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)
  
  Figure 3 shows the variation of the corrosion potential of MoSi$_2$ in a 0.6 mol/l K$_3$Fe(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 underlying 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 each rate 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.

- 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 dielectrics (high-k and stacks) and DI/O$_3$ chemistries

ERC Tele Seminar

H.F. Okorn-Schmidt, 10/26/2000
How new is this technique?

- Rest Potential measurements (OCP) have been and are very common in metal electrochemistry.


![Diagram](image.png)

**Fig. 15**
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 NH₄⁺ solution, pH = 4.
Introduction

(a) charge

- Gouy - layer
- Helmholtz - layer
- semiconductor space charge - layer

(b) potential

- $\Phi_{Ga}$
- $\Phi_S$
- $\Phi_G$
- $\Phi_H$
Introduction

Energy band model for an n-type semiconductor.

\[ E_{fb} \quad e\Phi_{SC} \quad E_{C} \quad E_{F} \quad E_{V} \]

\[ n_{o} \quad p_{o} \quad n_{s} \quad p_{s} \]
Experimental Set-Up

**Oxidation**

**Reference Electrode**
(e.g. gel-filled Ag/AgCl, Si-reference system, capillary-PFE salt bridge)

**Active area of working Electrode**
(e.g. Si/SiO\textsubscript{2} encapsulated in PFA)

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

$$\Delta_{\text{OCP}} = |PMP - V_{\text{OC}} @600\text{s immersion time}|$$
Oxidation Model
(solving the Poisson Equations)

\[ V = \frac{q}{8N_{\text{Sub}} \varepsilon_{\text{ox}} \varepsilon_{\text{Si}}} \left( 4Q_{\text{ox}}^2 \varepsilon_{\text{ox}} + 4N_{\text{ox}}Q_{\text{ox}} \varepsilon_{\text{ox}} d_{\text{ox}} + 8N_{\text{Sub}}Q_{\text{ox}} \varepsilon_{\text{Si}} d_{\text{ox}} + N_{\text{ox}}^2 \varepsilon_{\text{ox}} d_{\text{ox}}^2 \right) \]
Oxidation Model

\[ V = nd_{ox}^2 \quad \text{with} \quad n = \frac{qN_{ox}^2}{8N_{Sub}\varepsilon_{Si}} \]

\[ V = \Delta_{OCP} (V) \]

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

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

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

\[ N_{ox} \text{ the amount of charge in the oxide (nm}^{-3}) \]
Oxidation Model

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

OCP (mV) vs. Si ref.

Fit for $d_{ox}$:

$$y = a \cdot \log(1 + b \cdot x)$$

- $a = 0.627$ (err 0.002)
- $b = 0.137$ (err 0.002)
OCP in Oxidizing Environment

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

\[ d_{\text{ox}} = \left( \frac{(OCP - OCP_{\text{min}})}{327} \right)^{1/2} \]

fit for $d_{\text{ox}}$:
\[ y = a \times \log(1 + b \times x) \]
\[ a = 0.283 \text{ (err 0.001)} \]
\[ b = 0.261 \text{ (err 0.006)} \]
Experimental Set-Up
Etching, EDP-OCP

**Reference Electrode**
(e.g. gel-filled Ag/AgCl, Si-reference system)

Active area of working Electrode
(e.g. Si/SiO₂ encapsulated in PFA)

Example displayed: etching of SPM grown SiO₂ in 0.5 w% HF
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 $V_{OC}$

Johnson–Mehl: $X = 1 - \exp[\frac{-1}{(kt)\gamma}]$
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 $\Omega$ cm
  - (111), 125 mm, 30-100 $\Omega$ 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: $\sim 1.3$ ppm

HF concentration: 0.25 w%, std. light

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


- 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: $\sim 1.3$ 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: correlates to increasing RMS roughness *

* Much disussed @ UCPSS 1998
AFM details “during” interface layer etching

~ 1.2 ppm O₃  ~ 10.3 ppm O₃
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 its 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 $\text{Al}_2\text{O}_3$

$\text{Al}_2\text{O}_3$: ~ 3 nm (ALCVD), as deposited

*Interface*: HF-last (dotted), thin $\text{SiO}_2$ (solid)

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

- On HF-last: uniform deposition of $\text{Al}_2\text{O}_3$ without interface $\text{SiO}_2$ formation
- On thermal oxide: sharp interface with thermal $\text{SiO}_2$
  - $\text{Al}_2\text{O}_3$ etches significantly faster than thermal $\text{SiO}_2$
Al$_2$O$_3$ on bare Si (after HF last): HRTEM images

- Sharp interface
- Uniform film
- No evidence for interfacial SiO$_2$ during deposition
High Resolution Depth Profiling of Aluminum by Nuclear (Resonance) Reaction Analysis

$^{27}\text{Al}(p,\gamma)^{28}\text{Si}$ nuclear resonance (reaction) at 404.9 keV

E. Gusev, et al., APL 2000

* high depth resolution
* uniform $\text{Al}_2\text{O}_3$ films
* sharp interfaces
EDP-OCP of ZrO$_2$

- 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$_2$

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)
EDP-OCP and HRTEM of ZrO₂

ZrO₂: ~ 4 nm (ALCVD), as deposited
Interface: HF-last (dotted), 1.5 nm SiO₂ (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$_4$OH’ (~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

![Graph showing OCP (mV) vs. Ag/AgCl with and without megasonic agitation.](chart.png)
OCP of p-type Si in SC1 as function of the H$_2$O$_2$ concentration (0.25/x/5 = NH$_4$OH/H$_2$O$_2$/H$_2$O at room temperature)
OCP of p-type Si in 0.2% HF after SC1 with variable H₂O₂ concentration (0.25/x/5 = NH₄OH/H₂O₂/H₂O) at room temperature.
OCP of n-type Si in SC1 as function of the H₂O₂ concentration (\(0.25/x/5 = \text{NH}_4\text{OH}/\text{H}_2\text{O}_2/\text{H}_2\text{O}\) at room temperature
OCP of n-type Si in 0.2% HF after SC1 with variable H$_2$O$_2$ concentration 
(0.25/x/5 = NH$_4$OH/H$_2$O$_2$/H$_2$O) 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:
  – 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:
  
  – 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