The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific
and Cultural Organization

International Atomic
Energy Agency

SMR.1670 - 21

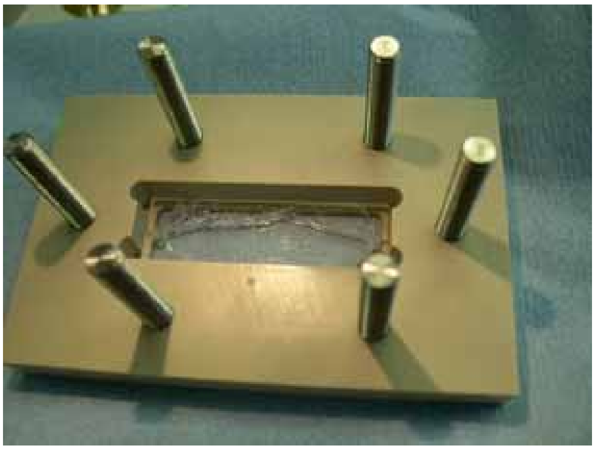
INTRODUCTION TO MICROFLUIDICS

8 - 26 August 2005

Reliability Issues

H. Gardeniers
University of Twente, Enschede, The Netherlands

Reliability issues



Han Gardeniers
MESA+ Institute for Nanotechnology
University of Twente

Summer School in Microfluidics
ICTP, Trieste, Italy

The fluids that go into the chip

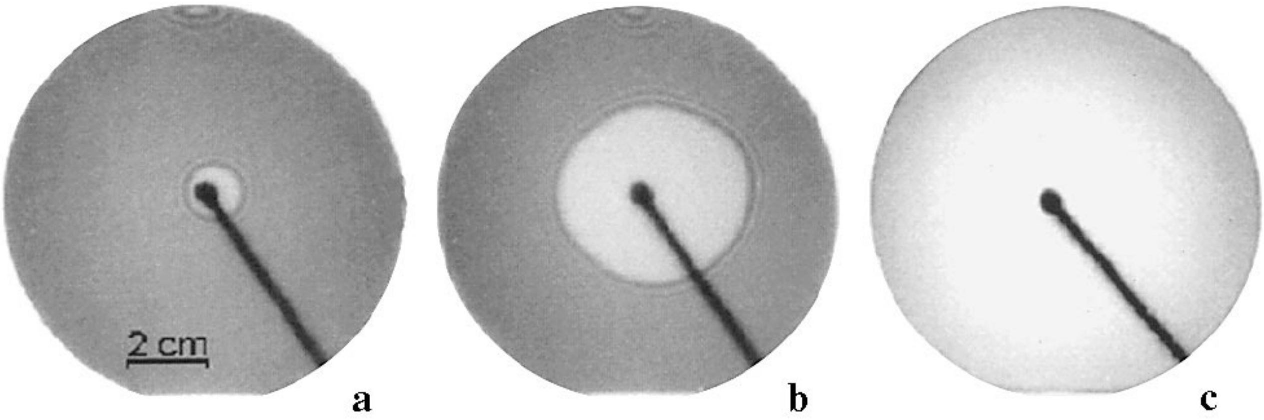
- Gases and liquids: viscosity
- Liquids with particles: blood, soil samples, crystallites
- Liquids with gas: bubbles, liquid film in gas stream
- Two phase flows (oil and water; droplets, interfaces)
- Highly viscous liquids: glue, ink
- Corrosive solvents: tetrahydrofuran, alkaline, acid

The conditions that may go on the chip

- Corrosive liquids
- High temperatures (microcombustor ~ 1000 ^{o}C)
- Low temperatures (microcooler for superconductors ~ 70K)
- High pressures (liquid chromatography 10~400 bar; microreactors ~ 10 kbar?)

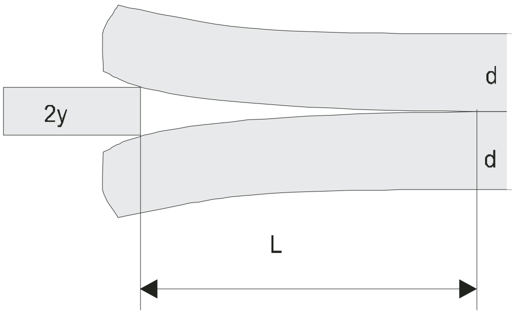
Wafer bond test methods

InfraRed microscopy: Newton rings



Blade insertion

But if the bond is too good...

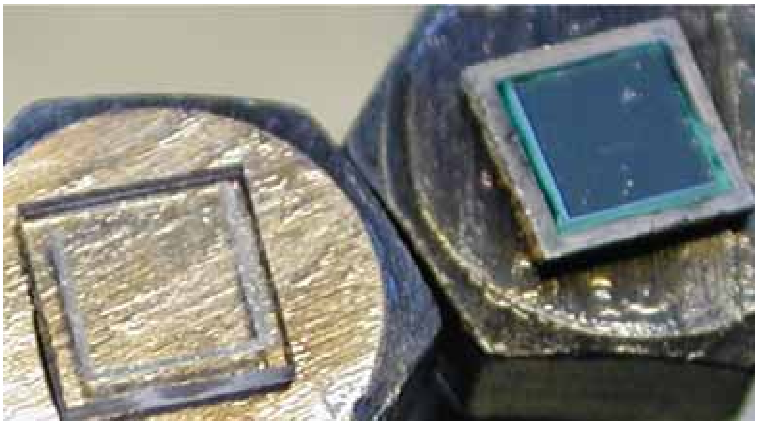


$$w_b = \frac{3Ed^3y^2}{8L^4}$$

Crack opening by blade or wedge insertion: width of opening is measure for effective bonding energy

Photographs from: Gabriel, Süss MicroTec, D

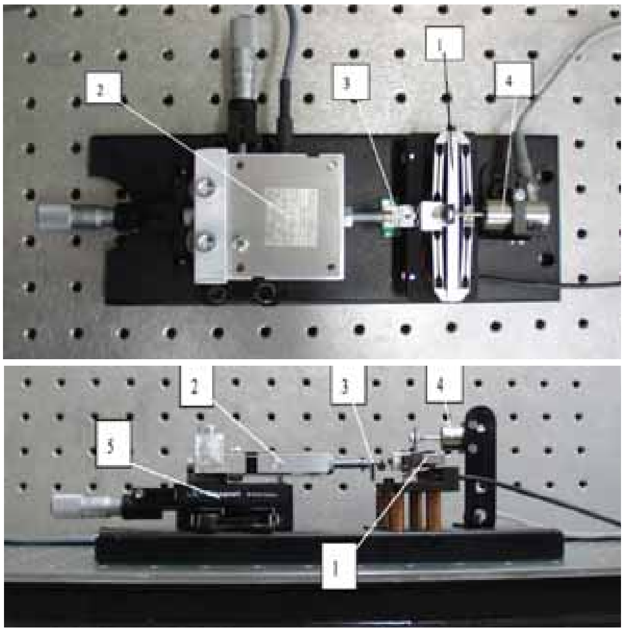
Pulling test - etched specimens (mesa)



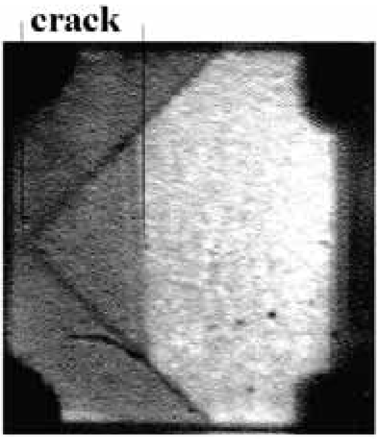
After the test

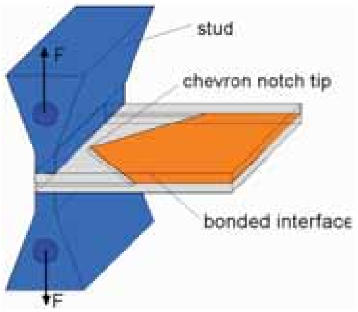
Figures from: K. Schjølberg-Henriksen, SINTEF, N

Pulling test - etched specimens (chevron)



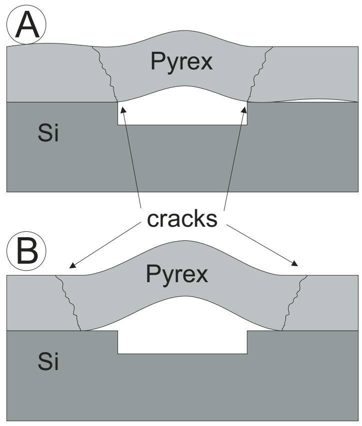
1. piezoelectric actuator; 2. 10 N load cell;
3. sample; 4. displacement sensor; 5 sample stage





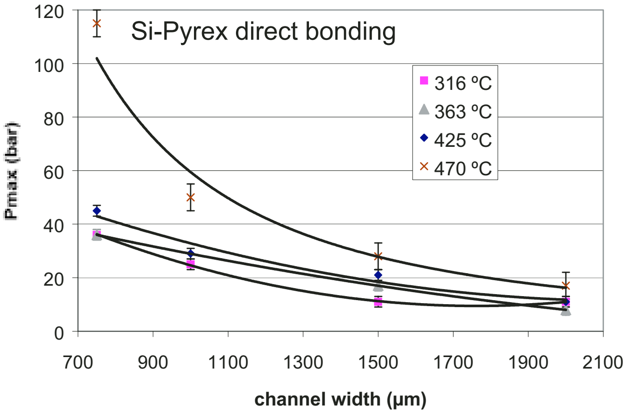
Source: J. Bagdahn e.a. Fraunhofer Institute for Mechanics of Materials, Halle, D

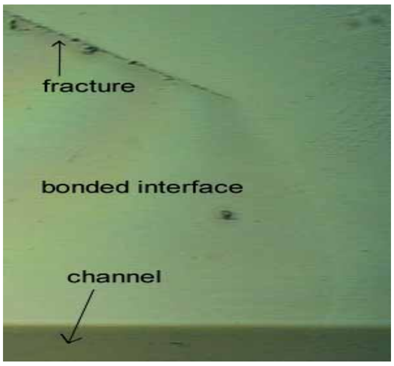
Hydraulic pressure on microchannel



Pressure at which interface starts to open:

$$p = \sqrt{\frac{2048 E t^3 \Delta\gamma_b}{77} \frac{1}{w^2}}$$

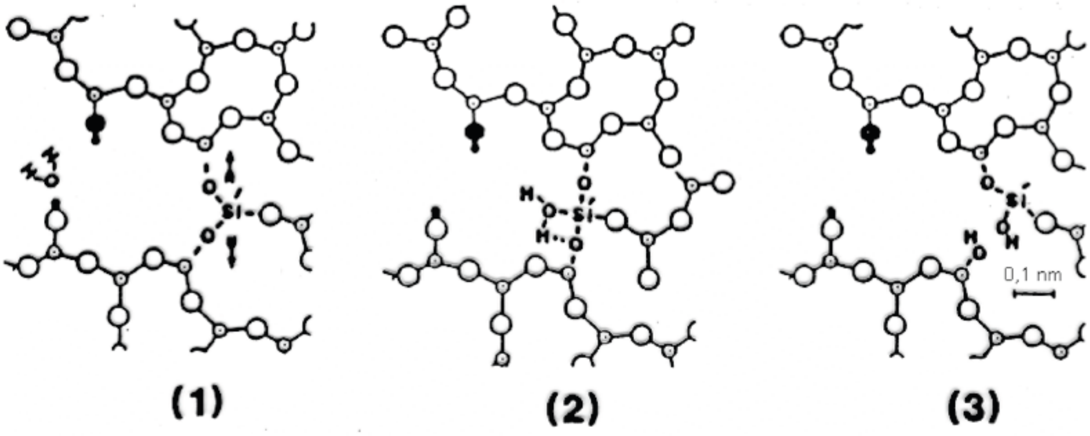




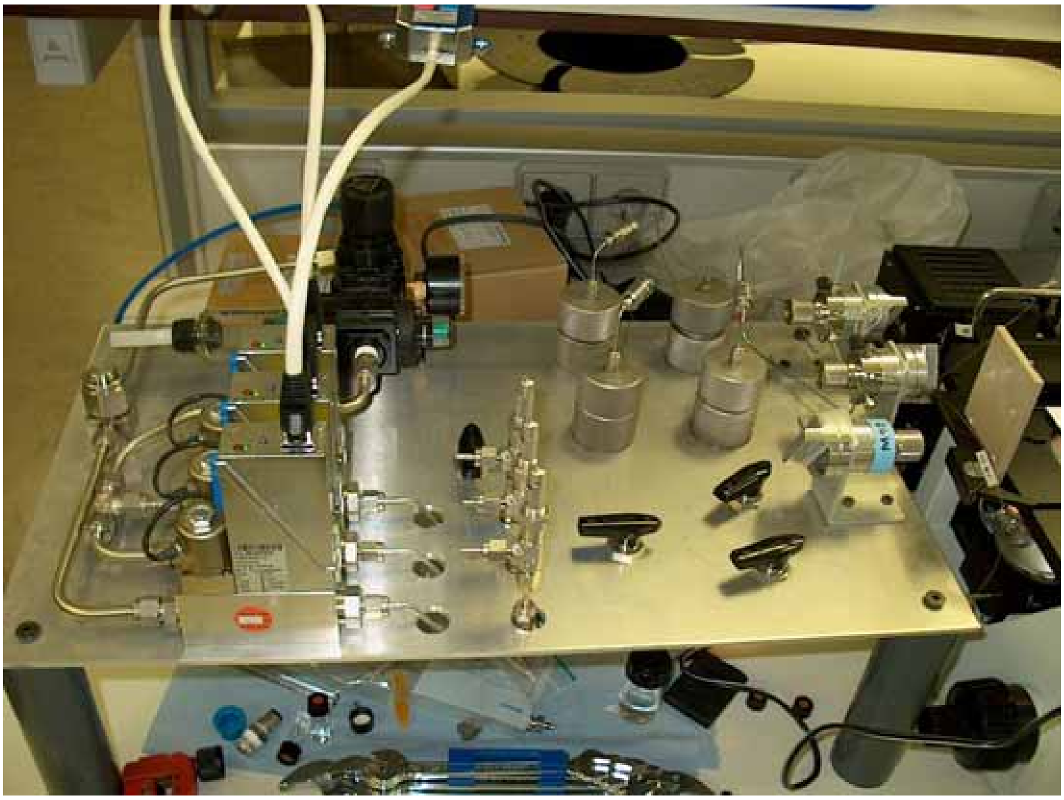
Blom e.a. J. MEMS 10, 158-164 (2001)

Crack opening + stress corrosion

$$\text{Si-O-Si} + H_2O \xrightarrow{\text{mech. stress}} \text{Si-OH : HO-Si}$$



Hydraulic test equipment



MESA+

University of Twente
The Netherlands

Case study:

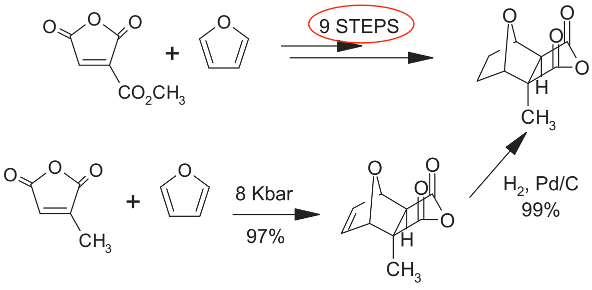
High pressure chemistry in a miniaturised system

The benefits of high pressure for chemistry

Molar activation volume: $$\left(\partial \ln k / \partial p\right)_T = -\Delta V^{\neq} / RT$$

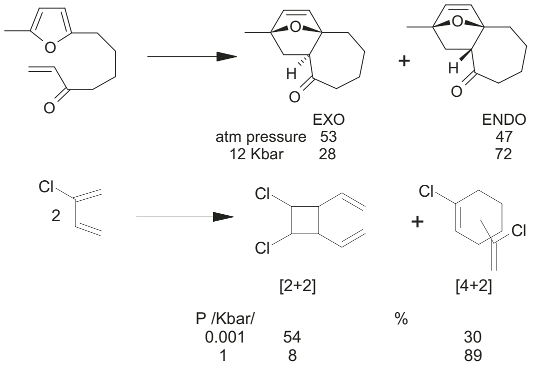
E.g. if molar activation volume = -20 cm^3/mol:
2870 atm —› factor 10 increase in kinetic constant
5740 atm —› factor 100

Example: less reaction steps (—› higher yield)



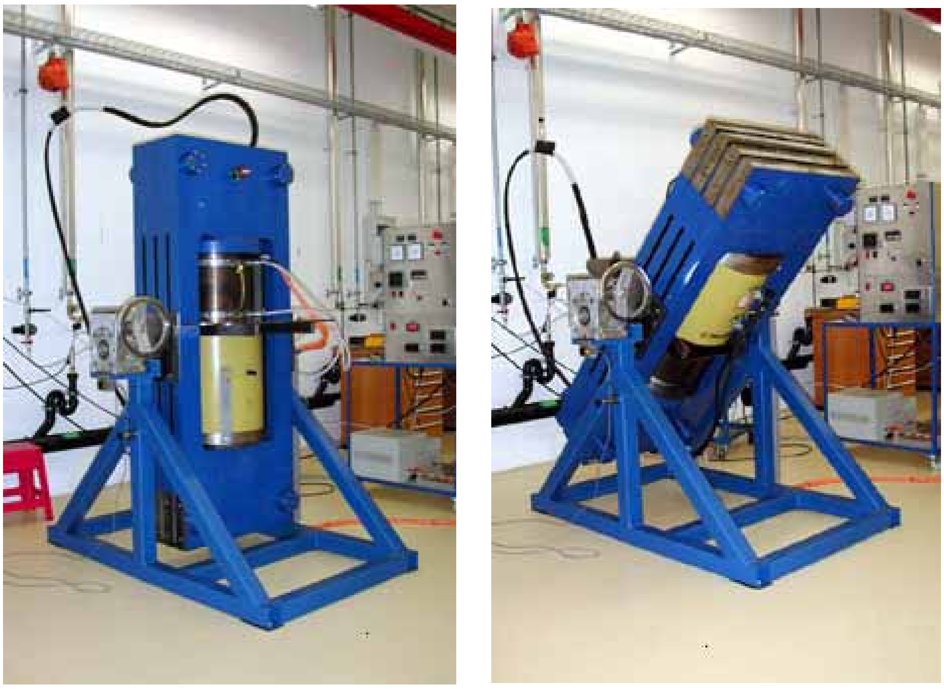
Grieco e.a. J . Am. Chem. Soc. 112, 4595-4596 (1990)

Example: higher selectivity

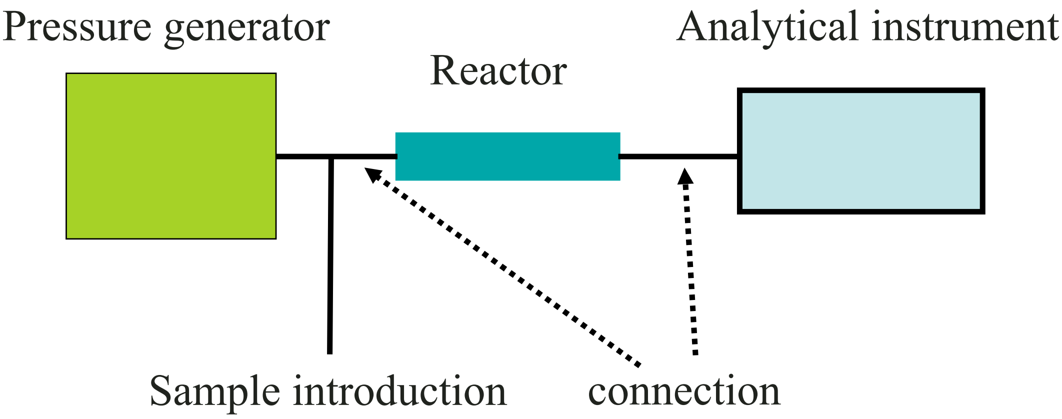


Jenner, Tetrahedron 53, 2669-2695 (1997)

Why miniaturisation?
Try shaking a high pressure reactor!



Possible set-up



Pressure generator

Reactor

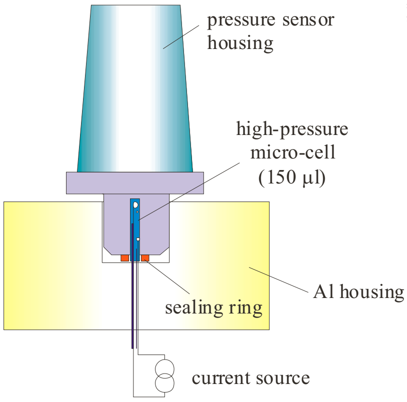
Analytical instrument

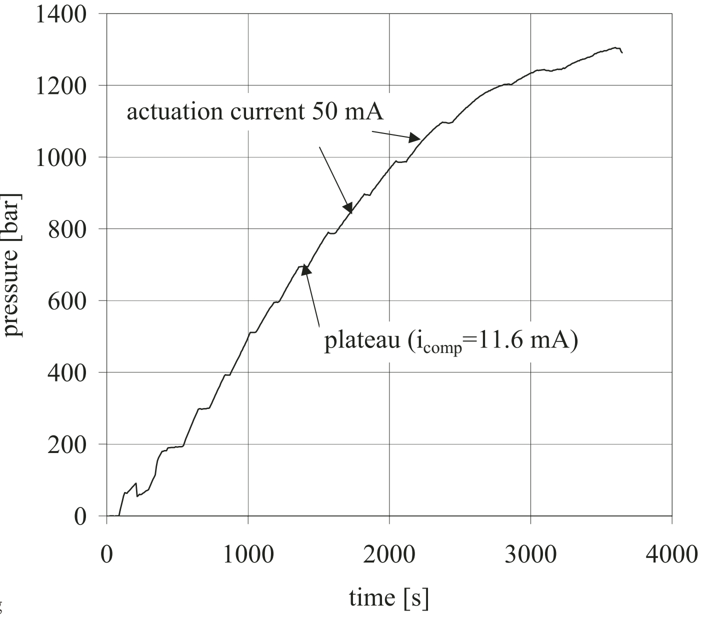
Sample introduction

connection

Which components should be integrated and miniaturised?

Miniaturised pressure generator using electrolysis



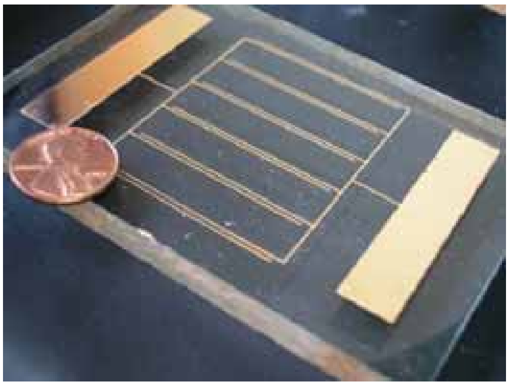


Böhm e.a. Proc. microTAS conf. 2000

Electrolytic pressure generation

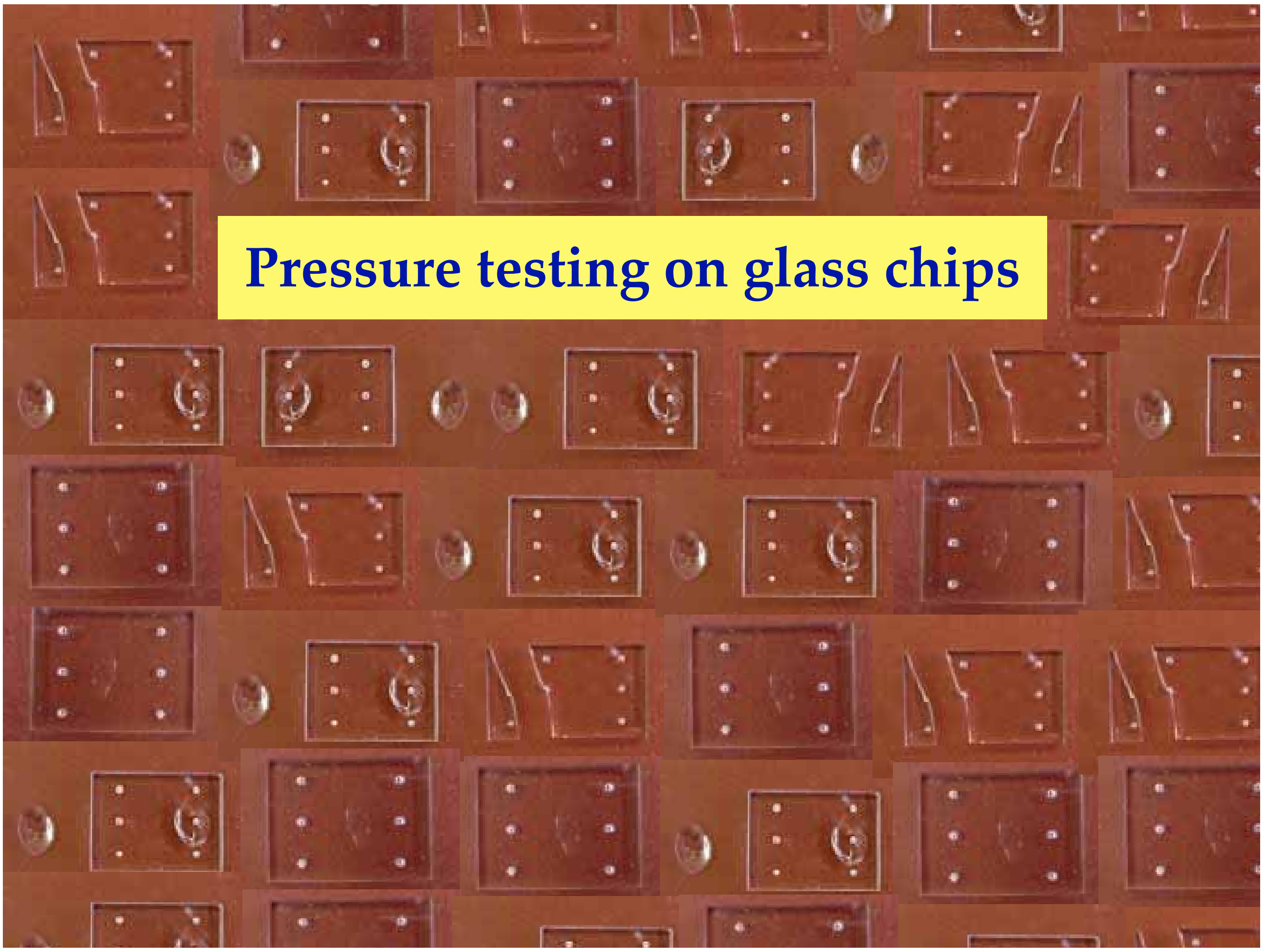
Drawbacks:
- slow (but miniaturisation and integration may help)
- separation of anode and cathode chambers is required

Advantages:
- reactive gases generated in-situ (Cl_2, F_2, D_2, CO_2, I_2, Br_2, etc.)
- local generation of gases



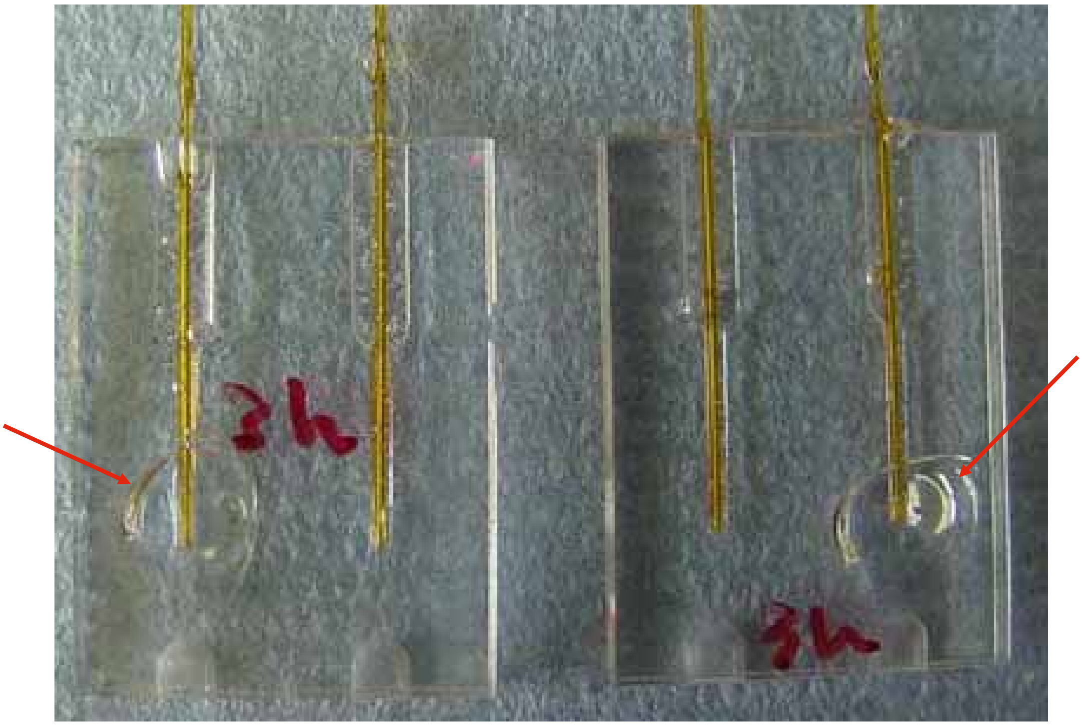
PMMA with gold pattern
-cracks at 200 bar

Pressure testing on glass chips

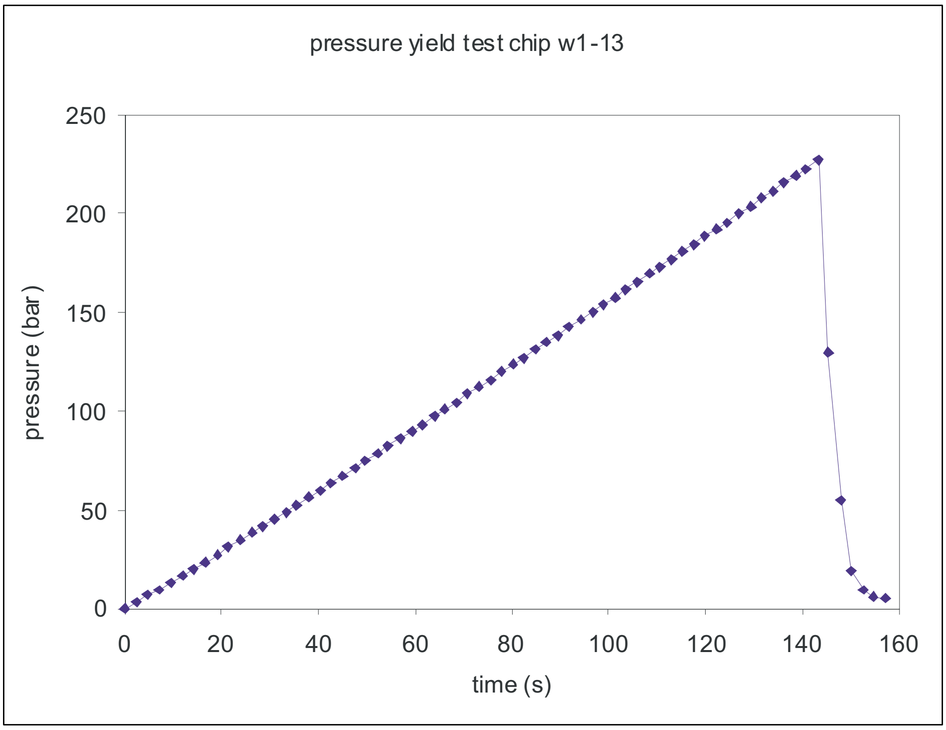


High-pressure (microreactor) setup

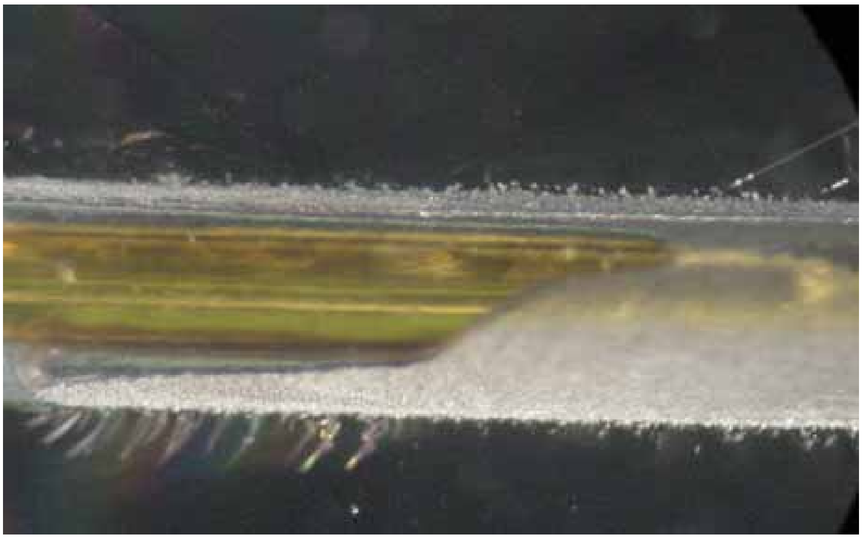
First high pressure tests on glass chips

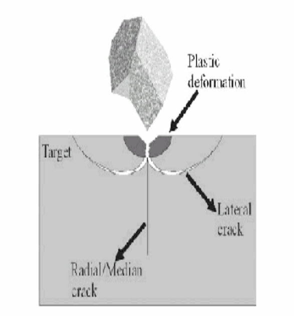


experimental yield strength << theoretical strength

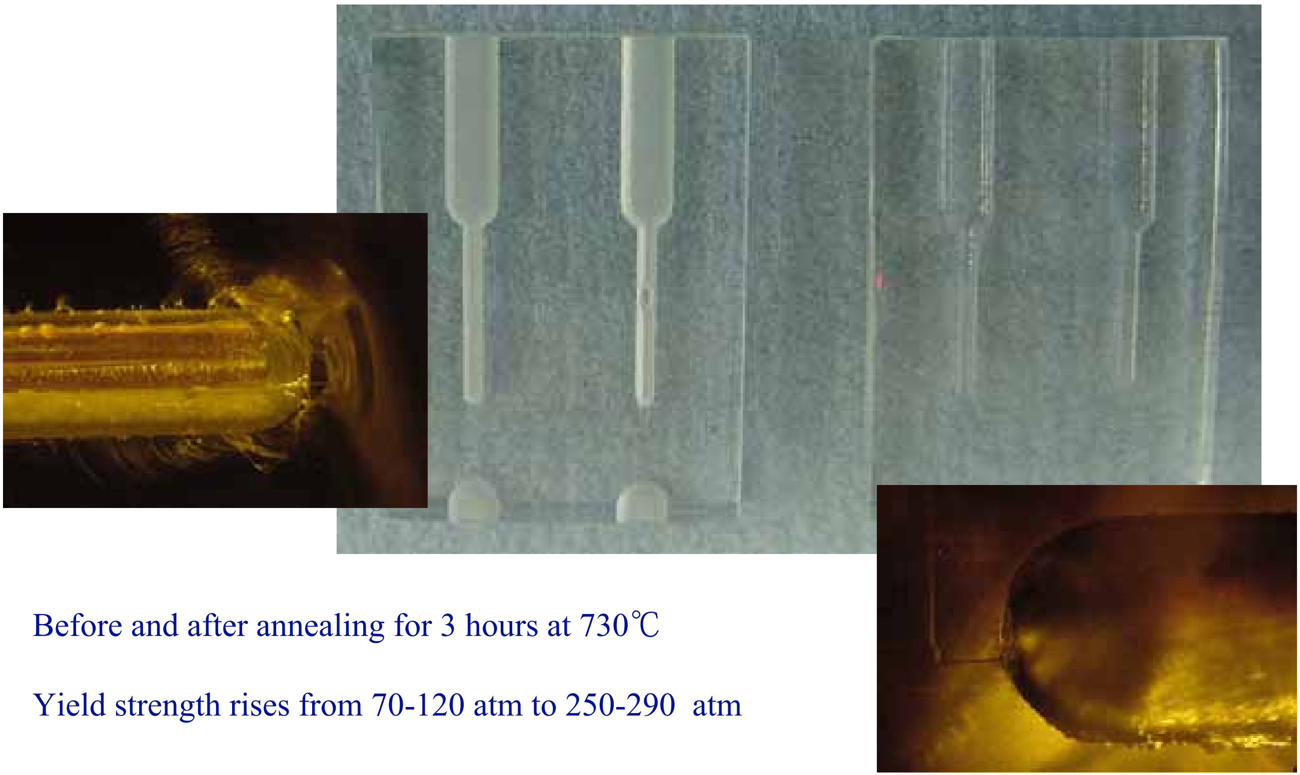


Reasons for low yield strength: micro cracks due to fabrication method (powder blasting)





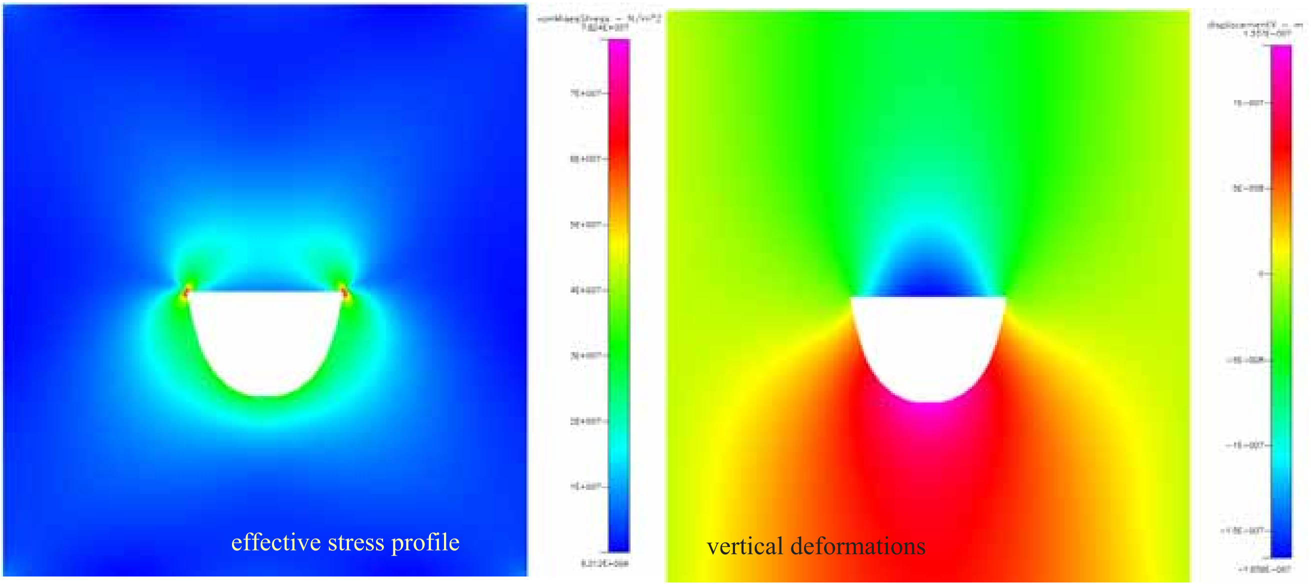
Annealing reduces roughness/cracks



Before and after annealing for 3 hours at 730℃

Yield strength rises from 70-120 atm to 250-290 atm

Stress concentration due to etching profile

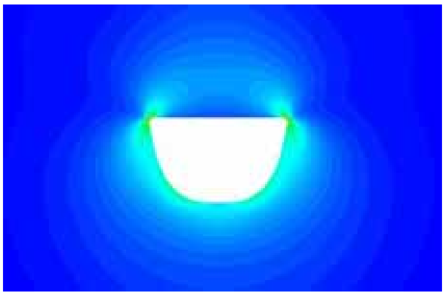


effective stress profile

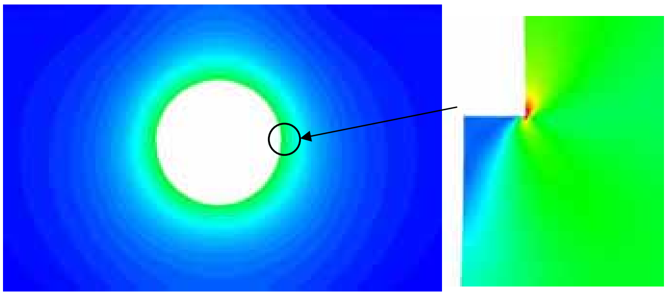
vertical deformations

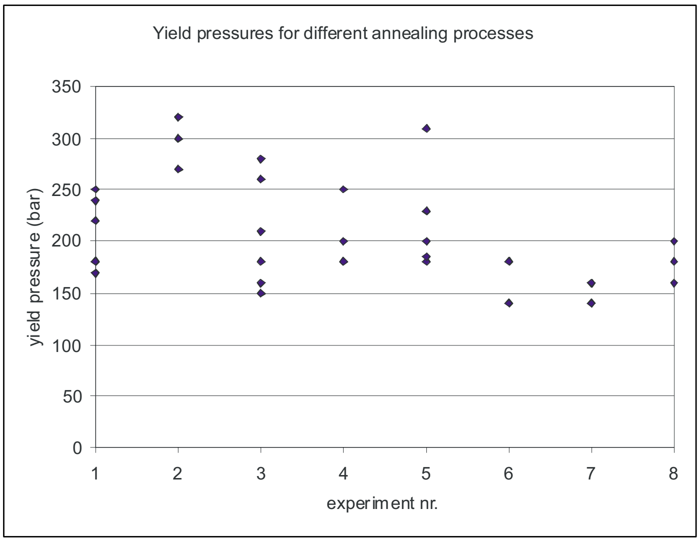
Stress profiles

- Standard channel: stress concentration at the edge



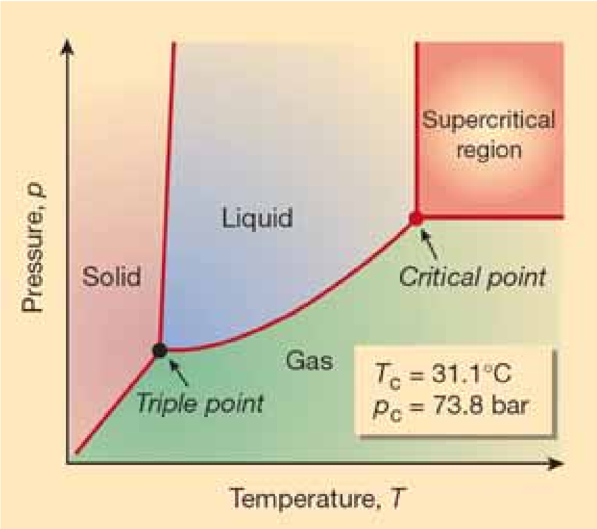
- Perfect circular channel: ideal but not feasible

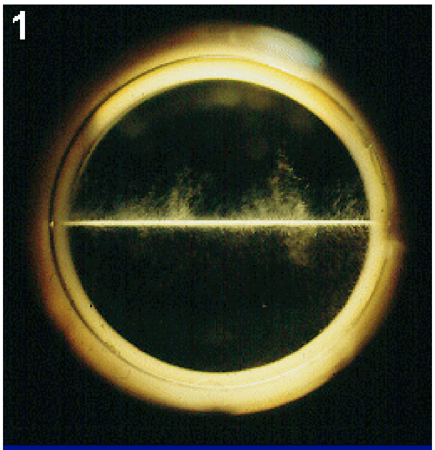




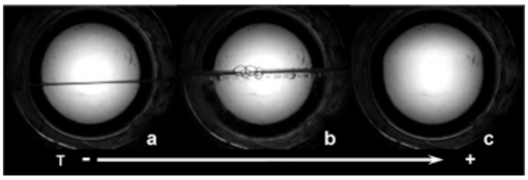
1) Standard annealing: 6 hrs 600 °C
2) 6 hrs 680 °C
3) 6 hrs 700 °C 4) 10 hrs 680 °C
4) 10 hrs 680 °C
5) 1:30 hrs 700 °C + 10 hrs 680 °C
6) 3 hrs 680 °C channel down during annealing
7) 3 hrs 680 °C channel up during annealing
8) 6 hrs 680 °C second batch

Current work: SC-CO_2



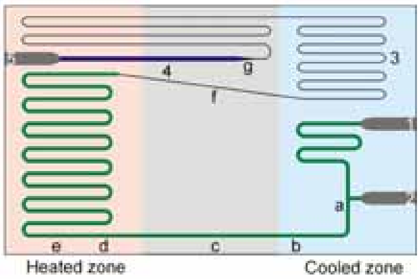


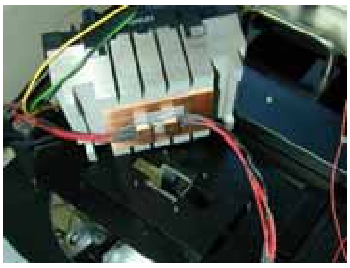
Below the critical parameters, two distinct phases exist

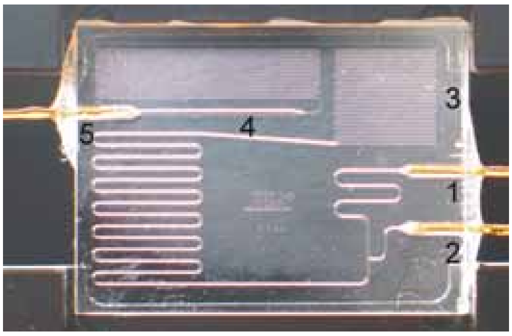


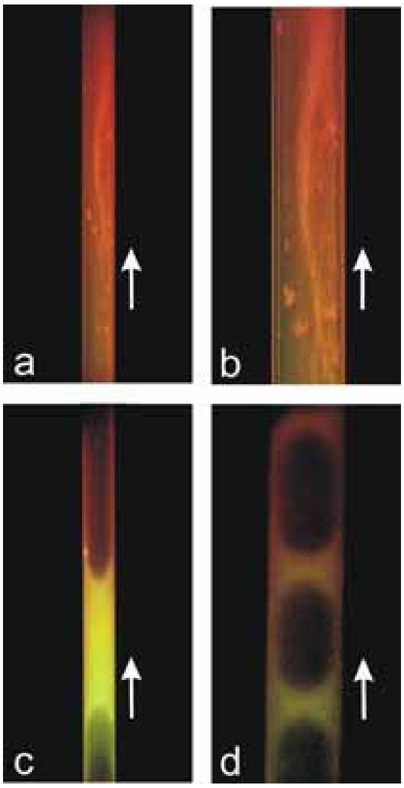
e.g. Poliakoff e.a. Nature 412, 125 (2001)

Visualisation critical transition





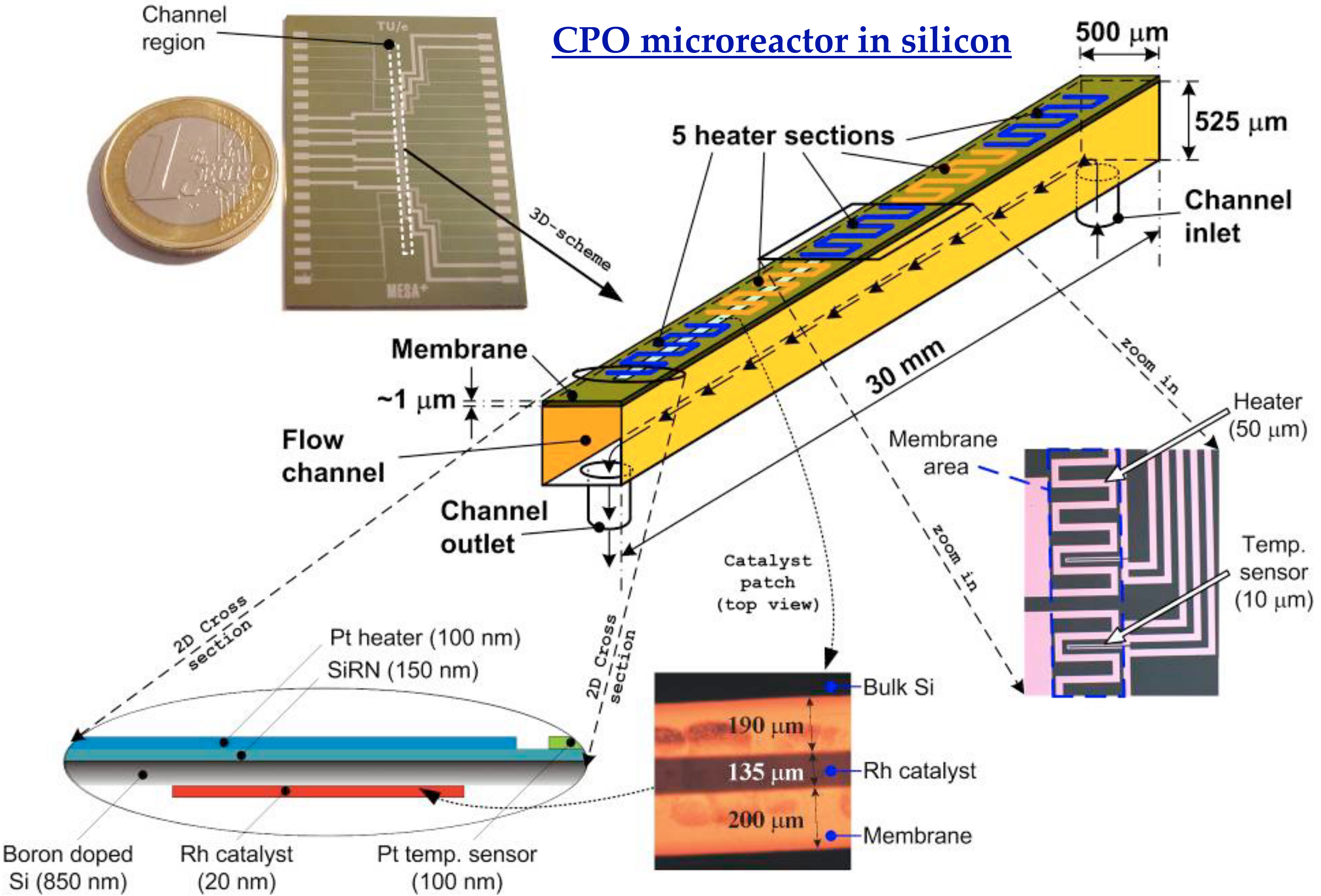




Flow patterns
below (c,d)
above (a,b)
critical point

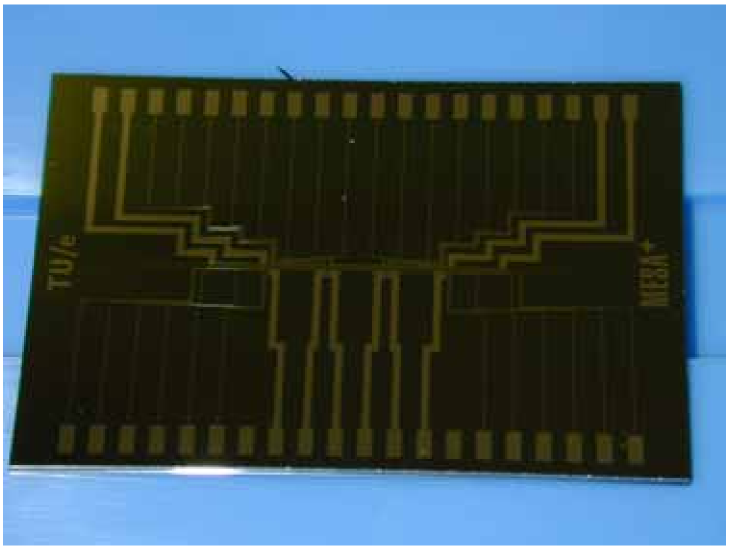
High-temperature microreactors for catalytic partial oxidation studies

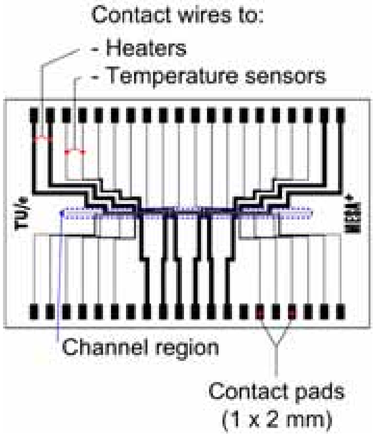
CPO microreactor in silicon

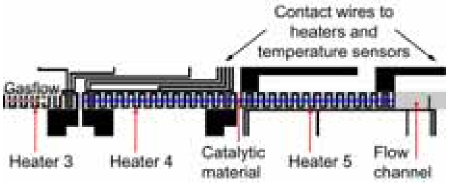


Tiggelaar e.a. Sens.Act.A 112, 267-277 (2004)

CPO microreactor in silicon

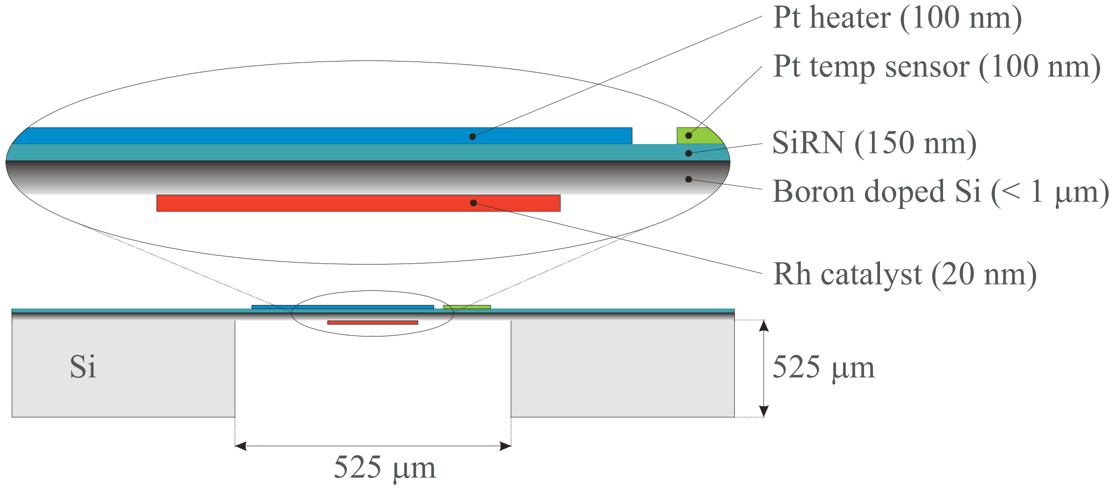






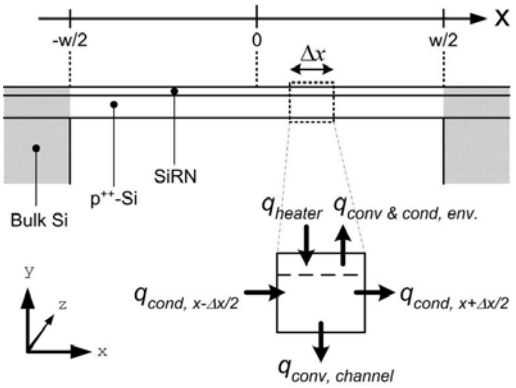
Tiggelaar e.a. Sens.Act.A 112, 267-277 (2004)

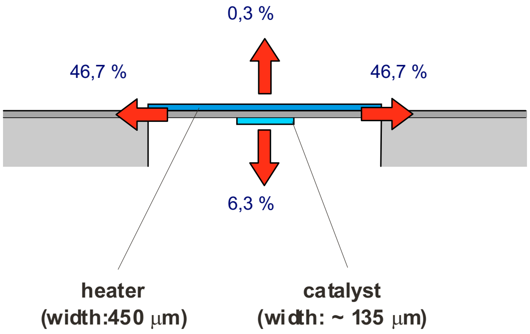
Cross-section of membrane



Tiggelaar e.a. Sens.Act.A 112, 267-277 (2004)

Thermal modelling

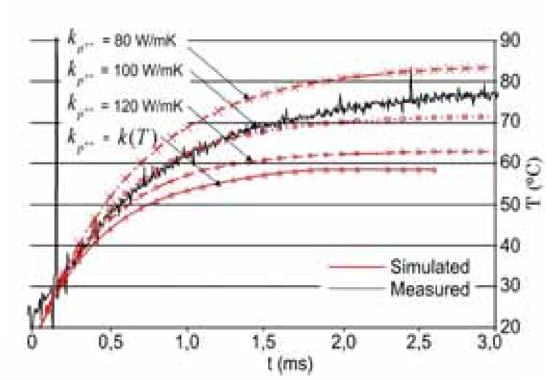


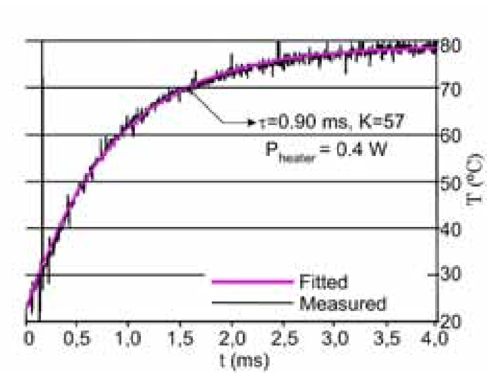


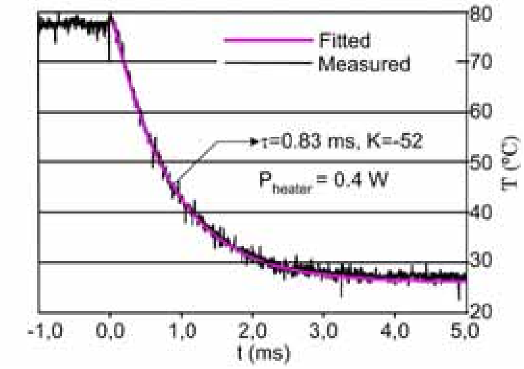
calculated heat losses in the membrane (150 nm SiRN and 850 nm p++-Si)

Tiggelaar e.a. Sens.Act.A 112, 267-277 (2004)

Transient effects







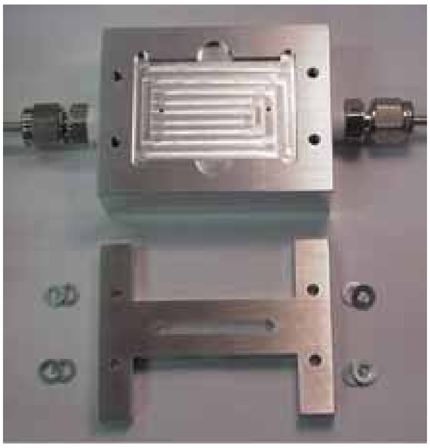
(a) heating curves for P = 0.4 W

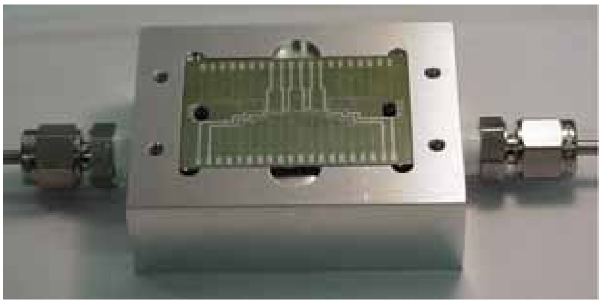
(b) open loop responses of the microreactor as a function of elapsed time when 0.4 W is applied

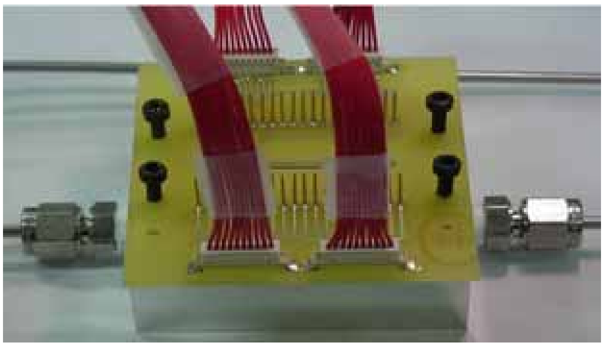
(c) or turned off

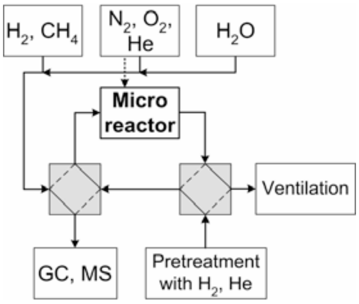
Tiggelaar e.a. Sens.Act.A 112, 267-277 (2004)

Microreactor testing set-up



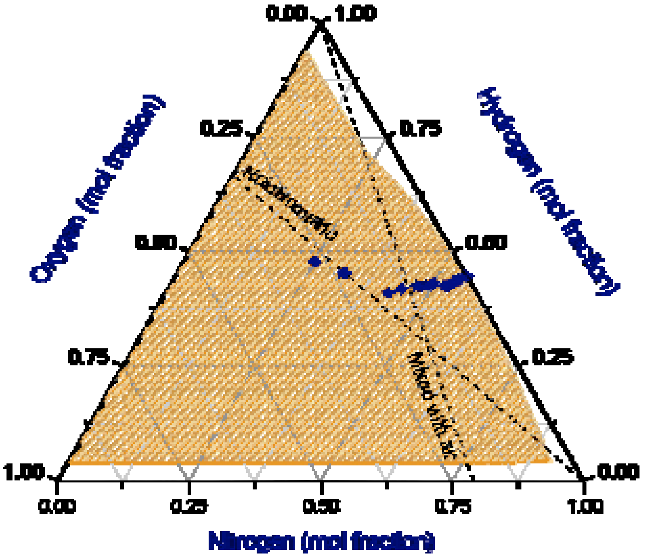






R.M. Tiggelaar, PhD Thesis University of Twente, 2004

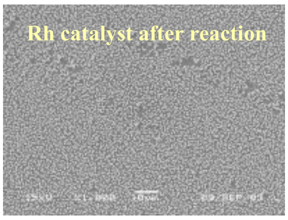
Safe hydrogen oxidation

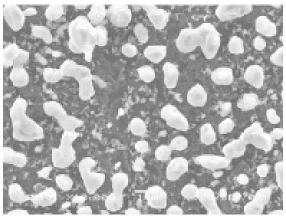


Ignition at 280°C

Temp. rises to 400°C

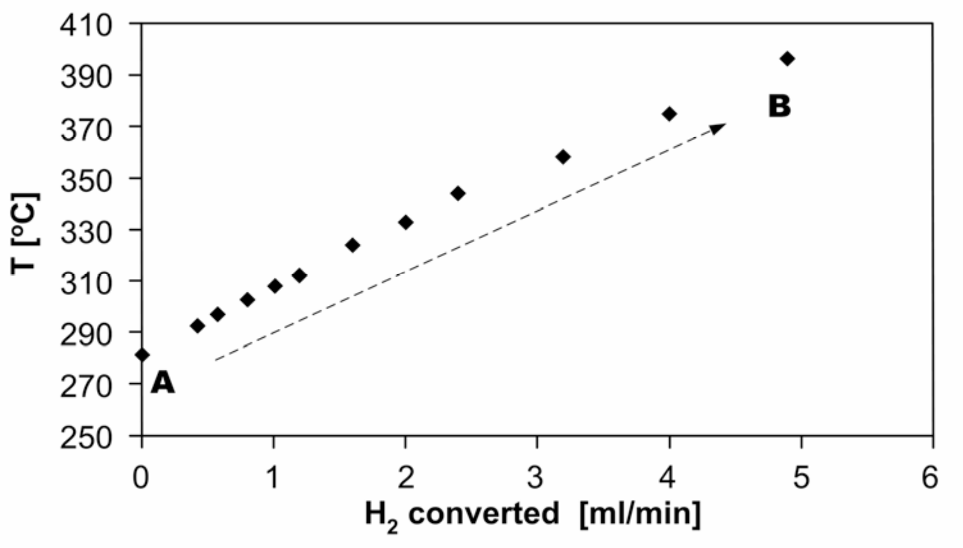
100% O_2 conversion



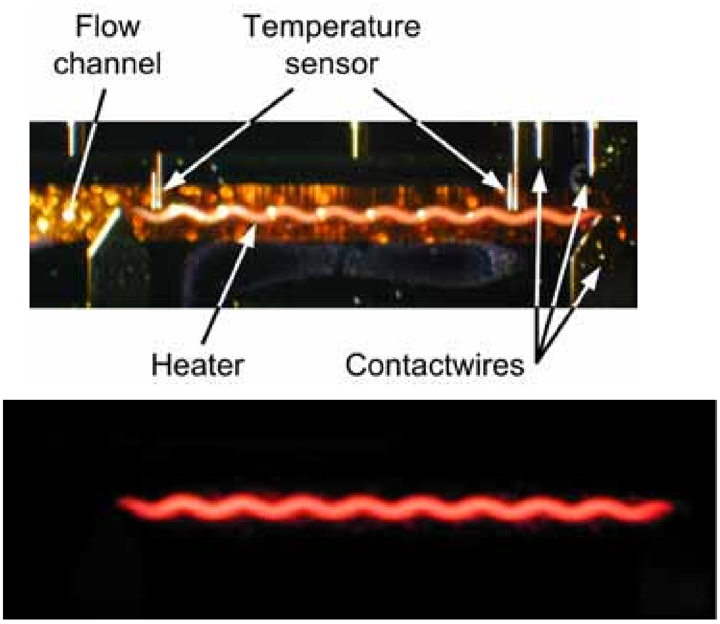


PhD work of Roald Tiggelaar (UT) and Poul van Male (TUE, Schouten) 2000-2004

Hydrogen conversion



Visible glow from heaters on membrane

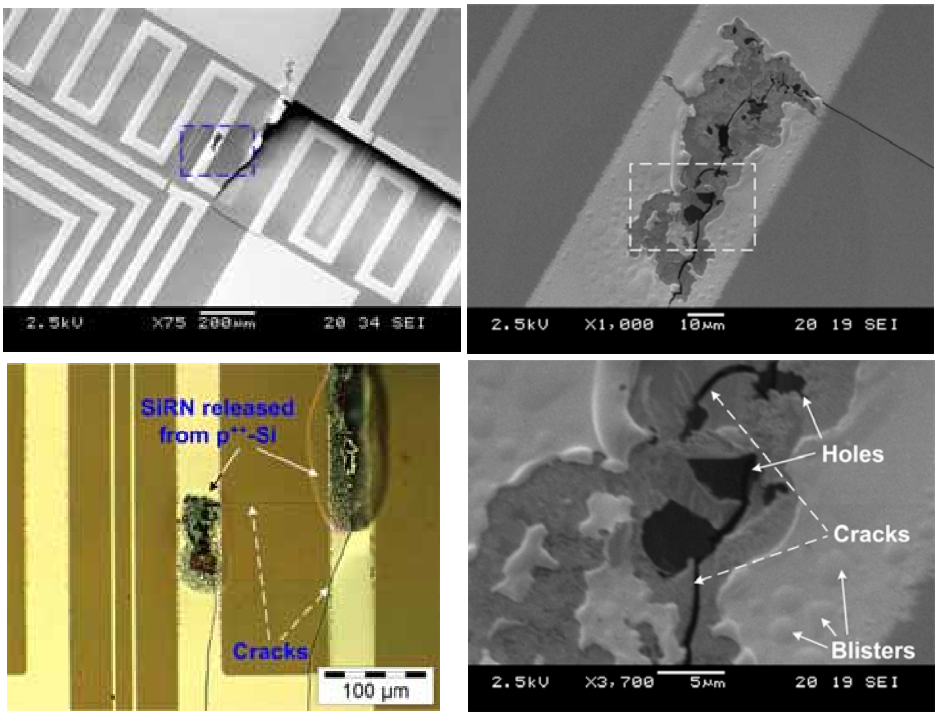


Estimated temperature > 725 ^{o}C

R.M. Tiggelaar, PhD Thesis University of Twente, 2004

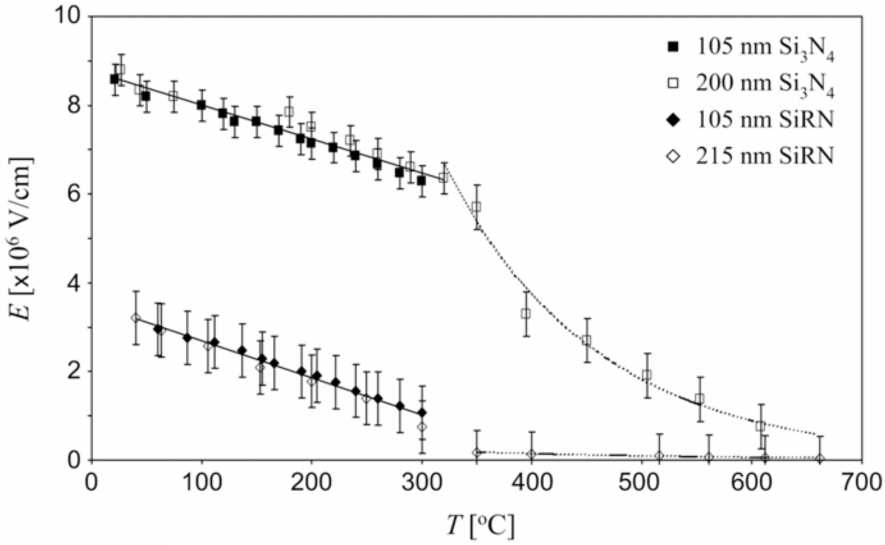
Materials aspects of high-temperature microreactors

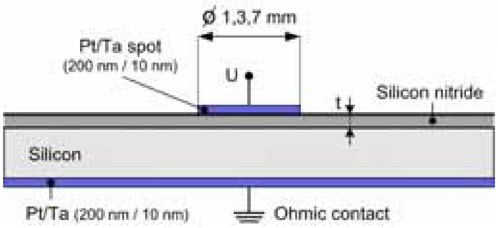
Breakdown of microreactors



R.M. Tiggelaar, PhD Thesis University of Twente, 2004

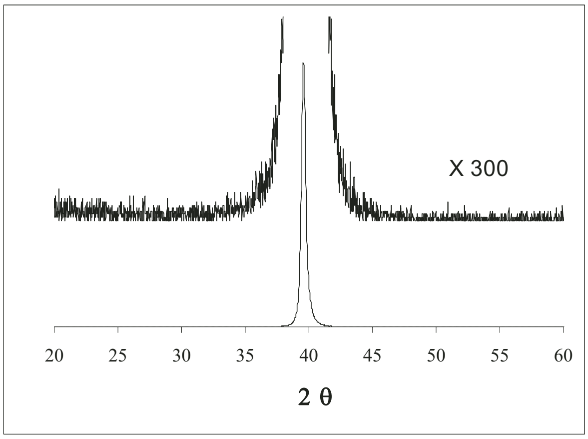
Breakdown of silicon nitride



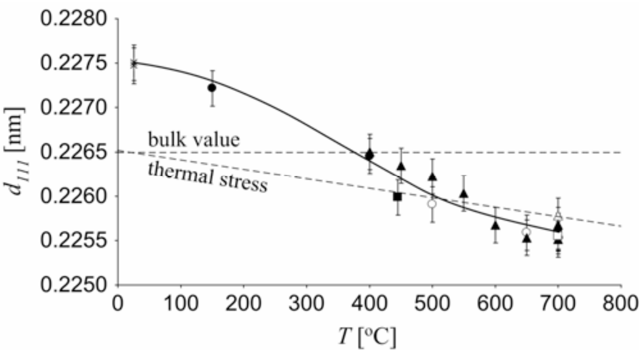


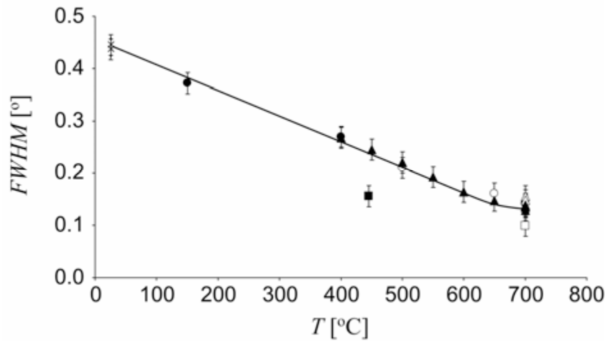
R.M. Tiggelaar, PhD Thesis University of Twente, 2004

Pt at high temperatures



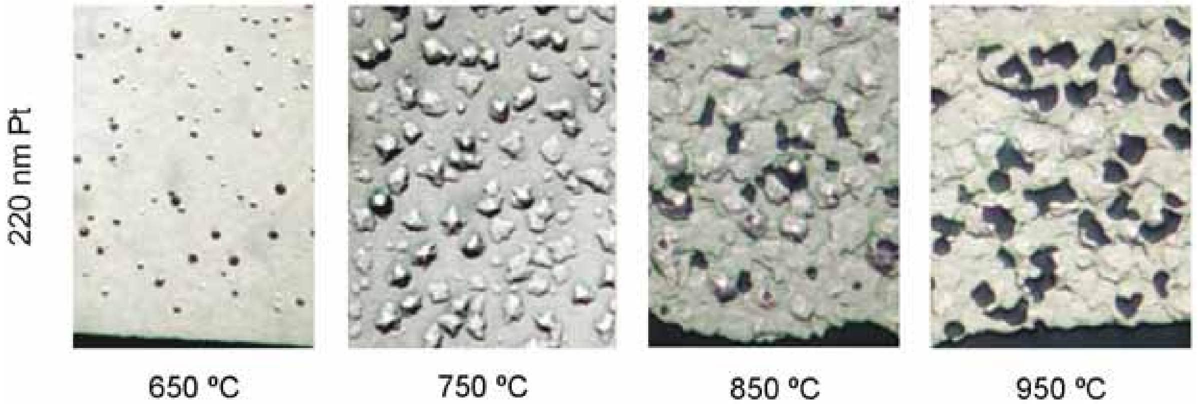
X-ray diffraction of Pt film





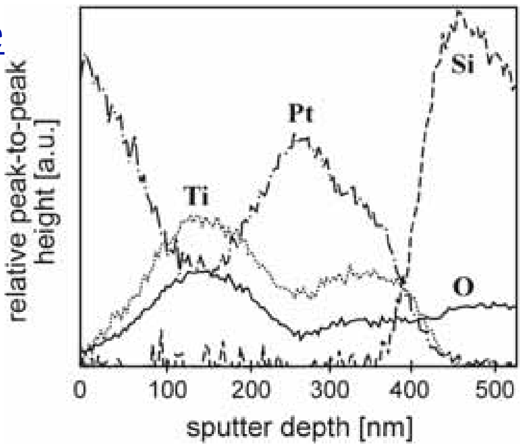
R.M. Tiggelaar, PhD Thesis University of Twente, 2004

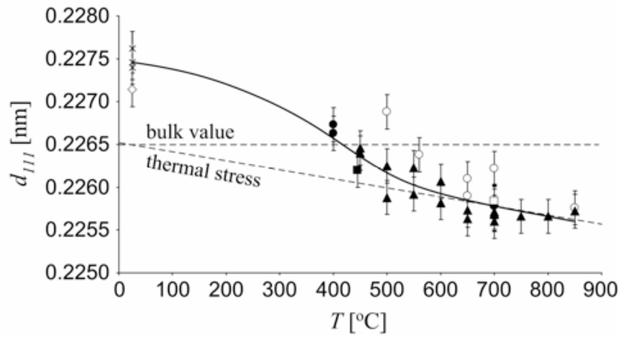
Pt at high temperatures (in air)

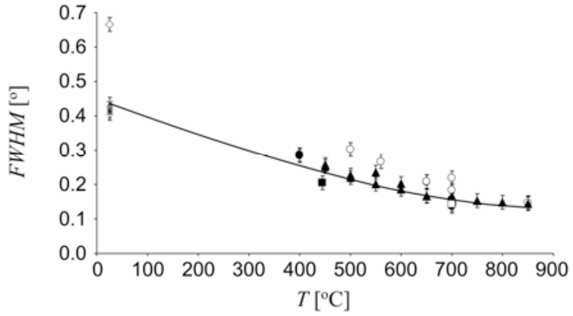


R.M. Tiggelaar, PhD Thesis University of Twente, 2004

Pt-Ti at high temperature

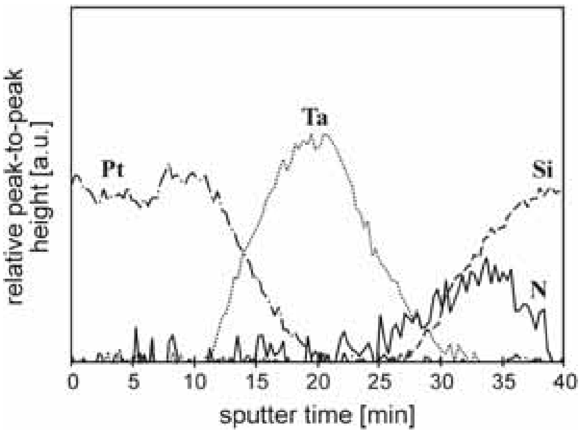




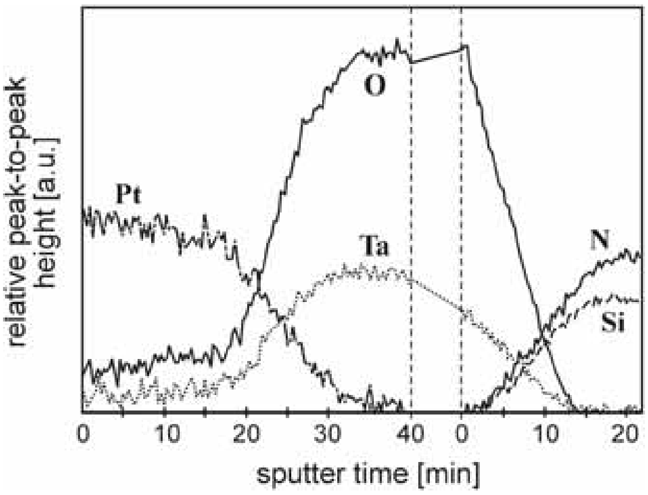


R.M. Tiggelaar, PhD Thesis University of Twente, 2004

Pt-Ta at high temperatures



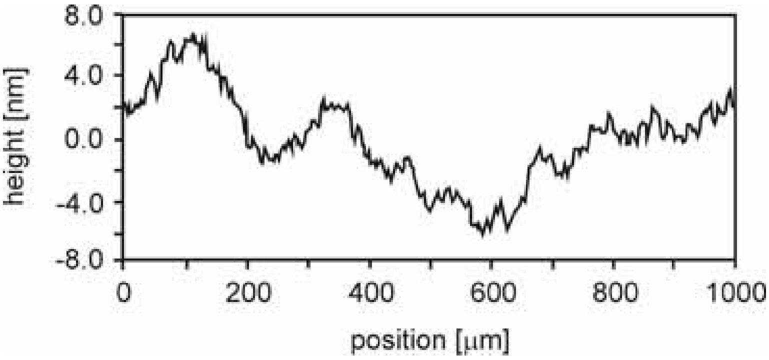
before annealing

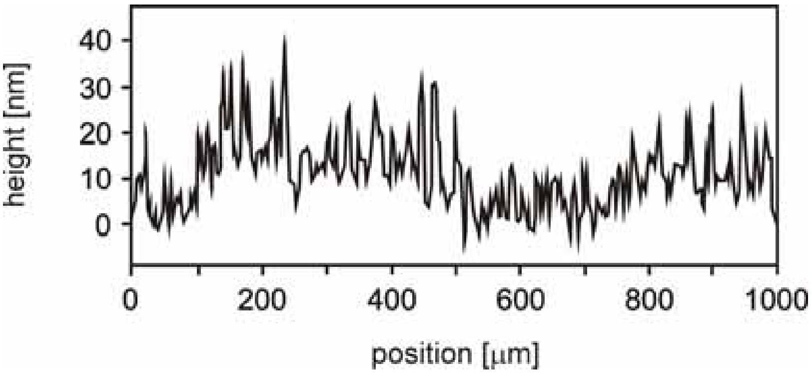


after annealing at 700 °C

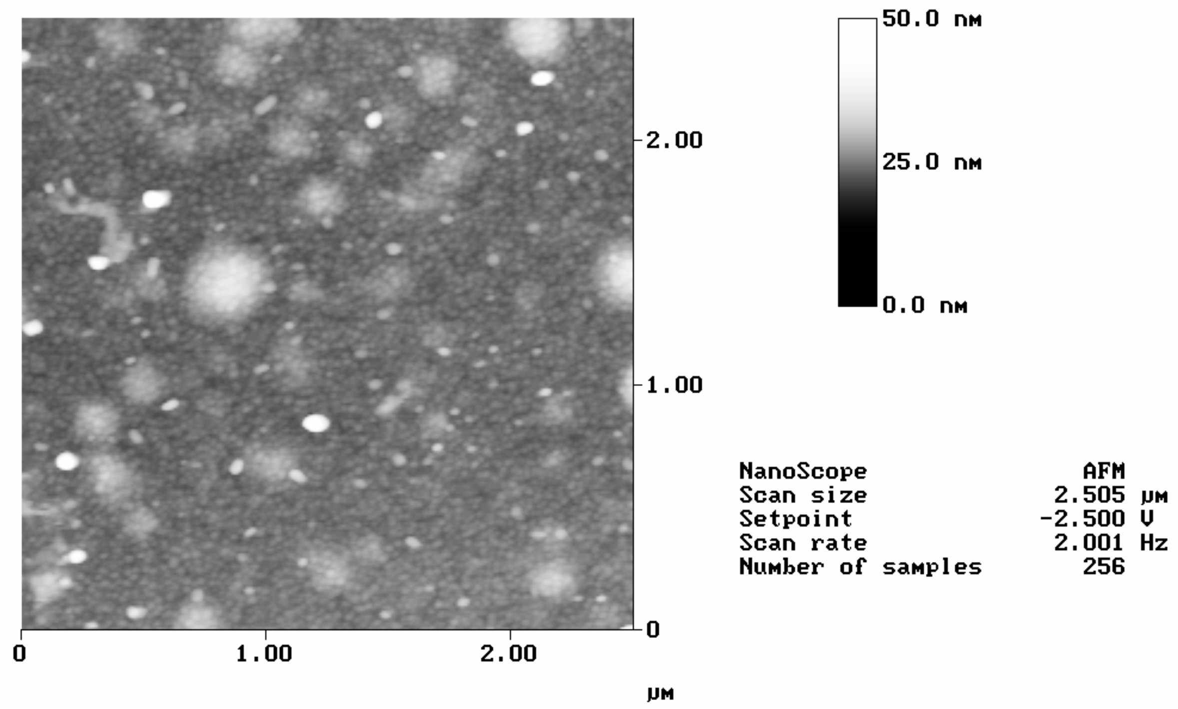
R.M. Tiggelaar, PhD Thesis University of Twente, 2004

Pt-Ta roughness before/after annealing at 700 °C



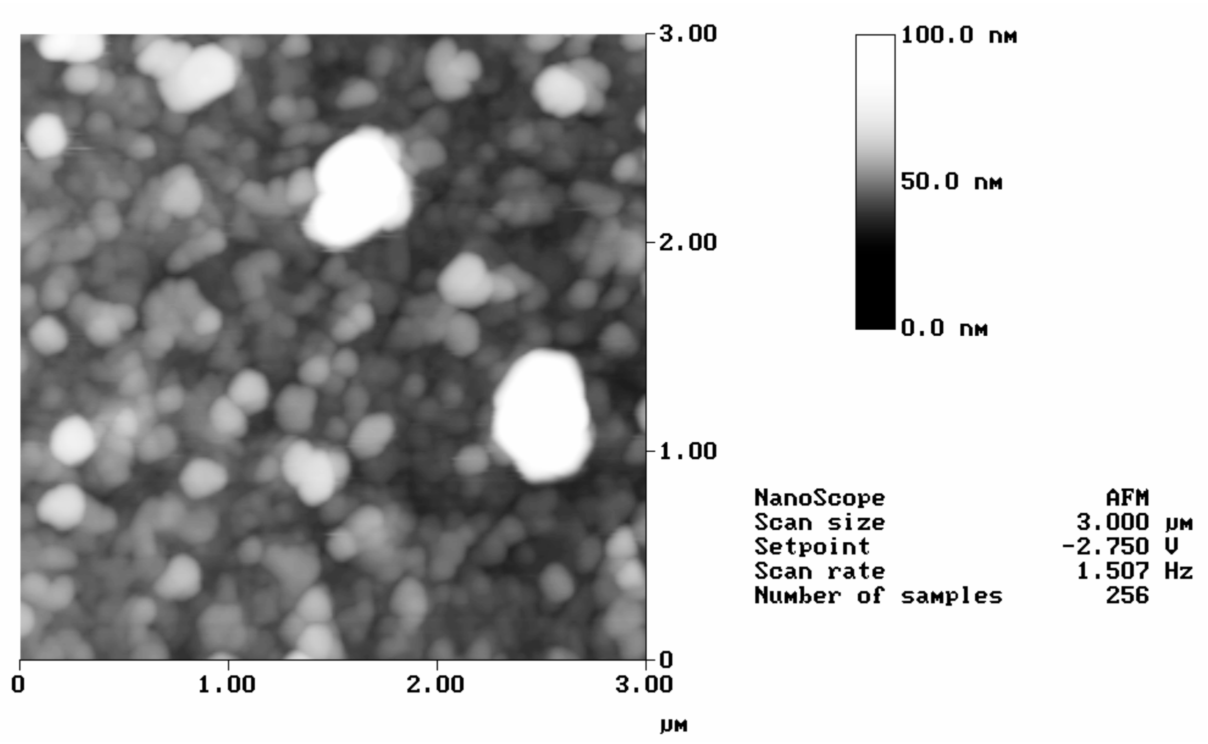


Pt-Ta before annealing -AFM image



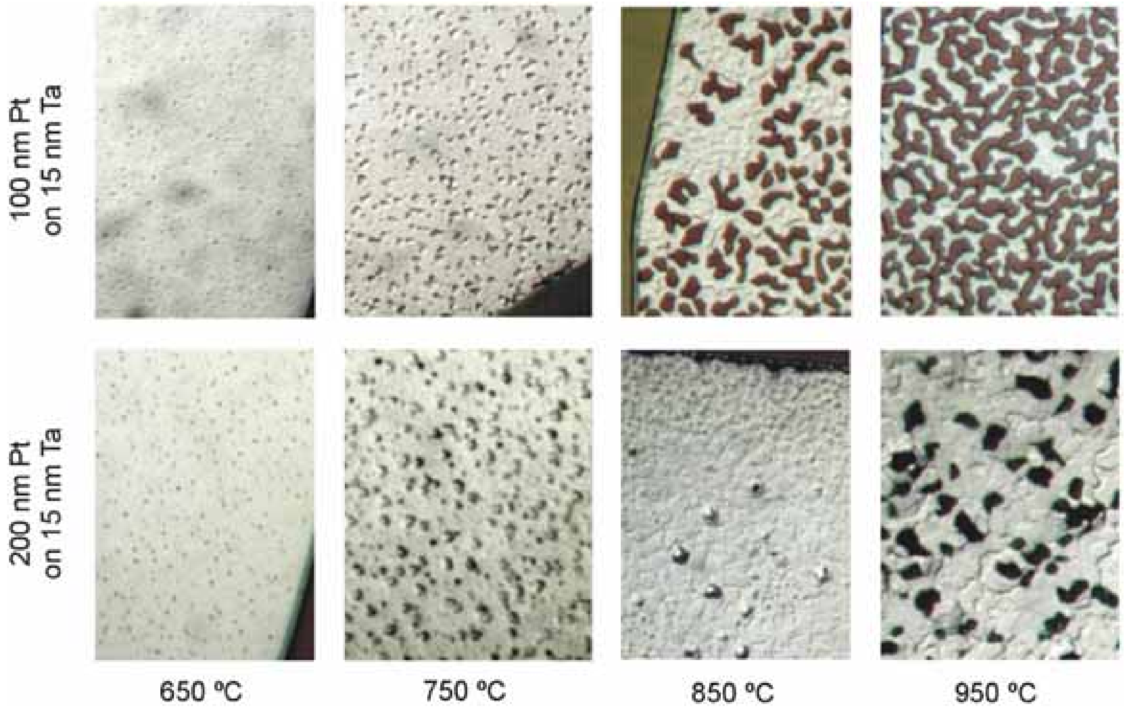
```
NanoScope                    AFM
Scan size                  2.505 µm
Setpoint                  -2.500 V
Scan rate                  2.001 Hz
Number of samples            256
```

Pt-Ta after annealing at 700 °C - AFM image



NanoScope	AFM
Scan size	3.000 μm
Setpoint	-2.750 V
Scan rate	1.507 Hz
Number of samples	256

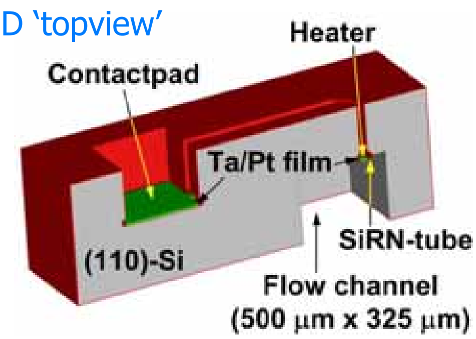
Pt-Ta at high temperatures



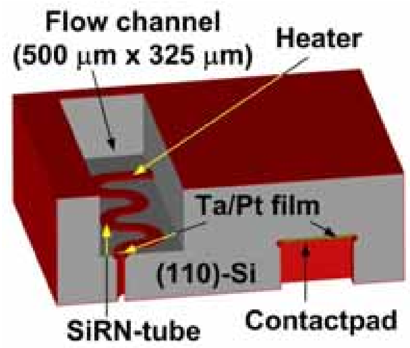
R.M. Tiggelaar, PhD Thesis University of Twente, 2004

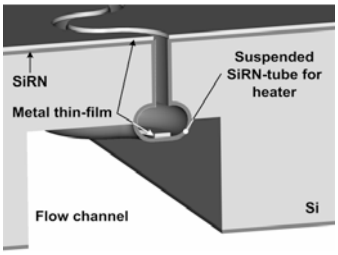
Re-designed microreactors

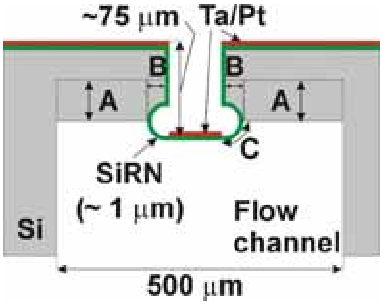
3D 'topview'



3D 'bottomview'

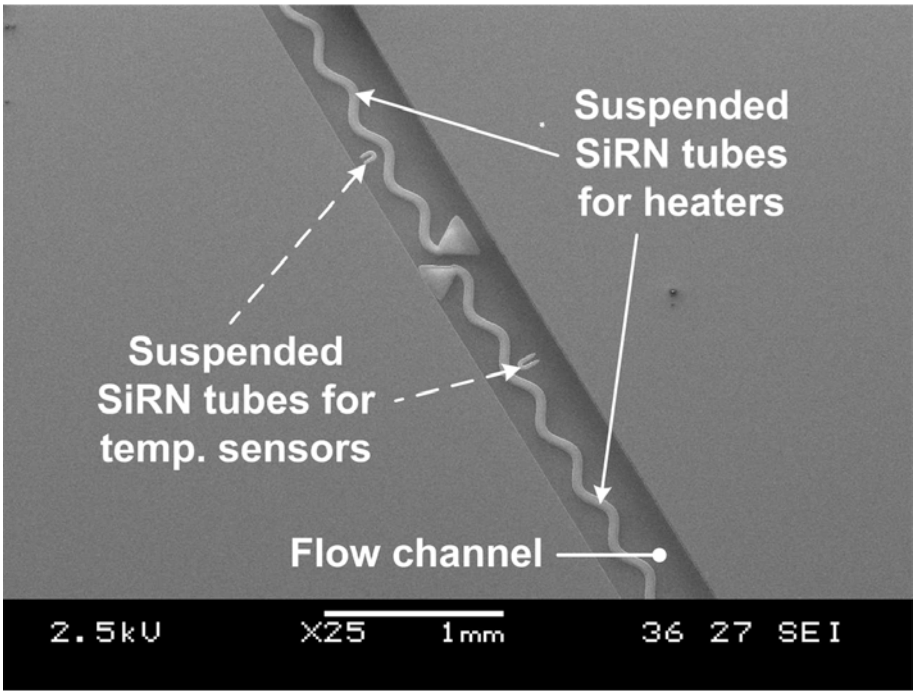






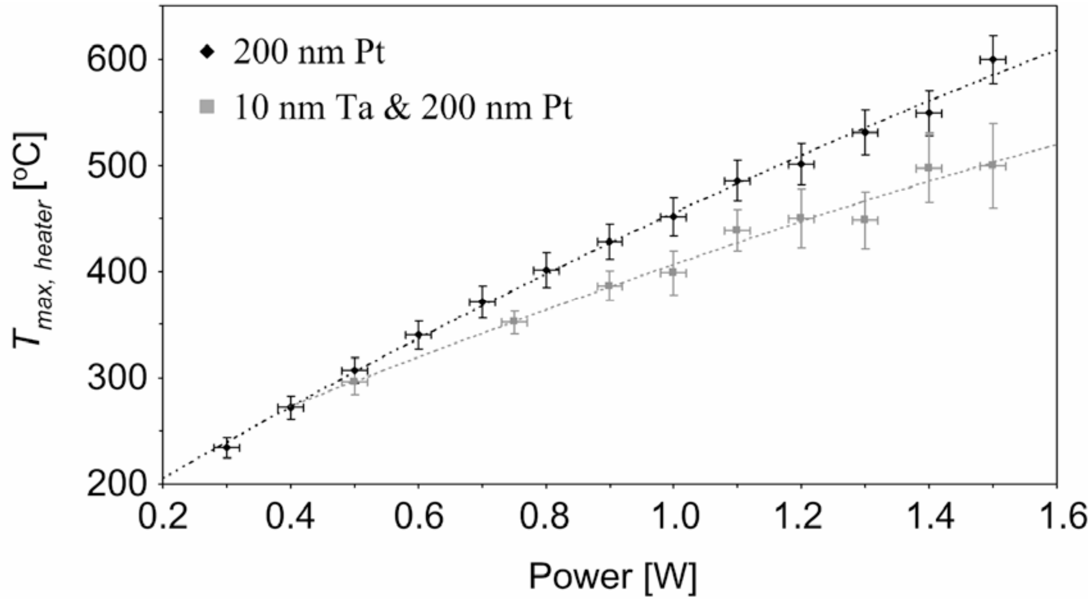
Cross section

Tiggelaar e.a. Lab Chip 5, 326-336 (2005)



Tiggelaar e.a. Lab Chip 5, 326-336 (2005)

Measured temperatures on re-designed reactor



Breakdown of re-designed microreactors