3D capacitors on silicon with high density pore network and ZrO2 dielectric films deposited by MOCVD

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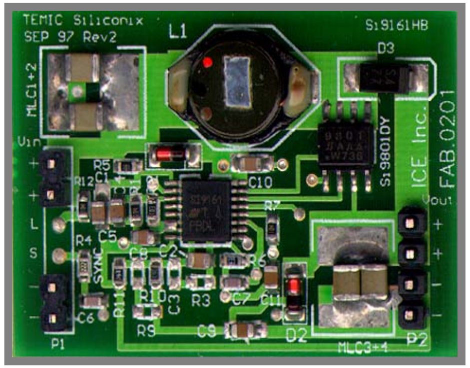
Introduction: Context

- Portable electronics
  - Numerous functionalities
  - Miniaturization of DC-DC converters

- Passive components (L,C,R): from discrete to integrated solutions
  - Low profile, miniaturization
  - Reliability
  - Cost reduction.



- How?
  - Increase of systems operating frequencies
  - New materials, adapted methods of microfabrication

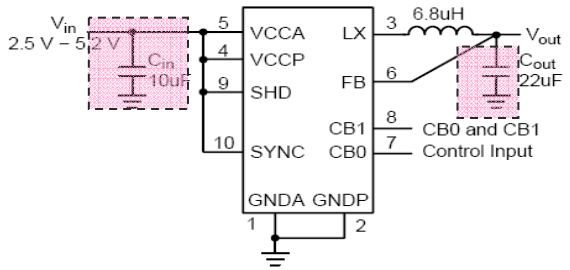


Figure 1. Typical Application Circuit

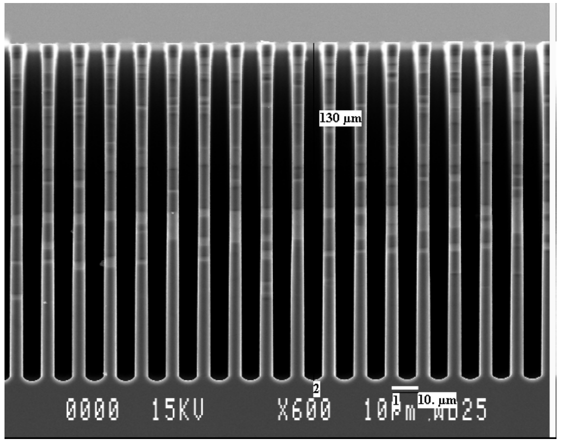
Converter PWM DC-DC On Semicond. step-down [NCP1508] 3mm x 3mm

High density capacitors

- Objectives:
  - High capacitance density : 1 µF/mm²
    - Operating frequencies (500 kHz – 10 MHz)
  - Power: few watts (V_{in}= 5V, I_{in} = 1 A)
    - Breakdown voltage: 20V
  - Efficiency: > 90%
    - Low losses in materials and structures

$$C = \varepsilon_0 \varepsilon_r \frac{S}{e}$$

- Solutions:
  - Increase electrode surface
    - Deep cavities in Si (bottom electrode)
  - Use of high-k dielectrics



Cross-section of silicon cavities etched by DRIE

Outline

I. Preliminary results and state of the art

II. Towards higher capacitance density for 3D capacitors:

II.a. Electrochemical etching of dense pore network in silicon.

II.b. Integration of high-k material.

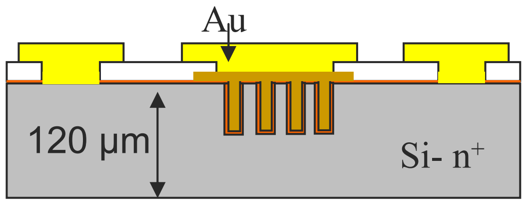
- ZrO_2 material characterization (2D and 3D) -Optimization of MOCVD conditions
- Electrical characterization (2D) of ZrO_2 films

III. Conclusions and future work.

I. Preliminary results: 3D capacitors

- **Fabrication**

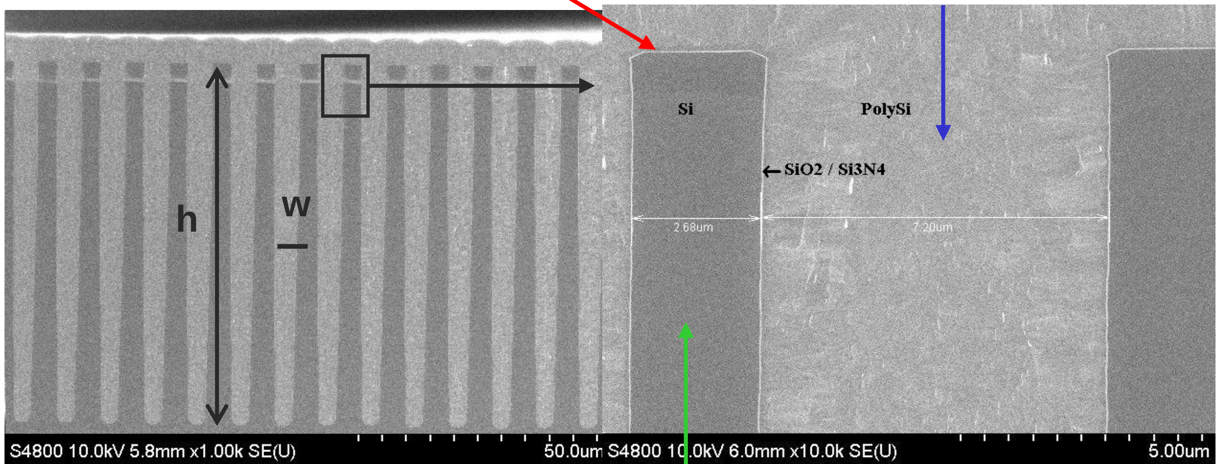
5 masks process



Pores aspect ratio (h/w) = 25

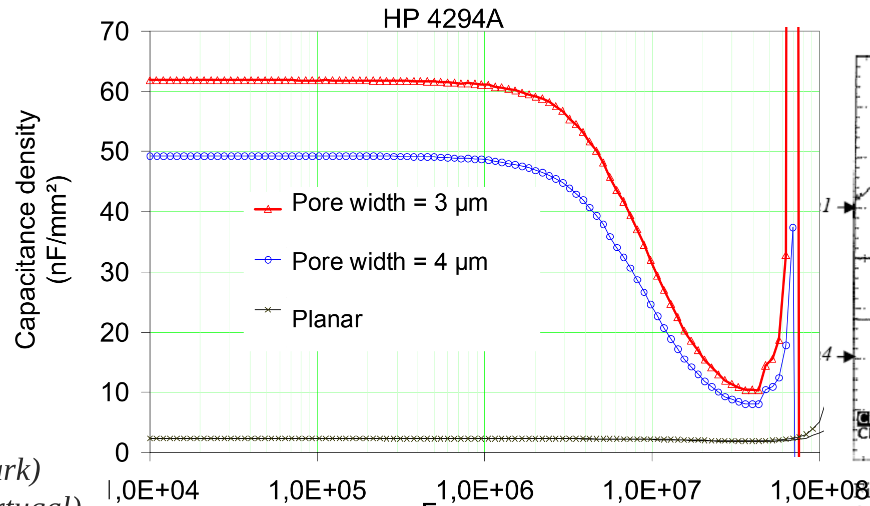
SiO_2 (5 nm) / Si_3N_4 (20 nm)

In-situ boron doped polySi
1.5 mΩ.cm



Antimony doped silicon
substrate - 6.5 mΩ.cm

- **Performances:**
  - 60 nF/mm²
  - f_{max} = 1MHz
  - ESR = 0.6Ω



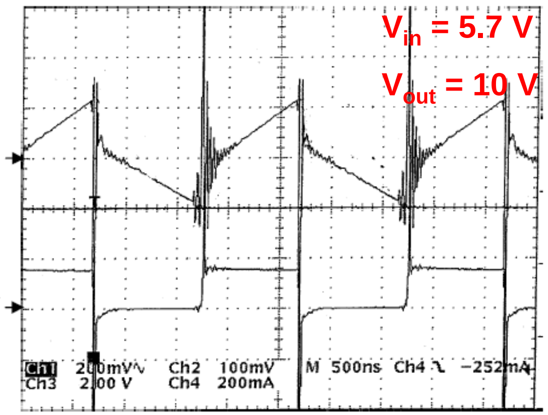
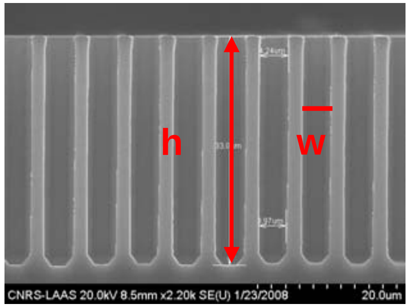


Fig. 6 : Waveforms of voltage output (Ch1) and diode current (Ch4) operating in continuous mode

A.Benazzi, EPE 2007, Aalborg, (Denmark)
M. Brunet, MME 2007, Guimaraes (Portugal).

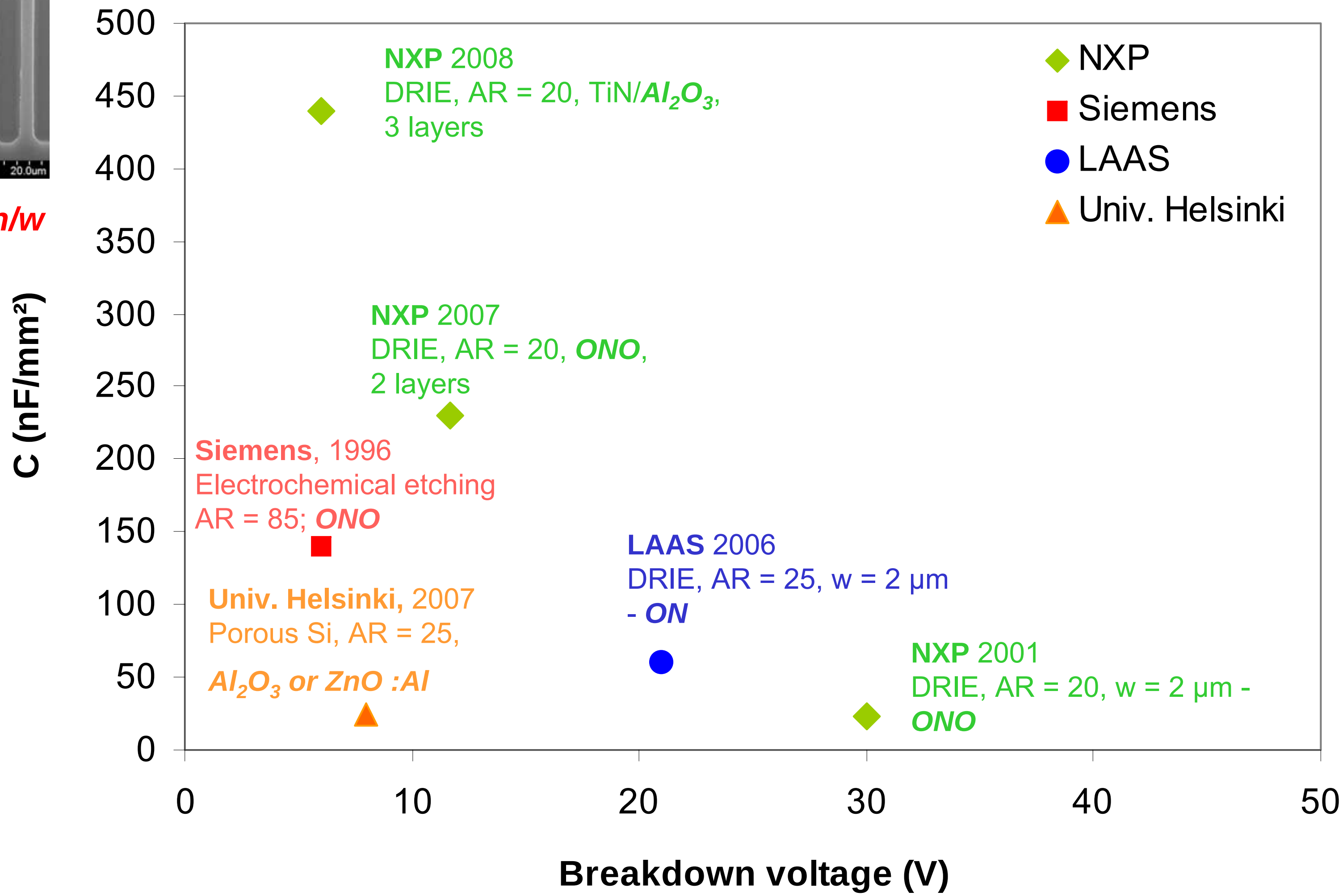
I. 3D capacitors: state of the art



AR = Aspect Ratio = h/w

Dielectric

O = SiO_2
N = Si_3N_4



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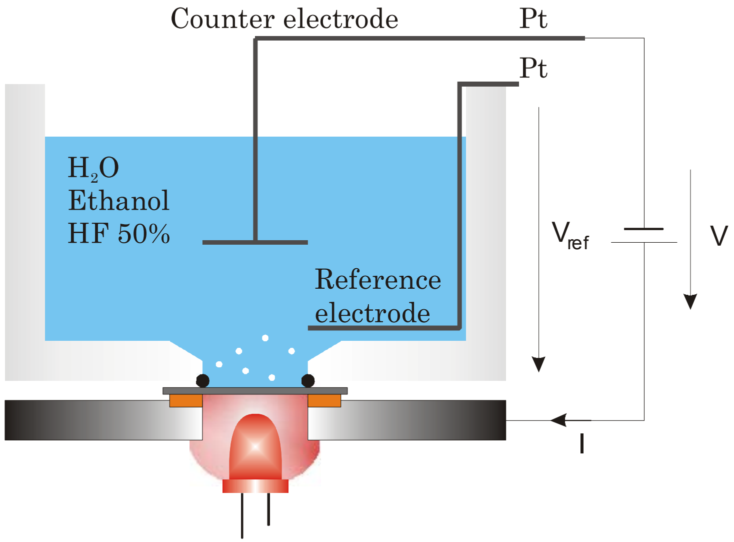
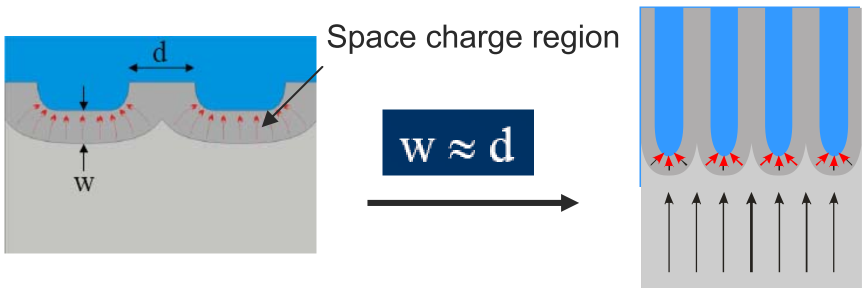
III. Conclusions and future work.

II.a. Electrochemical etching of Si

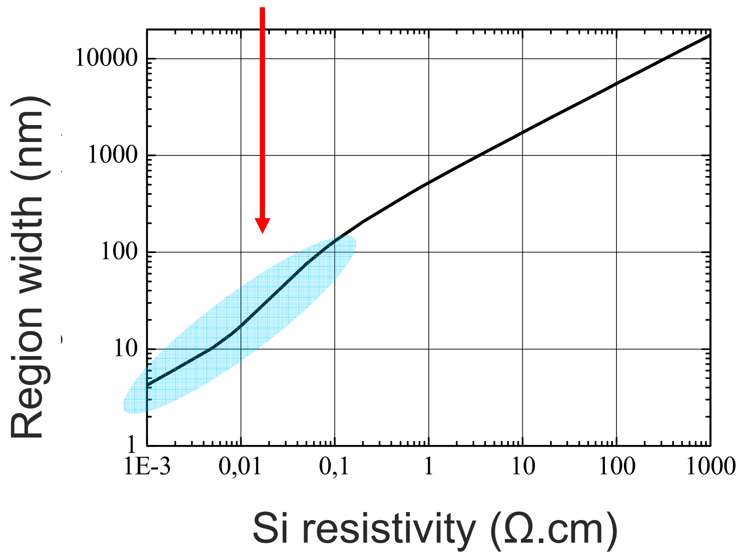


N-type substrate: Diffusion of minority carrier (holes) towards surface => Reaction with HF

3 regimes: electropolishing, etching (transition), porous silicon



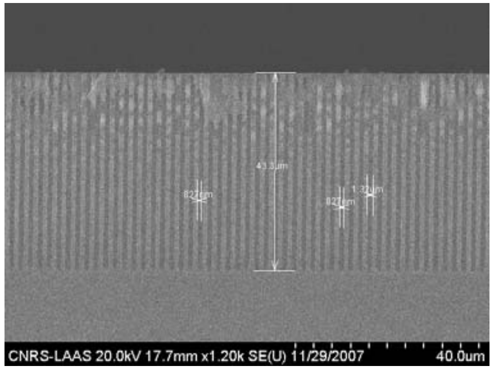
Higher density pore network

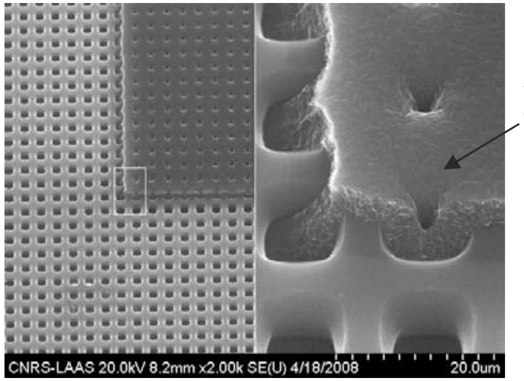


P. Kleimann, X Badel, J. Linnros, APL 86, 183108, 2005.

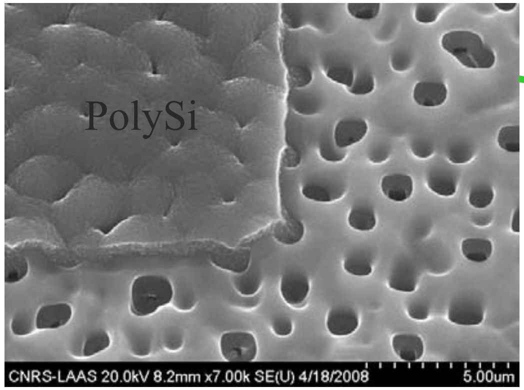
II.a. Electrical results

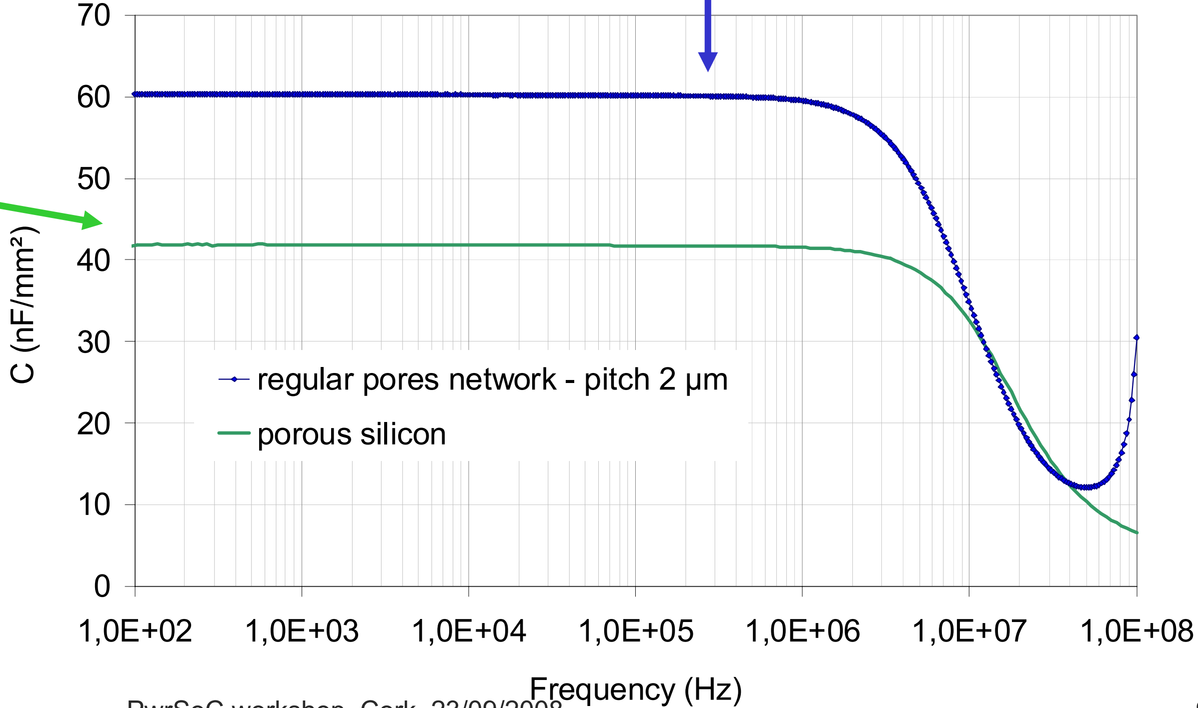
- 3D Capacitors
  - SiO_2/Si_3N_4
  - Pores : w = 1 µm
  - Aspect ratio = 43





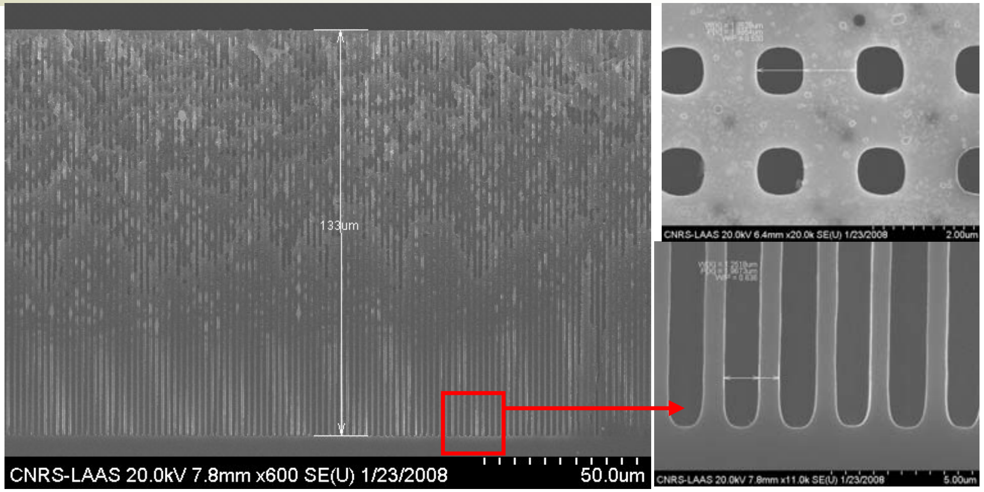
- Comparison Porous Si / Pore network



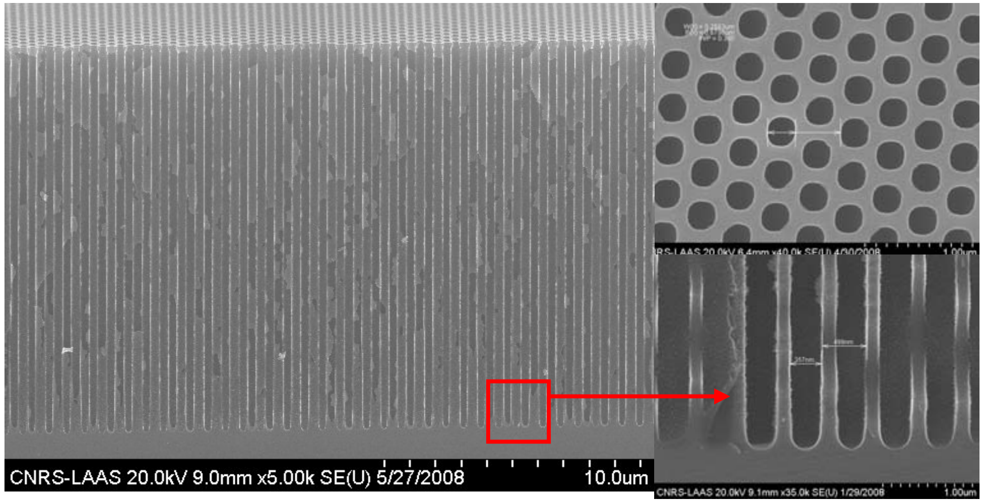


II.a. On-going developments

- 2 µm pitch pore network
  - Adapted resistivity = 1 Ω.cm
  - Maximum aspect ratio = 133
  - 260 nF/mm² expected (with SiO_2 / Si_3N_4)



- 500 nm pitch pore network
  - Ebeam lithography
  - Adapted resistivity = 50 mΩ.cm
  - Keeps component at the surface



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II.b. 3D deposition of high-k material

- High-k material: ZrO_2 - Polycrystalline material
  - Static dielectric responses :
    - $\varepsilon_{tetragonal} = 40$
    - $\varepsilon_{cubic} = 31.8$
    - $\varepsilon_{monoclinic} = 15$

  => Necessity to favour tetragonal phase for higher permittivities.

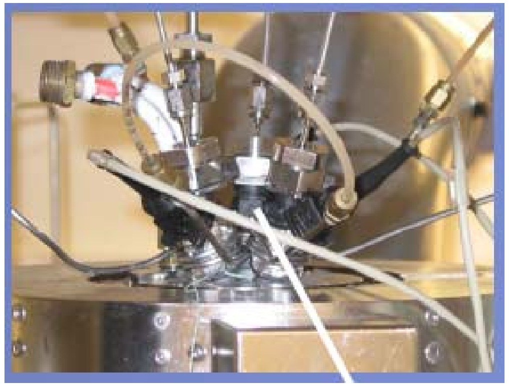
X. Zhao, D. Vanderbilt, Phys. Rev. B, 65, 075105, 2002

  - Breakdown voltage: 3 MV/cm
    - Minimum thickness = 70 nm

- 3D deposition:
  - Direct liquid injection MOCVD

II.b. MOCVD system

- Direct liquid injection MOCVD
  - Precursors evaporation: 250°C
  - Gas carrier: O_2 and N_2
  - Fractionnal injection
  - Substrate Temperature : 400°C – 700°C

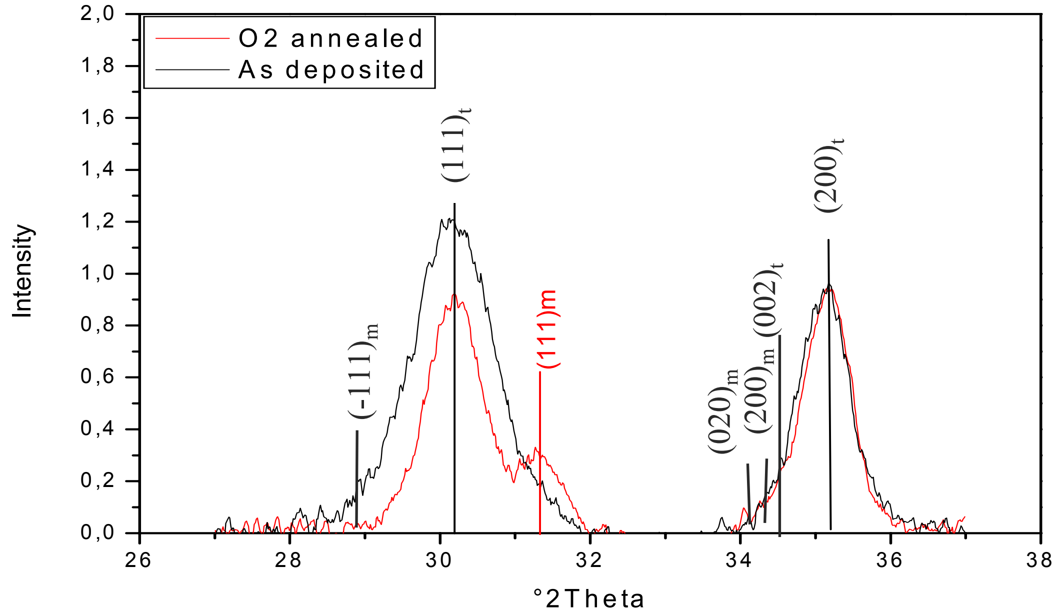


- Precursors tried:
  - $Zr(thd)_4$ *
  - $Zr(thd)_2(O^iPr)_6$

*(thd =2,2,6,6-tetramethylheptane-3,5-dionate)

II.b. Structural analysis ZrO_2

- X-Ray Diffractogramms - ZrO_2 on Si(100)

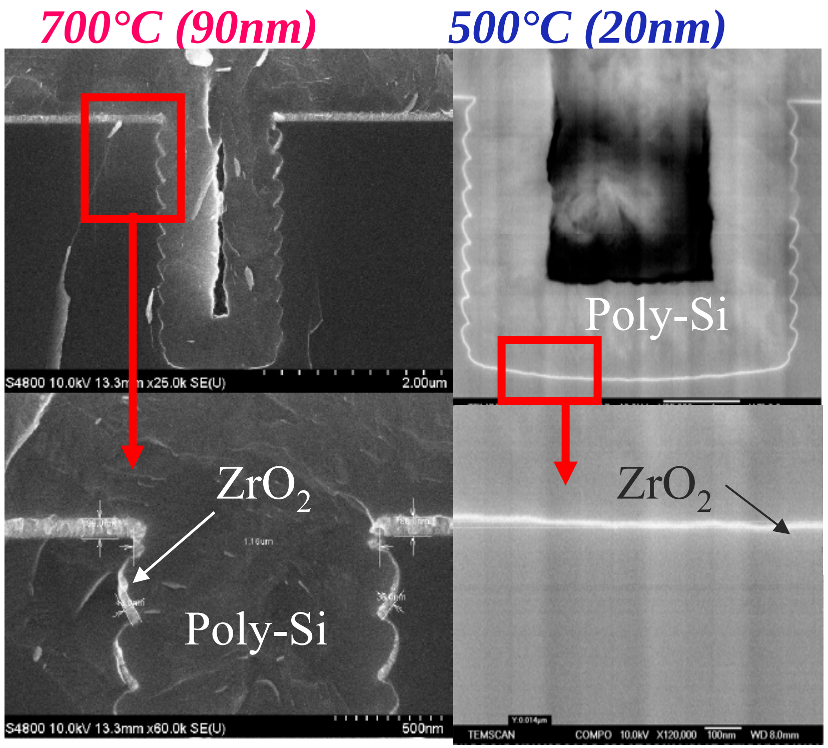


- Tetragonal phase favoured thanks to:
  - Low O_2 partial pressure
  - Low deposition rate (0.6 nm/min) : low injection frequency - low temperature
  - Characterised by smaller crystallites *
- After annealing at 900°C under O_2 :
  - Monoclinic + tetragonal phase

*L. Rapenne, M. Andrieux, Int Symp. EUROCVD 14, ECS, 2003, p. 325

II.b. 3D deposition - Coverage

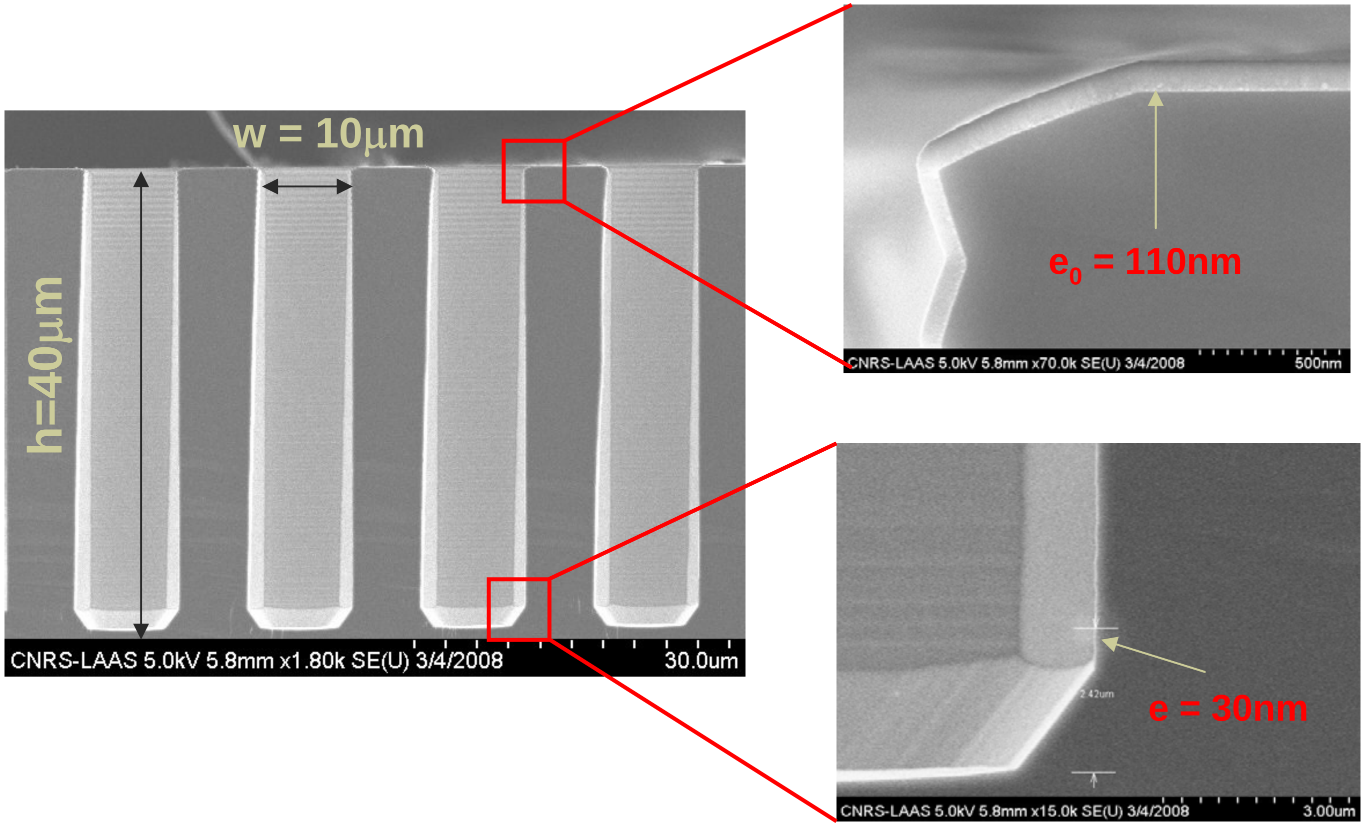
- Influence of temperature on coverage.



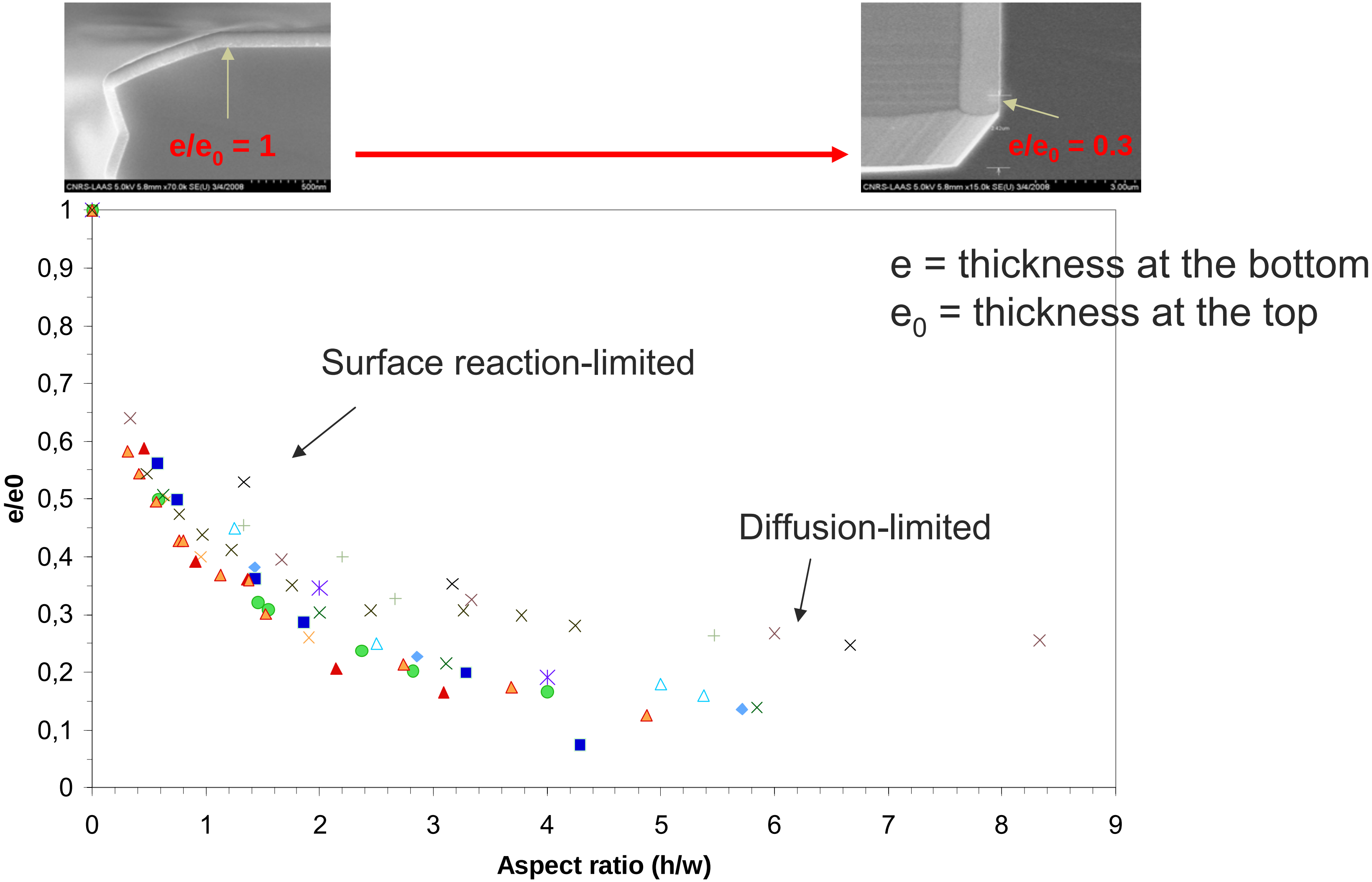
  - Decrease of surface reactivity with lower temperatures
  - Work at temperatures around 500 - 550°C

II.b. 3D deposition - Coverage

- Pores with depth h > 10 µm
  - Deposition of ZrO_2 : T = 550°C , P < 100 Pa



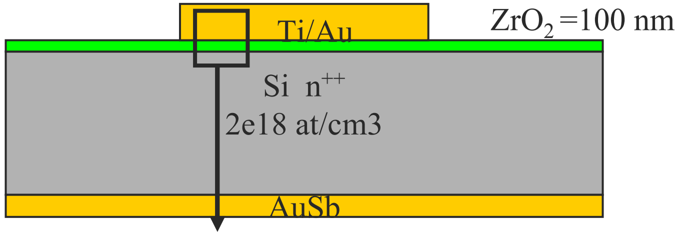
II.b. 3D deposition - Coverage

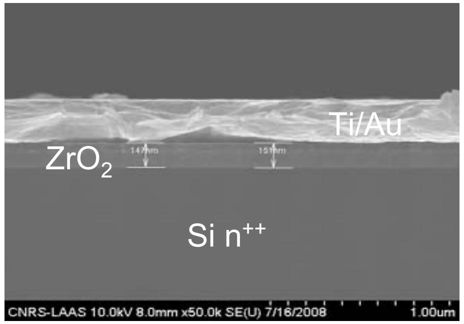


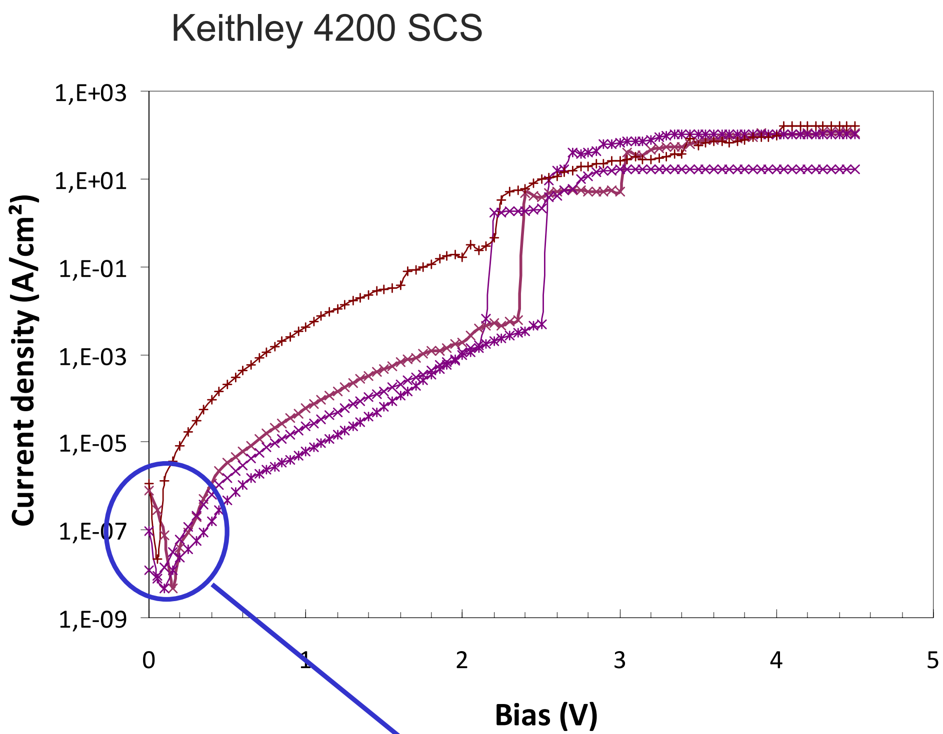
- Constant thickness for aspect ratio > 2

II.b. Electrical measurements ZrO_2

- Leakage current





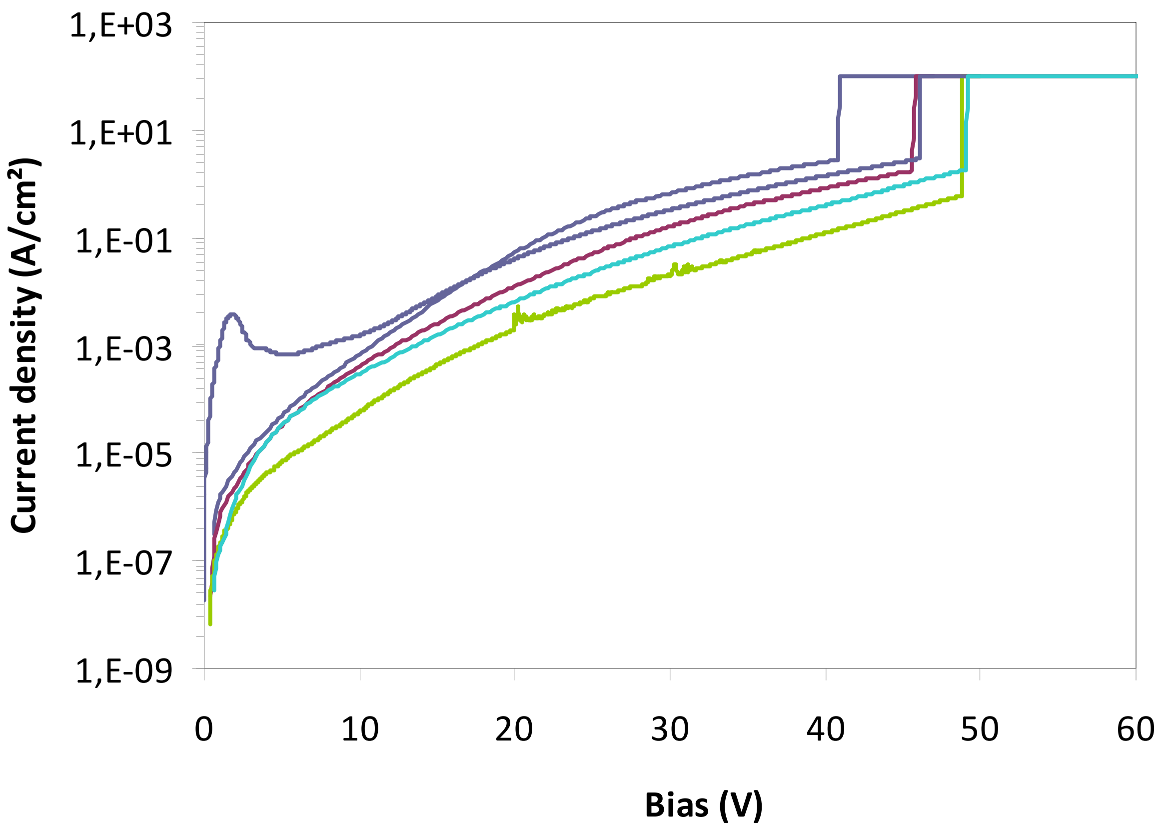


- Leakage current due to :
  - Extrinsic defects
  - Polycrystalline structure of ZrO_2
  - Grains boundaries
  - Si/ZrO_2 interface not controlled

Estimation at 200 mV of $R_{leakage}$ = Rp = 0.1 - 10 MΩ

II.b. Electrical measurements ZrO_2

- Breakdown voltage
  - Structure tested: ZrO_2 (195 nm) / Pt



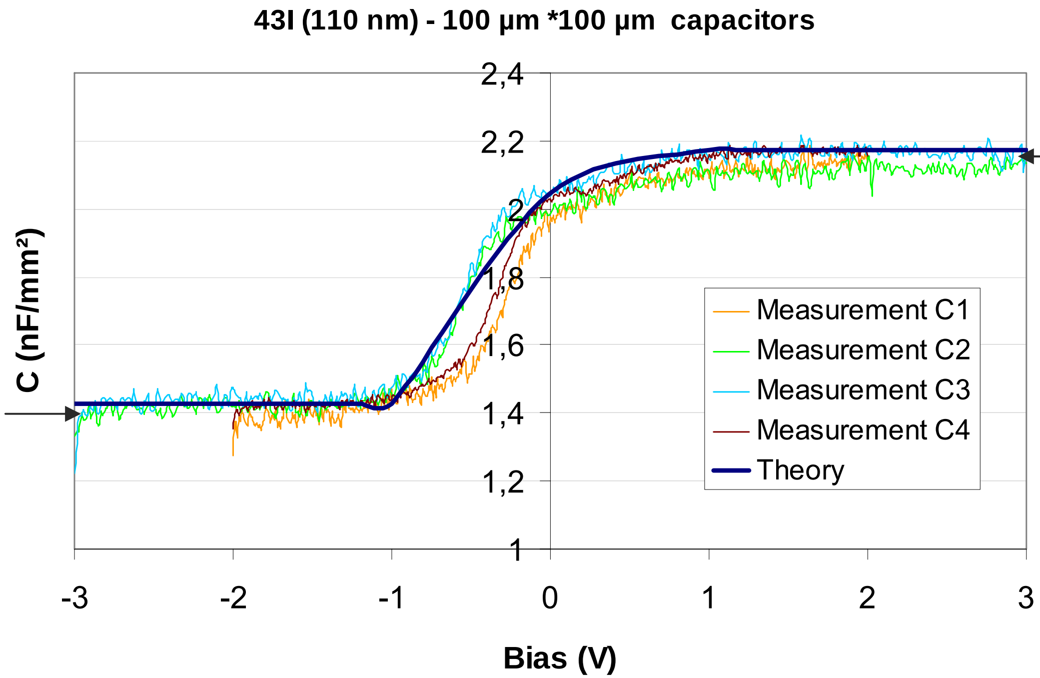
2.3 MV/cm

II.b. Electrical measurements ZrO_2

- C(V) on silicon substrates at 1MHz

$$C_{\min} = \frac{C_{ZrO_2} C_{inv}}{C_{ZrO_2} + C_{inv}}$$

C_{inv} = 4.17 nF/mm²



C_{ZrO2} = 2.2 nF/mm²

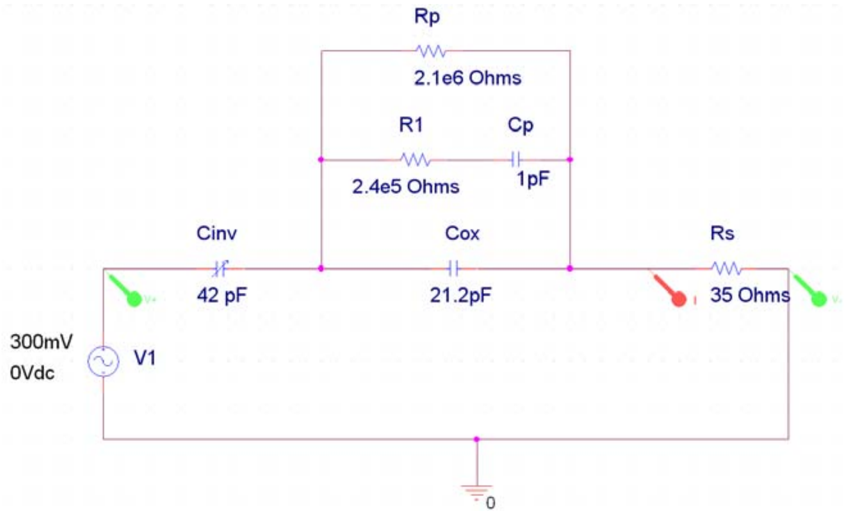
- Shifts due to oxide charges and interface states
- For MIM like structure => increase substrate doping

II.b. Electrical measurements ZrO_2

- Frequency behaviour: Z(f)

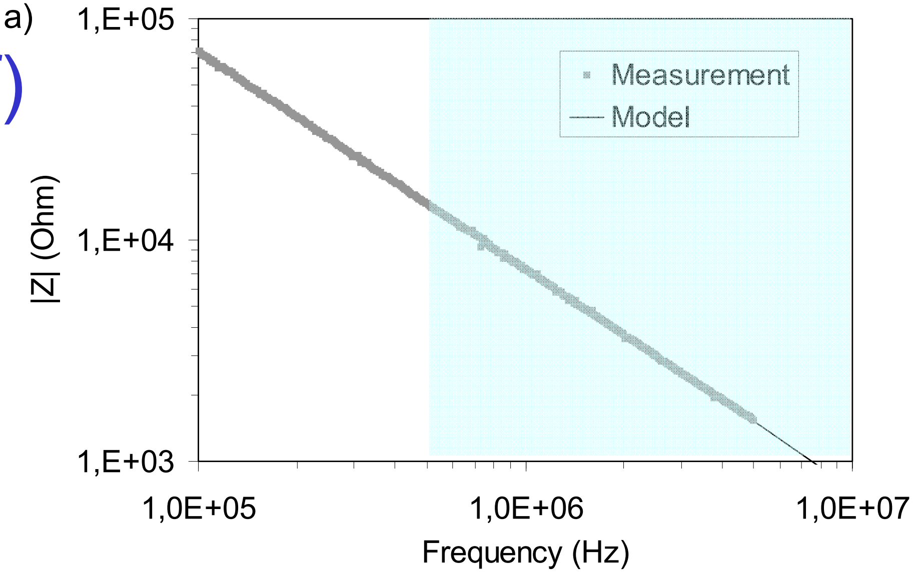
Impedance analyser HP 4294A

Equivalent model

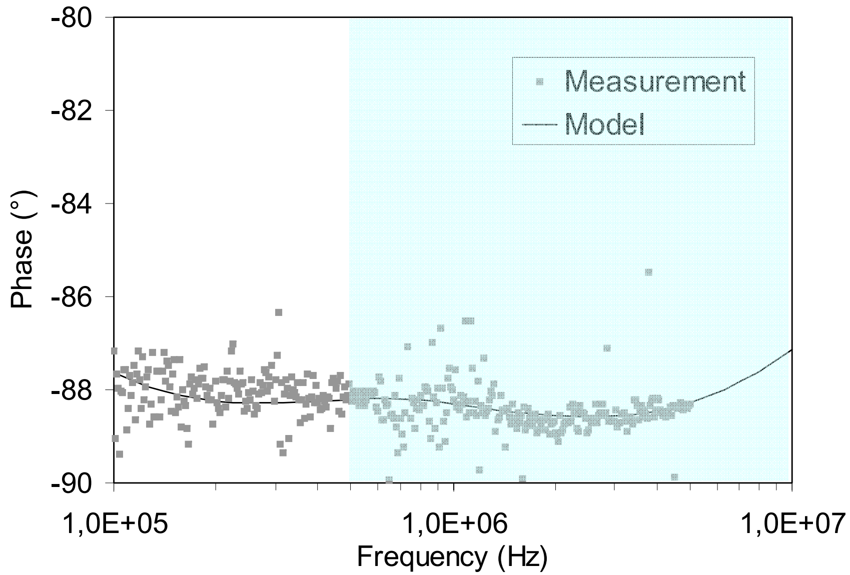


$\varepsilon_{ZrO2} = 27$

a)



b)



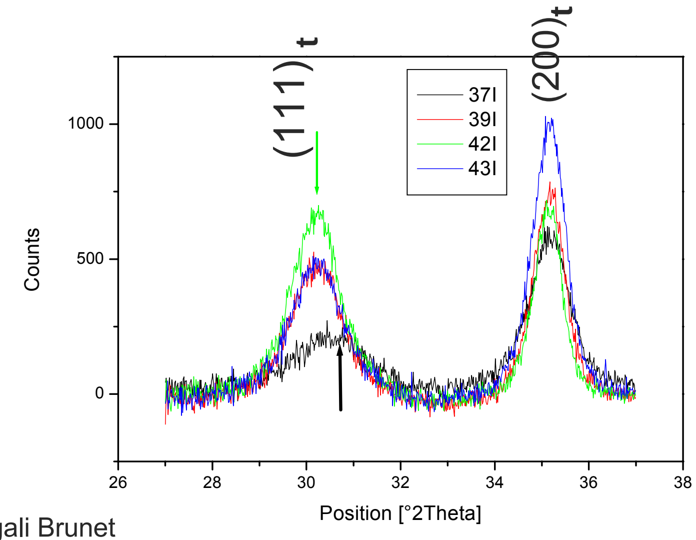
II.b. Electrical measurements ZrO_2

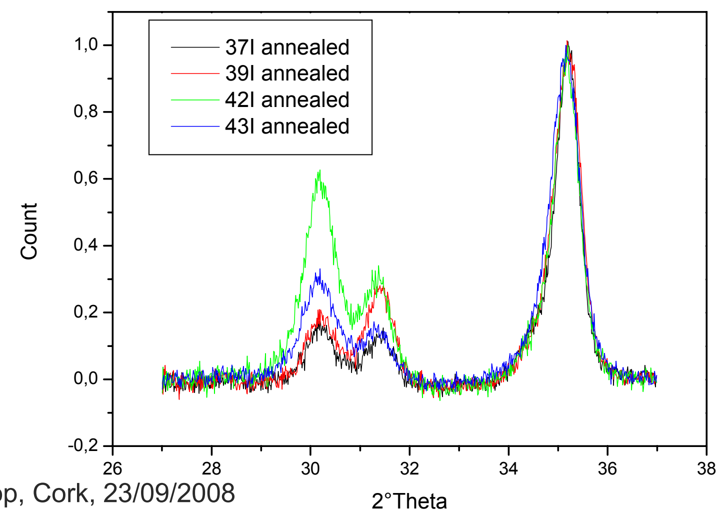
- Summary

Thickness (nm)	Leakage current density (A/cm²) at 200 mV	Breakdown voltage (MV/cm)	C (nF/mm²)	Permittivity
110	10^{-8} - 10^{-5}	2.3	2.2	27

Theory
ε_{tetra} = 40
ε_{cubic} = 31.8
ε_{mono} = 15

Sensitivity to monoclinic phase ?

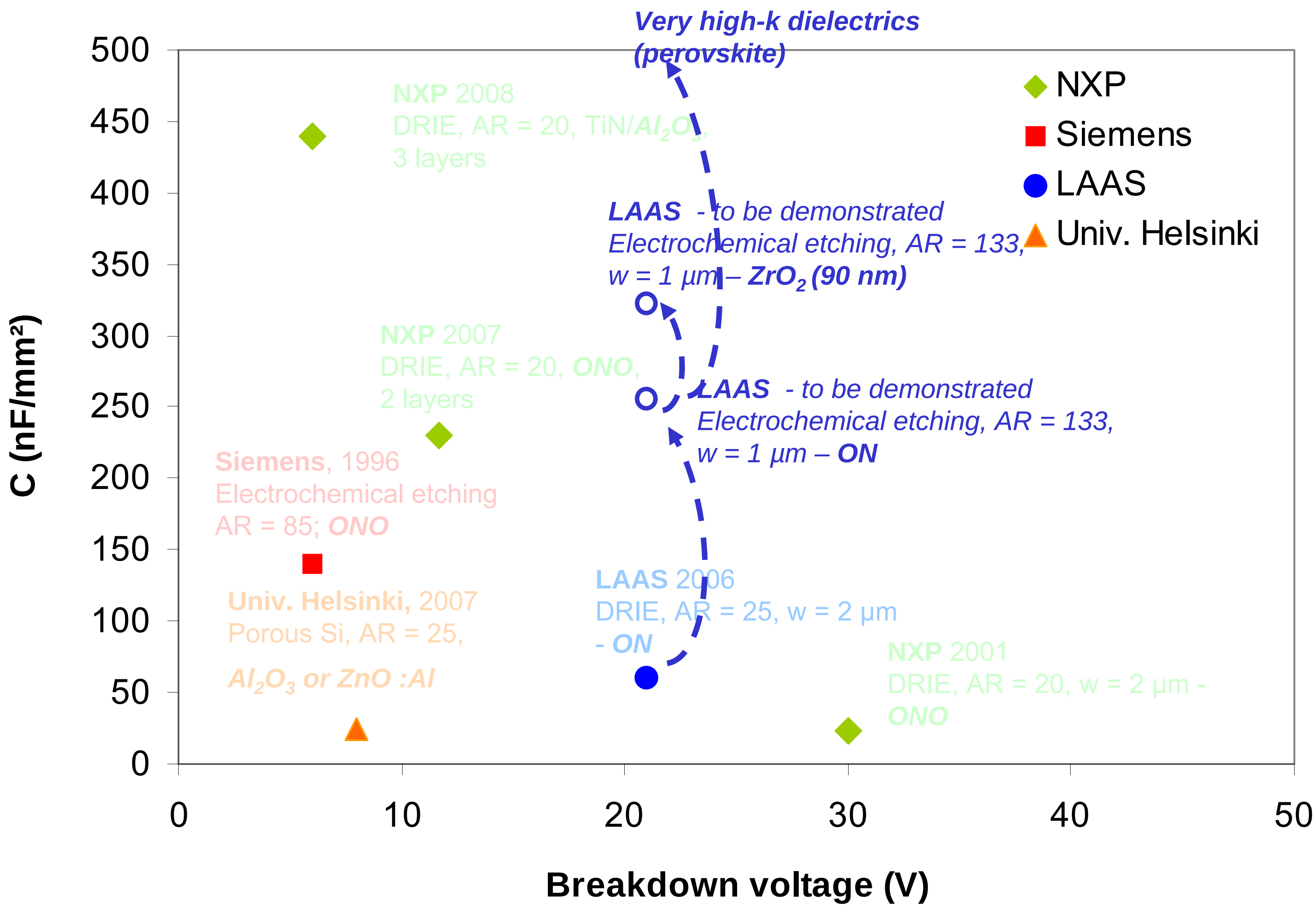




III. Conclusions / futur work

- High aspect ratio pores in a dense network
  - Electrochemical etching / DRIE
  - Validation of capacitors with aspect ratio 133
  - Denser pore network : pitch 500 nm
- MOCVD of ZrO_2 :
  - Tetragonal phase favoured
  - Necessity to improve 3D deposition
- Electrical characterisation:
  - Leakage and shifts in CV curves show necessity to improve interface chemistry and microcrystalline structure
  - Electrical characterisation of ZrO_2 on 3D structures.
    - Change of phase => change of permittivity ?
    - 3D breakdown voltage ?

III. Performances



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