The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific
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International Atomic
Energy Agency

SMR.1670 - 11

INTRODUCTION TO MICROFLUIDICS

8 - 26 August 2005

Glass Microfabrication and Other Microfabrication Techniques

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2. Glass microfabrication and other microfabrication techniques

Topics in this lecture

Glass and other less established materials in microfabrication
Choice of material substrates are particular interesting from the application point of view in chemistry and biochemistry. Besides plastics, glass is the most popular of all materials in Lab-on-a-Chip 'microfluidic' devices.

The MEMS tricks
Same concepts other goals…

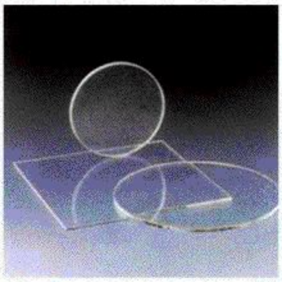
Structural elements
From design to device- how to select the appropriate technique?

- Introduction
- Strategic developments:
  - Utilizing microelectronic techniques for non-silicon materials.
- Tackling glass integration.
- Other materials and diversity of techniques.
- Outlook: Future developments
- Summary

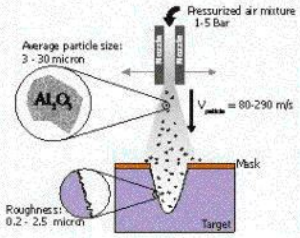
Introduction

Topics in this section

Glass as material



Fabrication principles



- Glass micromachining:
  - Material preparation,
  - Established patterning techniques,
  - Specially developed techniques for fast, through-wafer structuring in glass and other brittle materials.
- Miscellaneous used techniques in microfluidics.

Why glass ?

- Bulk and thin-film processing in glass popular due to generally chemical inertness of the material and existing record of glass surface chemistry.
- Micromachining based on developments in semiconductor microelectronic industry where glass is used as:
  - as an electrical isolation material,
  - as chemical inert material (capping),
  - as material with low interference (electromagnetic waves, acoustic pick up),
  - ??

Glass etymology

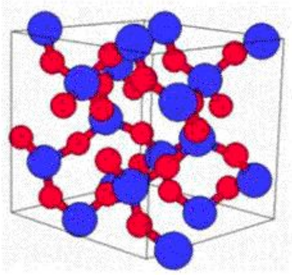
Glass is one of the most ancient of all materials known and used by mankind. The geologic glass, obsidian was first used by man thousands of years ago to form knives, arrow tips, jewelry etc. Manmade glass objects appear to be first reported in the Mesopotamian region as early as 4,500 BC. glass objects dating as old as 3,000 B.C. have also been found in Egypt. Surprisingly these glasses have compositions very similar to those of modern **soda lime silicate glass**. No doubt the readily available soda ash, from fires, limestone, from seashells and silica sand, from the beaches are the cause of this agreement.

Earlier **glass coated objects** have been dated to as early as 12,000 B.C. and are in the form of glazes and enamels on ceramic pottery, used presumably to improve the water tightness of various jugs, bottles and vases. Glass is 'etched' by various means of altering the surface. The earliest techniques were **acid etching** and copper wheel engraving. Acid etching produces a variety of different obscure frosted grey and semi obscure tones depending on the acid formulation employed. Where the glass is to remain clear it has to be **masked** off with material **to resist the acid**.

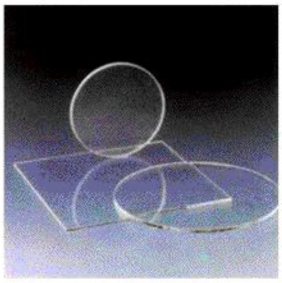
Copper wheel engraving uses a small rotating abrasive head to incise decorative patterns in the glass. This 'cut' glass is then polished by progressively smoother wheels.In the1860's acid etching and brilliant cutting started to be done on a semi industrial scale for the burgeoning house market. The invention of the large rotating stone wheel for the technique of 'brilliant cut' glass bore fruit in the very elaborate panels mostly seen in pubs. In the late 1870's craftsmen invented means of **imitating acid etching more cheaply with sandblasting**

From the Glass Encyclopedia {http://www.encyclopedia.netnz.com/}

Glass: the material



Crystal Lattice Structure of quartz
http://cst-www.nrl.navy.mil/



- Quartz is pure and crystalline SiO_2. It is very hard, piezoelectric and does not absorb UV radiation.
- Fused silica is pure and amorphous SiO_2. It is very hard, and does not absorb UV radiation.
- Glass is a mixture of various compounds. Pyrex and Borofloat are chemically inert and has the same low thermal expansion coefficient as silicon (so suitable for bonding).
- Material is delivered as wafers (substrates, blanks) at about 3-10 x the prize of a conventional silicon wafer.

Composition of glasses

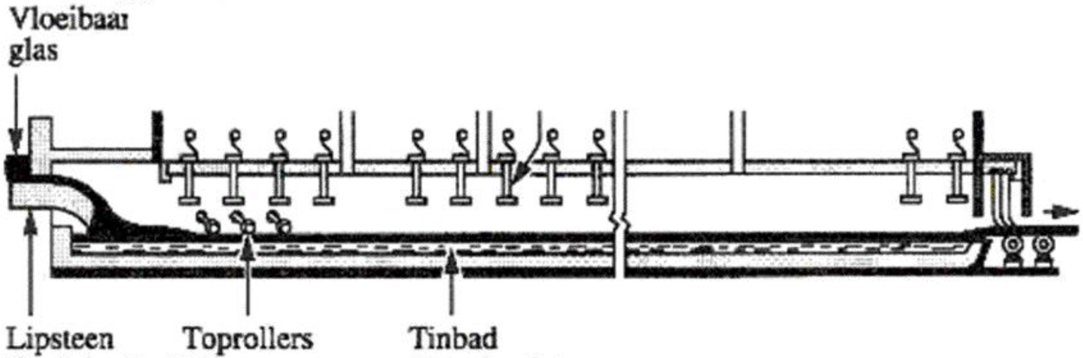
	SiO_2	Na_2O	B_2O_3	MgO	CaO	K_2O	Al_2O_3
Quartz/fused silica	100	-	-	-	-	-	-
Pyrex/borofloat	80.2	4.5	12.3	-	0.1	0.3	2.6
Window glass	72.8	12.8	-	3.8	8.2	0.8	1.4
Grolsch bottle brown	72.7	13.8	-	-	10.0	1.0	1.9

Float glass manufacture

Established industrial process for many glass types

- From window glass and other household appliances to high tech applications.

"Floating glass, melt"



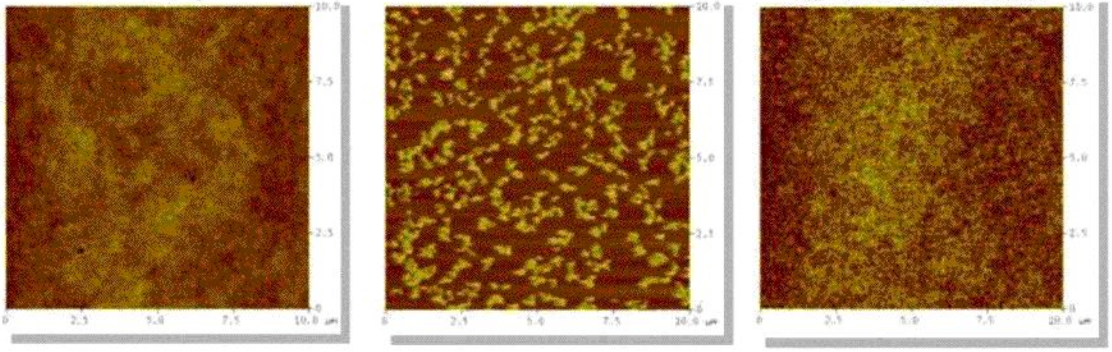
"Slit inlet" "Upper transport roles" "Tin bath"

"Vademecum voor de Glastechniek", 1992

Floatglass quality

- The good and the bad side of float glass

AFM of top side | AFM of float side | AFM of chemical mechanical polishing (CMP) of the float side

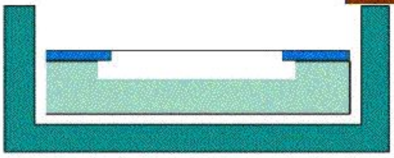


roughness = 0.23 nm | roughness = 4.2 nm | roughness = 0.49 nm

J.W. van Nieuwkasteele, University of Twente, 2004, unpublished

Pattern definition by lithography

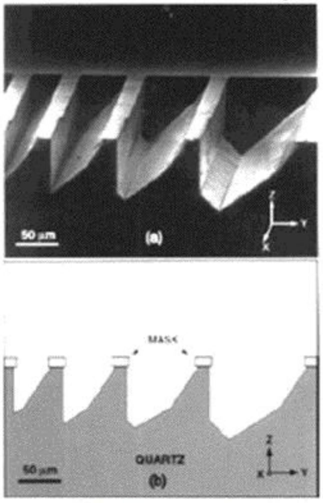
- Mask materials for glass
  - Shadow masks, photoresists
  - Au, Cr
  - Silicon as a mask
- Hydrofluoric acid wet etching
- Plasma dry etching
- Powder blasting



IC-adapted methods for glass (classical)

Wet etching ⇔ **Dry etching**

Quartz: anisotropic



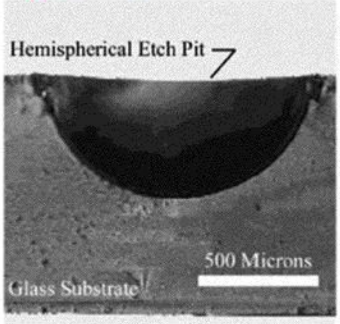
Rangsten et al, JMM 8, 1998

Glass: wet isotropic

50% HF in water

$SiO_2 + 6HF \rightarrow H_2SiF_6 + H_2O$

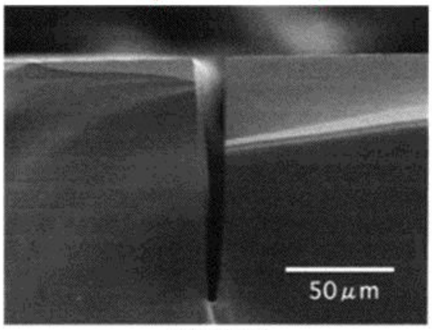
Etch rate about 7 µm/min!



Pyrex etch pit
Walton et al., Anal.Chem 75, 2003

Glass: dry anisotropic

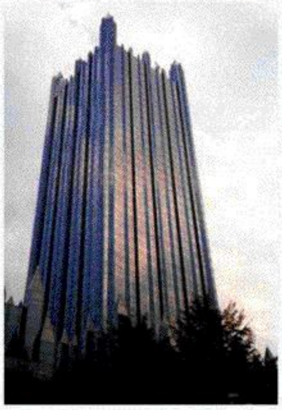
Not yet a fully developed technique!



Pyrex trench
Li, S&A A 87, 2001

Topics in this section

Glass microfluidic chip fabrication & integration

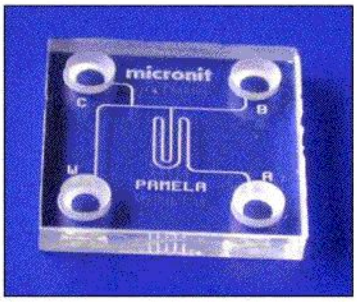


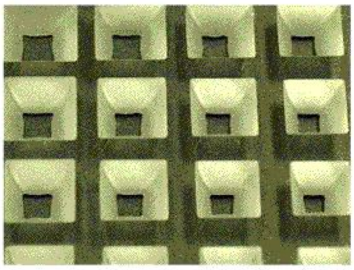
"Glass cathedral"

Strategic developments

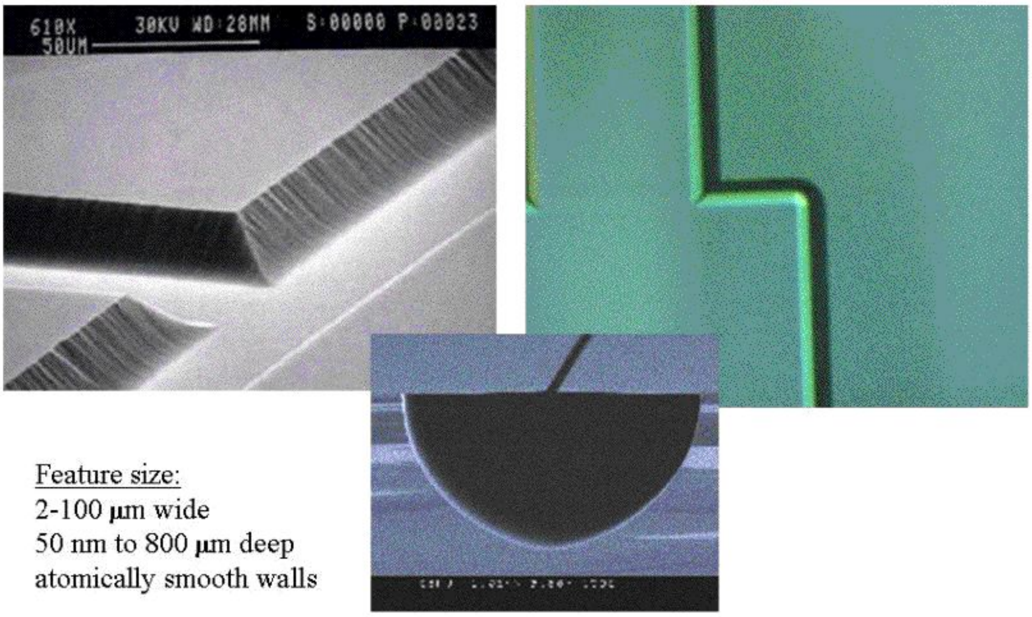
- Glass microfludic chip fabrication techniques
- From MEMS to spin-offs
- Selection of fabrication techniques is based on pattern feasibility and critical dimensions in the design
  - Choice of material often restricts the fabrication technique used.
  - Critical dimensions often restrict the material-fabrication combinations to choose from.

Micromachining of microfluidic products in glass





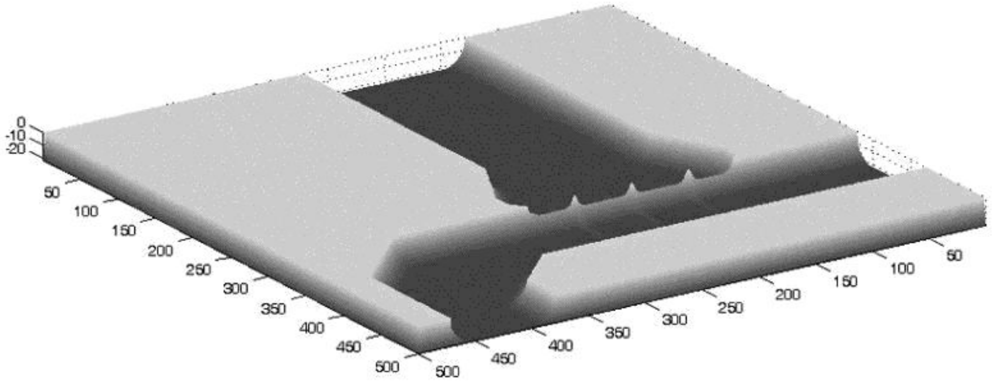
Wet-chemically etched channels



Feature size:
2-100 μm wide
50 nm to 800 μm deep
atomically smooth walls

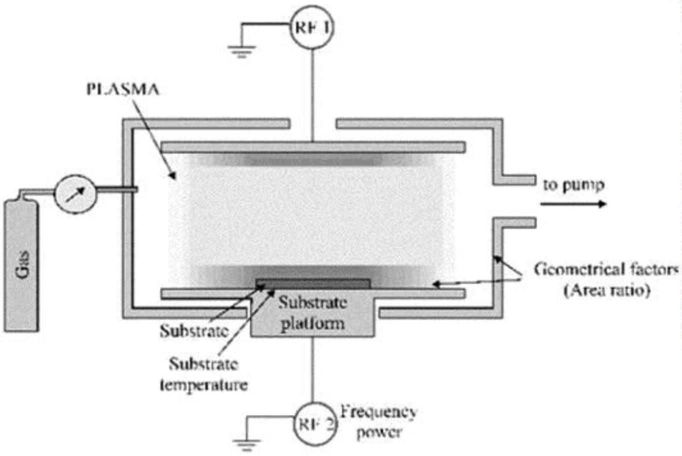
Wet-chemically etched structures

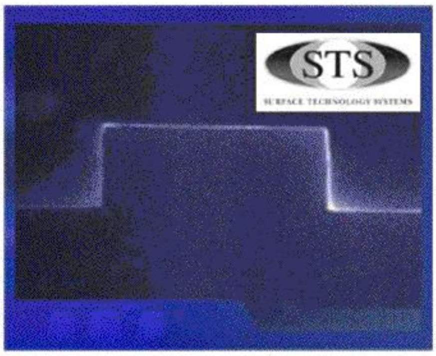
- **Simulation of an HF-etched channel structure with integrated particle trap**



(Deep) Reactive Ion Etching (dry)

- Versatile
- Isotopic/anisotropic
- High etch rates





$8 \mu m$ deep etch in SiO_2

Criteria for plasma etched glass

Etch Rate and Surface Morphology of Substrates

- Transparent substrates permit fabrication of novel MEMS devices with promising applications in optical communication and microbiological systems.
- To be useful, the transparent substrate must be compatible with conventional lithographic and micromachining techniques.
- Compatibility with thin film silicon electronics is desired as this permits one to build intelligent systems.
- Topography of the etched surfaces must be smooth (1/10 to 1/20 of the wavelength of light) to minimize scattering loss and cross talk.
- Microfluidic biological systems also require smooth surfaces.

Thus, both the etch rate and surface morphology of dry-etched glass and glass ceramics are of interest to investigate!

J. Liu et al., Mat. Res. Soc. Symp. Proc. Vol. 657, 2001

Etch results of the Magnetron Ion Etcher (MIE) at Cornell Nanofabrication Facility

- **Corning Glass Ceramic substrate (GC-6), new glass developments and their characterization**

Table I. Substrates compositions and etch results

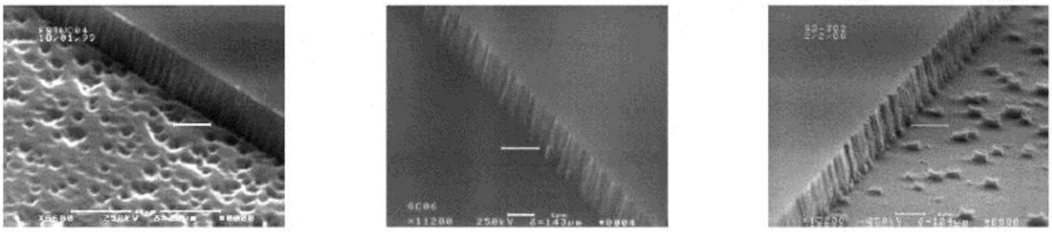
	Structure	$CHF_3 + O_2$ etch rate (Å/min)	CF_4 etch rate (Å/min)	Surface Morphology
Fused Silica	Amorphous SiO_2	1714	3676	Smooth
"Green" glass substrate	SiO_2, Al_2O_3, ZnO, MgO, TiO, ZrO_2, BaO	500	797	Smooth or rough; depending on pre-etch cleaning procedure used.
Glass-ceramic substrate	Solid solution of spinel crystals (~10nm) with glass	553	717	Smooth or rough; depending on pre-etch cleaning procedure used

Note: All samples used in above experiments were cleaned with our "standard" procedure
Recipe 1: CHF_3 20 sccm, O_2 2 sccm, RF power 1 kw [3]
Recipe 2: CF_4 40 sccm, RF power 1 kw [4]

[3] Greg Williams, Ph.D thesis, Cornell University, 1995
[4] MIE recipe book, Cornell Nanofabrication Facility

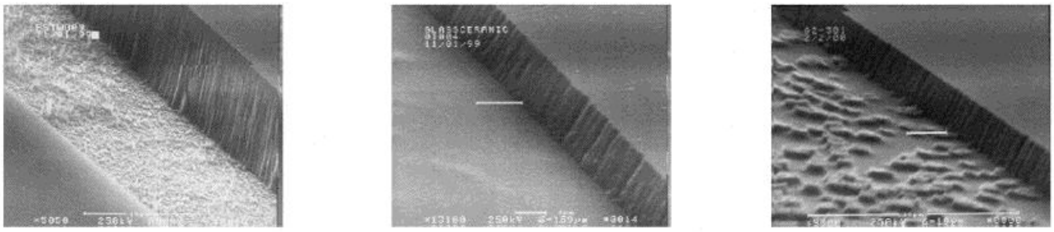
J. Liu et al., Mat. Res. Soc. Symp. Proc. Vol. 657, 2001

Surface morphology



a) Fused silica *b) Glass-ceramics* *c) "Green" glass*

Figure 1. SEM images of substrates etched in $CHF_3 + O_2$ for 20 minutes



a) Fused silica *b) Glass-ceramics* *c) "Green" glass*

Figure 2. SEM images of substrates etched in CF_4 for 20 minutes

J. Liu et al., Mat. Res. Soc. Symp. Proc. Vol. 657, 2001

Material analysis

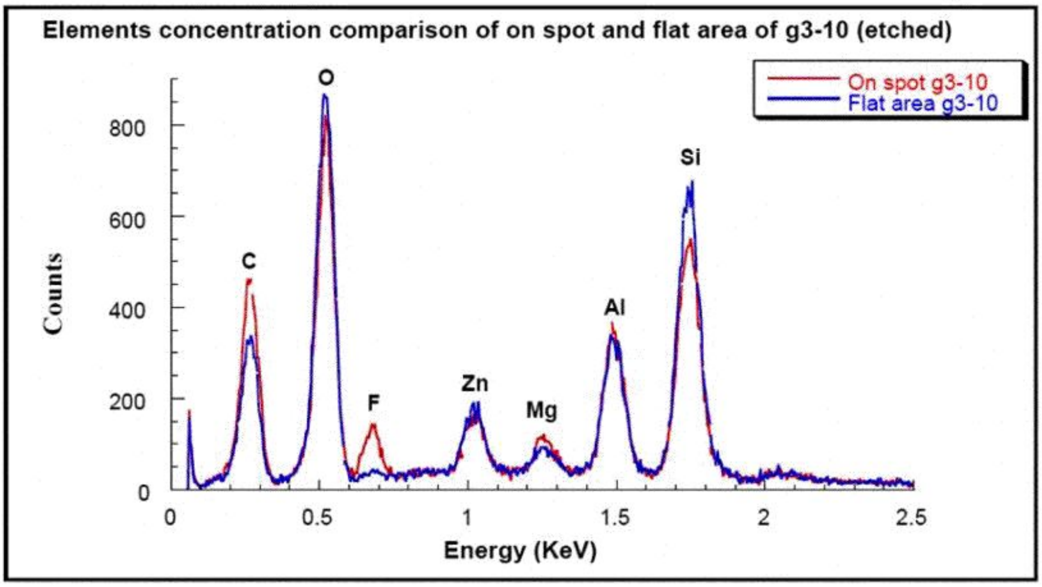


Figure 3 Microprobe analysis results of elemental concentration at the protrusions and in the flat area of a "green" glass sample blanket etched in CF$_4$ for 60 minutes.

J. Liu et al., Mat. Res. Soc. Symp. Proc. Vol. 657, 2001

Pre-etching cleaning treatments

- The 1x1cm samples were than treated in 13 different ways prior to being MIE etched using CF4:

1. Null experiment – no further cleaning.
2. Exposure to an oxygen plasma for 20 minutes (All oxygen plasma treatments were performed in situ in the PlasmaTherm 72 Reactive Ion Etcher at CNF)
3. "Standard" clean:
    1. A 5 minute rinse in Acetone, a 5 minute Isopropyl alcohol (IPA) rinse, and a final deionized (D.I.) water rinse, followed by
    2. An ultrasonic, 5 minute, clean in NH_4OH/H_2O_2 (volume 1:1) followed by a D.I. water rinse.
4. "Standard" clean, oxygen plasma treatment for 20 minutes
5. "Standard" clean, buffered HF (6:1) dip, D.I. water rinse
6. "Standard" clean, buffered HF (6:1) dip, D.I. water rinse, oxygen plasma treatment for 60 minutes
7. "Standard" clean, buffered HF (6:1) dip, D.I. water rinse, H2O2 (30%) solution soak for overnight, D.I. water rinse

J. Liu et al., Mat. Res. Soc. Symp. Proc. Vol. 657, 2001

Treatments (continuous)

8. Buffered HF (6:1) dip, D.I. water rinse
9. Buffered HF (6:1) dip, D.I. water rinse, oxygen plasma clean for 20 minutes
10. RCA[3] cleaning
11. RCA cleaning, oxygen plasma treatment for 20 minutes
12. RCA cleaning, buffered HF (6:1) dip, D.I. water rinse
13. Treatment 12, oxygen plasma treatment for 20 minutes

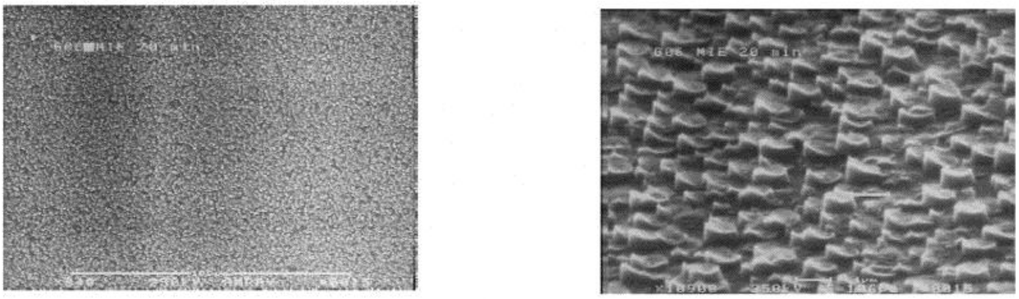
J. Liu et al., Mat. Res. Soc. Symp. Proc. Vol. 657, 2001

[3] *The RCA clean is commonly set up using series of bath in which the wafer is immersed. The first bath contains a mixture of $H_2O/NH_4OH/H_2O$, heated to about 75°C. This solution removes organic residues from the surface, and also dissolves many metals such as Ni, Cd, Zn, Co, Cr, Au and Ag [6]*

[6] J. G. Couillard, D. G. Ast, C. Umbach, J. M. Blakely, C. B. Moore and F. P. Fehlner, *J. of Non-Cryst. Solids* **222** (1997) 429

Results of the treatment experiment

- **After the CF_4 etch, only samples cleaned using procedures 5, 6, 7, 12, 13 had smooth surfaces. All other samples had a rough surface and looked opaque (transmission) or milky (reflection). The opaque samples contained a very high density of particles, as shown in Figure 4.**



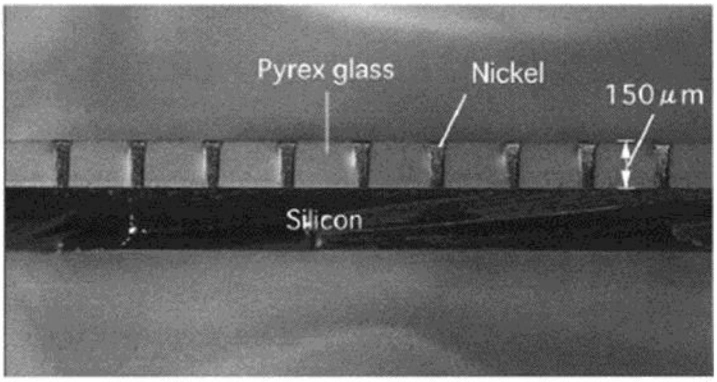
a) SEM image at x 840 *b) SEM image at x 10900*

Figure 4. SEM images of etched "green" GC6 glass sample cleaned by procedure #8

J. Liu et al., Mat. Res. Soc. Symp. Proc. Vol. 657, 2001

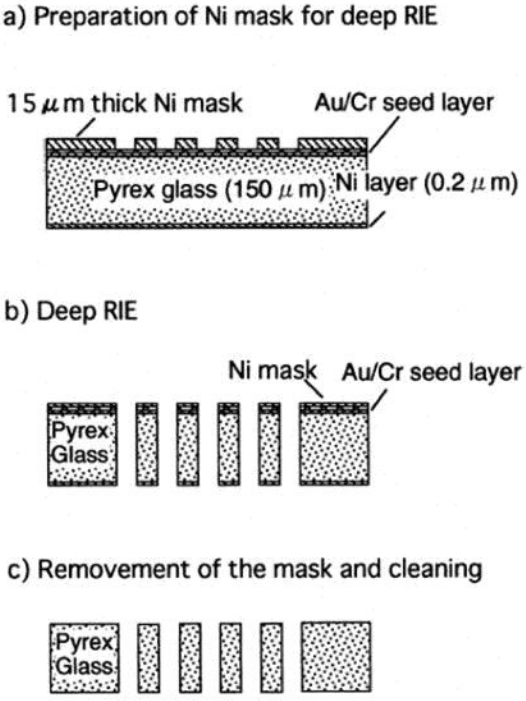
Deep glass etching for feed-through

- Classical MEMS development: spin-off for microfluidic chip fabrication.
- Feed-throughs is one of the key processes in the field of MEMS.



X. Li et al., J MEMS, VOL. 11, NO. 6, 2002

DRIE for glass

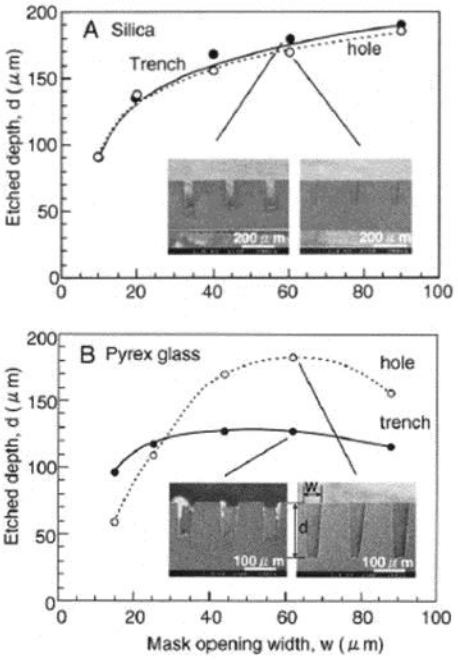


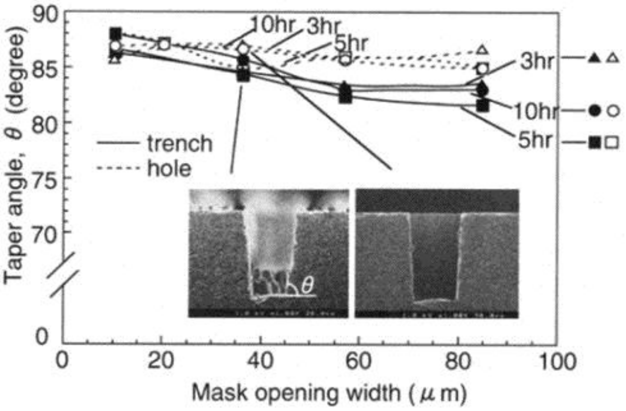
- Sulfur hexafluoride (SF6) plasma.
- Aspect ratios: 5-7 for a hole pattern and 10 for a trench pattern.
- Through the wafer etching of a hole pattern of 50 mm diameter was carried out using 150mm-thick Pyrex glass wafers.

X. Li et al.,,J MEMS, VOL. 11, NO. 6, 2002

DRIE results

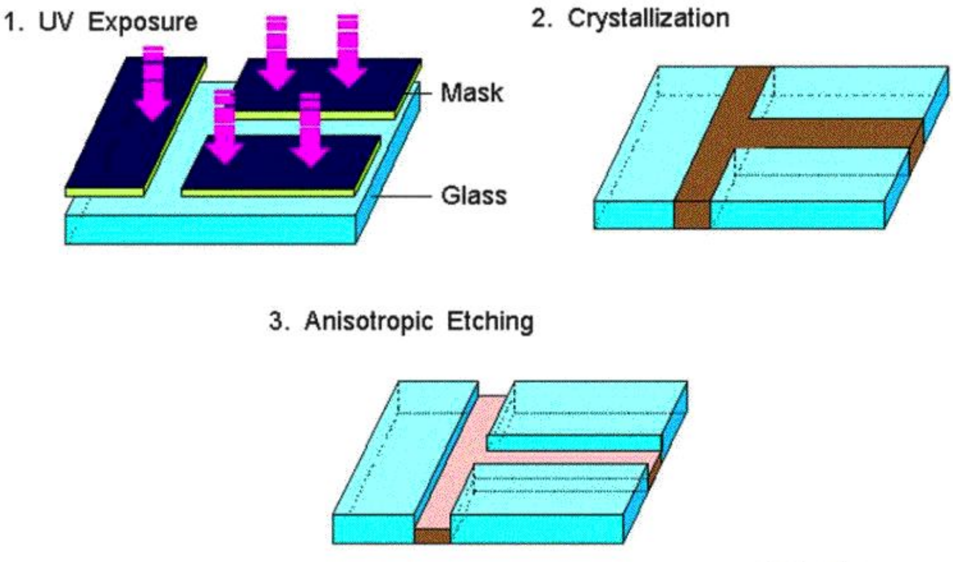
Etch characterisation





X. Li et al., J MEMS, VOL. 11, NO. 6, 2002

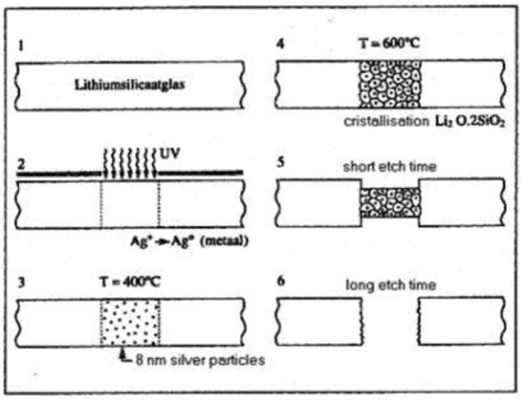
Photo sensitive glass FOTURAN



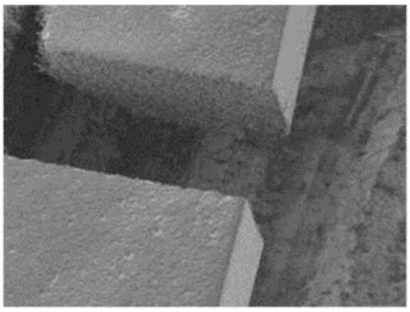
www.mikroglas.com

Photostructurable glass

Trade names: Foturan, FotoForm, PEG-3



"Vademecum voor de Glastechniek", 1992

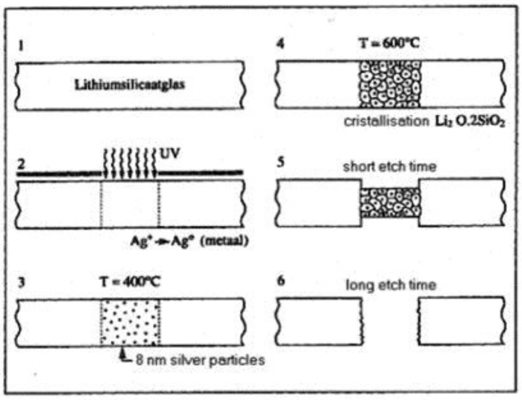


J.Bomer (2002), University of Twente

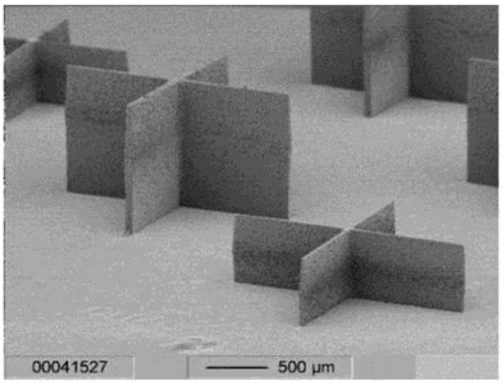
Glass surface becomes very rough!

Photostructurable glass

Trade names: Foturan, FotoForm, PEG-3



"Vademecum voor de Glastechniek", 1992

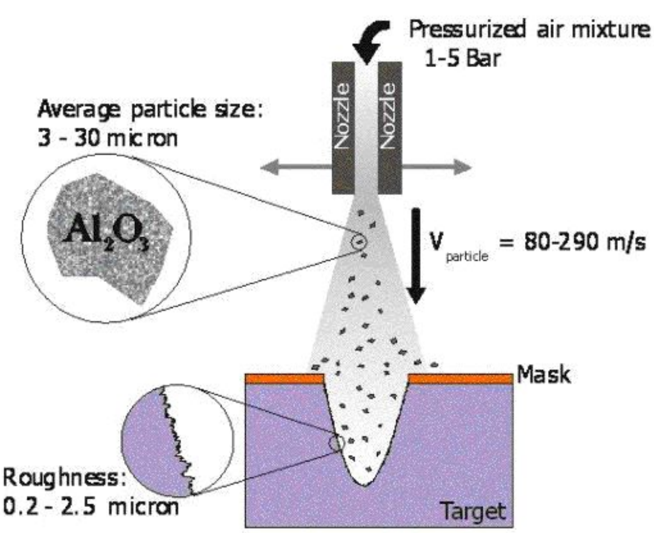


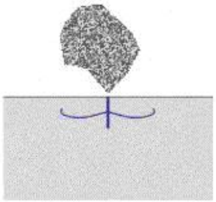
Mikroglas.com

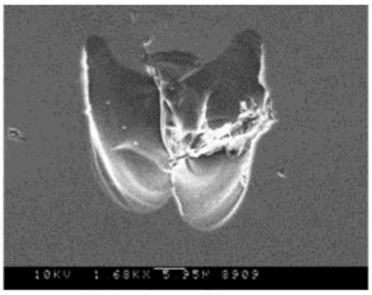
Structures of different height!

Powder blasting

- Unconventional technique (not allowed in cleanroom)







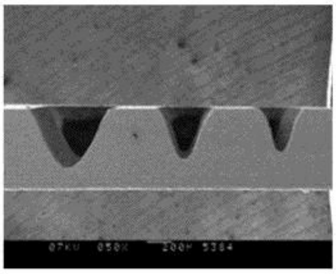
Single particle impact

Wensink et al., University of Twente

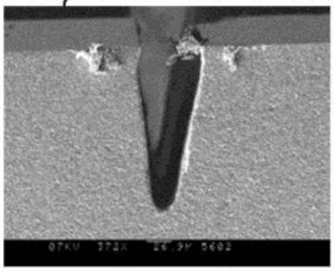
Powder blasting properties

- Etch rate is about 20 μm/min, minimum feature size is about 30 μm.
- Suitable for *any* brittle material (silicon, glass, ceramics)
- Mask material is rubber foil or a thick metal layer.

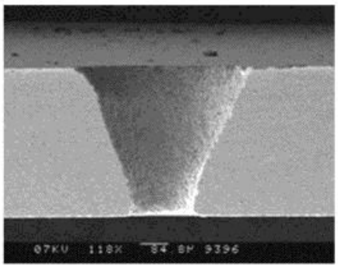
Blast lag: a wider channel became deeper compared to smaller channels.



Maximum depth to width ratio is only 2.5

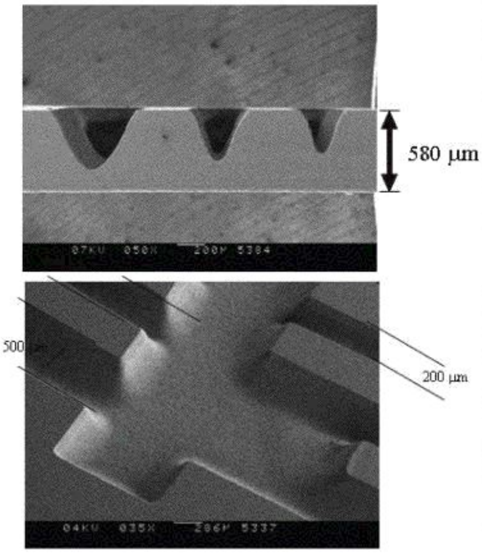


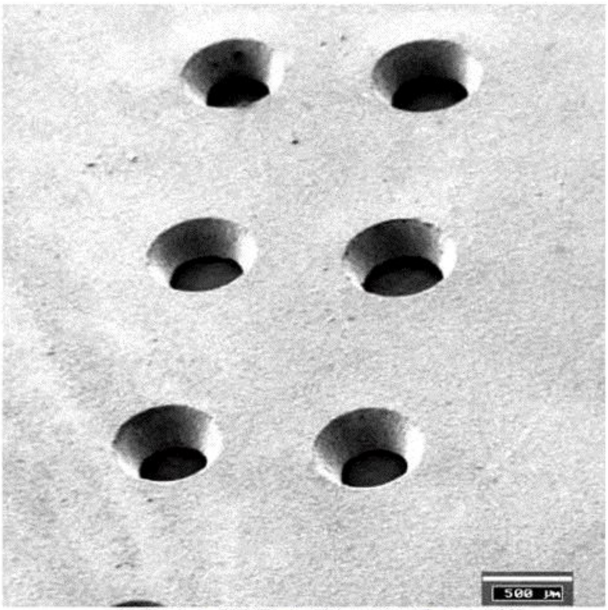
Very suitable to make through holes



H. Wensink, PhD Thesis, University of Twente, 2002

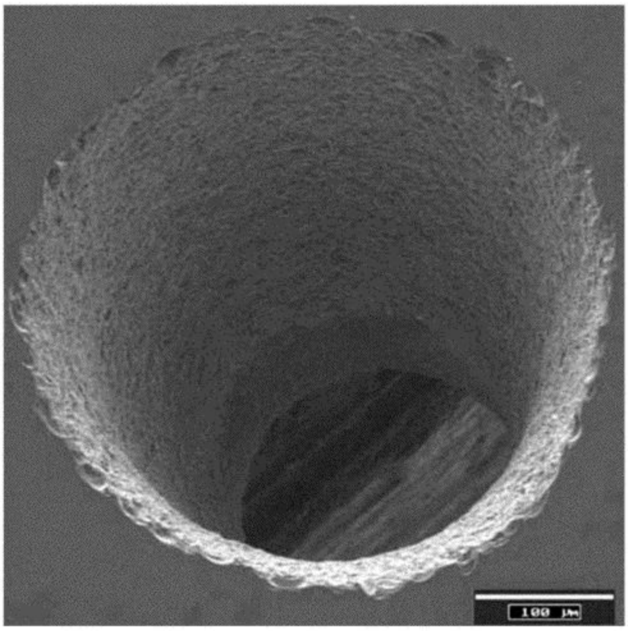
Critical Dimensions in powder blasting





H. Wensink, PhD Thesis, University of Twente, 2002

Surface properties



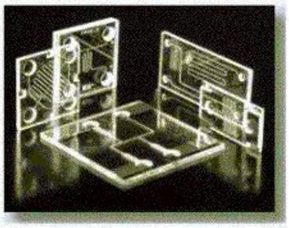
- Powder blasting in Pyrex
- Roughness 2-5 µm
- Angle with surface ~70°

H. Wensink, PhD Thesis, University of Twente, 2002

Topics in this section

Glass devices

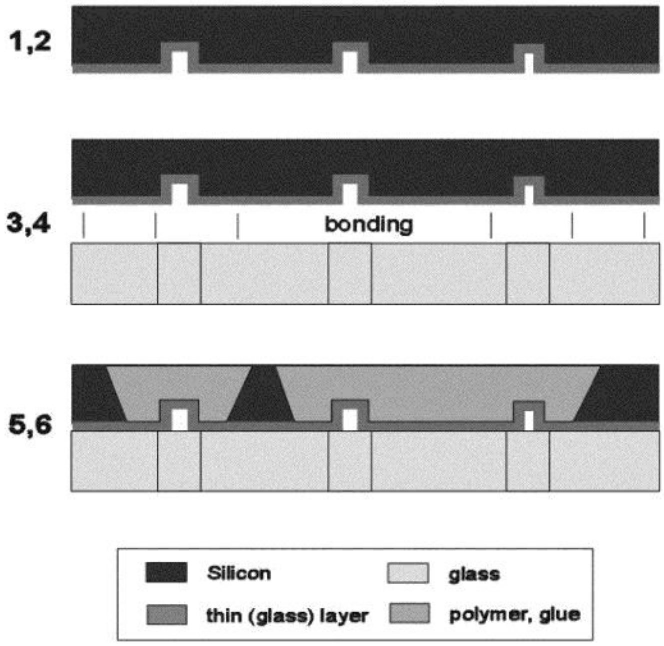
Thin-film processing versus bulk…no simple answers!



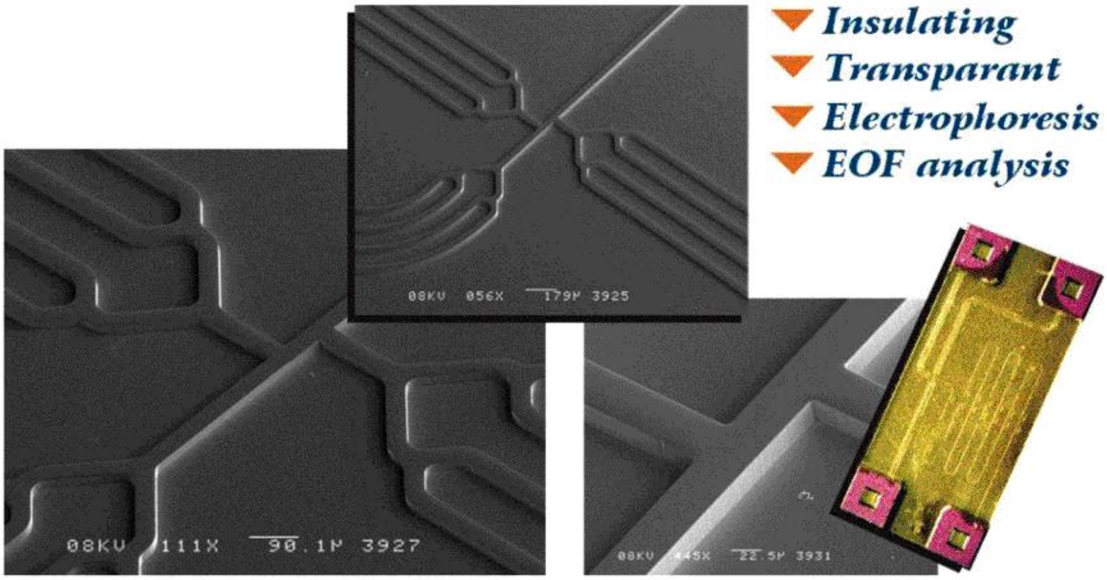
Tackling glass integration

- Leak tight microfluidics:
  - Integrated Circuit (IC) processing philosophy,
  - Combined techniques.

Silicon-integrated glass channels



Transparent insulating channels (µTICs)



- ***Insulating***
- ***Transparant***
- ***Electrophoresis***
- ***EOF analysis***

www.c2v.com

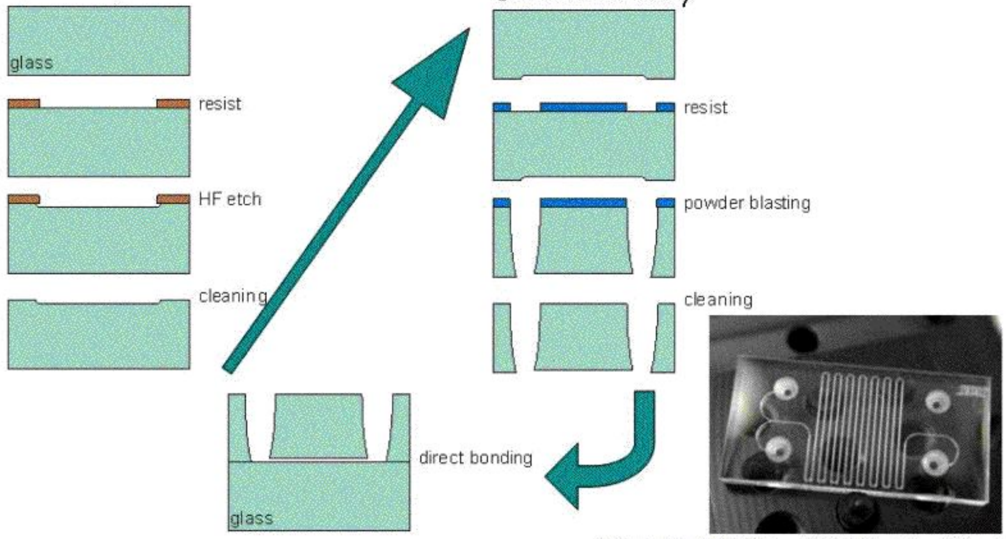
Bulk-integrated “simple” glass chip

Making a channel

Requirements:
1 µm deep and smooth

Making holes

Requirements:
Should be easy



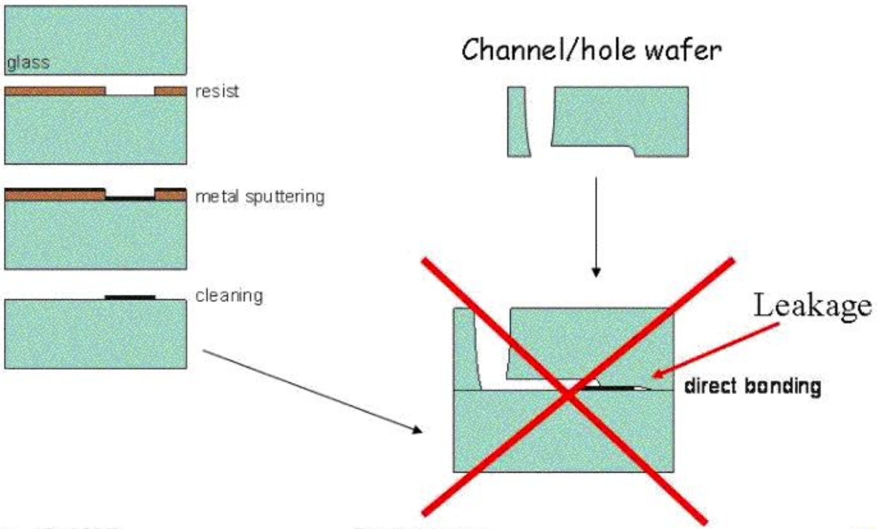
E.Oosterbroek/M. Brivio, 2003, University of Twente

Metal-integrated: Trial 1

The glass chip with integrated electrodes

Making an electrode

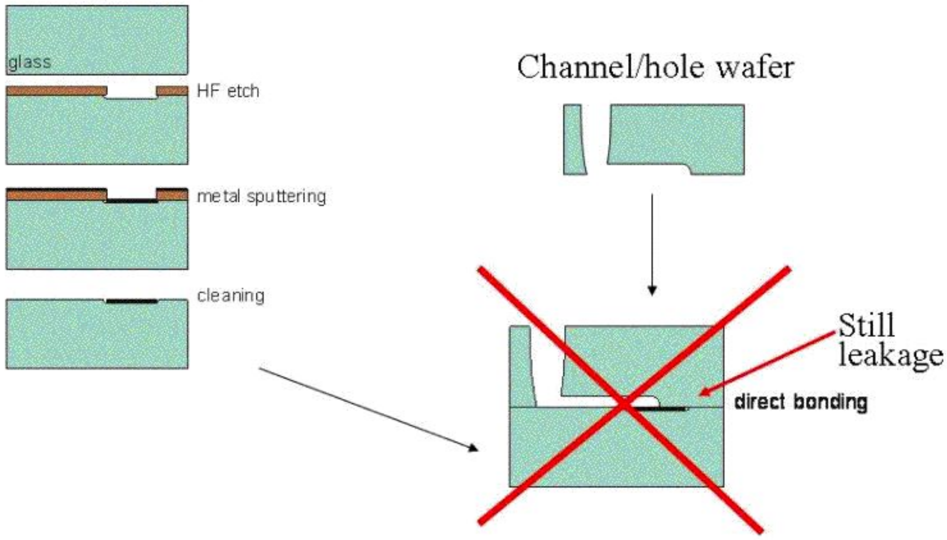
Requirements: metal



Metal-integrated: Trial 2

The glass chip with integrated electrodes

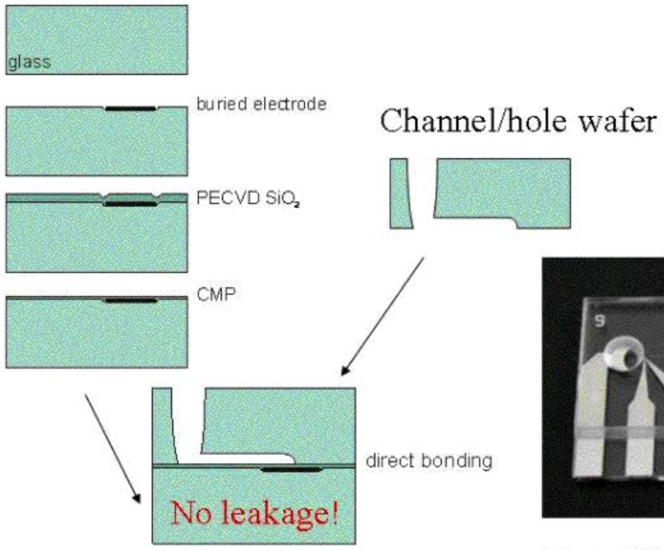
Making a buried electrode

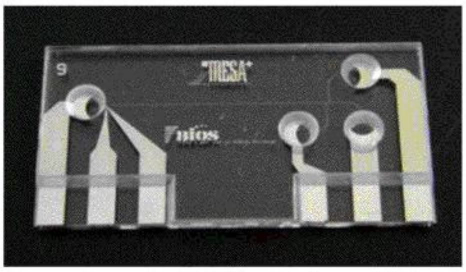


Metal-integrated: Trial 3

The glass chip with isolated integrated electrodes

Making an isolated electrode





E.Vrouwe, 2003, University of Twente

Topics in this section

Diversity in clean room processing

New developments
Many possibilities little restrictions- an entire mechanical machining workshop can be dedicated to microfabrication today. *Off-limits:* microfluidics fabrication gets out of the classical cleanroom environment.

Other materials and diversity of techniques

- Modular systems architecture.
- Driving force is functionality.
  - Precursor ceramics processing
  - Mix & match techniques
  - Coatings
- Rapid prototyping

Fine-machining

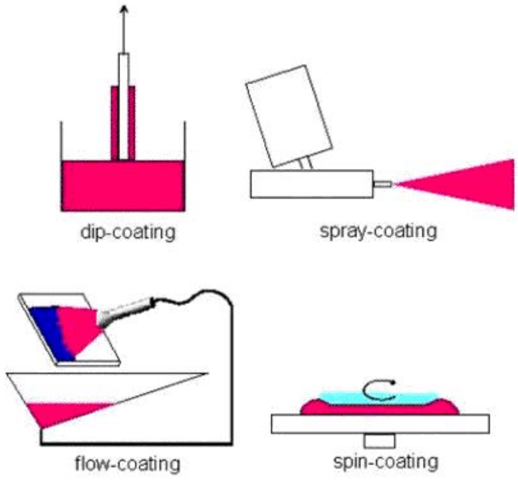
- Characterized by a piece-by-piece approach
  - Laminating/Casting
  - High-precision CNC (micromilling)
  - Micro-stenciling (punching)
  - Electrochemical discharge drilling
  - Laser ablation/cutting
  - Electroplating
  - Stereo-lithography and rapid prototyping

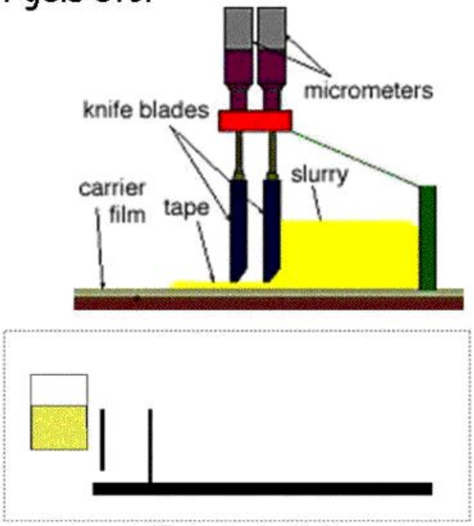
Source:IMM

Punched metal sheets, stacked & laminated

Simple deposition/casting techniques

Polymers, ceramic slurries and sol-gels etc.



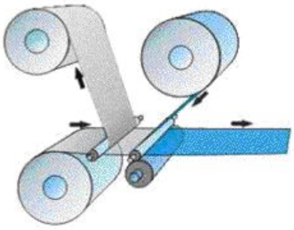


Tape casting

www.ikm.uni-karlsruhe.de

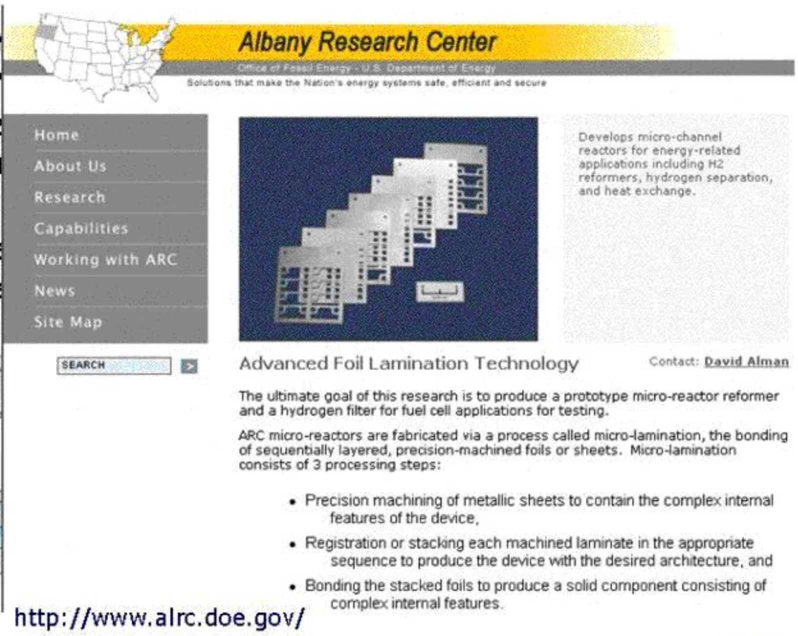
Laminating

- Laminating is a process for bonding sheets of materials together to produce large multi-layer panels.
- Adhesive is usually applied to the bonding surfaces and the sheets are stacked in some kind of press which compresses the panel while the adhesive cures.
- The sheets can also be bonded by other means, e.g. thermo-compression bonding of stainless steel.



Laminating

- Laminati
together
- Adhesive
sheets a
the pane
- The shee
compress



Develops micro-channel reactors for energy-related applications including H2 reformers, hydrogen separation, and heat exchange.

Advanced Foil Lamination Technology

Contact: David Alman

The ultimate goal of this research is to produce a prototype micro-reactor reformer and a hydrogen filter for fuel cell applications for testing.

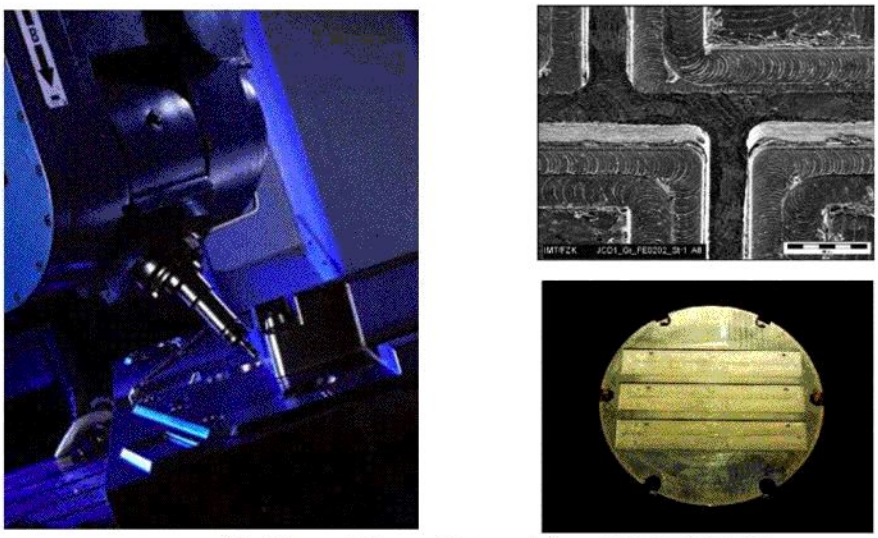
ARC micro-reactors are fabricated via a process called micro-lamination, the bonding of sequentially layered, precision-machined foils or sheets. Micro-lamination consists of 3 processing steps:

- Precision machining of metallic sheets to contain the complex internal features of the device,
- Registration or stacking each machined laminate in the appropriate sequence to produce the device with the desired architecture, and
- Bonding the stacked foils to produce a solid component consisting of complex internal features.

http://www.alrc.doe.gov/

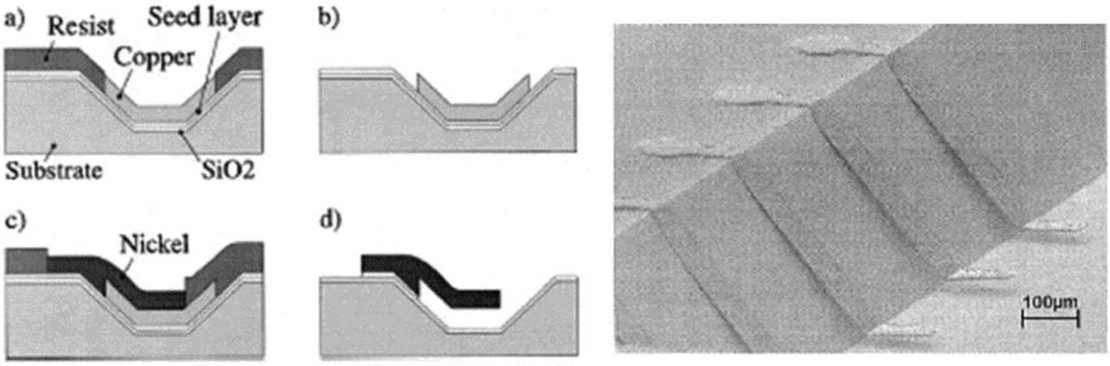
Precision CNC (high-speed milling)

Metal micro mold insert made of brass by milling



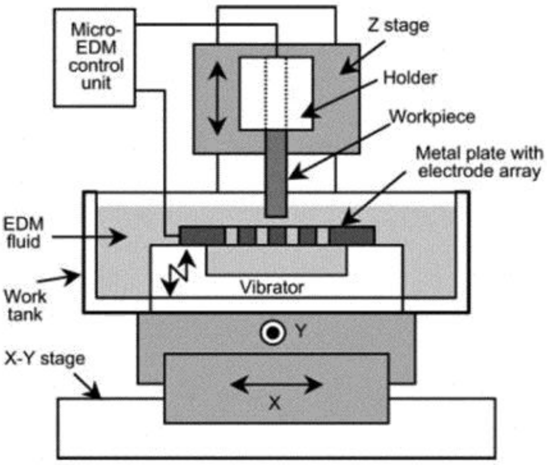
A.E. Guber et al. / Chemical Engineering Journal 101 (2004) 447–453

Electroforming on pre-processed wafer



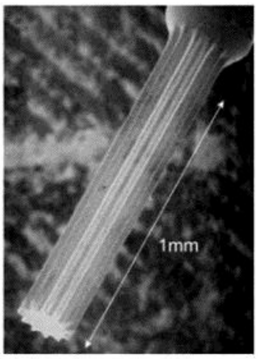
L.S. Johansen et al. Sensors and Actuators 83 2000 156–160

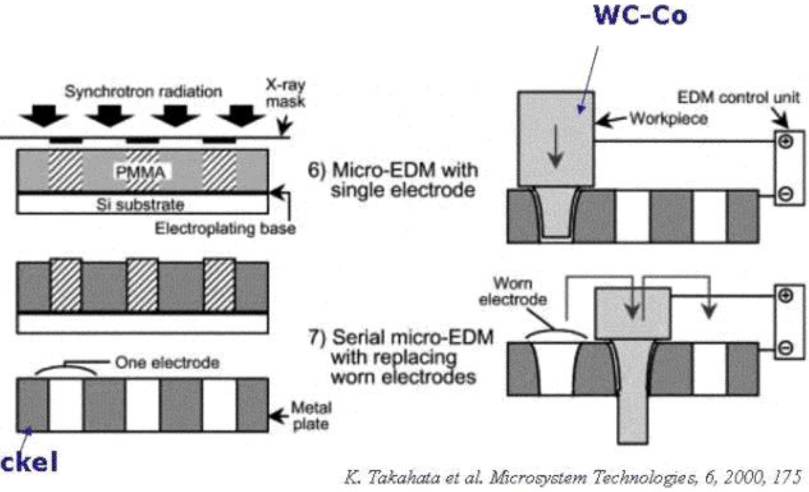
Electrodischarge



K. Takahata et al. Microsystem Technologies, 6, 2000, 175

Electrodischarge processing example

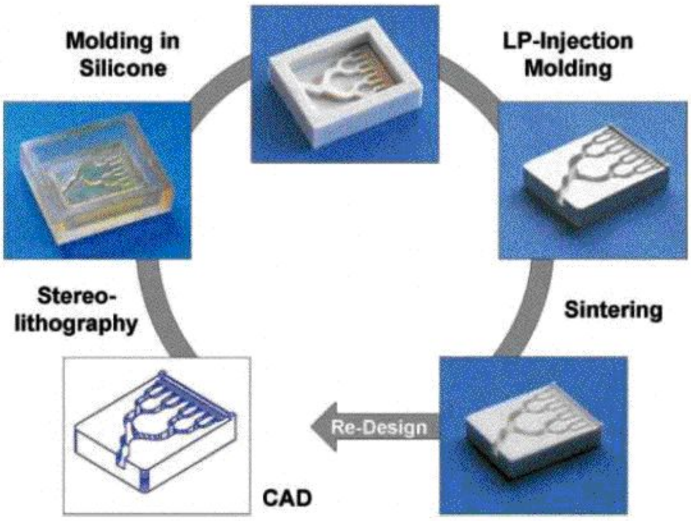




K. Takahata et al. Microsystem Technologies, 6, 2000, 175

Rapid prototyping chain – molding processes

Ceramic microcomponents



Molding in Silicone

LP-Injection Molding

Sintering

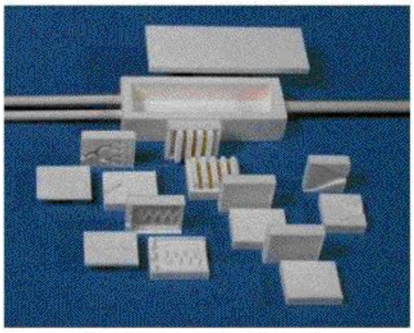
Re-Design

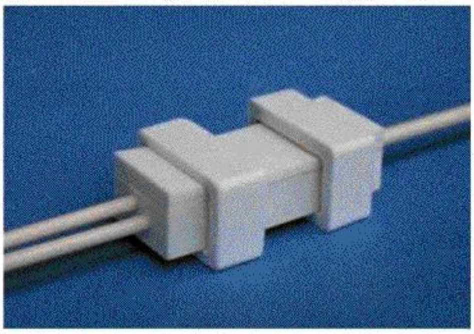
CAD

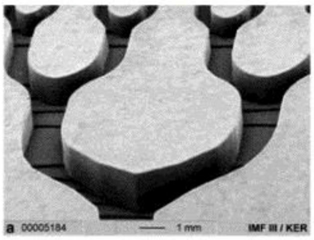
Stereo-lithography

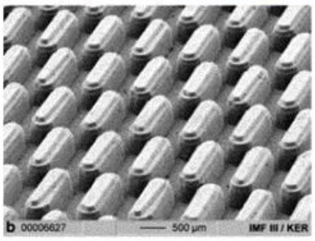
R. Knitter et al. / Microsystem Technologies, 7, 2001, 85

Modular ceramic microreactor









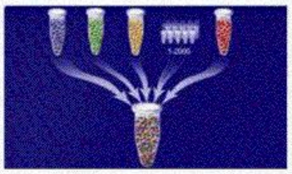
Al_2O_3

Sintered at 1700 °C/24h

R. Knitter et al., Microsystem Technologies, 7, 2001, 85

Outlook: Future developments

Micro-and nanofabricated devices to contain and process liquids must deliver what conventional techniques cannot do!

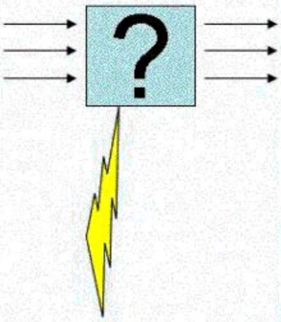


?

- Fundamental research in micro-and nanofabrication characterization for ever new materials and material combinations continuous.
- However, the implementation in commercial microfluidic products will be only driven by cost and functional needs: rapid and high-throughput!
- More and more work on characterization must take place to deliver product requirements.

Summary

Black box: microfluidics



- Still many trial and error experiments in microfluidics device fabrication.
- Microfluidics does not support its own fabrication lines:
  - Processes are highly adopted from either microelectronics or MEMS developments,
  - Processes are not respected as functional dedicated and often exchanged,
  - Some first systematic efforts are made to characterize established MEMS materials for the application in microfluidics.
- From pure glass processing microfluidics takes on a great many diversity of material choices and processing, often on the basis of facilities availability.