Microfabrication by wet etching

- Hydrofluoric acid etching mechanism
- Effect of etchant and glass composition
- Etching process sequence
- Applications

- glass chip for living cell measurements
- photosensitive glass

- References

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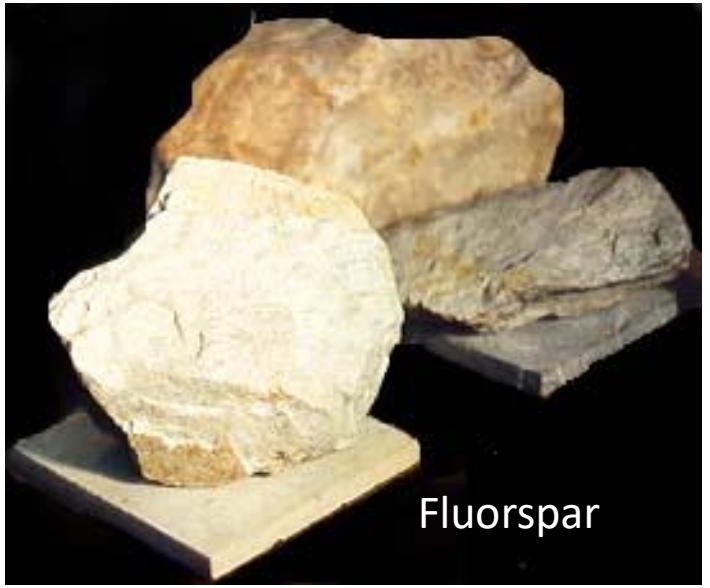
Historically

- In 1771, Scheele showed means to identify fluorspar (a "fluate" of lime):
  - glass is etched by fumes (= HF) developed after addition of some acid to the sample
  - release of silica if the fumes, after contact with glass, are led into water
  - precipitation of fluorspar if the fumes - or solutions of the fumes- are led into lime water.
- Fluorspar (fluorite) : mineral containing CaF_2
- Lime water : a solution of $Ca(OH)_2$ in water


Fluorspar

Overall reaction

- Glass is dissolved by HF or HF-containing solutions
- HF, dissolved in water, is weak acid; solution contains H^+, F^- and HF_2^- ions.
- Vitreous SiO_2 and multicomponent silica glasses are etched. Overall reaction :

$$SiO_2 + 6HF \rightarrow H_2SiF_6 + 2H_2O$$

- Reaction constants at 25°C :

$$K_1 = [H^+][F^-]/[HF] = 6.7 \times 10^{-4} \text{ mol/l}$$

$$K_2 = [HF][F^-]/[HF_2^-] = 0.26 \text{ mol/l}$$

- NaF or NH_4F do not etch SiO_2 → reactivity of F^- ions is negligible
- Insensitivity of etch rate to agitation →etching is kinetically controlled

HF-SiO_2 etching mechanism (i)

- Silica etches in acidic and basic solutions without HF → dissociated water species are reactants
- Mica and coesite etch only slightly in HF →surface structure of silica is important
- Thermally densified silica has very slow etching rate →'open' surfaces favour etching
- Types of surfaces: I, II, III, IV.

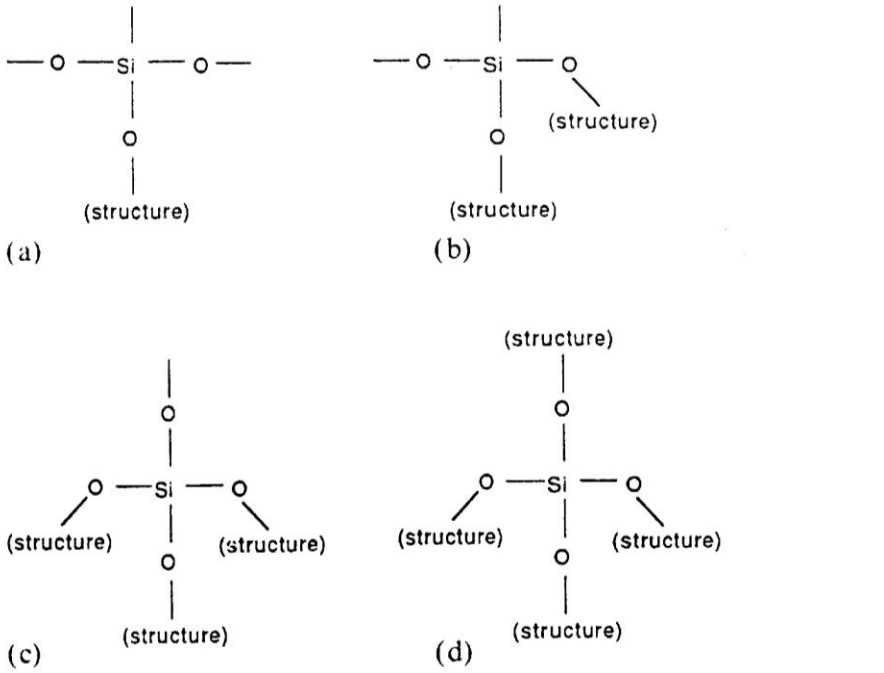


Fig. 5. Four possible surface exposures of the silica tetrahedron: (a) type I; (b) type II; (c) type III; (d) type IV.

HF-SiO_2 etching mechanism (ii)

- HF provides combination of nucleophilic and electrophilic attack

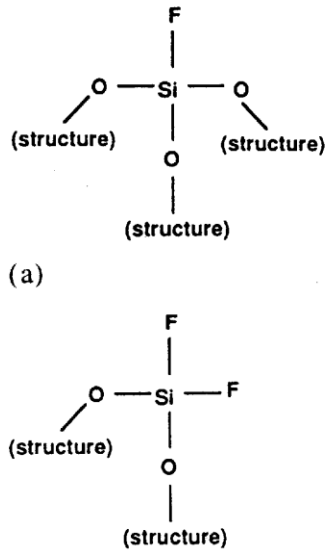


Fig. 6. Two variations of "hybrid" silica tetrahedra resulting from the replacement of the OH^- by F^-.

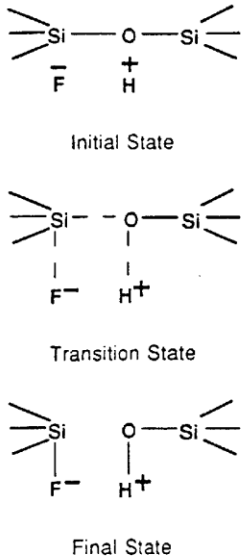


Fig. 8. Simultaneous nucleophilic and electrophilic attack by hydrofluoric acid on the silicon–oxygen network.

HF-SiO_2 etching mechanism (iii)

- Dissociated water creates open surface, with enhanced etching in HF

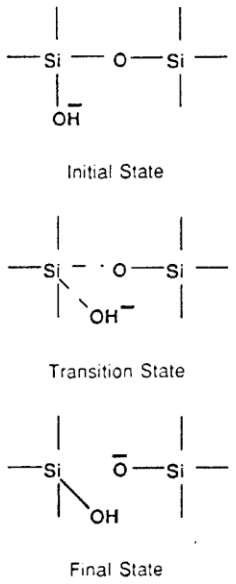


Fig. 7. Nucleophilic attack by the hydroxyl ion on a network silicon atom.

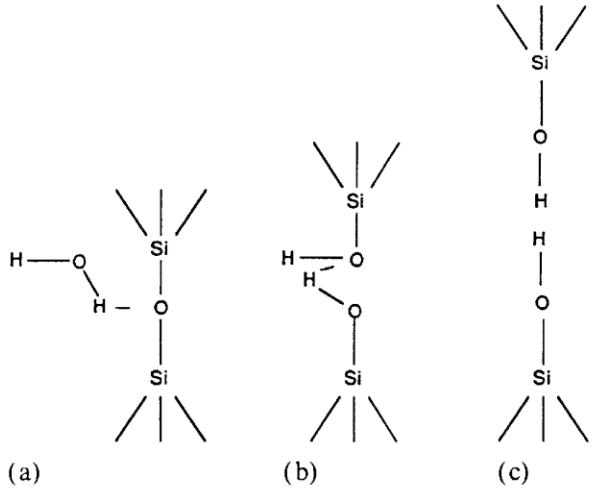


Fig. 9. Representation of the proposed reaction between water and strained Si–O–Si bonds at a crack tip. The reaction steps involve (a) adsorption of water to the Si–O bond, (b) concerted reaction involving simultaneous proton and electron transfer, and (c) formation of surface hydroxyl groups.

HF-SiO_2 etching mechanism (iv)

- Adding HCl enhances etching rate → increasing $[H^+]$ 'opens' surface

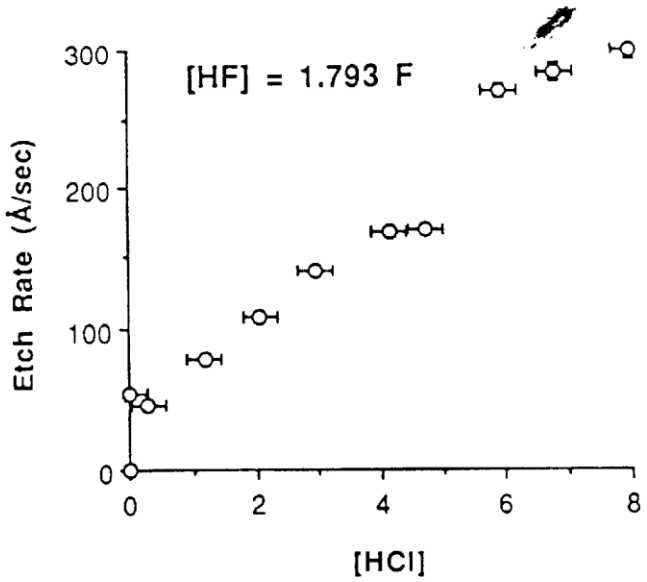


Fig. 11. By adding hydrochloric acid to an HF etchant [76, 77], the etch rate of silicon dioxide thin films is increased [102]. In this case, several solutions of 1.793 F HF were used with varying concentrations of HCl. The silicon dioxide etch rate increased with increasing acidity. This was caused by an increase in the silicon dioxide "surface opening" reaction that resulted from increasing H^+ (*i.e.* decreasing pH).

HF-SiO_2 etching mechanism (v)

- 3 possible mechanisms :
  - Chemical replacement of OH^- groups with F^- anion (not probable)
  - Hydrogen bonding of HF to silanol groups (probably not strong enough)
  - Nucleophilic chemisorption of HF to the Si (most probable)

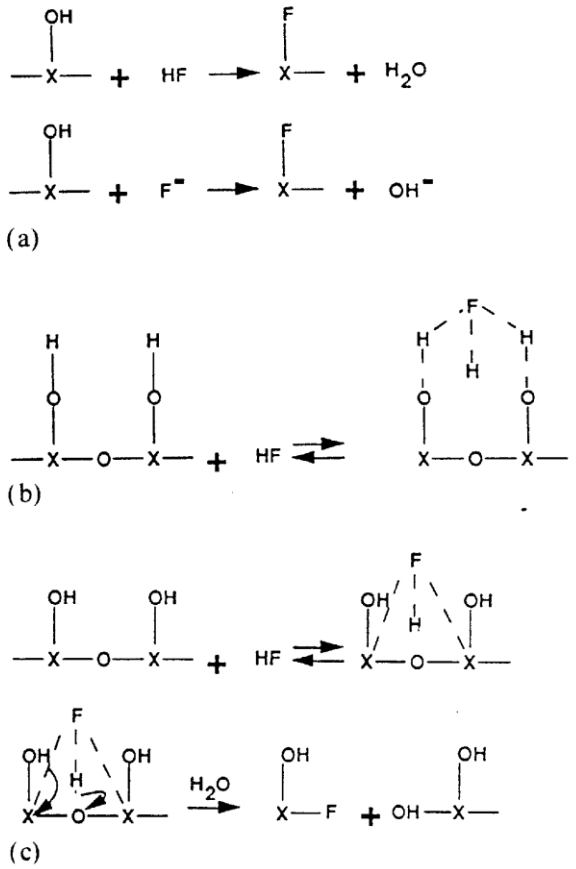


Fig. 12. (a) Chemical replacement of surface hydroxyl groups. (b) Hydrogen bonding at lattice hydroxyl groups. (c) Nucleophilic chemisorption at the lattice bonds.

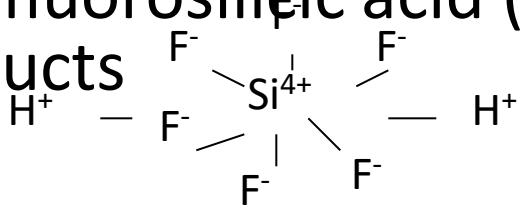
HF-SiO_2 etching mechanism (vi)

- Opening of silica surfaces from dissociated water species
- H^+, HF_2^- and HF adsorb on lattice bonds
- Rate-determining step : breakage of siloxane bond by combined action of the adsorbed species.
- Etching rate :

$$v_E = k_1 \cdot \theta(H^+) \cdot \{k_2 \cdot \theta(HF_2^-) + k_3 \cdot \theta(HF)\} + k_4 \cdot \theta(H^+)$$

$$\theta : \text{degree of coverage of active adsorption sites}$$

- Formation of fluorosilicic acid (H_2SiF_6) and other reaction products



Surface morphology (i)

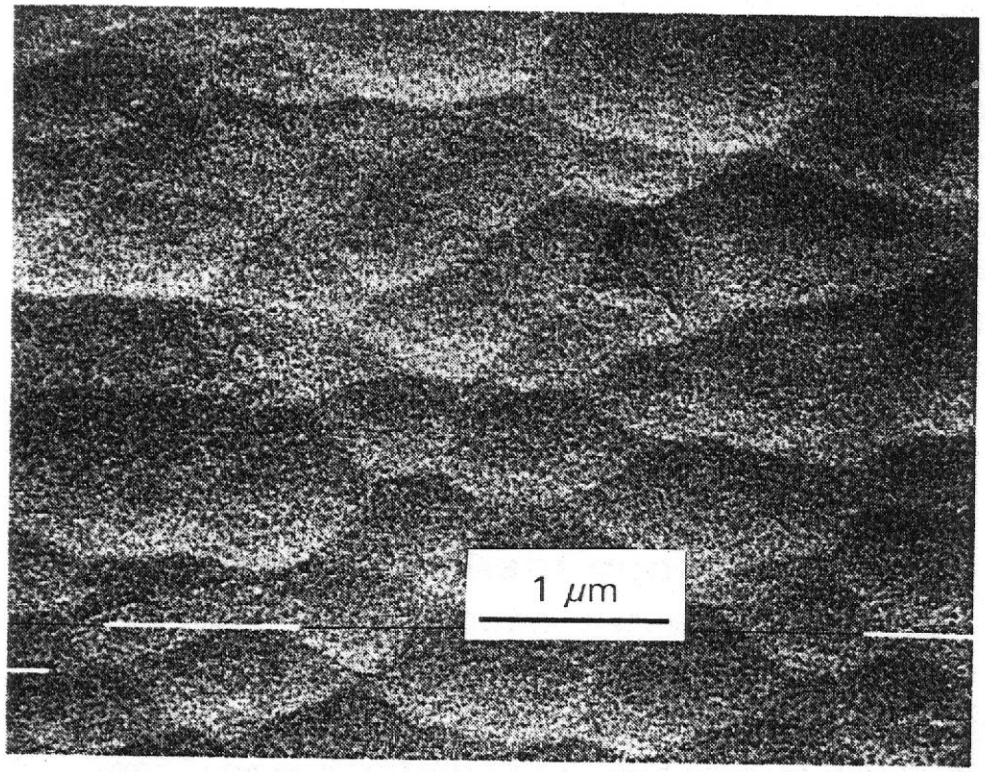


Figure 1 SEM micrograph showing the cusp-like surface obtained after etching a polished soda lime silicate glass surface [14].

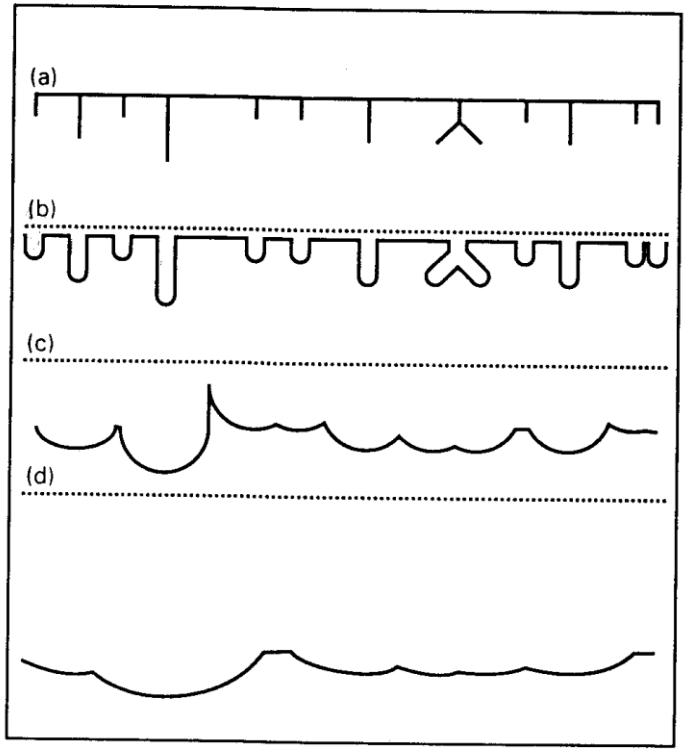


Figure 2 Transformation of a surface with closed microcracks or flaws into a cusp-like glass surface by wet chemical etching. (a) Initial surface. (b) After etching 0.2 time units. The dashed line indicates the initial glass surface. (c) After etching 1 time unit. (d) After etching 3 time units.

Surface morphology (ii)

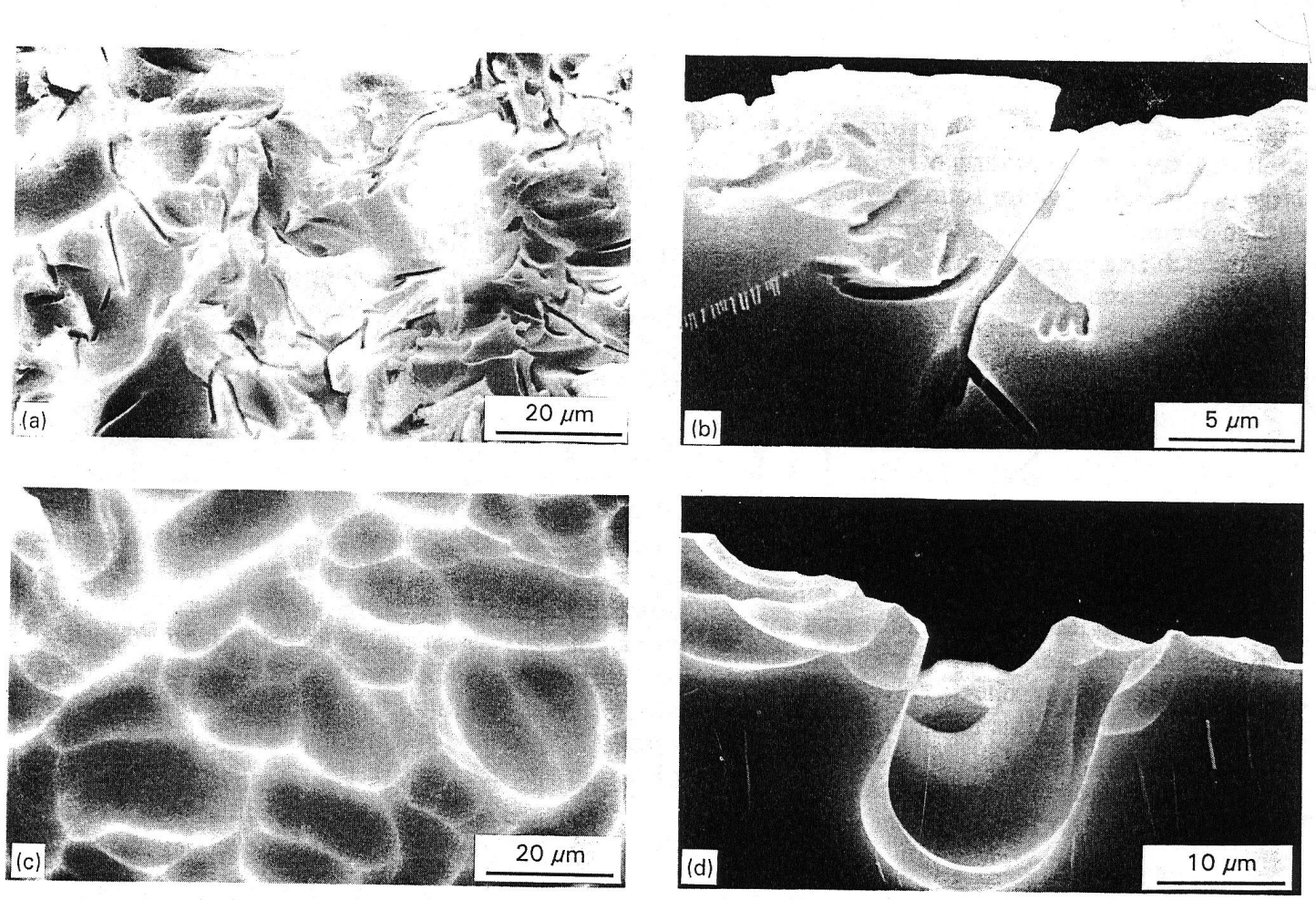
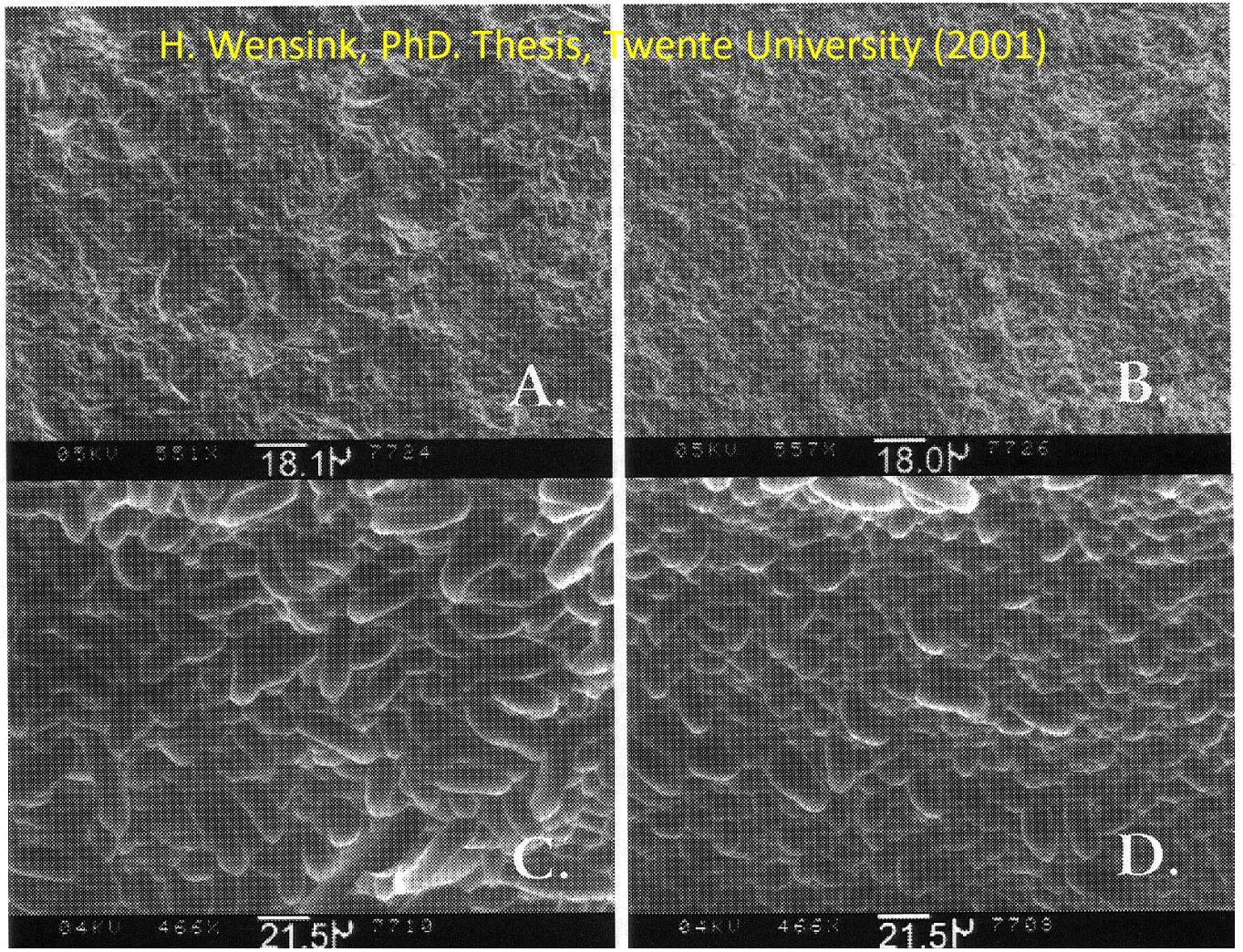


Figure 3 SEM micrographs of the surface of a soda lime silicate glass after particle erosion and etching in 2 wt % HF. (a) After 2 min, surface view showing the opened microcracks. (b) After 2 min, cross section. (c) After 30 min, surface view showing the cusp-structure. (d) After 30 min, cross section.

Effect of etching on surface roughness

Original surface:

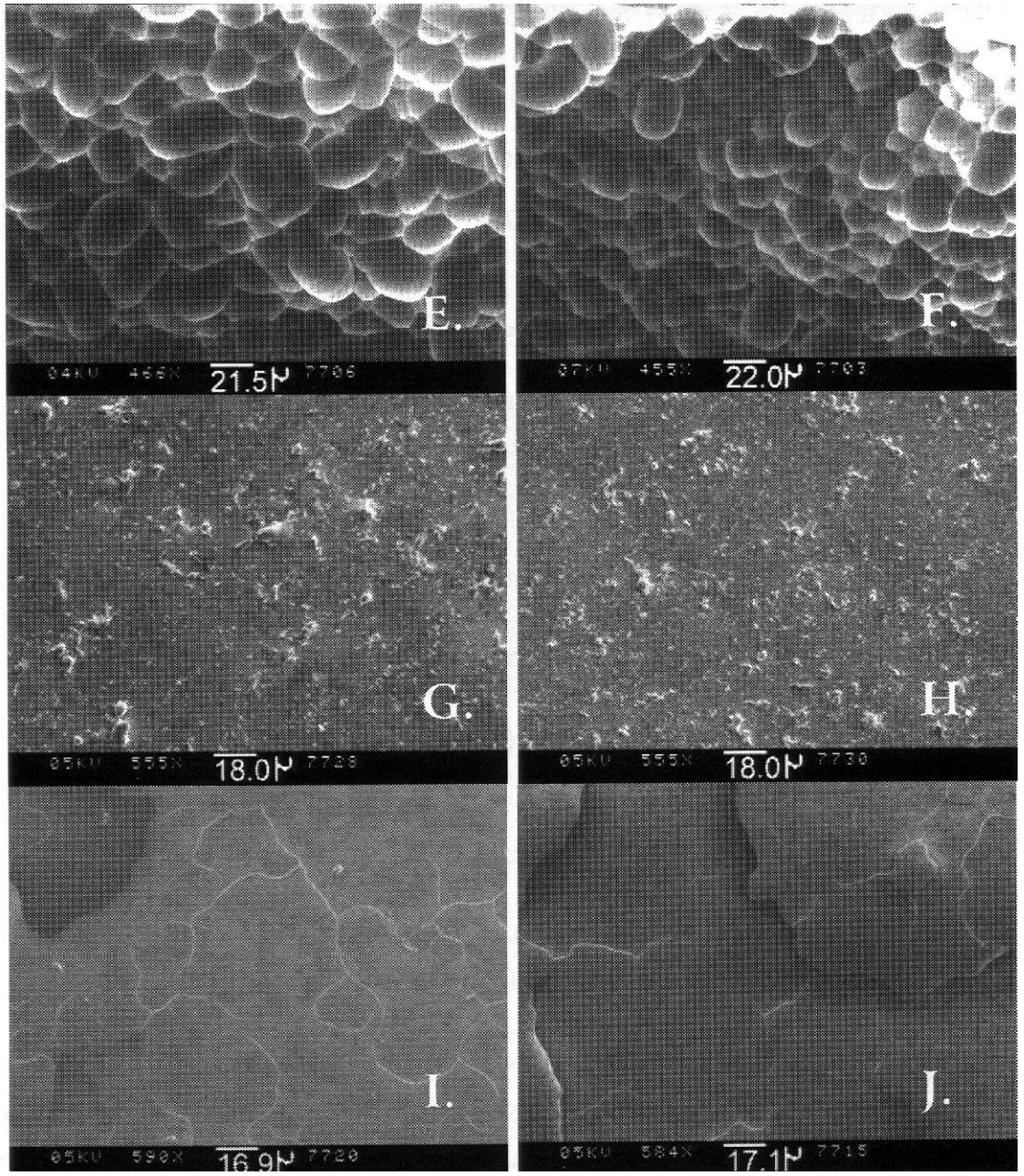
1 hour 5% HF etch



3 hours
5% HF etch

Anneal
750°C

Anneal
800°C



Decrease surface roughness by thermal annealing

Table 5-1. Roughness measurements

Particle size / speed [μm]/[m/s]	**9 / 290**	**29 / 220**
R_a after blasting [μm]	1.2 ± 0.2	2.5 ± 0.6
R_a after finishing with 9 μm particles [μm]	-	2.0 ± 0.3
R_a after finishing with 3 μm particles [μm]	0.9 ± 0.2	1.8 ± 0.5
R_a after 1 hour at 5% HF [μm]	1.7 ± 0.1	3.2 ± 0.2
R_a after 3 hour at 5% HF [μm]	2.2 ± 0.1	3.9 ± 0.5
R_a after 1 hour at 700°C [μm]	1.1 ± 0.1	2.6 ± 0.5
R_a after 1 hour at 750°C [μm]	0.58 ± 0.1	1.8 ± 0.4
R_a after 1 hour at 800°C [μm]	0.091 ± 0.02	0.49 ± 0.3

Effect of HF concentration

- Etching rate scales approximately linear with HF concentration
- At high HF concentration, increased etching due to presence of higher polymeric $H_nF^-_{n+1}$ ions
- Reaction activation energy depends on HF content

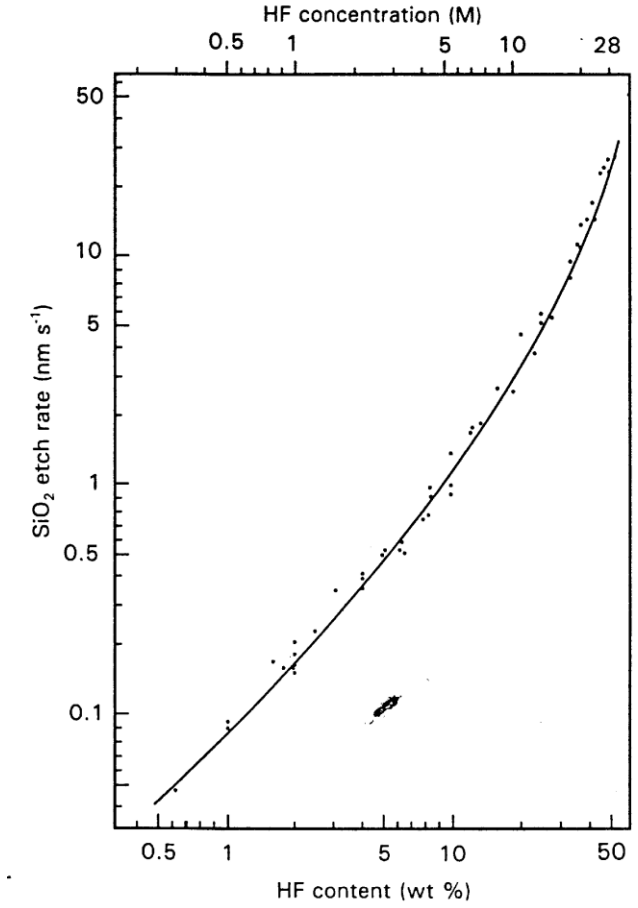


Figure 4 Collected etch rate data of SiO_2 in HF aqueous solutions at 23 ± 2 °C as a function of the HF content of the etchant [6, 16, 32, 39–45].

Addition of NH_4F

- Shift of reaction equilibria :

$$K_1 = [H^+][F^-]/[HF] = 6.7\times10^{-4}\ \text{mol/l}$$
$$K_2 = [HF][F^-]/[HF_2^-] = 0.26\ \text{mol/l}$$

→ Increase in HF_2^- concentration and pH

- Mix of 40 wt% NH_4F with 49 wt% HF (in ratios from 6:1 to 10:1) : buffered oxide etches (BOEs) or buffered HF (BHFs).
- At high NH_4F-concentration : lower etch rates ← complexation of HF_2^- with NH_4^+ ions.

Effect of glass composition

- SiO_2 interconnect structure is changed by 'network modifiers' and 'network-forming oxides'
- Network-forming oxide A_xO_y creates ≡Si-O-A- and -A-O-A- bonds, which need to be broken
- Network-modifying oxides such as Na_2O, K_2O, CaO and BaO are incorporated by breaking a siloxane bond, forming non-bridging oxygen, e.g.

$$Na_2O + \equiv Si - O - Si \equiv \quad \rightarrow \quad 2 \equiv SiO^- \cdot Na^+$$

→ strong increase of etch rate

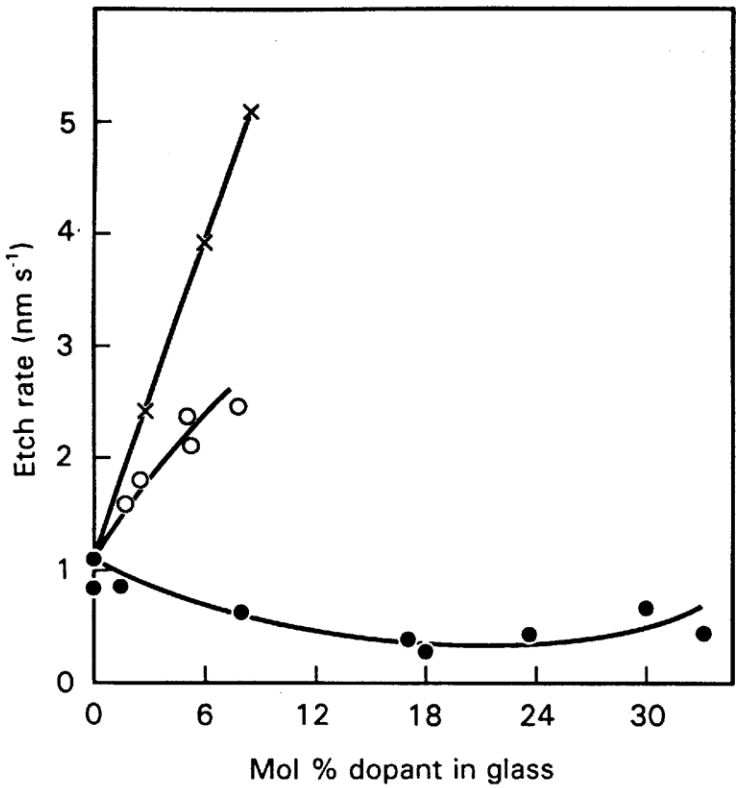
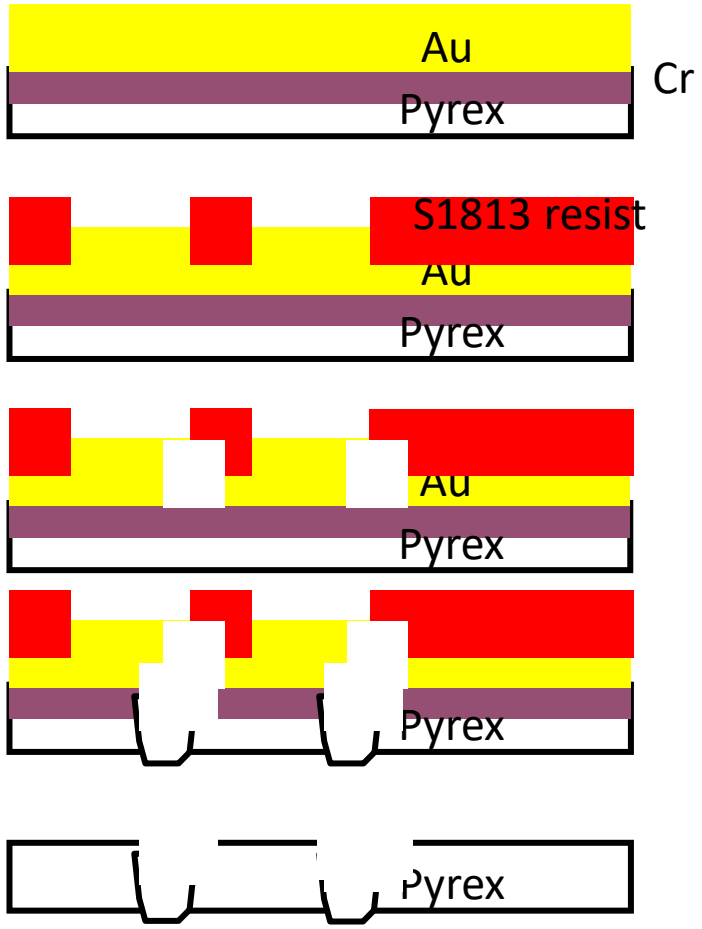


Figure 6 Effect of B_2O_3 (●) [33, 54], P_2O_5 (×) [33] and As_2O_3 (○) [29] content on the etch rate (at 23 ± 2 °C) of annealed doped SiO_2 films in BOE (10:1).

Etching process sequence (HF)



Pyrex Corning 7740, 525 mm, Cr 60 nm, Au 200 nm

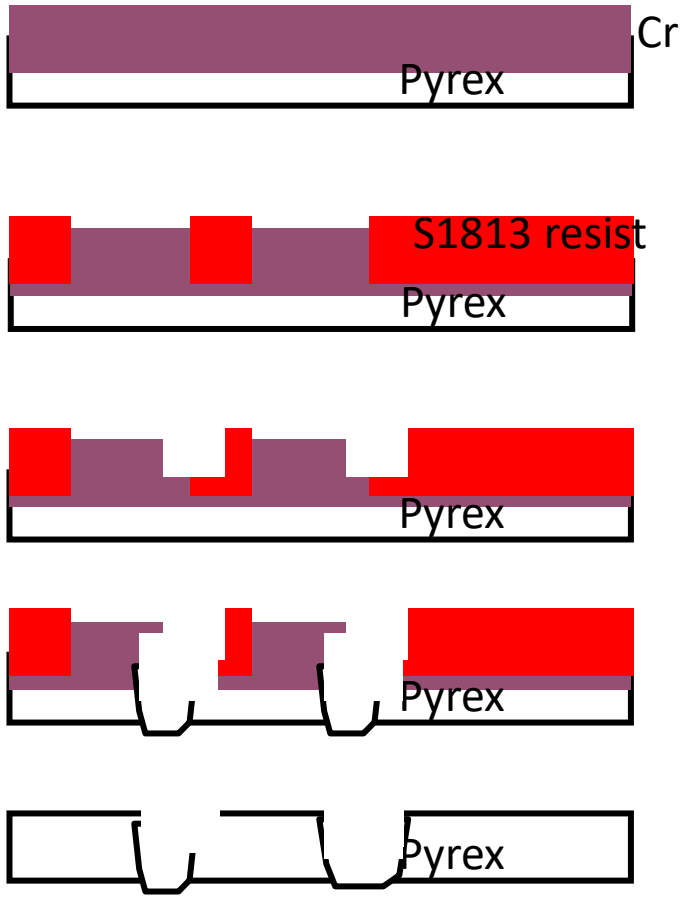
Spin coat with S1813 positive photoresist, prebake, development, postbake, O_2 plasma, descum

Au-etching with KI + I_2 solution, Cr-etch

Bake, Pyrex etching with 49 % HF; etch rate 5-10 μm/min

Stripping of resist with remover, Au etch with KI+I_2, Cr-etch.

Etching process sequence (BHF)



Pyrex Corning 7740, 525 mm, Cr 60 nm

Spin coat with S1813 positive photoresist, prebake, development, postbake, O_2 plasma, descum

Cr-etch

Bake, Pyrex etching with BHF [1:7 49 % HF : NH_4F]; etch rate 5 μm/hour. Strong mask underetching.

Stripping of resist with remover, Cr-etch.

Etching profiles

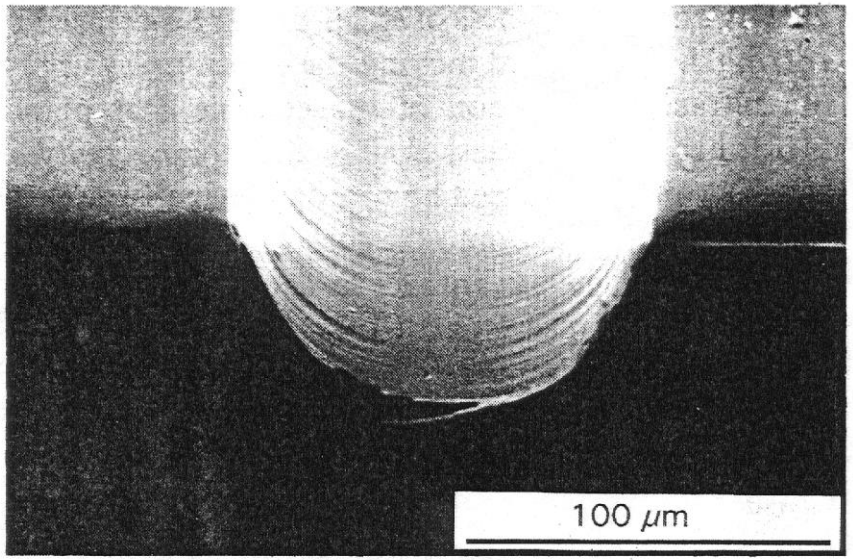


Figure 8 Semicircular groove etched into Pyrex glass using a chromium mask which was structured using photolithographic means.

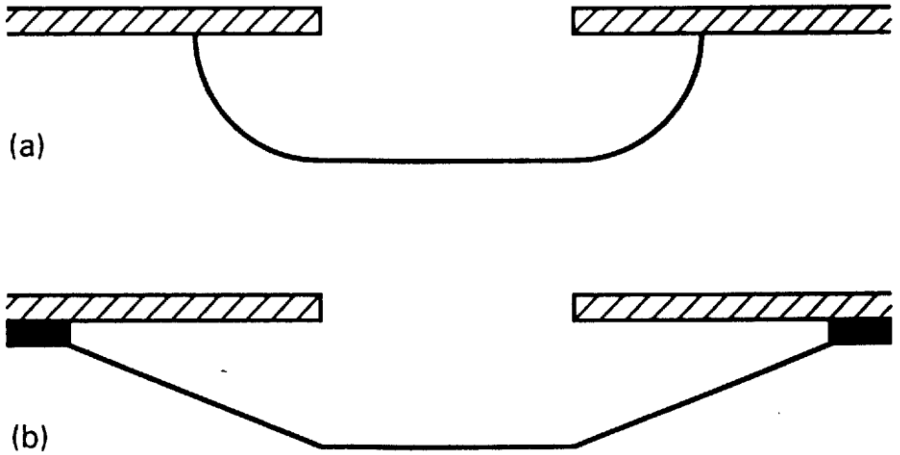


Figure 11 The contour of the wall at the edge of a window etched in an HF solution. (a) Good adhesion of the masking material. (b) Controlled etchant penetration between masking material and glass either by controlled delamination or the addition of an extra fast dissolving film.

Typical etching rates

SiO_2 film deposition method	Etch rate in BHF (20:1) [nm/s]
Thermal oxide	0.28
LPCVD ($TEOS+O_2$)	0.53
APCVD (SiH_4+O_2) [porous, ≡SiOH groups]	0.95
APCVD + anneal 500 °C [densification]	0.74
APCVD + anneal 600 °C	0.71
PECVD (SiH_4+N_2O) [Si-H groups]	0.41

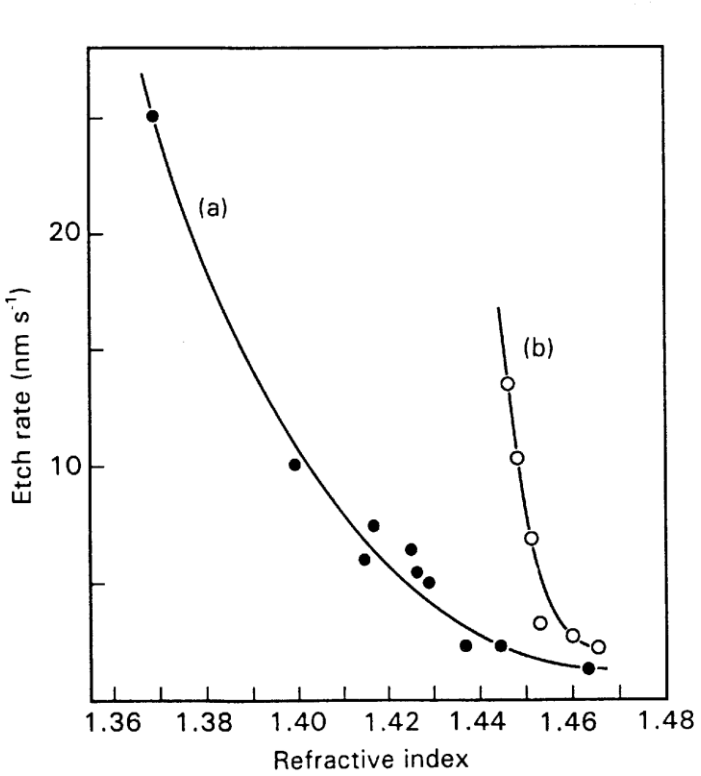


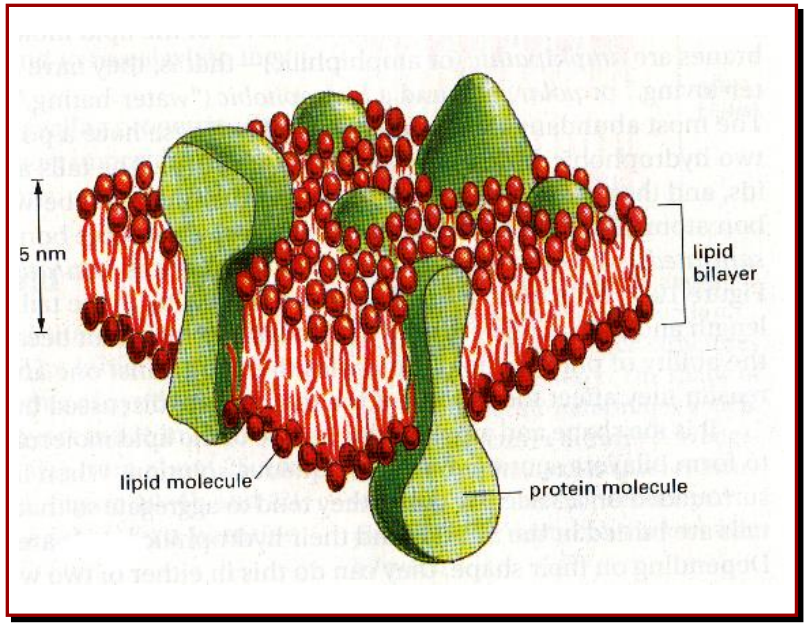
Figure 9 Dependence of the etch rate at 23 ± 2 °C on the refractive index for SiO_2 films, reflecting the influence of the porosity of the films for: (a) Sol–gel films prepared from solutions with different water/silicon alkoxide ratios, etchant BOE [75]; (b) APCVD films prepared with different anneal temperatures, etchant P-etch [89].

P-etch : 2 HNO3 (70 wt%):3 HF(49 wt%):60 H2O)

Application 1: microstructured glass chip for ion-channel electrophysiology

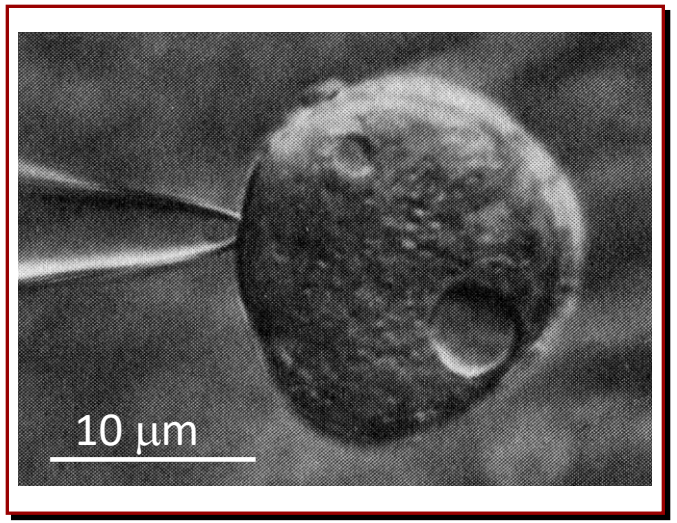
Background

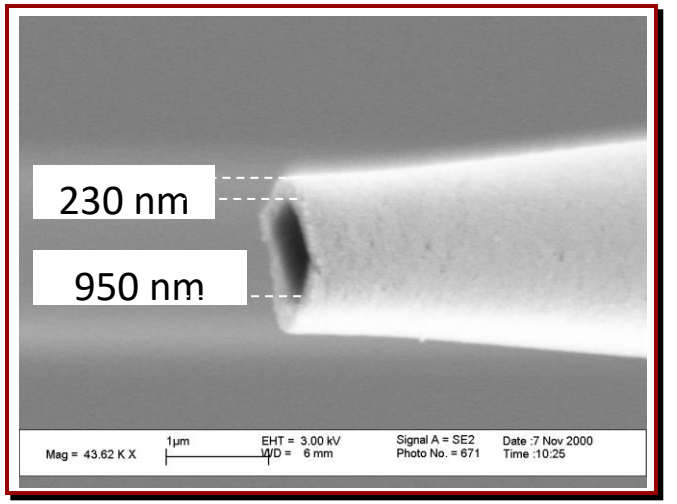
- Investigation of ion transport through cell membranes
- Dysfunction of ion channels may result in serious diseases
- Powerful electrophysiological method for drug screening



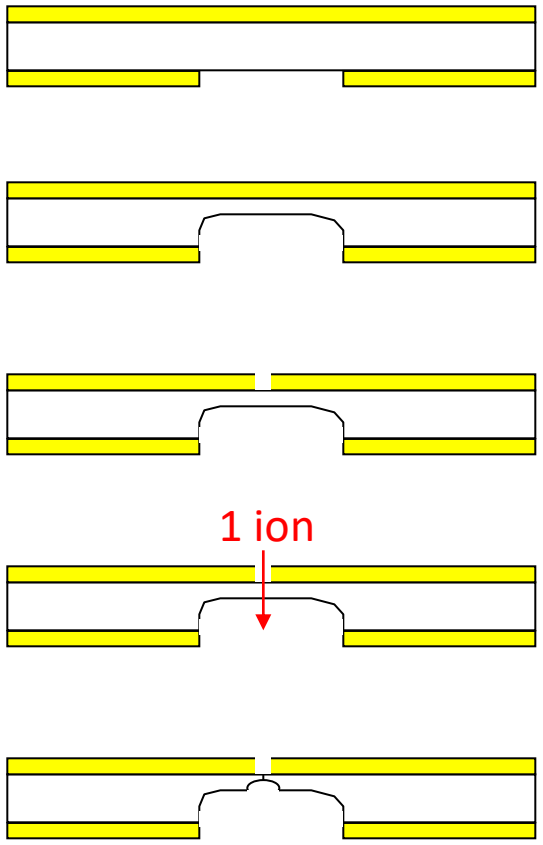
Conventional technique

- Cell fixed by suction to glass pipette
- Measurements on small membrane patches ($\approx \mu m^2$)
- Single channel or whole-cell recording
- Manual µ-positioning
- Ion currents and dynamics (pA / µs to ms range) :
  ⇒ 💣 *low noise wanted, high seal resistance (GΩ) required*





Process sequence



200 μm thick glass wafer + Au mask

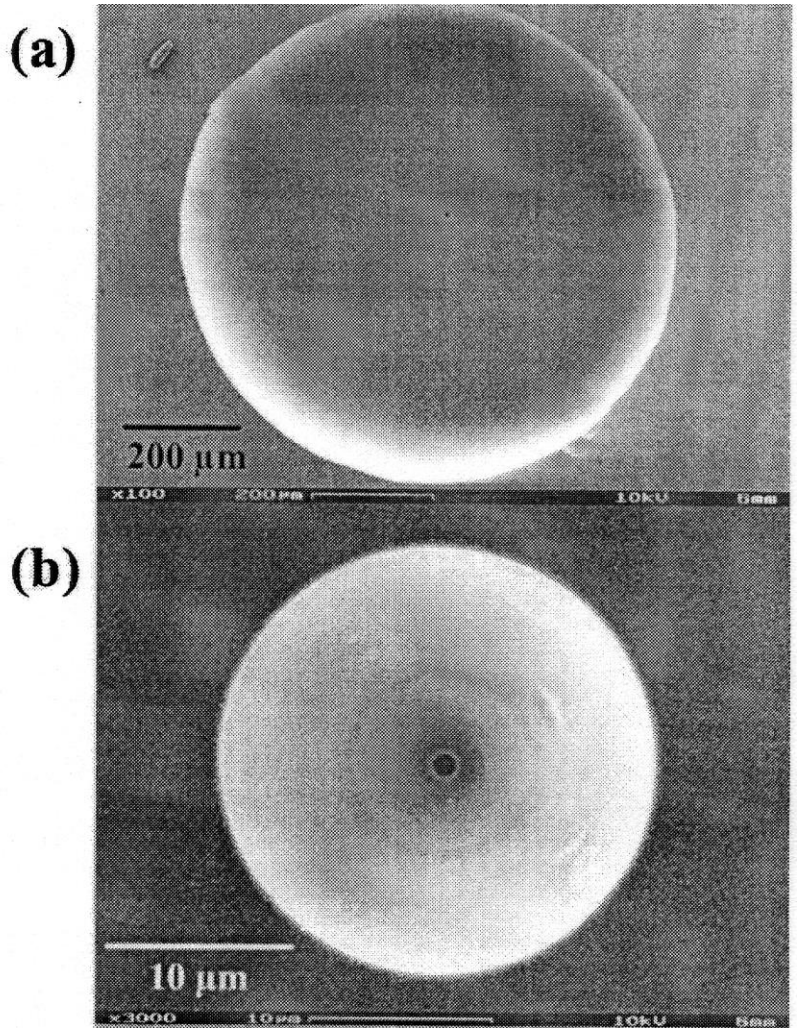
Thinning to 80 μm by HF (10 vol%) at 60 °C

Lithography of upper Au layer

Exposure to Au ion beam (2260 MeV)

HF etching of latent track

N. Fertig, Ch. Meyer, R.H. Blick, Ch. Trautmann, J.C. Behrends, Phys. Rev. E 64, 040901 (2001).



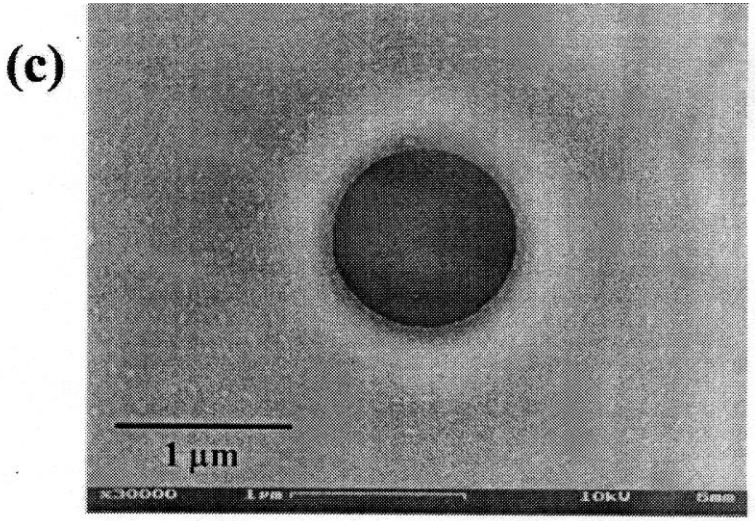


FIG. 1. Scanning electron micrographs of a glass chip microstructured with the ion track technique. The sequence shows the complete pre-etched groove (a), defined by the Au etch mask, the etched ion track in the glass (b), and its small, round aperture (c).

C = 1 pF

R = 100 kΩ in 1 M CsCl solution

Electrical measurements

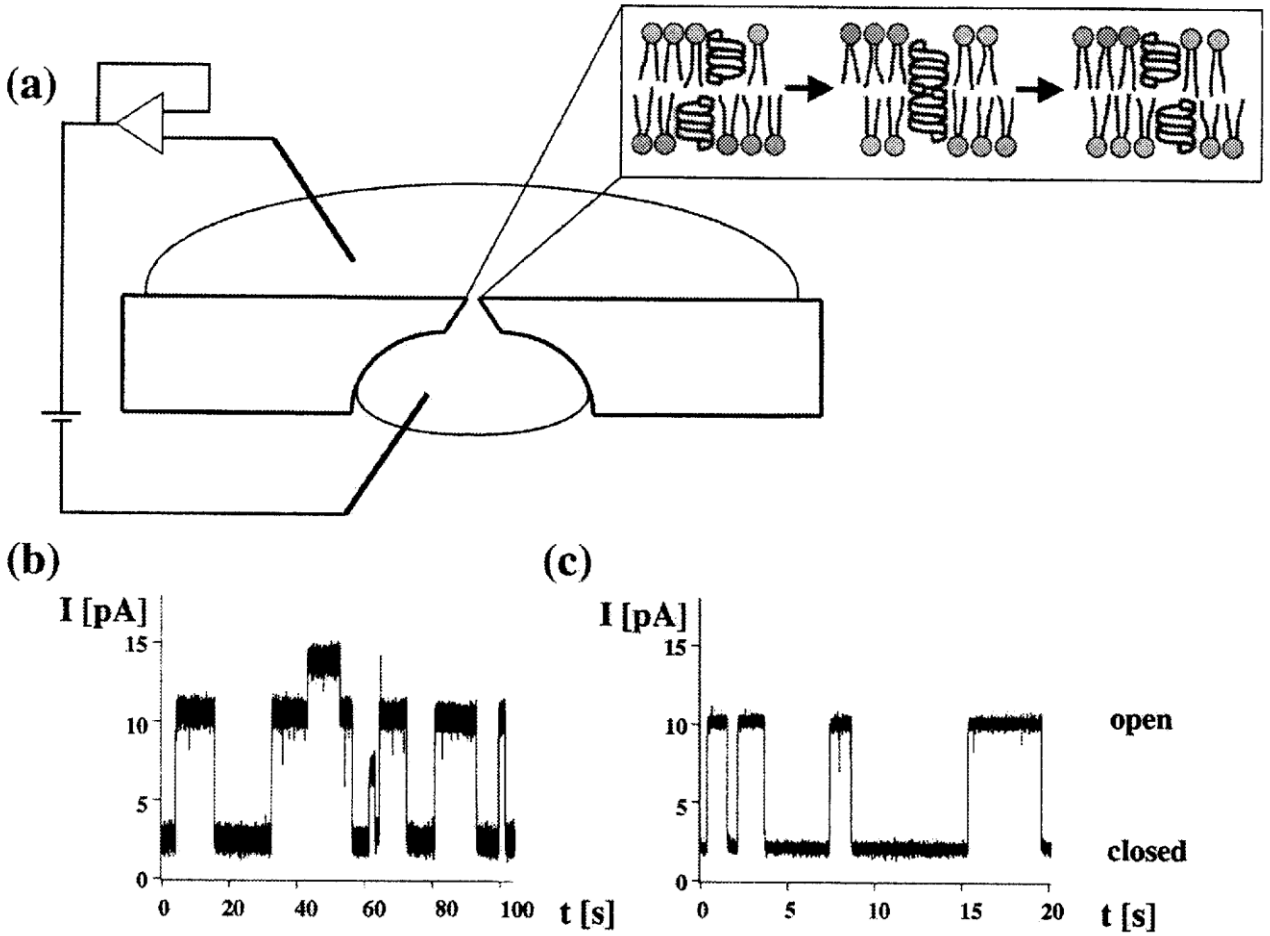


FIG. 2. (a) Schematic of the chip and the recording setup. The inset shows the gramicidin monomers in an artificial bilayer and the formation and dissociation of an ion conducting dimer. Current vs time recordings from gramicidin A channels in the CsCl solution (3M) with different filter cutoff frequencies [3 kHz (b), 1 kHz (c)] are performed with a 200-mV potential applied.

Application 2 : Photosensitive glass

Glass manufacturing

- Defects generated during melting : devitrification, striae and bubbles**.**
- **Devitrification** (= crystal growth) depends on glass composition and can be managed by adequate temperature time regime, e.g. fast crossing of crystallisation regions.
- **Striae** (= regions with different index of refraction, caused by a local change in chemical composition) can be prevented by stirring of the melt.
- **Bubbles** consist of gases generated by decomposition of raw materials. Melt is kept at relatively low temperature so that smaller bubbles are eliminated by dissolution.

Photosensitive glass (ii)

- Annealing step is done to :
  - eliminate residual strain in the sheets
  - import same chemical composition to the entire glass specimen
- Annealing prevents deformation of the wafers during later photo-etchable machining.
- Glass composition : Li_2O/Si_2O with traces of noble metals

SiO_2	75-85 %
Li_2O	7-11 %
K_2O	3-6 %
Al_2O_3	3-6 %
Na_2O	1-2 %
ZnO	0-2 %
Sb_2O_3	0.2-0.4 %
Ag_2O	0.05-0.15 %
CeO_2	0.01-0.04 %

http://www.mikroglas.com/foturane.htm

Photosensitive glass (iii)

UV exposure

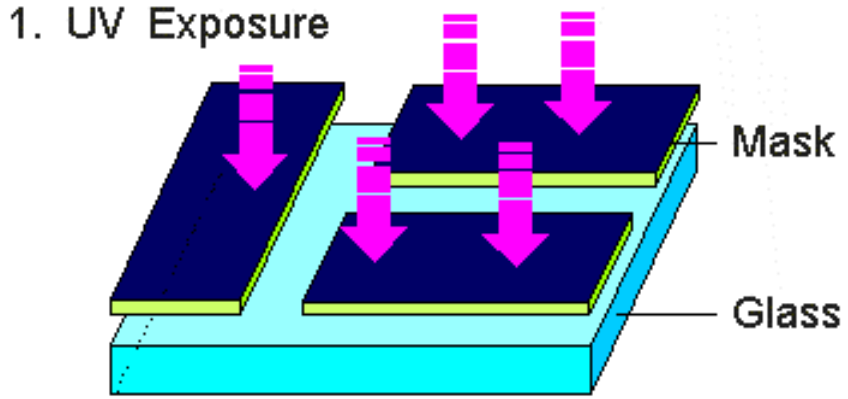
- Foturan absorbs UV light at about 310 nm. During melting

$$2Ce^{4+} + Sb^{3+} \Leftrightarrow 2Ce^{3+} + Sb^{5+}$$

- Illumination with 2 J/cm^2 energy density :

$$Ce^{3+} + h\nu(312\,nm) \Rightarrow Ce^{4+} + e^-$$

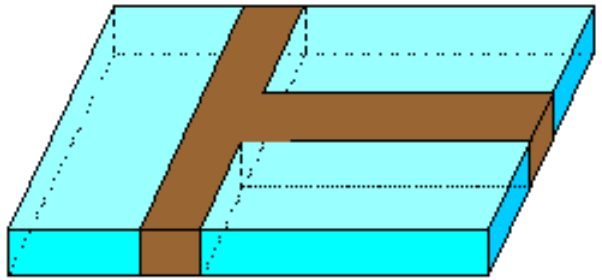
$$Ag^+ + e^- \Rightarrow Ag$$

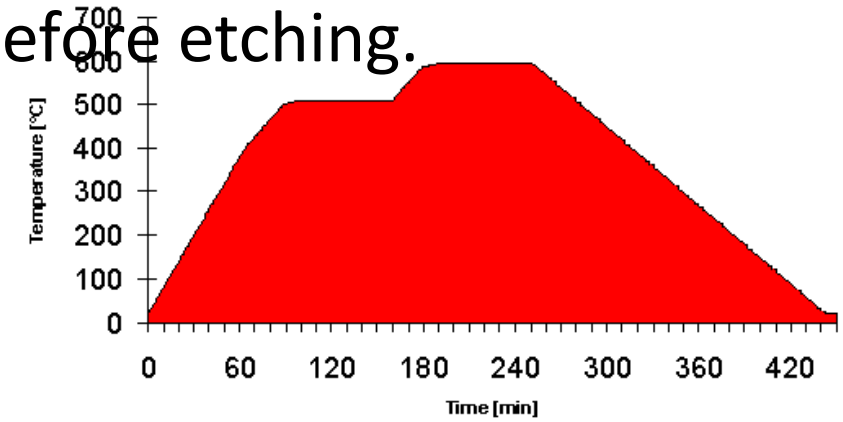


Photosensitive glass (iv)

Temperature treatment

- Heating up to 500 °C : Ag atoms form bigger Ag nuclei.
- Heating up to 600 °C : Glass crystallises around Ag nuclei, forming Li_2SiO_3 crystals (1-10 μm).
- Surface becomes rough, so grounding and polishing is necessary before etching.





Photosensitive glass (v)

Etching

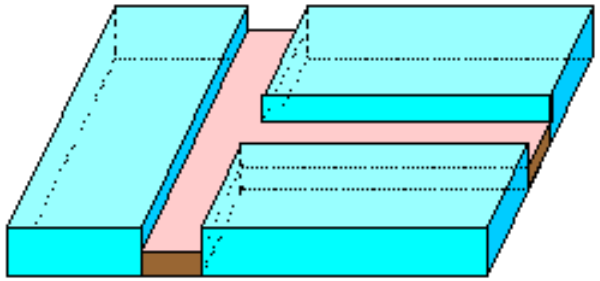
- In 10 % solution of HF

$$SiO_2 + 4HF \Rightarrow SiF_4 + 2H_2O$$

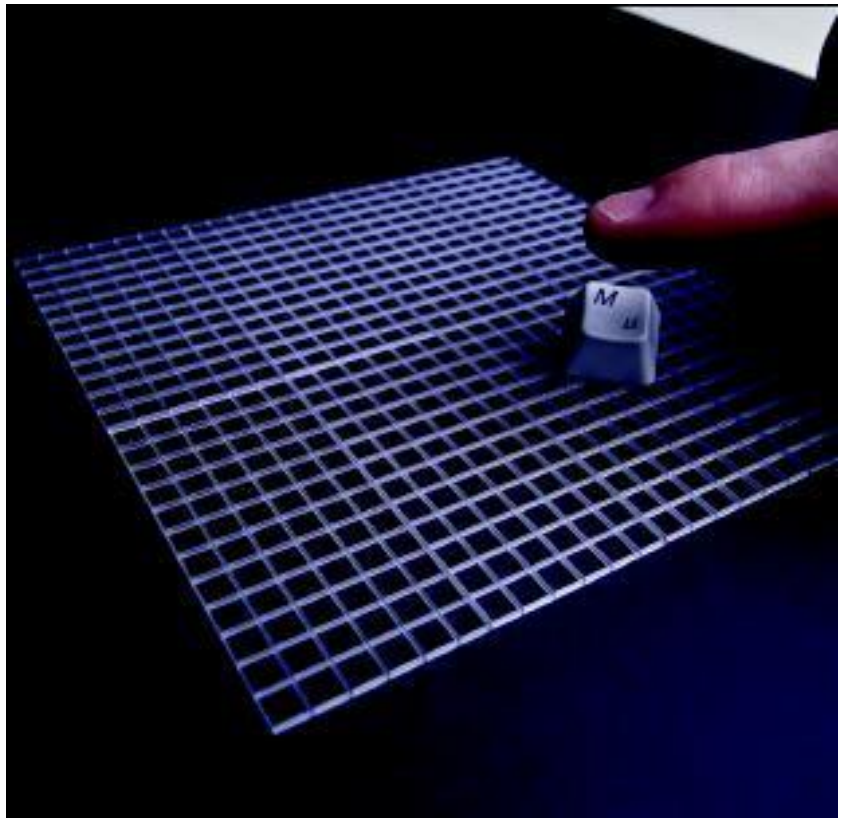
$$SiF_4 + 2HF \Rightarrow H_2SiF_6$$

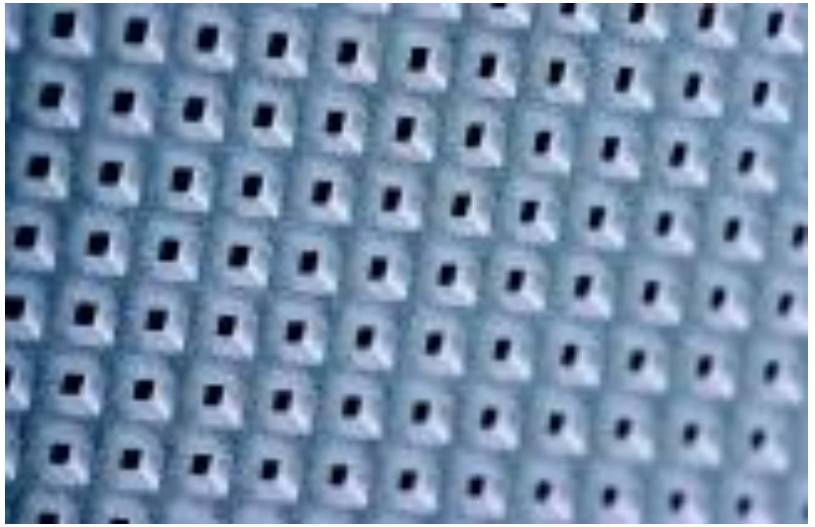
- 1 mm substrate etched in 50 min
- etching ratio vitreous phase/crystalline phase is 1:20

3. Anisotropic Etching



Photosensitive glass (vi)





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