
Oxidation





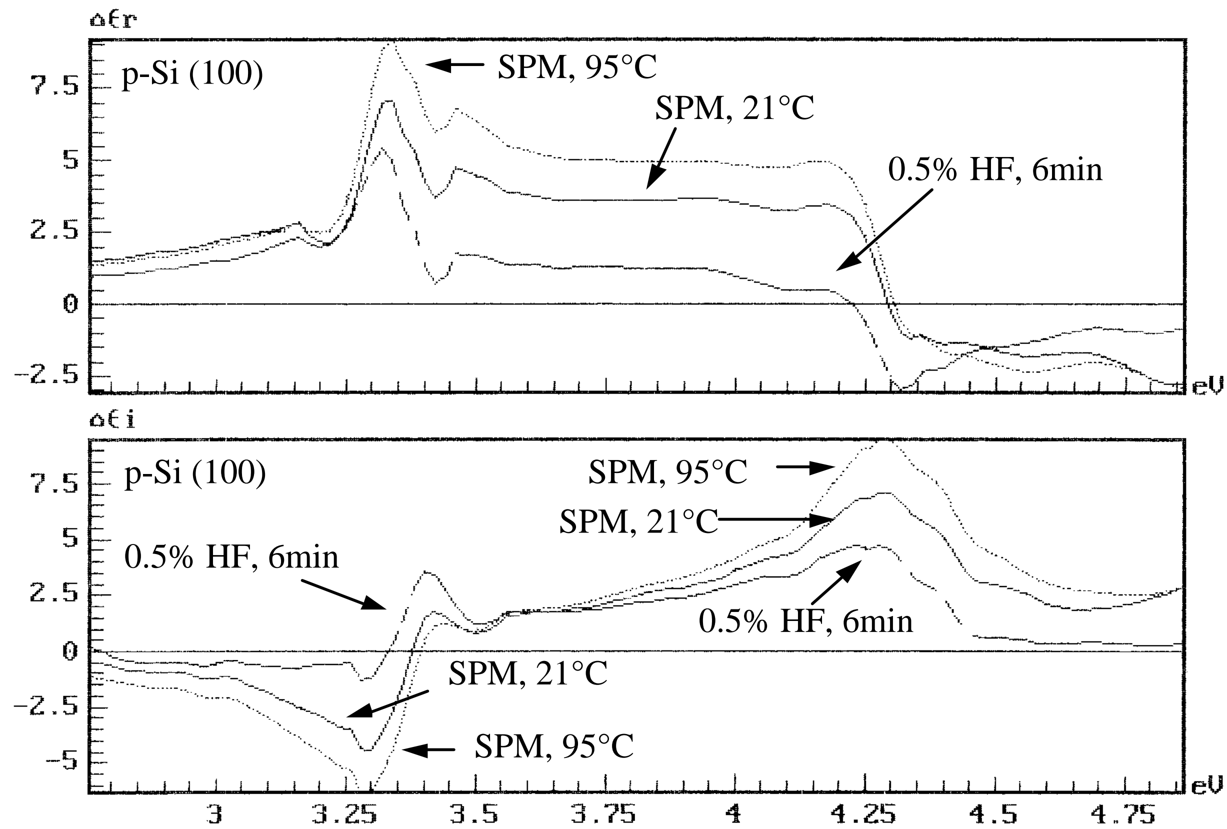


Example displayed: oxidation of Si (100) in SPM after H-passivation in HF

H.F. Okorn-Schmidt, 10/26/2000

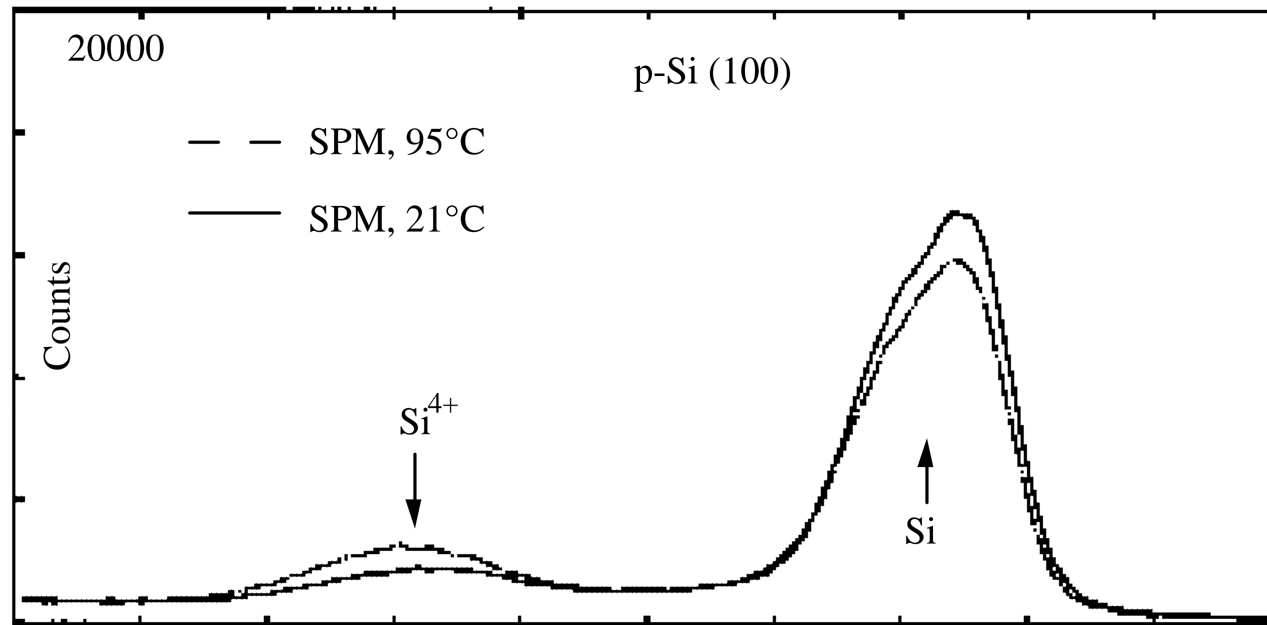
Ellipsometric Results

Pseudo-dielectric functions versus photon energy for p-type Si treated in different SPM mixtures



XPS Results

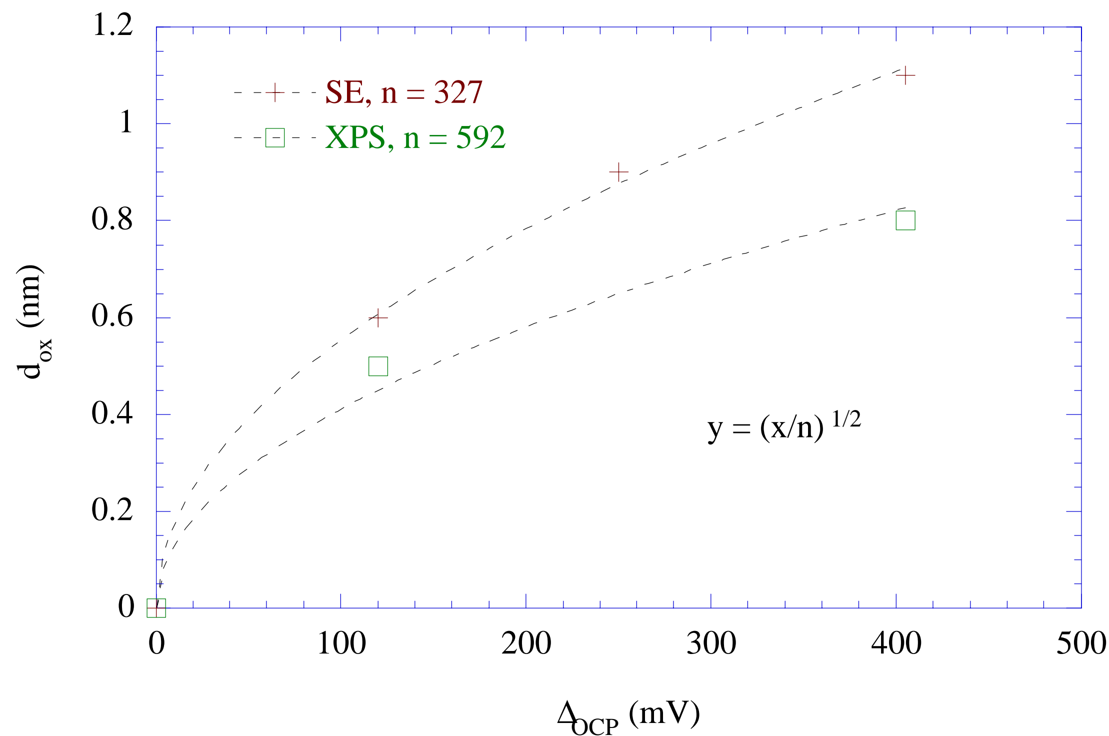
XPS spectra for p-type Si treated in different SPM mixtures



OCP in Oxidizing Environment

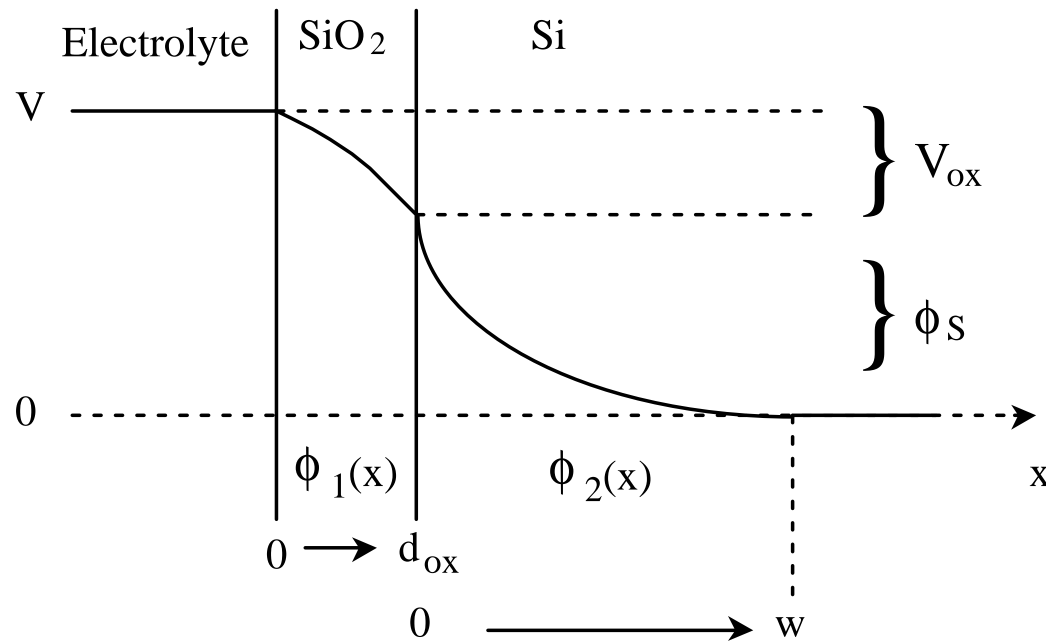
Correlation between potential difference and oxide thickness

(Δ_{OCP} = |PMP - V_{OC} @600s immersion time|)



Oxidation Model

(solving the Poisson Equations)



$$V = \frac{q}{8N_{Sub}\varepsilon_{ox}\varepsilon_{Si}}(4Q_{ox}^{2}\varepsilon_{ox} + 4N_{ox}Q_{ox}\varepsilon_{ox}d_{ox} + 8N_{Sub}Q_{ox}\varepsilon_{Si}d_{ox} + N_{ox}^{2}\varepsilon_{ox}d_{ox}^{2})$$

Oxidation Model

$$V = n d_{ox}^{2} \qquad \text{with} \qquad n = \frac{q N_{ox}^{2}}{8 N_{Sub} \varepsilon_{Si}}$$

$V = \Delta_{OCP}$ (V)

$q = 1.6022 \times 10^{-19}$ C (electronic charge)

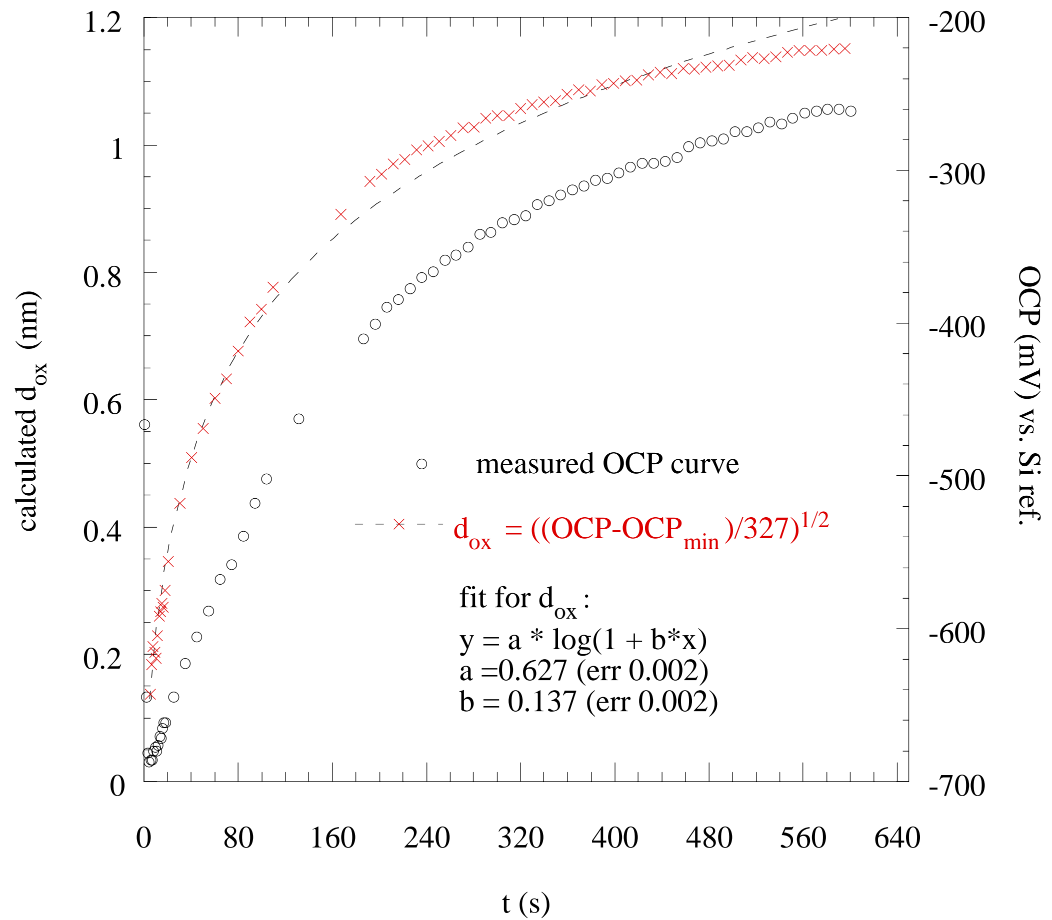
$\varepsilon_{Si} = 1.05 \times 10^{-19}$ F nm^{-1} (dielectric constant for Si)

$N_{Sub} = 6.5 \times 10^{-7}$ nm^{-3} (doping level of the Si substrate,
equals a Boron doping level of 7×10^{14} cm^{-3})

N_{ox} the amount of charge in the oxide (nm^{-3})

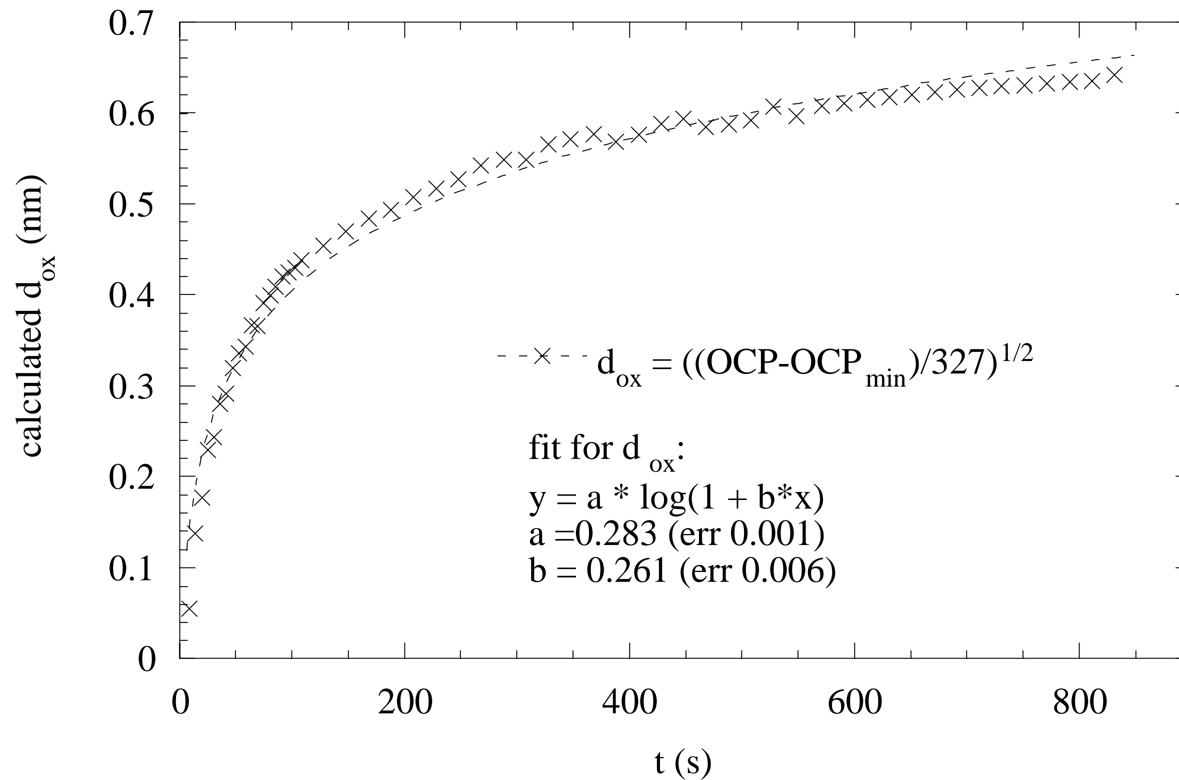
Oxidation Model

Oxide thickness (d_{ox}) as function of time calculated from V_{OC} trace

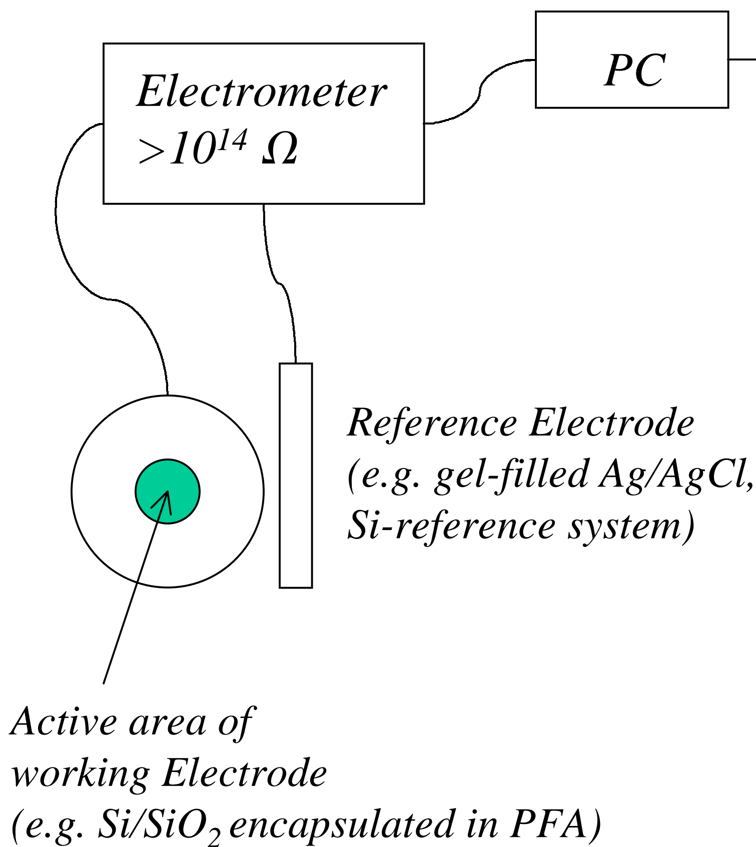


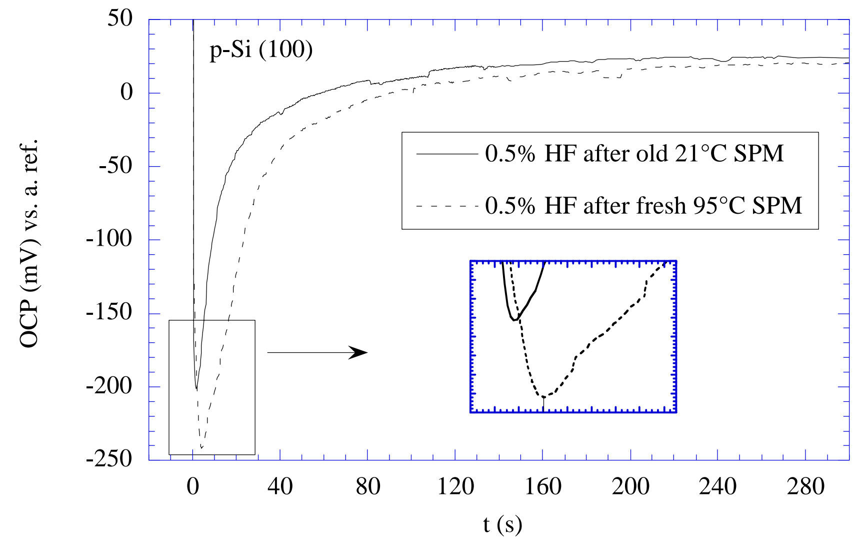
OCP in Oxidizing Environment

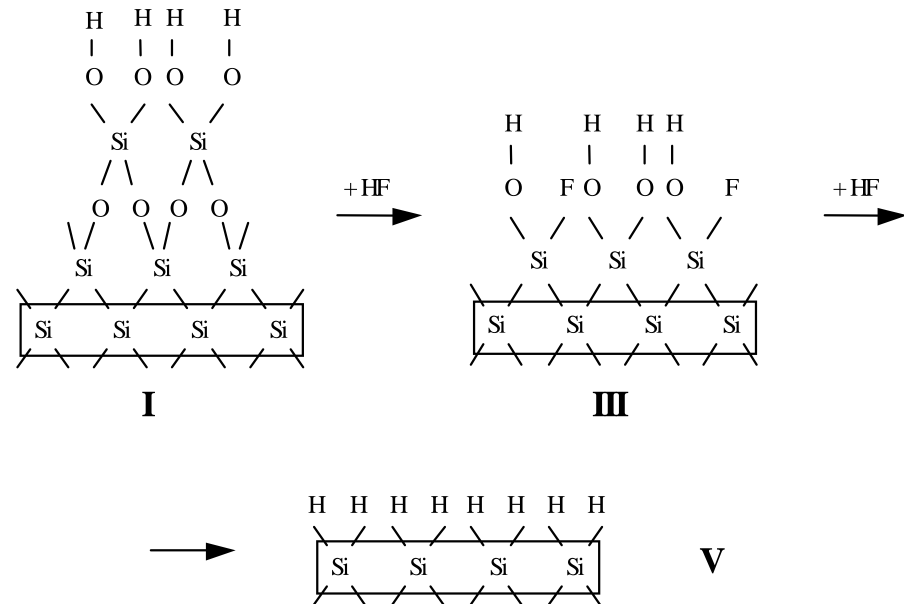
Oxide thickness (d_{ox}) as function of time



Experimental Set-Up
Etching, EDP-OCP





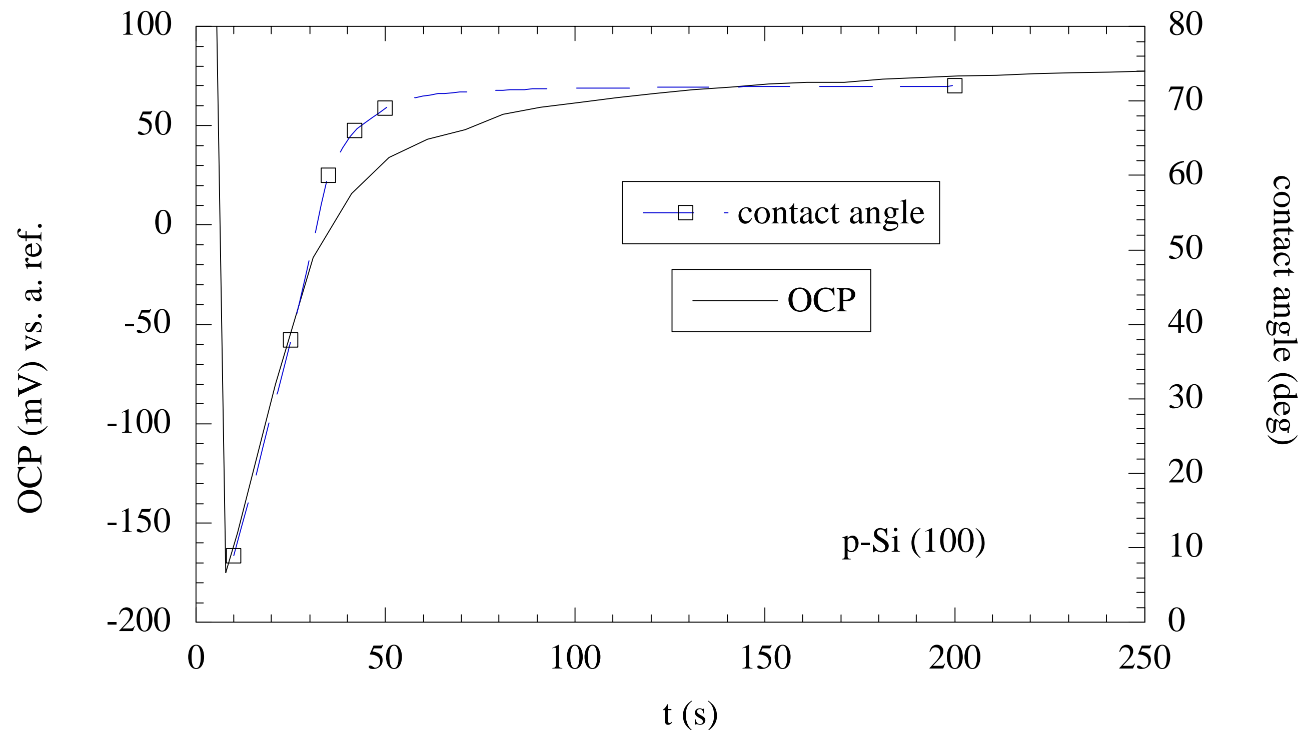


Example displayed: etching of SPM grown SiO_2 in 0.5 w% HF

H.F. Okorn-Schmidt, 10/26/2000

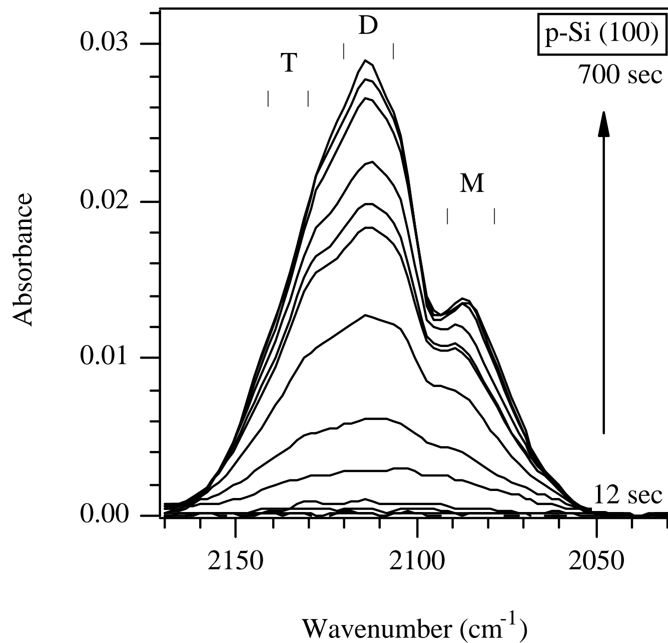
OCP in HF

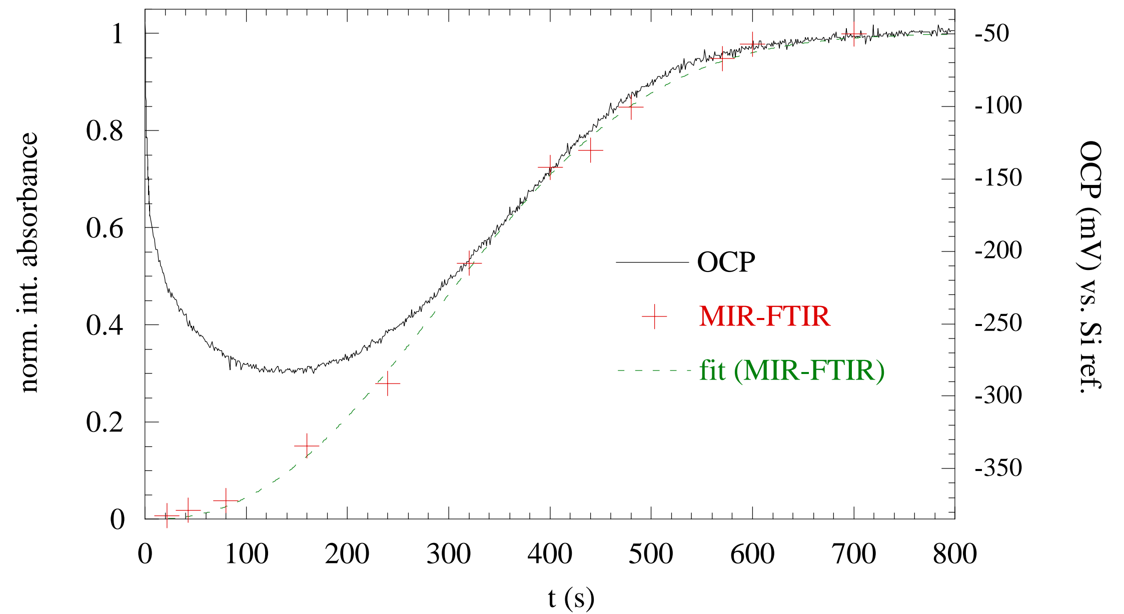
Correlation between the time evolution of the V_{OC} and the contact angle of a p-type Si wafer in 0.5 % HF (SPM oxide)



OCP in HF

p-Polarized FTIR spectra (SiH_x) as a function of the etching time in a 0.1% HF solution and correlation to the V_{OC}

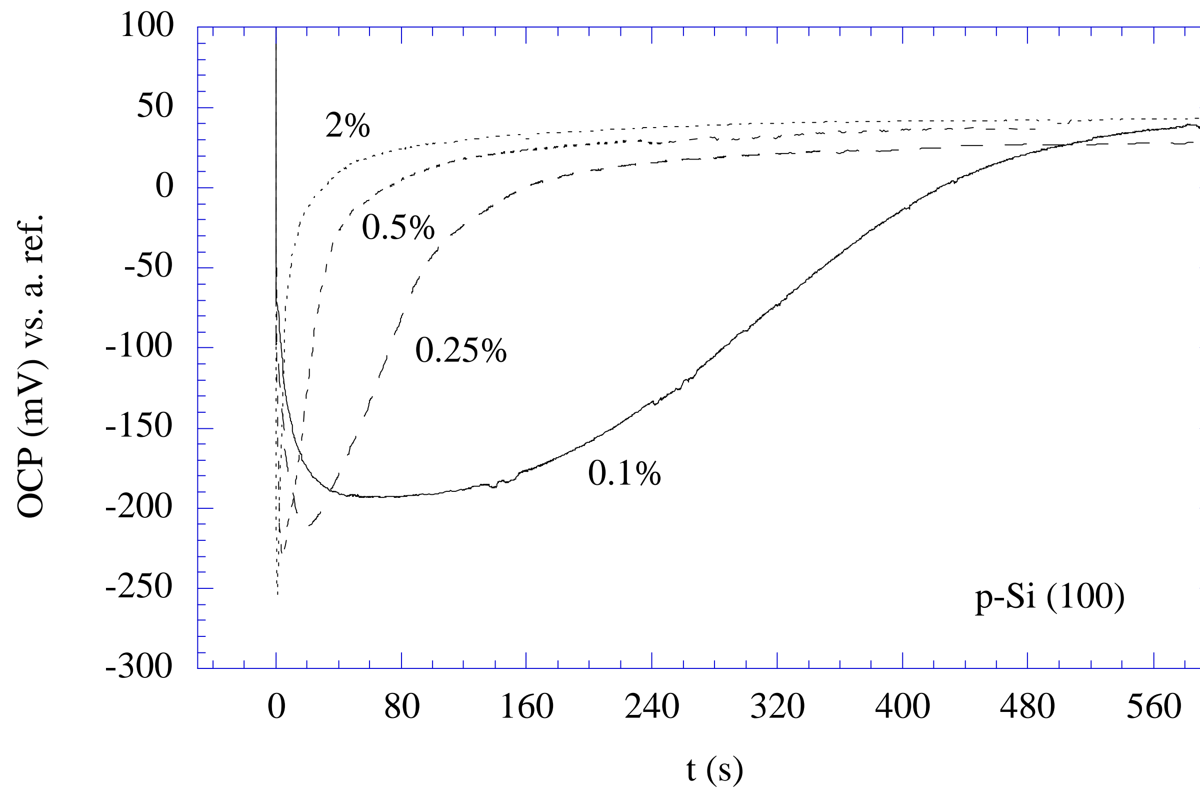




$$\text{Johnson–Mehl}: X = 1 - \exp[-(kt)^n]$$

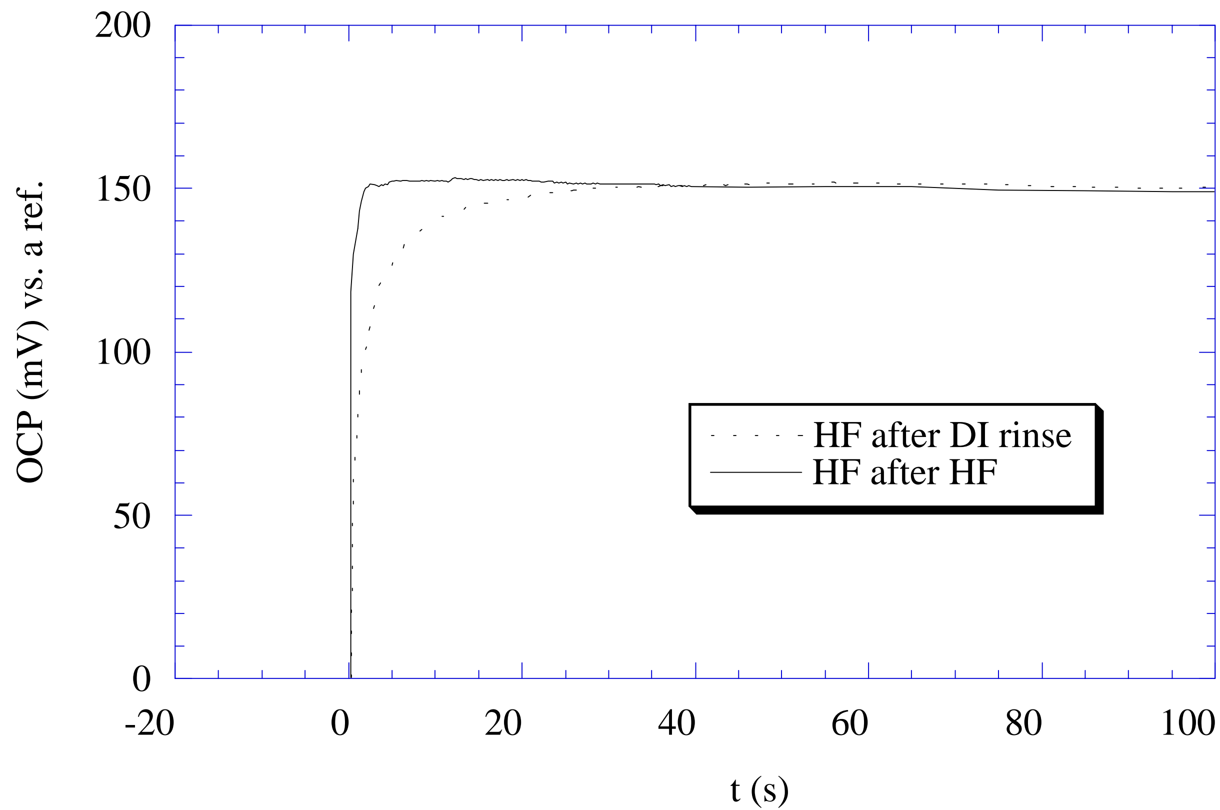
OCP in HF

V_{OC} traces as function of the HF concentration (in w-%)
(all measurements with equivalent chemically grown oxides)



OCP in HF

V_{OC} traces for p-type Si in 0.5% HF after 10 min DI rinse ('HF after DI rinse') and after HF ('HF after HF')



Experiments with DI/O_3

- O_3 concentrations tested (= in-tank concentrations):
  - ~1.3, ~4, ~5.3 and ~10.3 ppm
  - continuous overflow/rinse-tank

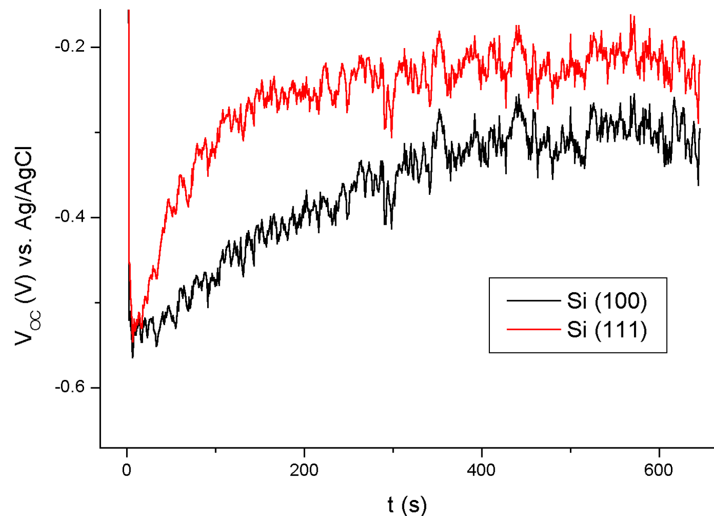
- Si substrates:
  - (100), 125 mm, 11-16 Ω cm
  - (111), 125 mm, 30-100 Ω cm

- Analytical techniques:
  - Oxidation-OCP: relative oxidation rates
  - EDP-OCP (0.25w% HF): relative/qualitative t_{chemox}, relative interface etching kinetics
  - Ellipsometry and AFM: quantitative t_{chemox}, surface morphology (RMS roughness)

Chemical Oxide Growth and Etching

V_{OC} traces for Si (100) and (111)

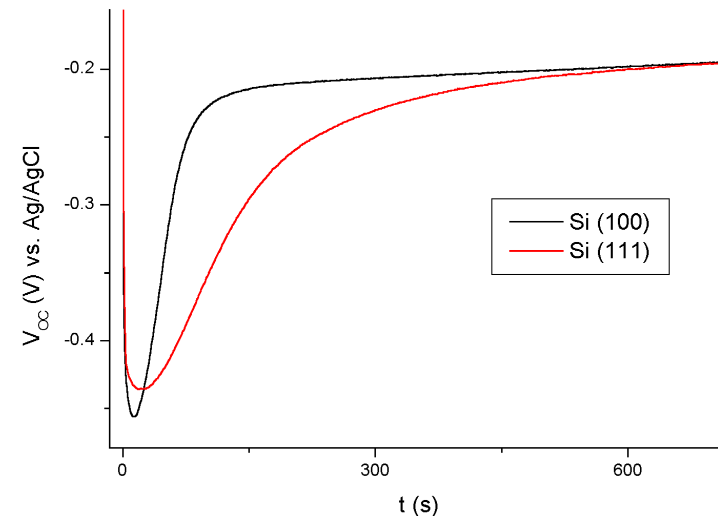
O_3 concentration: ~ 1.3 ppm



- faster initial oxidation rate on (111) (equivalent to gas-phase*)
- similar t_{chemox} after about 8 to 10 min

*A. Kurokawa et al., Mat. Res. Soc. Proc. Vol. 513 (1998) p. 37

HF concentration: 0.25 w%, std. light

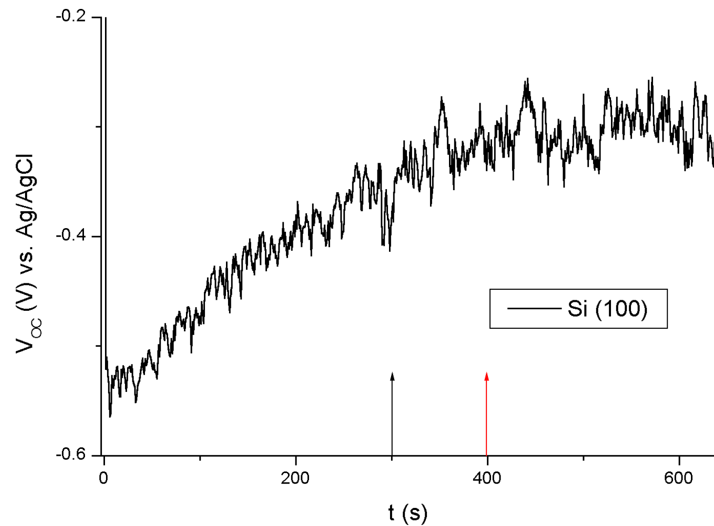


- similar t_{chemox}
- maybe less uniform etching of oxide
- significant slower H-passivation kinetics on (111)

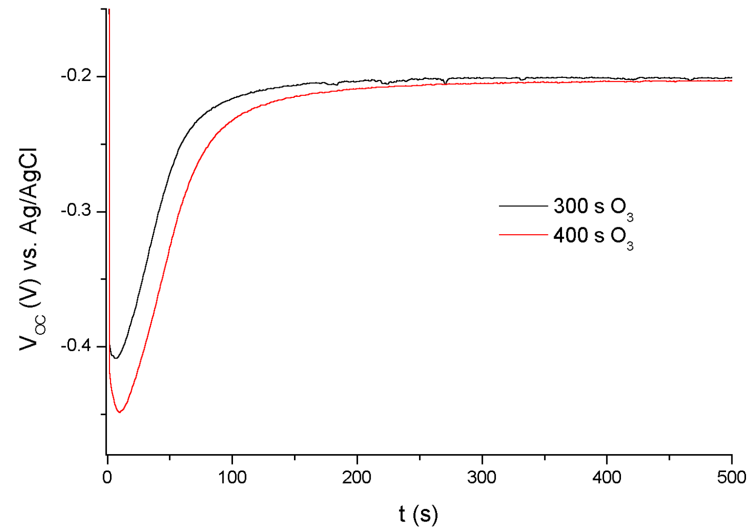
Chemical Oxide Growth and Etching

V_{OC} traces for Si (100)

O_3 concentration: ~ 1.3 ppm



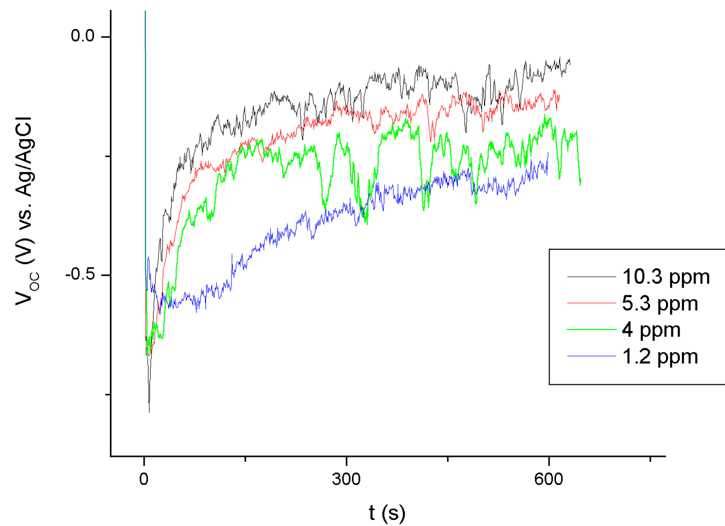
HF concentration: 0.25 w%, std. light

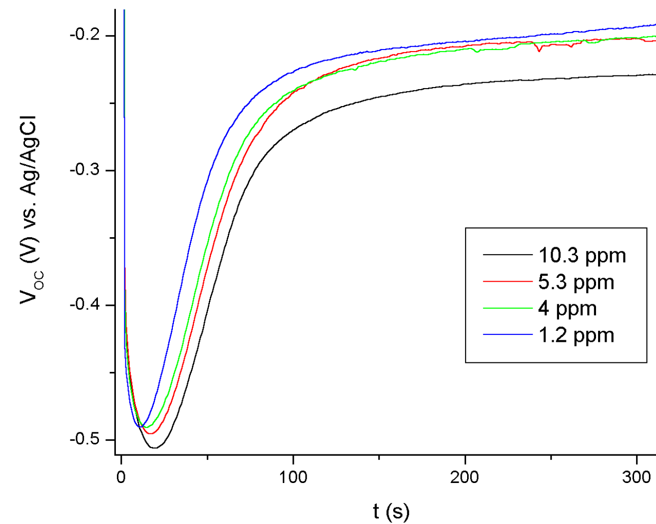


relative t_{chemox} can be visualized

EDP-OCP in HF

V_{OC} traces for Si (100) as function of the O_3 concentration





with increasing O_3 concentration:

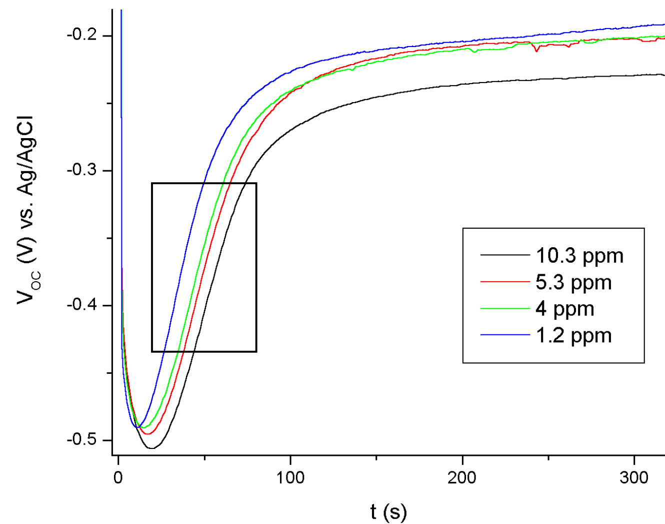
- significant increase of the initial oxidation rate *
- significant increase in the final t_{chemox} **

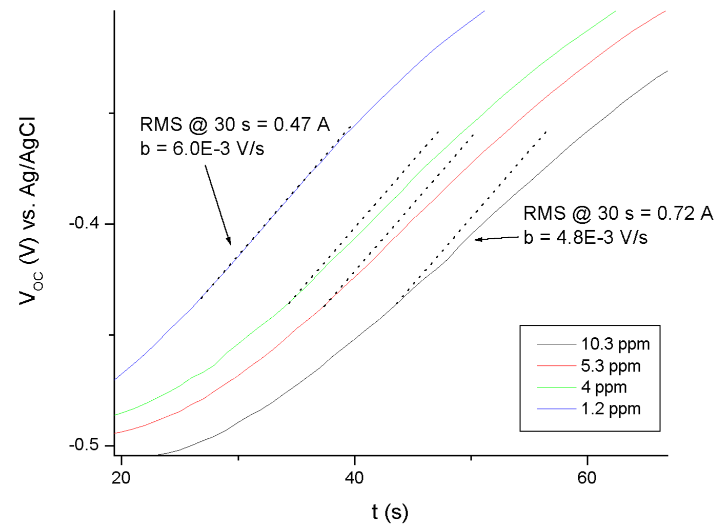
* F. De Smedt et al., UCPSS 1998

** S.L. Nelson et al. UCPSS 1996

EDP-OCP in HF

V_{OC} traces for SiO_2 etching on Si (100) as function of the O_3 concentration



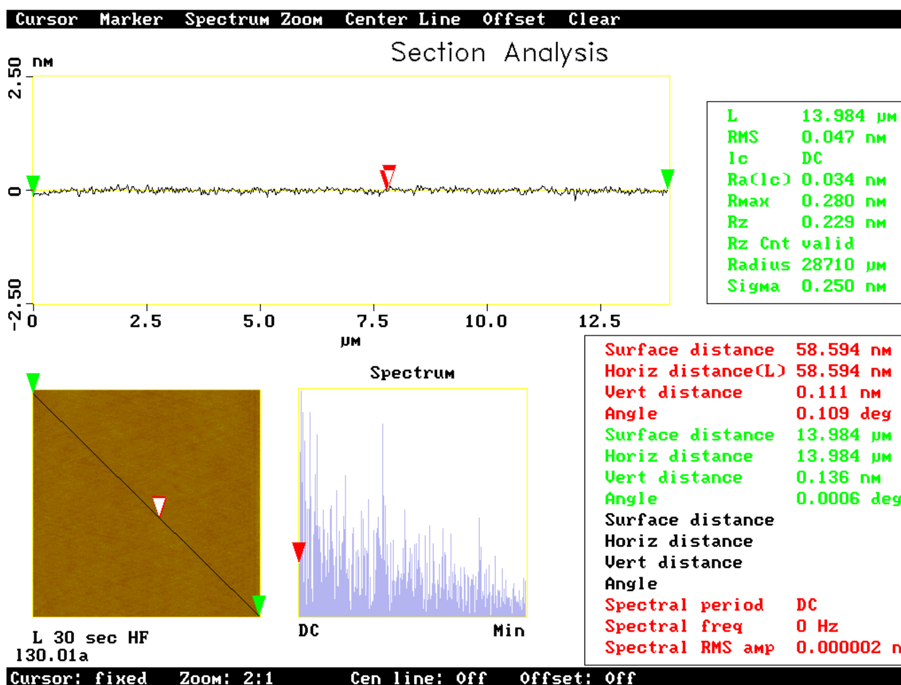


Slope of the *interface etching*-V_{OC} becomes more (111) like with higher O_3 concentration: <u>correlates to increasing RMS roughness</u> *

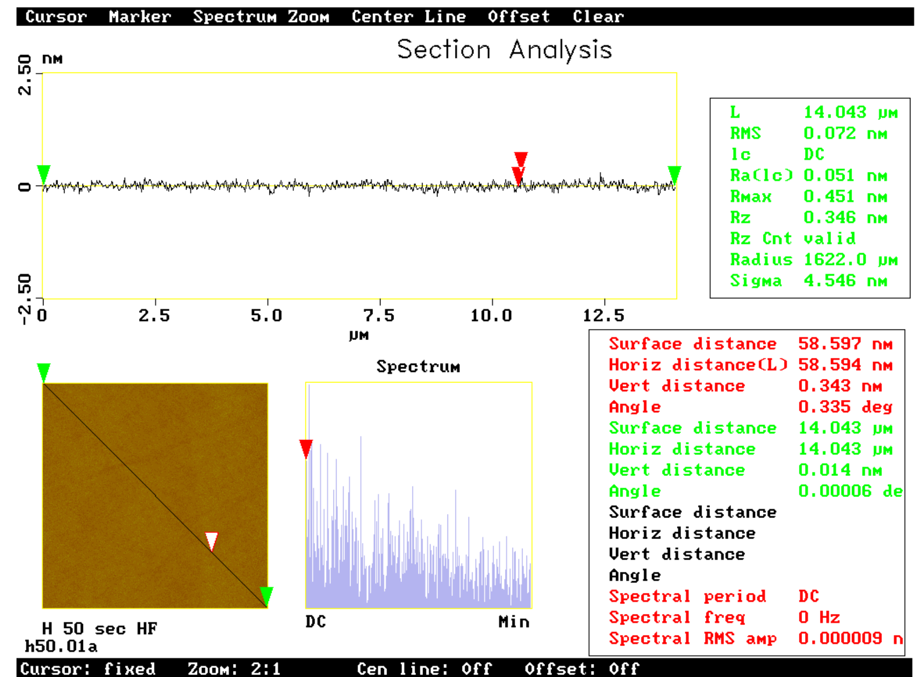
* Much disussed @ UCPSS 1998

AFM details "during" interface layer etching

~ 1.2 ppm O_3

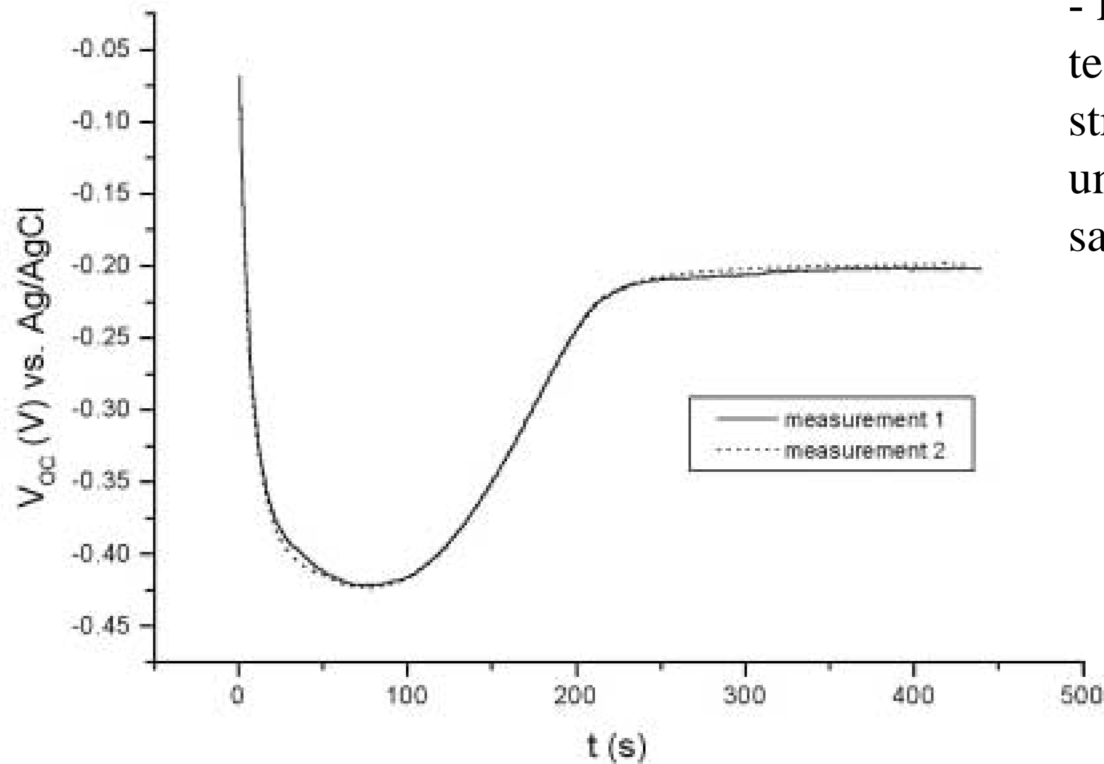


~ 10.3 ppm O_3



EDP-OCP of Thermal Oxides

Typical change of the V_{OC} with time while slowly removing about 1.2 nm nitrided oxide from a Si (100) surface in HF (0.5 w%)



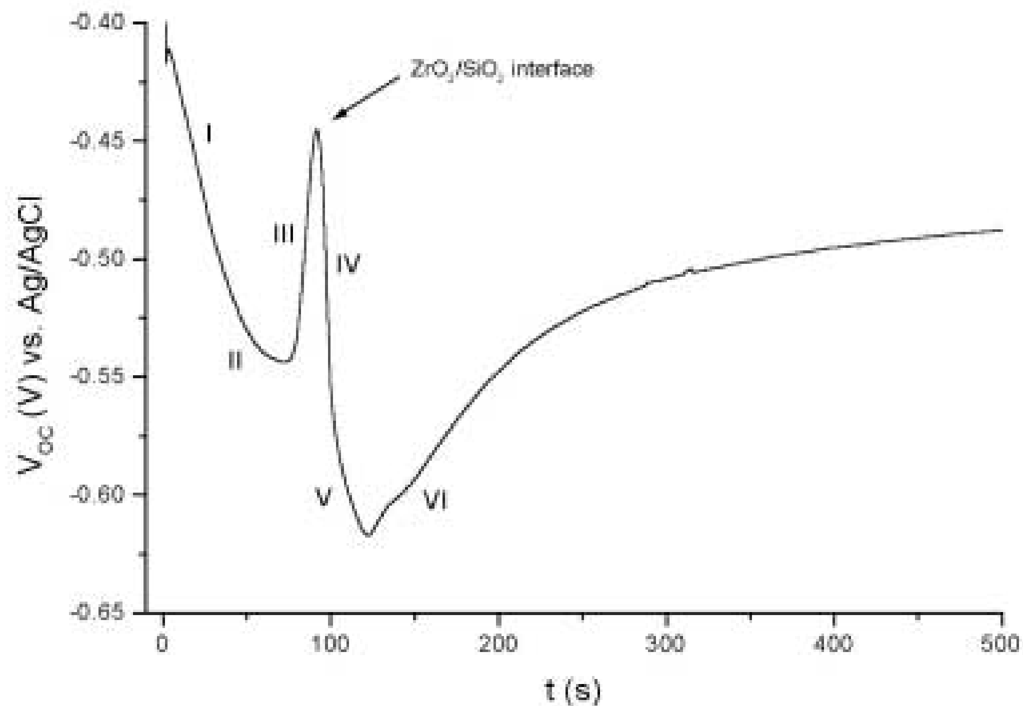
- Due to the sensitivity of the technique the reproducibility is strongly dependent on the uniformity/equivalency of the samples

EDP-OCP Measurements

- Electrochemical Depth-Profiling Open Circuit Potential Measurements:
  - following the V_{OC} (Open Circuit Potential, OCP) of a semiconductor sample during the removal of a dielectric layer on it's surface as a function of time
- Applicable to stacks of dielectric layers:
  - each dielectric material has a specific surface charge (potential) in a given chemical solution
  - V_{OC} adjust when new surface is exposed (change in capacitance)
- Valuable tool for fast screening of:
  - interface properties
  - interface mixing
  - film homogeneity
  - ...

Example of EDP-OCP
Characterization of Dielectric Stacks

V_{OC} depth profile for a ~ 4 nm ZrO_2 film deposited on thin thermally grown SiO_2



I: Etching of ZrO_2

II: Initial breakthrough to SiO_2, majority of surface still ZrO_2

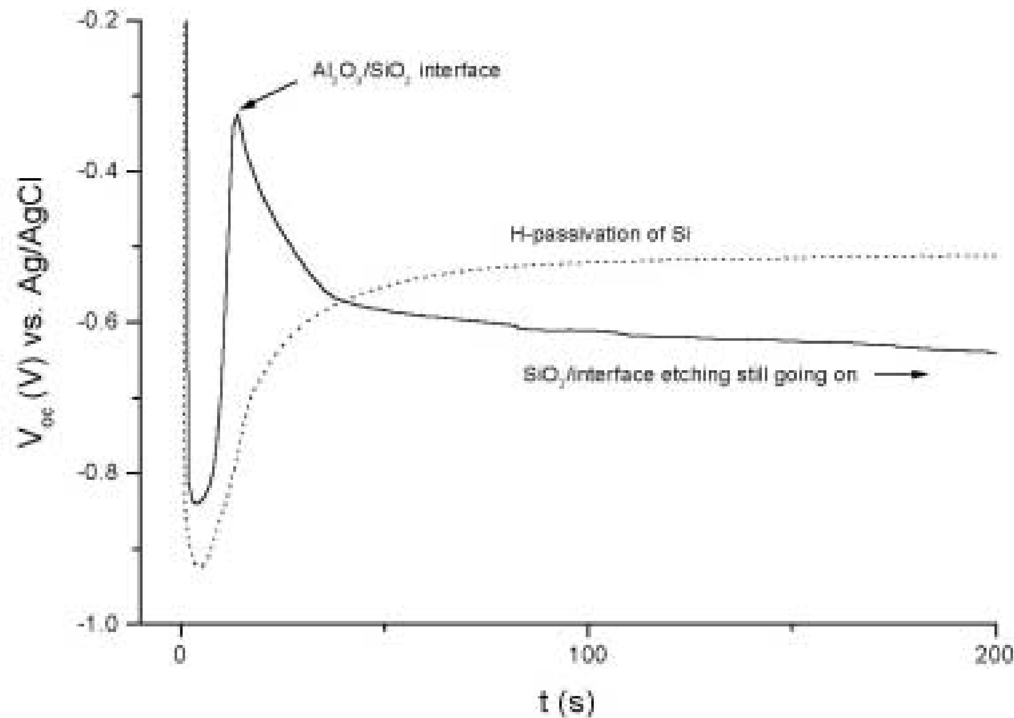
III: Adjustment of surface potential to new majority species Si-$(OH)_x$

IV: Etching of SiO_2

V: Initial breakthrough to Si

VI: H-passivation reaction becomes dominating

EDP-OCP of Al_2O_3



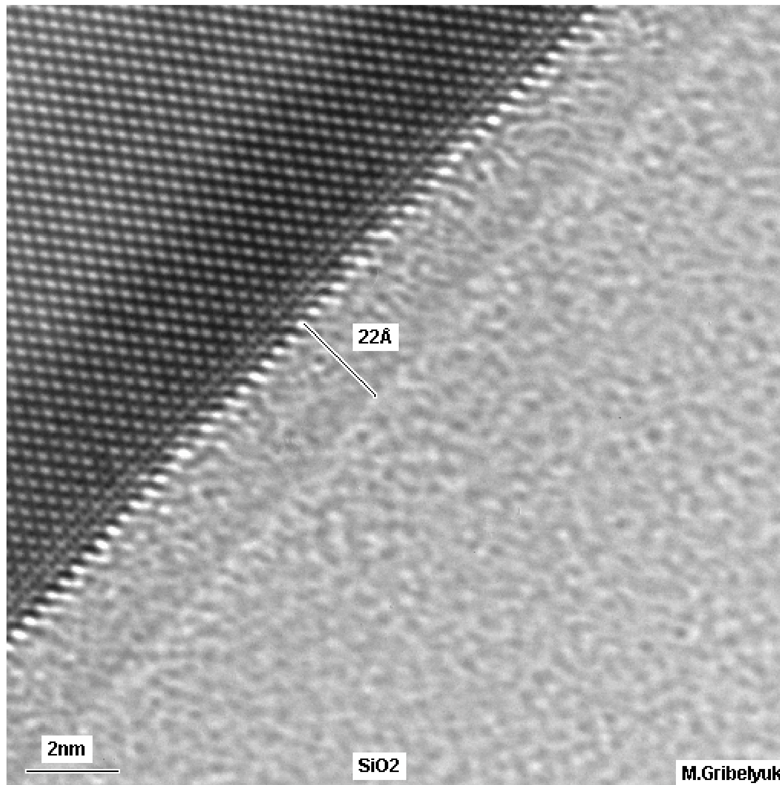
Al_2O_3: ~ 3 nm (ALCVD), as depositied

Interface: HF-last (dotted), thin SiO_2 (solid)

V_{OC} : in 0.1 w% HF, p-Si(100)

- On HF-last: uniform deposition of Al_2O_3 without interface SiO_2 formation
- On thermal oxide: sharp interface with thermal SiO_2
  - Al_2O_3 etches significantly faster than thermal SiO_2

Al_2O_3 on bare Si (after HF last): HRTEM images

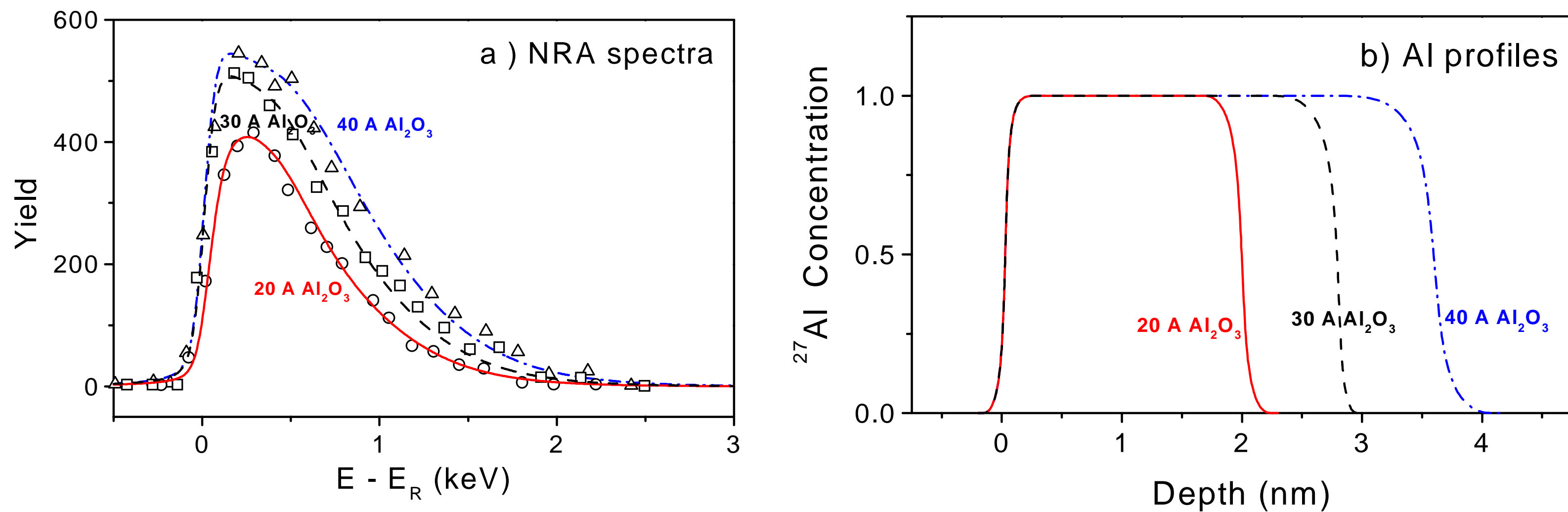


- Sharp interface
- Uniform film
- No evidence for interfacial SiO_2 during deposition

High Resoluton Depth Profiling of Aluminum by Nuclear (Resonance) Reaction Analysis

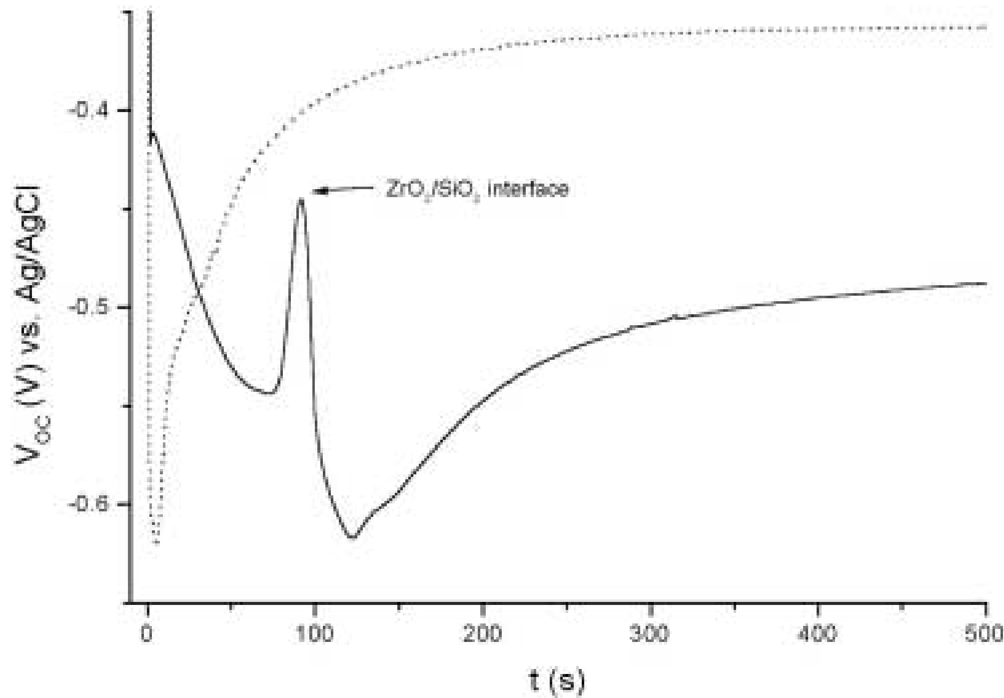
^{27}Al(p,γ)^{28}Si nuclear resonance (reaction) at 404.9 keV

E. Gusev, et al., APL 2000



* high depth resolution
* uniform Al_2O_3 films
* sharp interfaces

EDP-OCP of ZrO_2



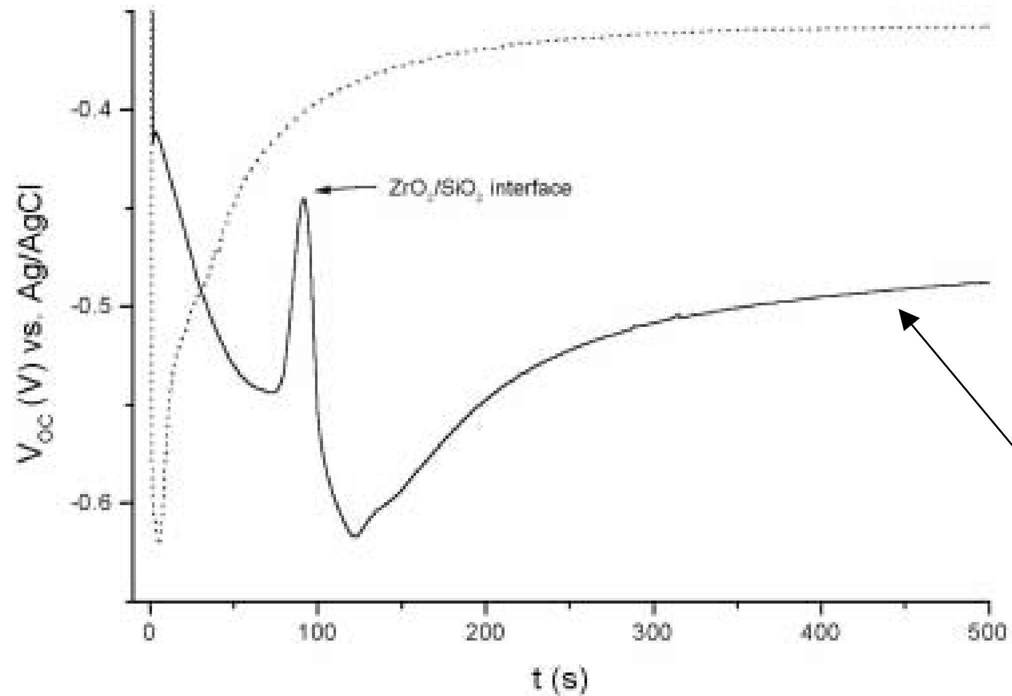
ZrO_2: ~ 4 nm (ALCVD), as deposited

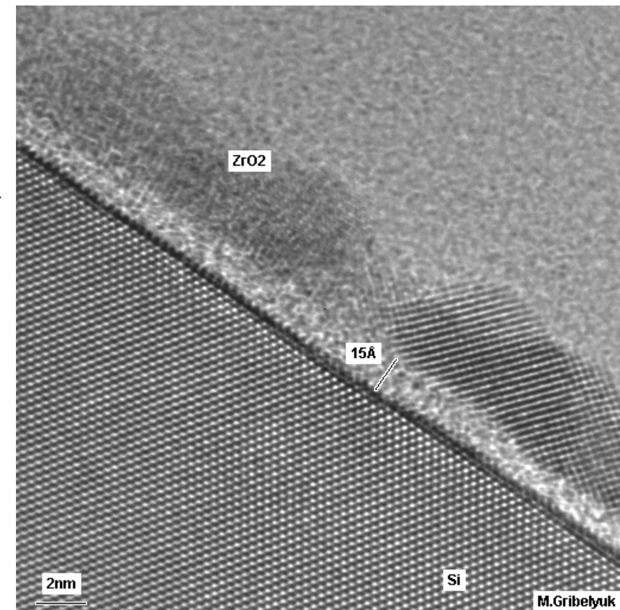
Interface: HF-last (dotted), 1.5 nm SiO_2 (solid)

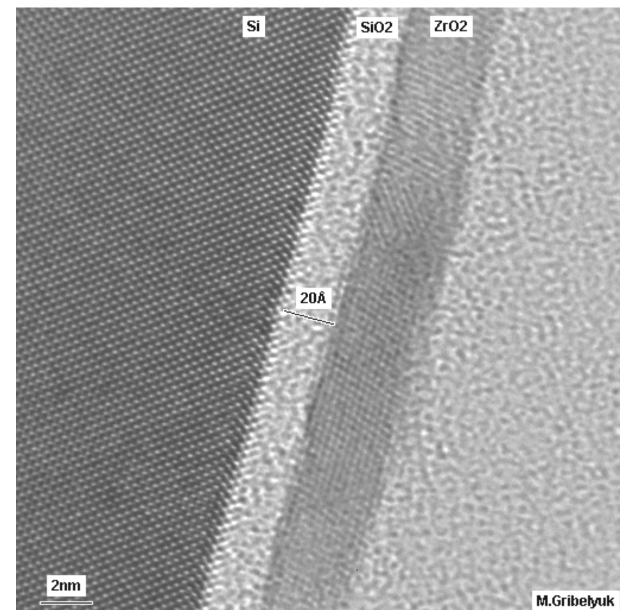
V_{OC} : in 0.5 w% HF, p-Si(100)

- On HF-last: non-uniform deposition of ZrO_2 with very fast "break-through" of HF to the substrate
- On thermal oxide: sharp interface with thermal SiO_2
  - as dep. ZrO_2 etches at similar rate than thermal SiO_2

EDP-OCP and HRTEM of ZrO_2







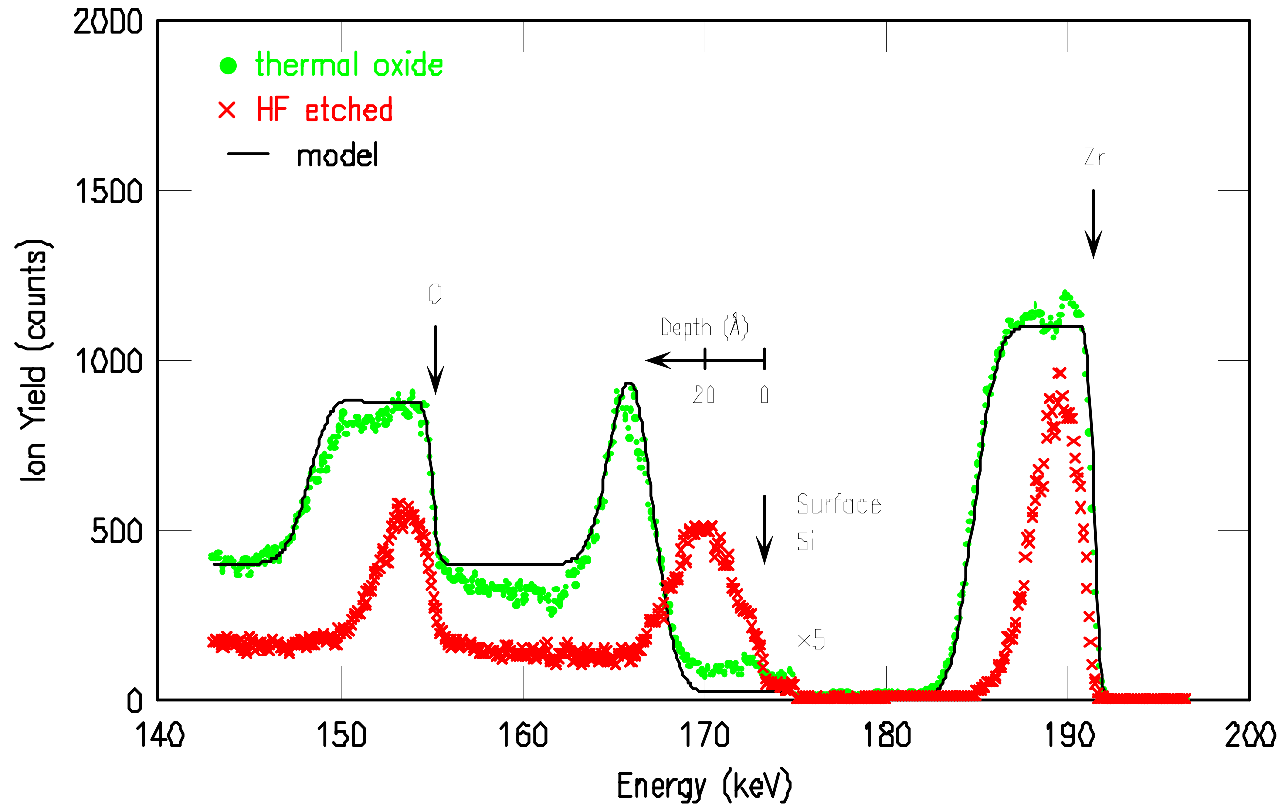
ZrO_2: ~ 4 nm (ALCVD), as deposited

Interface: HF-last (dotted), 1.5 nm SiO_2 (solid)

V_{OC} : in 0.5 w% HF, p-Si(100)

ZrO_2 on "HF last"/Si: MEIS depth profiling results

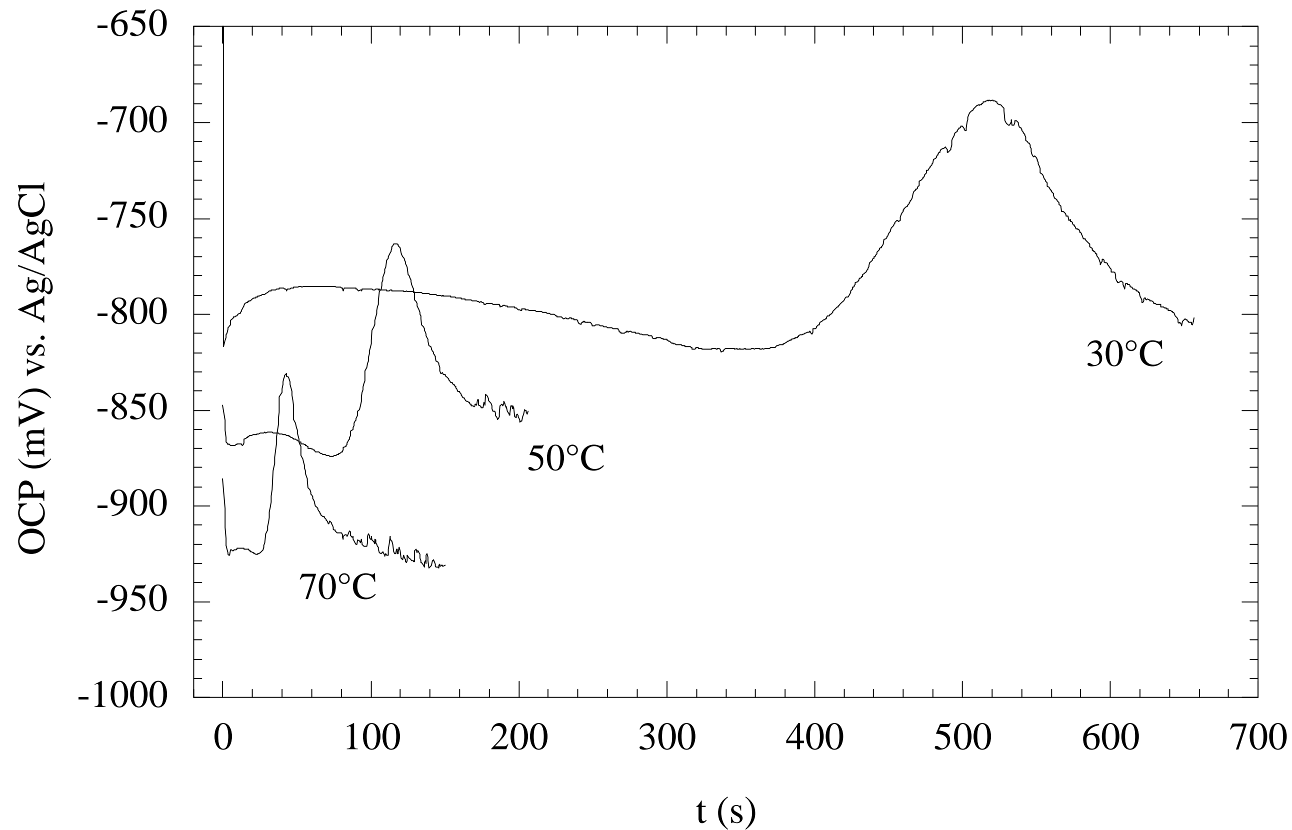
as deposited film 40 A ZrO2 on ~15 A SiO2 (green) and HF last (blue)
(M. Copel)



* nucleation problem of AL-CVD ZrO_2 of “HF last” Si
* ZrO_2 on thin SiO_2 is OK

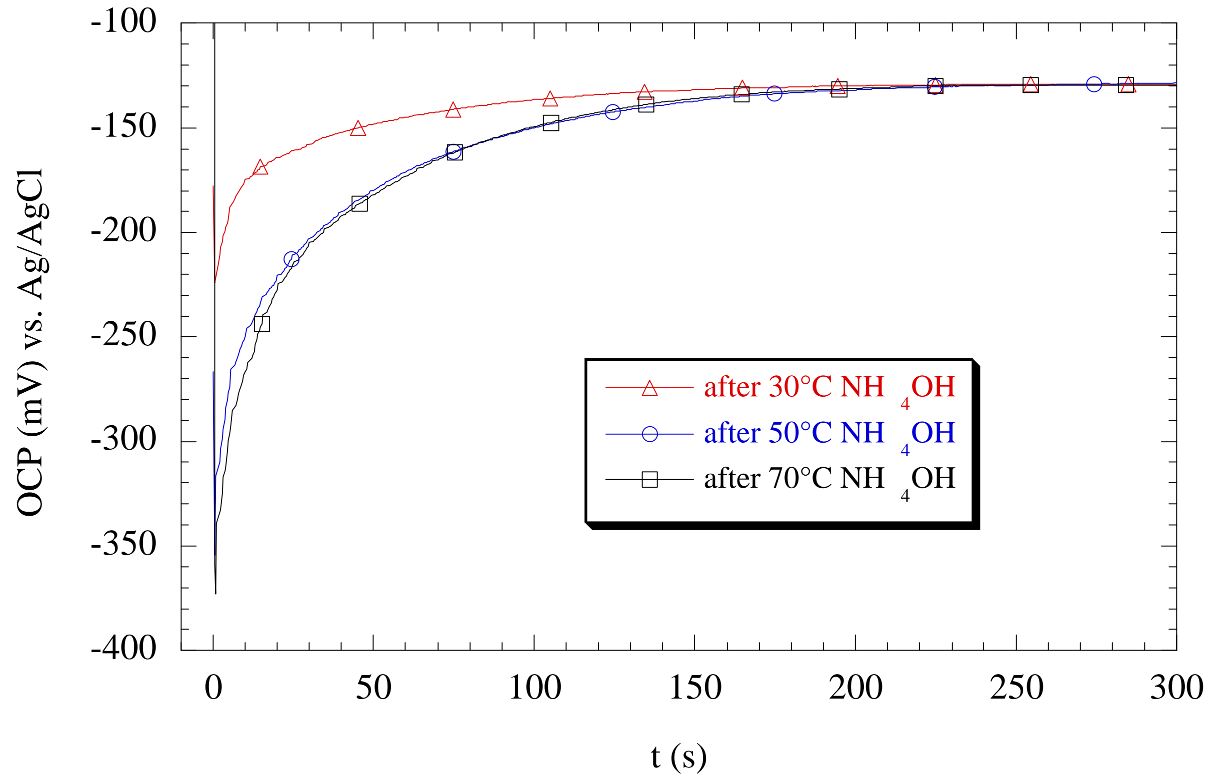
OCP in Aqueous NH_3

V_{OC} traces for the dissolution of SiO_2 (chemically grown) in 'NH_4OH' (~1.4M) as function of temperature



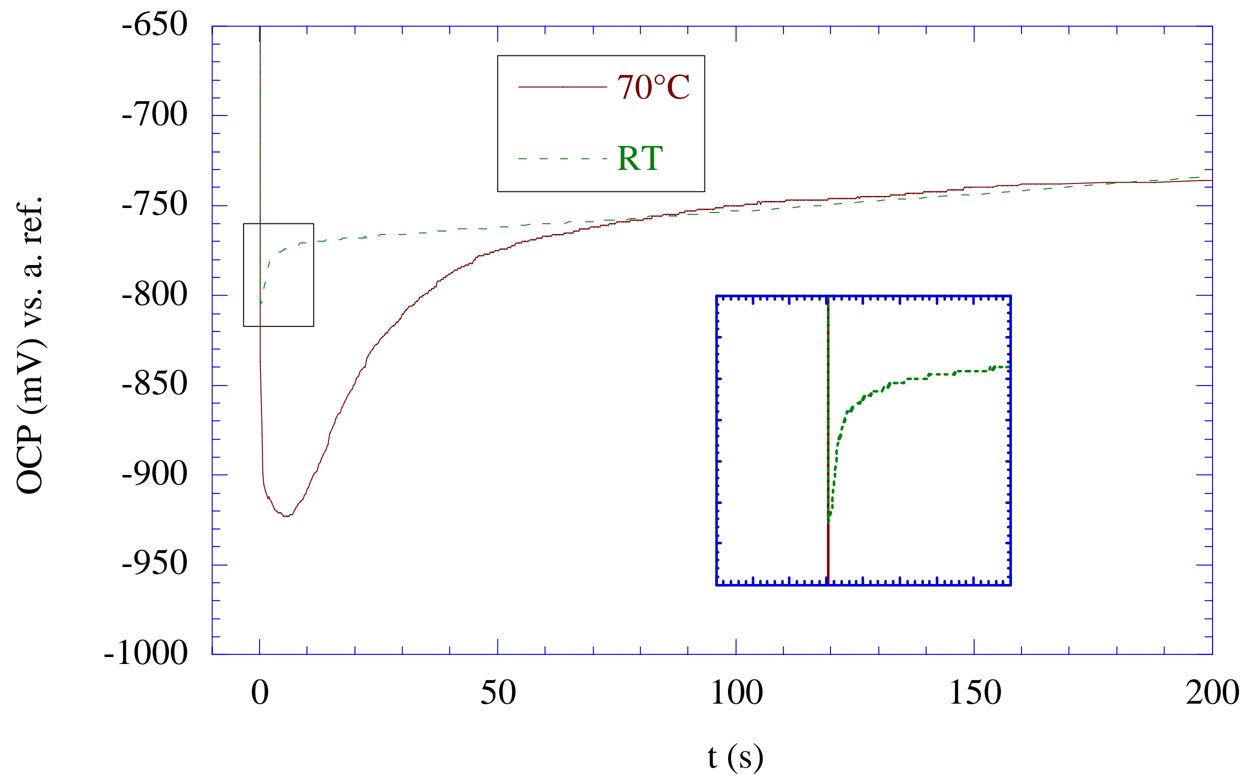
OCP in HF after Aqueous NH_3

V_{OC} traces of p-type Si being immersed into 0.25 % HF after treatment in aqueous ammonia



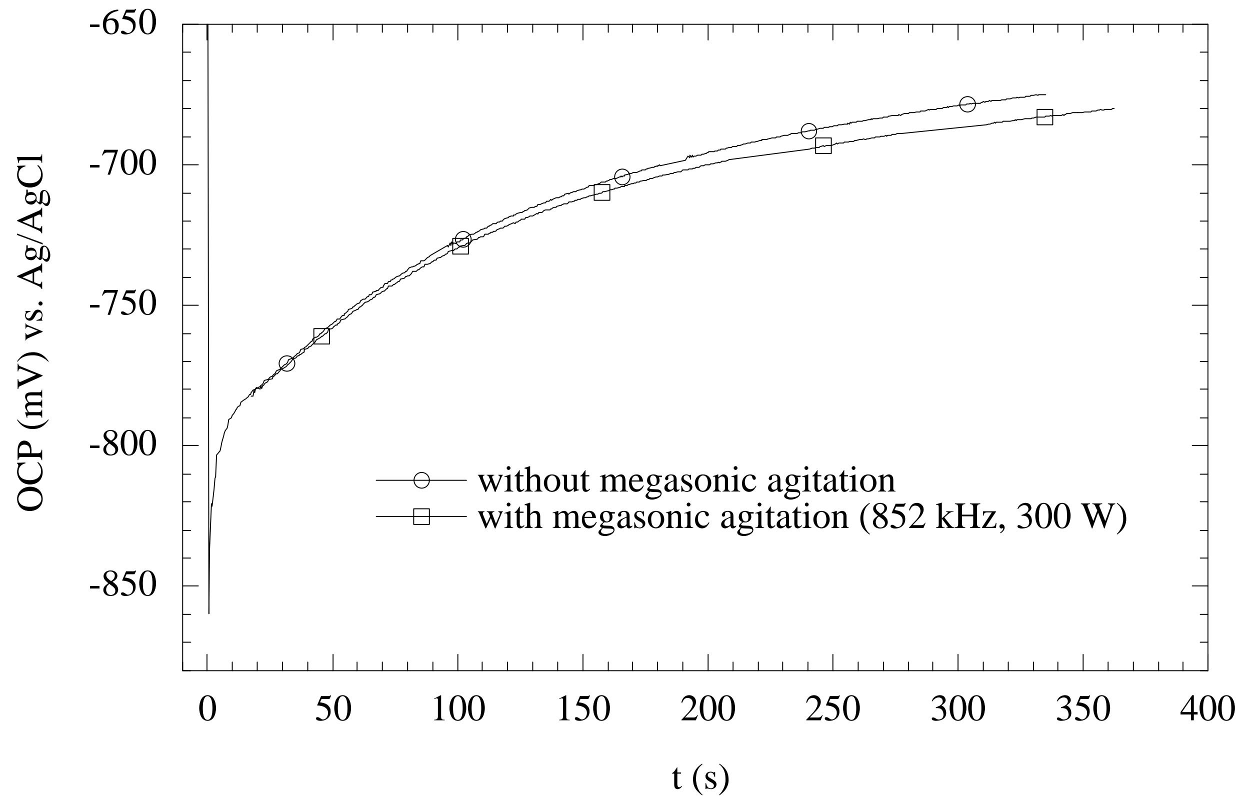
OCP in SC1

V_{OC} traces for a p-type substrate immersed in hydrophobic state into SC1 @ different temperatures



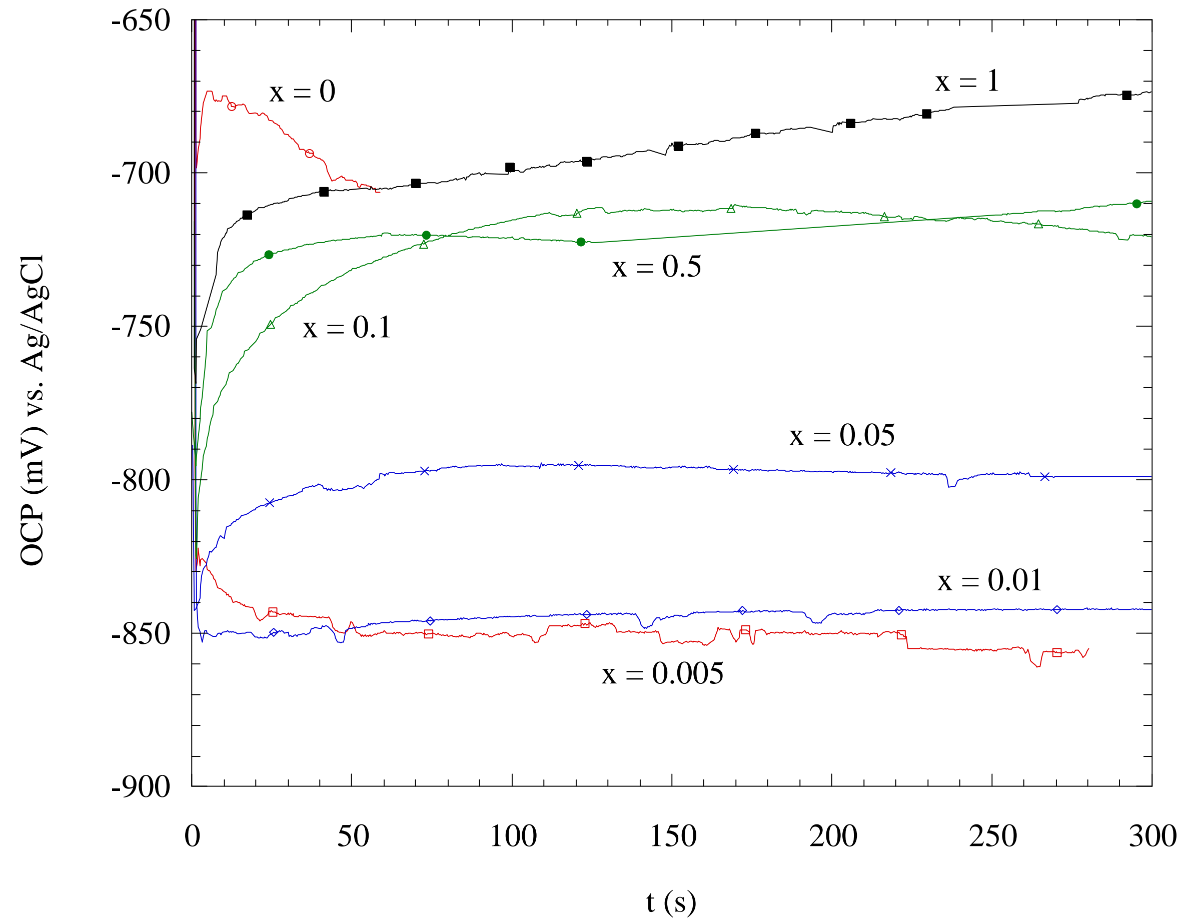
OCP in SC1

No influence of megasonic agitation on the SC1 oxidation



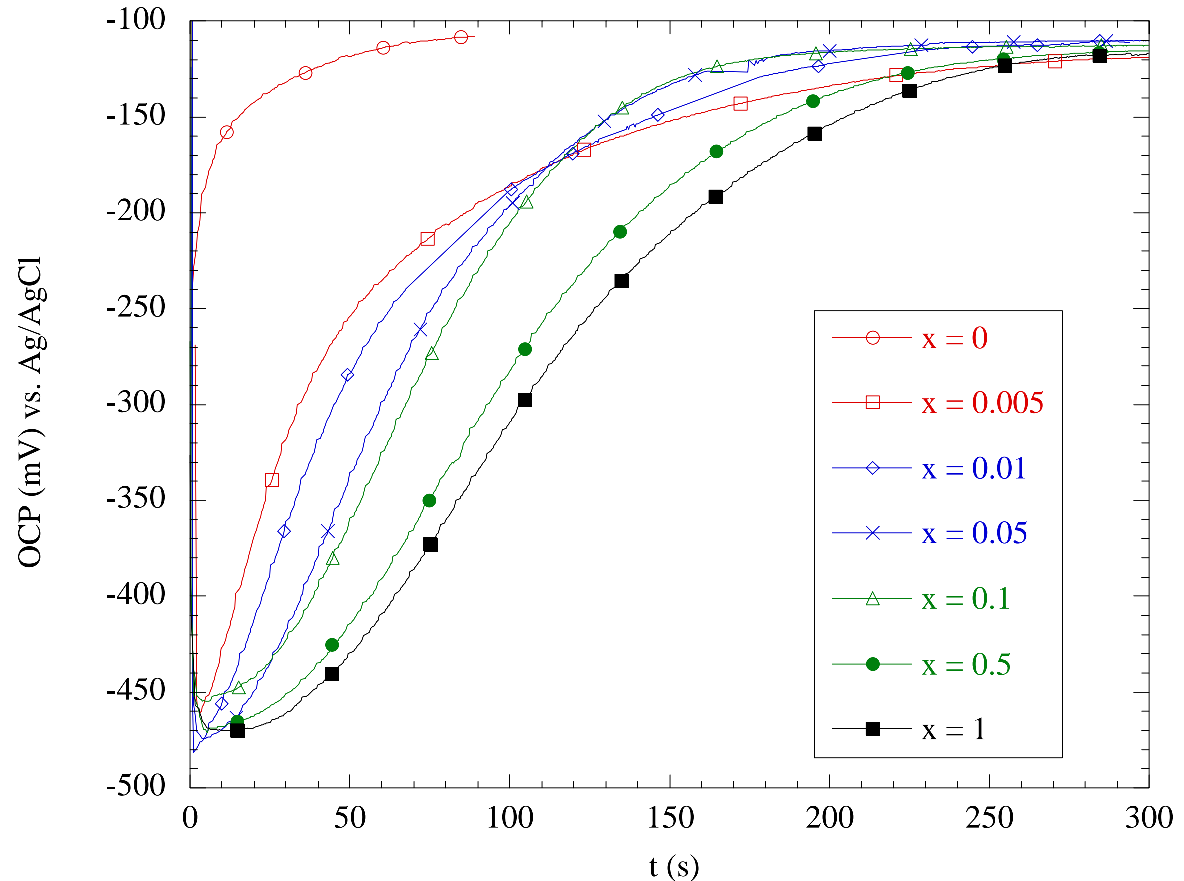
OCP in SC1 / p-type Si

OCP of p-type Si in SC1 as function of the H_2O_2 concentration ($0.25/x/5 = NH_4OH/H_2O_2/H_2O$ at room temperature)



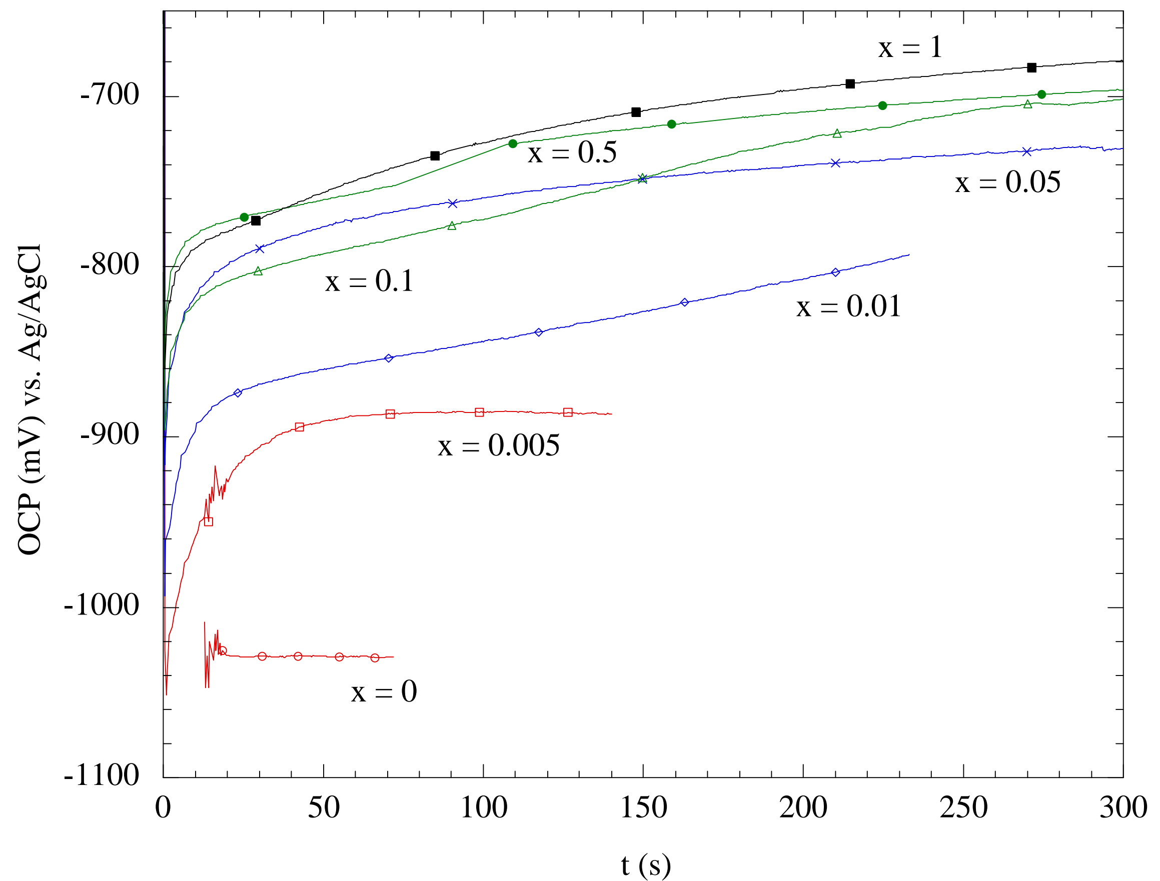
OCP in HF after SC1 / p-type Si

OCP of p-type Si in 0.2% HF after SC1 with variable H_2O_2 concentration
(0.25/x/5 = $NH_4OH/H_2O_2/H_2O$
at room temperature



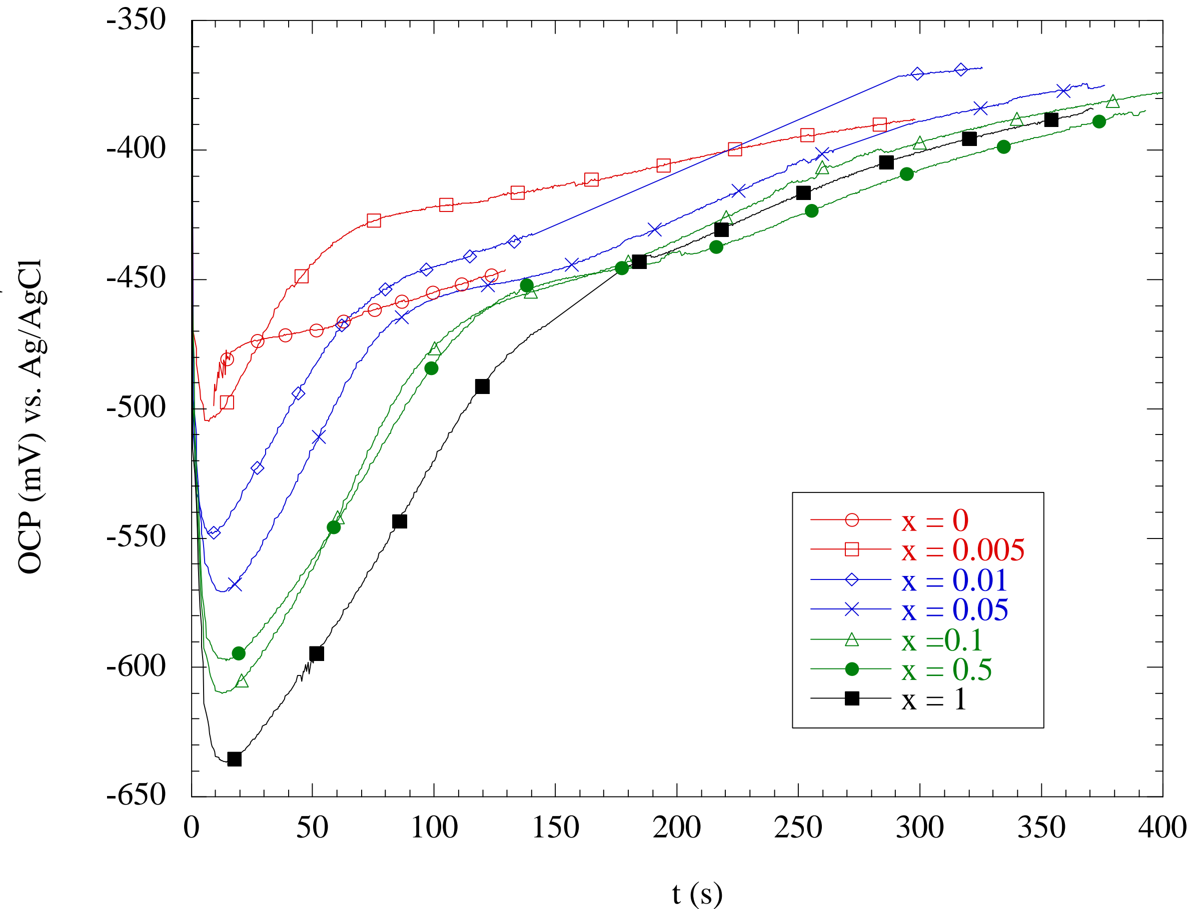
OCP in SC1 / n-type Si

OCP of n-type Si in SC1 as function of the H_2O_2 concentration
($0.25/x/5 = NH_4OH/H_2O_2/H_2O$
at room temperature



OCP in HF after SC1 / n-type Si

OCP of n-type Si in 0.2% HF after SC1 with variable H_2O_2 concentration
(0.25/x/5 = $NH_4OH/H_2O_2/H_2O$ at room temperature



Summary 1/2

- V_{OC} measurements enable the *real time* and *in-situ* observation of semiconductor cleaning and etching processes:
  - ideal for the determination of oxidation/etching kinetics
    - first visualization of 2-step HF etching process
    - faster initial oxidation rate of Si(111) compared to Si(100)
    - slower H-passivation kinetics for Si(111)compared to Si(100)
    - qualitative estimate of resulting surface roughness possible (!)
    - determination of oxide thickness during growth
- References:
  - Review of OCP work until 1997:

H.F. Okorn-Schmidt, IBM J. Res. Develop. **43**, 354 (1999)

  - DI/O3 study:

H.F. Okorn-Schmidt et al., UCPSS 2000, to be published in the conference proceedings (Solid State Phenomena)

Summary 2/2

- V_{OC} measurements enable the fast screening of dielectric materials (EDP-OCP, electrochemical depth-profiling - Open Circuit Potential measurements)
  - etch rates/ etch behavior
  - interface properties
  - interface mixing
  - film homogeneity
  - …
- References:
  - High-k stacks:

  H.F. Okorn-Schmidt et al., The Electrochem. Soc., Pennington, NJ, Vol. **2000-2**, p.505
  - Work until 1996:

  PhD thesis, University of Technology Graz/Austria (1996, in english)
  - Work from 1989 to 1991:

  Diploma Thesis, University of Technology Graz/Austria (1991, in german)

  Presentation at the NATO Summerschool, 1-13 July, 1991,Erice/Italy