Introduction to the Micro and Nano Fabrication: WET ETCHING

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Purpose of Etch

- To remove material from areas identified by the lithography process
  * Areas of photoresist exposed to light
  * Developing leaves only these areas open
  * Etching removes substrate areas not masked
- To create structures for functional use
- To remove oxide layers below features to allow for motion

ETCHING

Dry Etching:

"The material is removed from the solid surface directy into gas phase"

- Plasma chemical etching
- Sputter etching
- Ion beam etching

Wet Etching

Wet etching

⇩

"Etching using liquid chemicals"

Why use wet etching?

- Simplest etching technology: all you need is a container of liquid chemicals!
- Good for thin films
- Selectivity

There are complications

- Selectivity:
  - → Must find mask that will not dissolve (Poor resolution)
- Undercutting!
- Geometries.

Etch Parameters

- Etch Rate:

  - rate of material removal (μm/min)

  - function of concentration, agitation, temperature, density and porosity of the thin film or substrate,…

- Etch Selectivity:

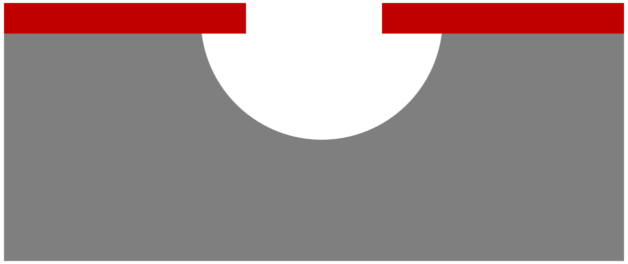
  -relative (ratio) of the etch rate of the thin film to the mask, substrate, or another film

- Pattern Geometry
- Etch mask!

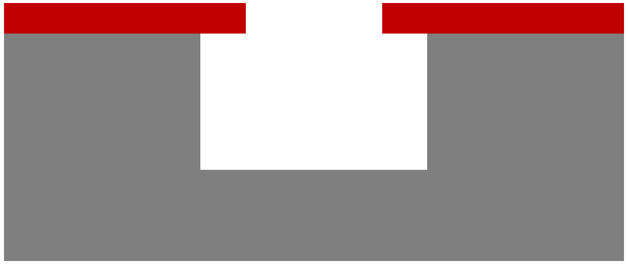
  - Selection of right mask for each material

WET ETCHING

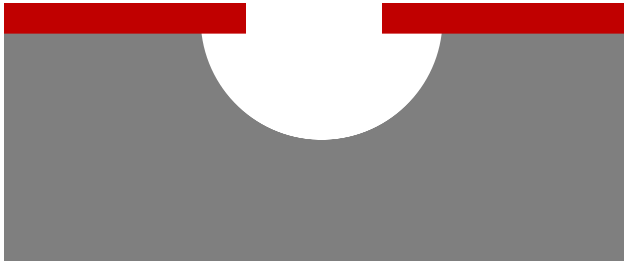
Isotropic Wet Etching



Anisotropic Wet Etching



Isotropic Etching



- Etch rate is independent of direction
- Isotropic etch profile

Mask undercut, rounded etch profile

Applications

- Flow channels →microfluidic devices
- Removal of sacrificial layers in surface micromachining

Provides a high degree of selectivity and etch rate: can be controlled by composition, temperature, dopant concentration.

- Etching proceeds by
    1. Reactant transport to surface
    2. Surface reaction
    3. Reaction product transport from the surface

If 1 or 3 is rate determining step:

↓

it's diffusion limited

↓

Can improve by stirring, gas evolution

If 2 is rate determining step:

↓

it's reaction rate limited

↓

Parameters: temperature, etchant composition

Prefer to be reaction rate limited – higher etch rates, better controlled

ETCHANTS

→ Mixtures of acids, bases, solutions in water or solvents

HF, H3PO4, H2SO4, KOH, H2O2, HCl, ..

→ Can be used to etch many materials

Si, SiO_2, Si_3N_4, Al, Au, Cr…

MASK

Can be used:

- ✓Photoresist (or polymeric resist)
- ✓Metals (gold, chromium, nickel)
- ✓Ceramics (oxides, nitrides)

Silicon oxide (glass,quartz…)

Hydrofluoric Acid

$SiO_2 + 6HF \rightarrow H_2SiF_6(aq) + 2H_2O$

- **Selective**

- etches SiO2 and not Si
-will also attack Al, Si3N4,..

- **Etch Geometry**

-completely isotropic

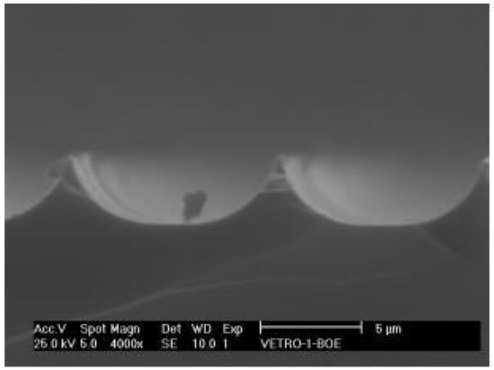
- **Dangerous !**

penetrate skin (adsorption) and attacks slowly

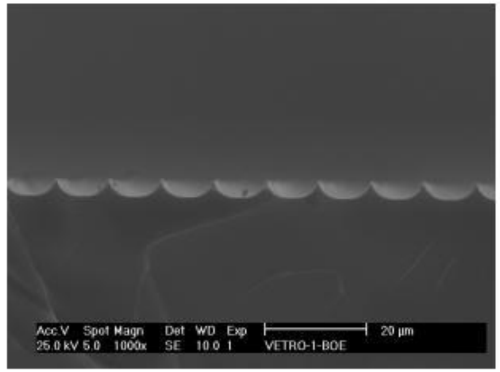
- **Rate:** depends strongly on concentration

- maximum: 49% HF ("concentrated) ~ >2 μm/min
- controlled: 5 to 50:1 ("timed") ~ <0.1 μm/min

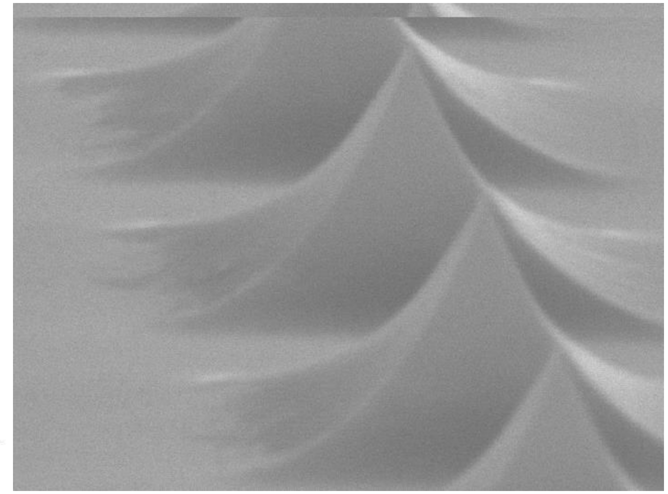
Buffered HF (**BHF**), also called Buffered oxide etch (**BOE**) addition of NH_4F to HF solution: it replenishes the depletion of the fluoride ions to maintain stable etching performance

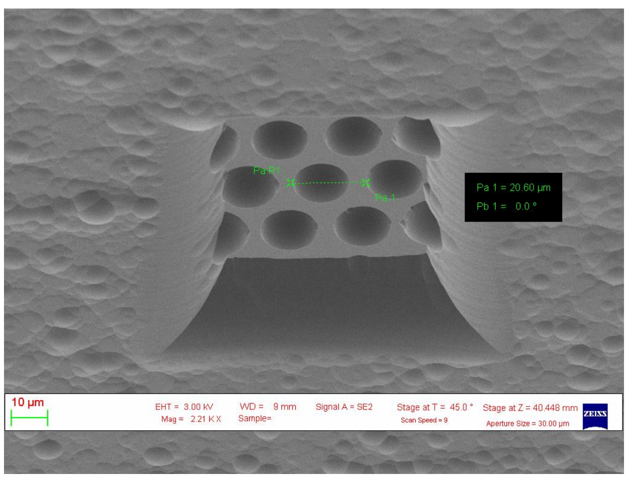


Acc.V Spot Magn Det WD Exp
25.0 kV 5.0 4000x SE 10.0 1
5 µm
VETRO-1-BOE

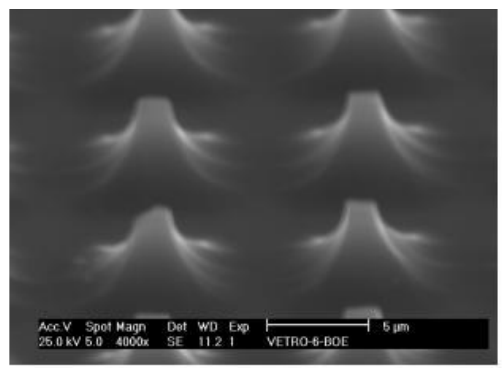


Acc.V Spot Magn Det WD Exp
25.0 kV 5.0 1000x SE 10.0 1
20 µm
VETRO-1-BOE

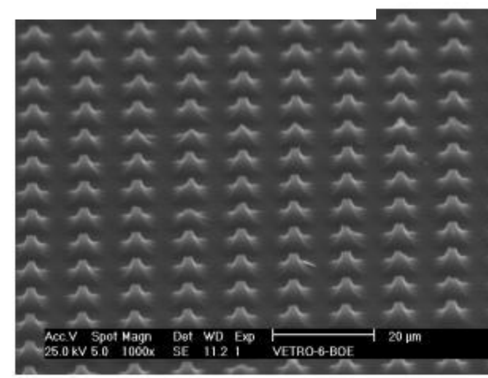




Pa 1 = 20.60 µm
Pb 1 = 0.0 °
10 µm
EHT = 3.00 kV
Mag = 2.21 K X
WD = 9 mm
Signal A = SE2
Stage at T = 45.0 °
Stage at Z = 40.448 mm



Acc.V Spot Magn Det WD Exp
25.0 kV 5.0 4000x SE 11.2 1
5 µm
VETRO-6-BOE

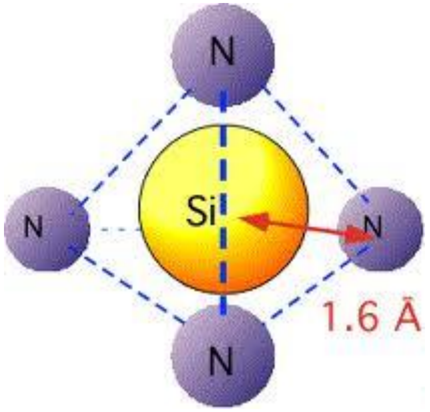


Acc.V Spot Magn Det WD Exp
25.0 kV 5.0 1000x SE 11.2 1
20 µm
VETRO-6-BOE

Silicon nitride (glass,quartz…)

Phosphoric Acid

- Selectively
  - etches SixNy and not Si or SiO_2
  - etches Al and other metals much faster
- Rate
  - Slow ! Rate>0.0050 µm/min for H_3PO_4 at 160°C
- Tough masking materials needed
  - PR will not survive
  - Oxide is typically used



Gold

- *aqua regia:* HCl/HNO3

Mixtures of nitric acid and hydrochloric acid (in a mixing ration of 1 : 3*).* The very strong oxidative effect of this mixture stems from the formation of nitrosyl chloride (NOCl) via

$$HNO_3 + 3\ HCl \rightarrow NOCl + 2\ Cl + 2\ H_2O$$

- KI/I_2

Gold and iodine form gold iodide via

$$2\ Au + I_2 \rightarrow 2\ AuI$$

- Cyanides

Aqueous solutions of the very toxic sodium cyanide (NaCN) or, respectively, the also very toxic potassium cyanide (KCN) dissolve gold via the formation of the soluble cyano-complex [Au(CN)2].

Silicon

HNA → Isotropic wet etching

It's a mixture of nitric (HNO3), hydrofluoric (HF) and acetic (CH3COOH) acids

1. HNO3 oxides Si

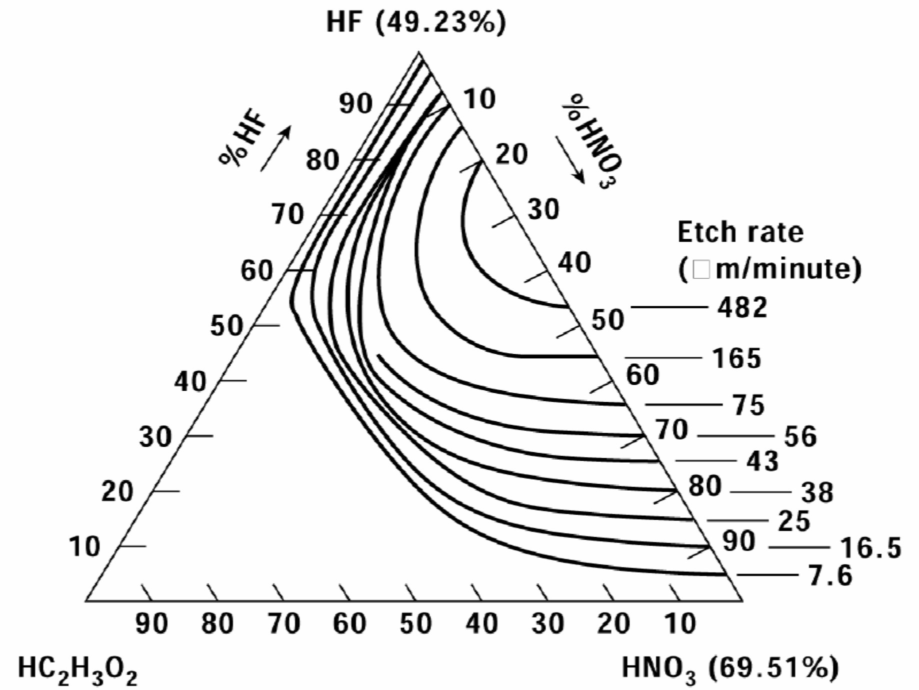
$$Si + 4HNO_3 \rightarrow SiO_2 + 2H_2O + 4NO_2$$

2. HF removes SiO2

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

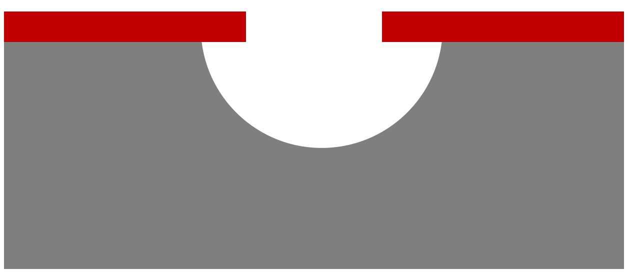
acetic acid (CH_3COOH)is preferred because it prevents HNO_3 dissociation

Iso-etch Curve

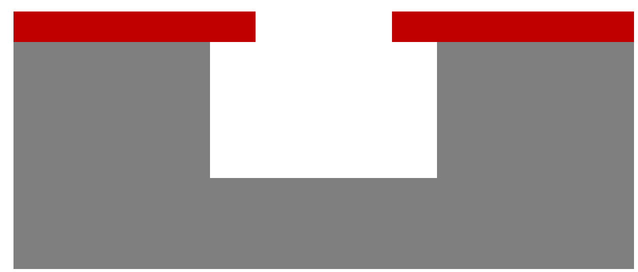


WET ETCHING

Isotropic Wet Etching



Anisotropic Wet Etching



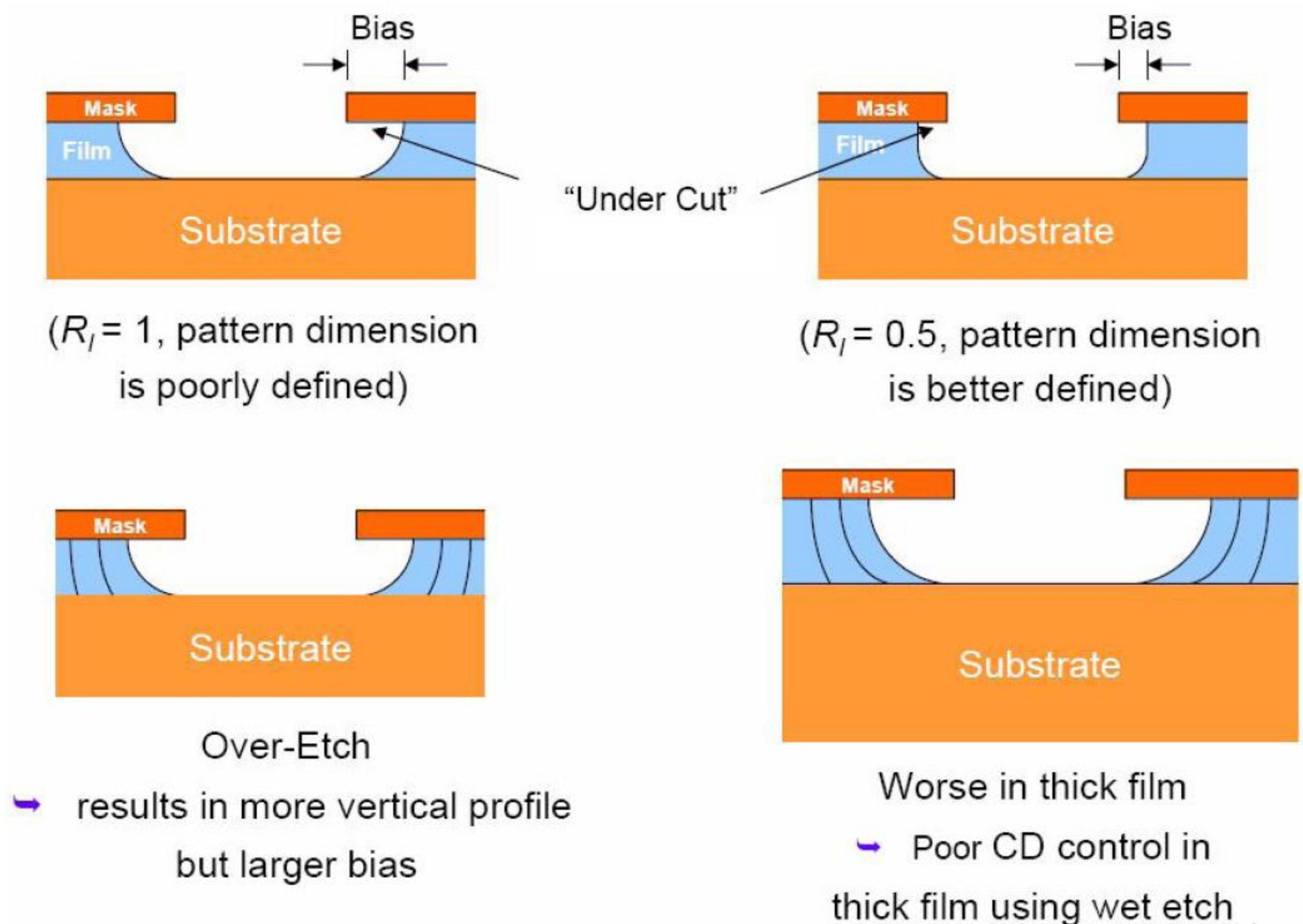
Figures of merit: anisotropy

Isotropic: etch rate is the same along all directions.
Anisotropic: etch rate depends on direction, usually vertical vs. horizontal.

$$R_l = \frac{Horizontal\ Etch\ Rate(R_h)}{Vertical\ Etch\ Rate(R_v)}$$

For isotropic, R_l=1.

For complete anisotropic, R_l=0.



CD: critical dimension

Figures of merit: anisotropy

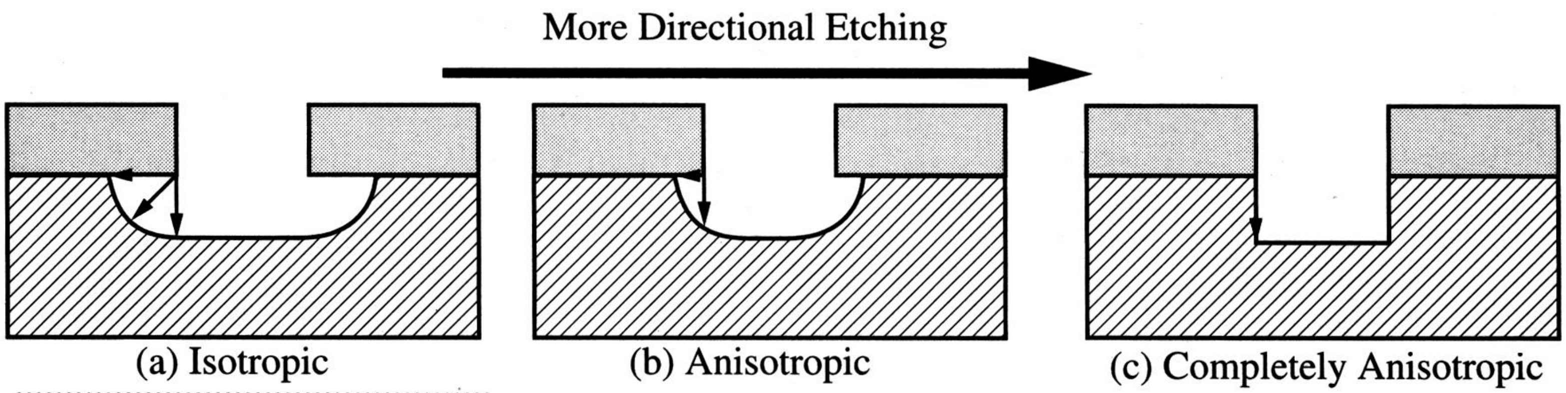


Figure 10–3 Etch profiles for different degrees of anisotropic, or directional, etching: (a) purely isotropic etching; (b) anisotropic etching; (c) completely anisotropic etching.

Generally speaking, chemical process (wet etch, plasma etch) leads to isotropic etch; whereas physical process (directional energetic bombardment) leads to anisotropic etch.

Isotropic:

- Best to use with large features when sidewall slope does not matter, and to undercut the mask (for easy liftoff).
- Large critical dimension (CD, i.e. feature size) loss, generally not for nano-fabrication.
- Quick, easy, and cheap.

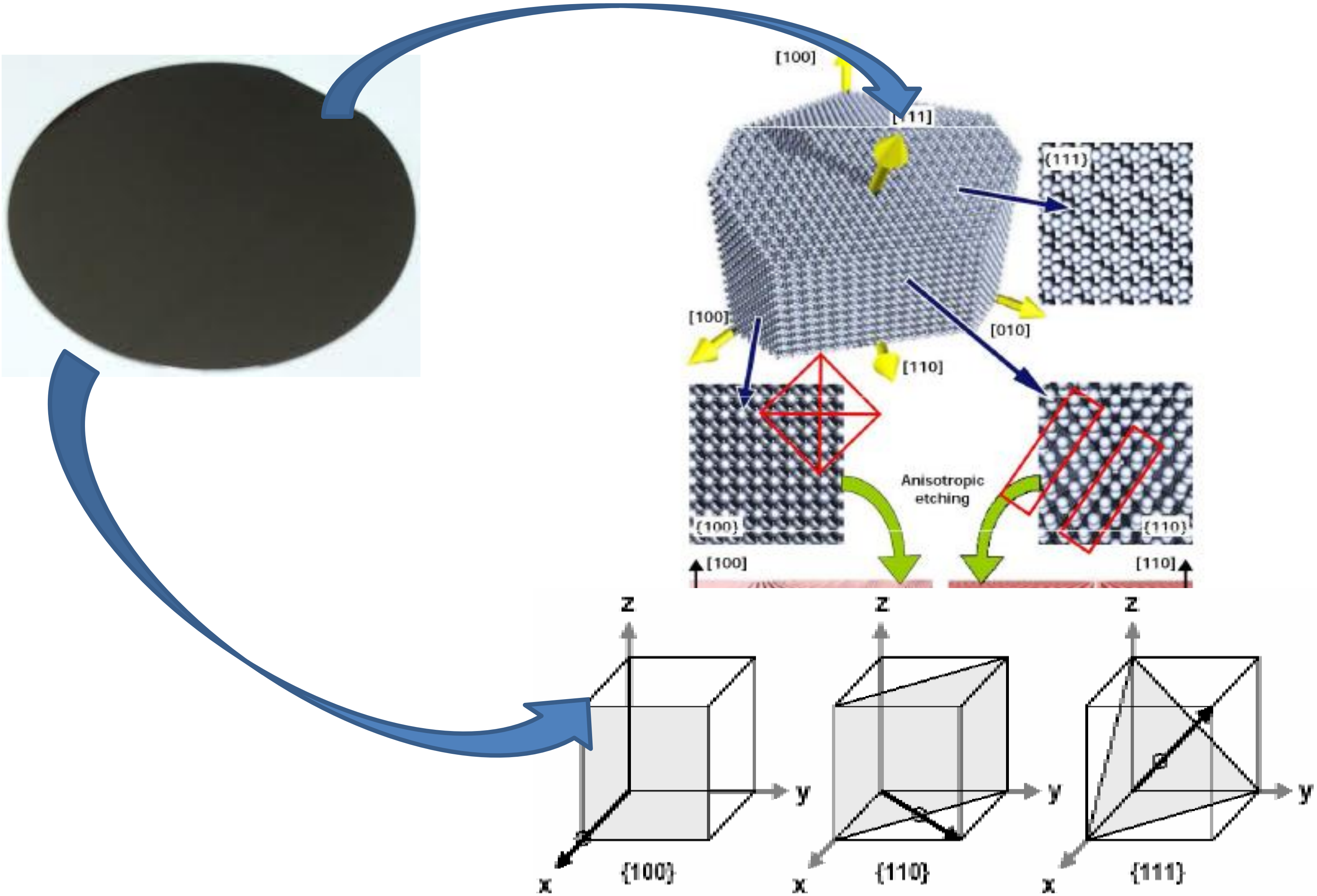
Anisotropic:

- Best for making small features with vertical sidewalls, preferred pattern transfer method for nano-fabrication and some micro-fabrication.
- Typically more costly.

Anisotropic wet etching of Silicon

- Depends on having a singe-crystal substrate
- The effect depends on the different etch rates of different exposed crystal planes
- Silicon etchants for which <111> planes etch slowly
  - -Strong bases (KOH, NaOH, NH_4OH)
  - - TMAH
  - - Ethylene diamine pyrochatechol
  - - Hydrazine

Silicon Crystal Planes



Etch rate of Si in KOH Depends on Crystallographic Plane

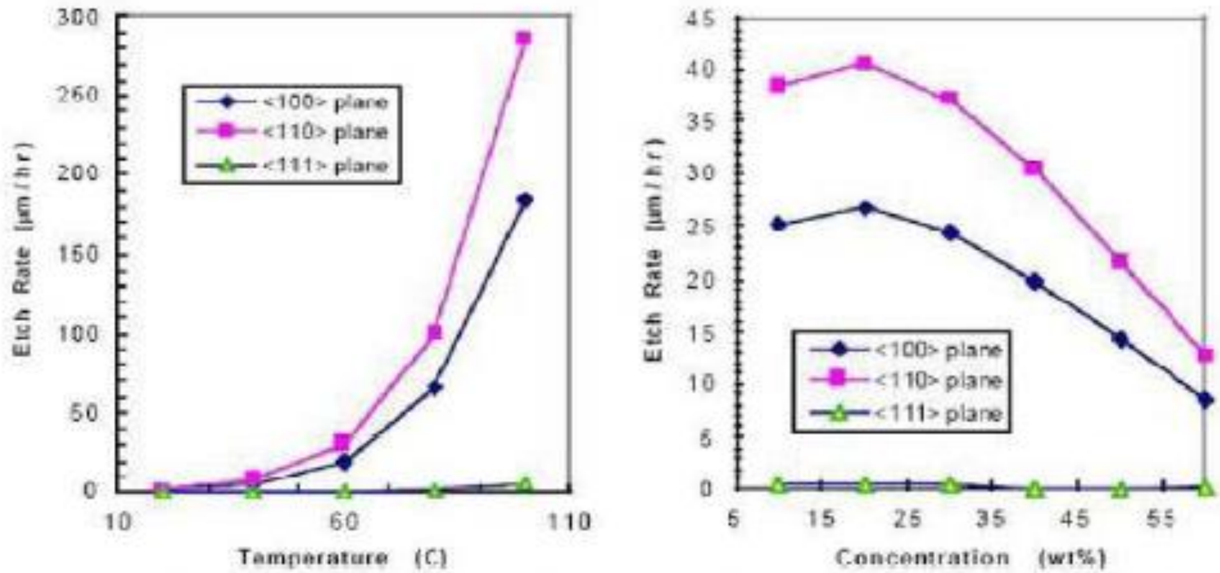


Figure 3. Silicon Etch rate in KOH vs. Temperature and Concentration

(left) Silicon etch rate as a function of temperature at fixed concentration of 40%
(right) Silicon etch rate as a function of concentration at fixed temperature of 60°C
From "Efficient process development for bulk silicon etching using cellular automata simulation techniques", J. Marchetti et al.

http://www.ee.byu.edu/cleanroom

Dissolution of silicon in hydroxydes:

1. Oxidation of silicon by hydroxyls to form a silicate:

$$Si + 2OH^- + 4h^+ \rightarrow Si(OH)_2^{2+}$$

For (100) and (110) surfaces there will be two dangling bonds, for (111) there will only be one

2. Reduction of water:

$$4H_2O \rightarrow 4OH^- + 2H_2 + 4h^+$$

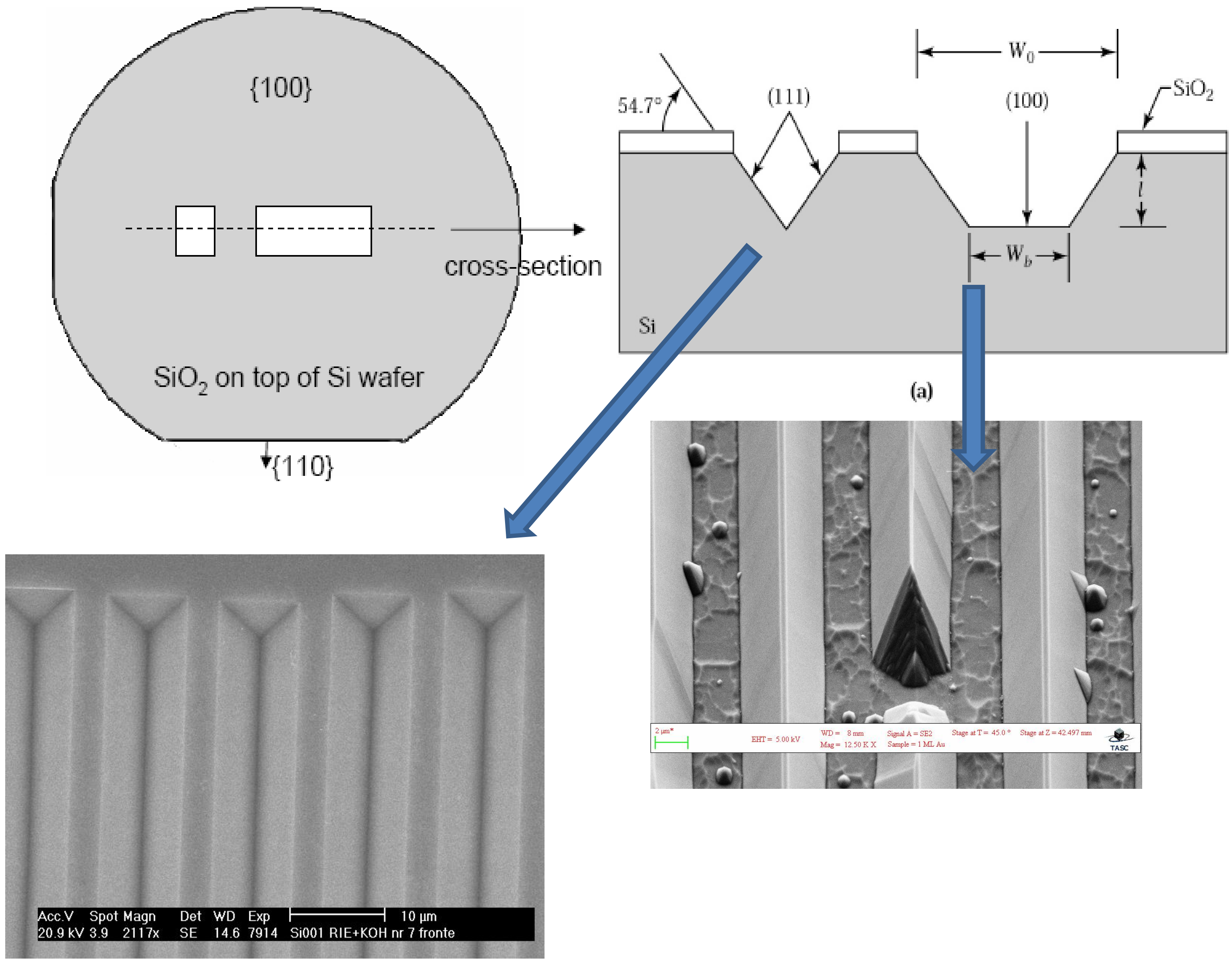
3. If sufficient energy available (thermal) Si-Si bonds break and silicate further reacts with hydroxyls to form a water soluble complex:

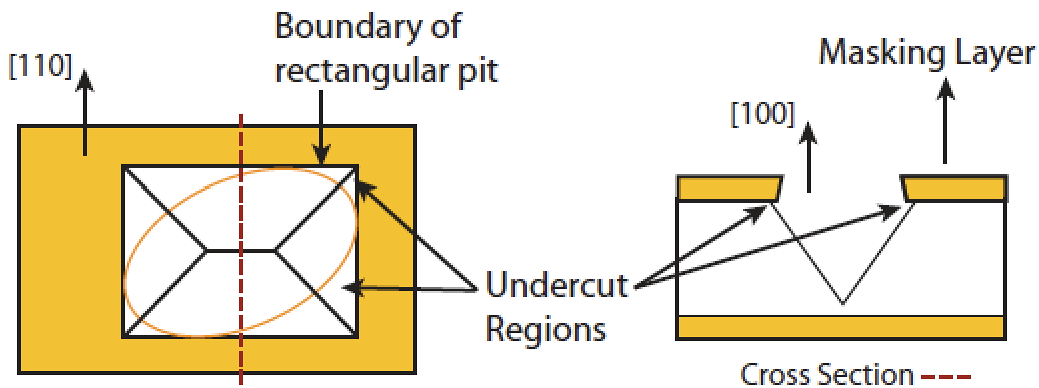
$$Si(OH)_2^{2+} + 4OH^- \rightarrow SiO_2(OH)_2^{2-} + 2H_2O$$

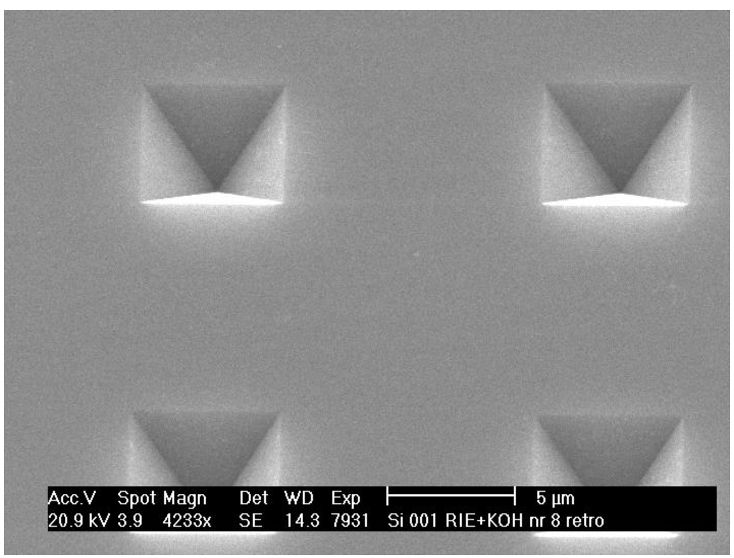
<u>The (111) surface requires 3 bonds to be broken => lower etch rate</u>

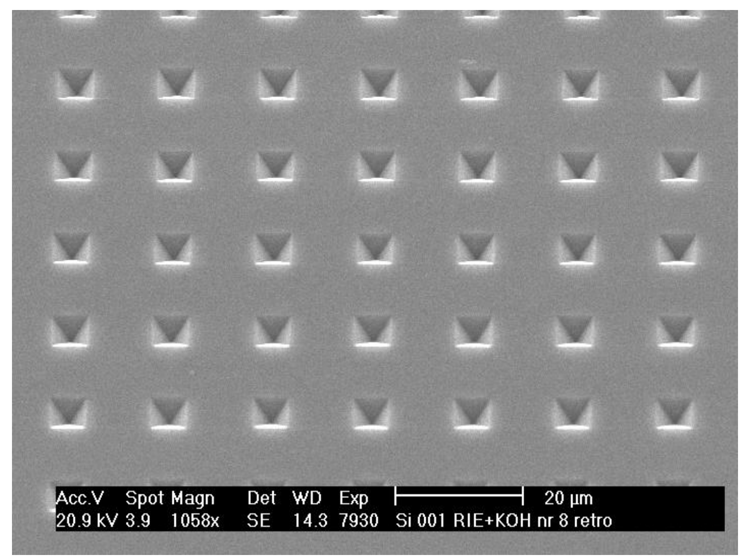
4. Overall redox reaction is:

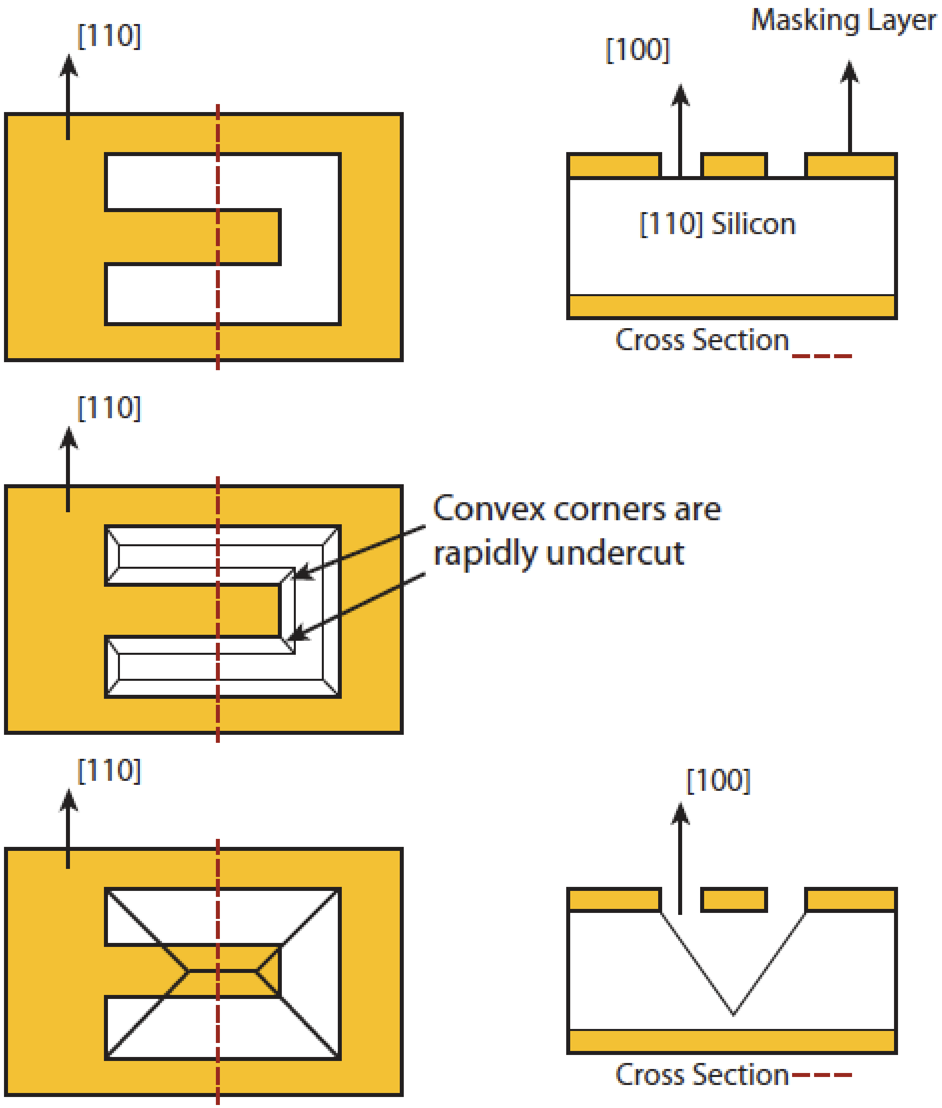
$$Si + 2OH^- + 4H_2O \rightarrow Si(OH)_2^{2+} + 2H_2 + 4OH^-$$


{100}
cross-section
SiO_2 on top of Si wafer
{110}
54.7°
(111)
W_0
(100)
SiO_2
l
W_b
Si
(a)
2 µm*
EHT = 5.00 kV
WD = 8 mm
Mag = 12.50 K X
Signal A = SE2
Sample = 1 ML Au
Stage at T = 45.0 °
Stage at Z = 42.497 mm
TASC
Acc.V Spot Magn Det WD Exp 10 µm
20.9 kV 3.9 2117x SE 14.6 7914 Si001 RIE+KOH nr 7 fronte

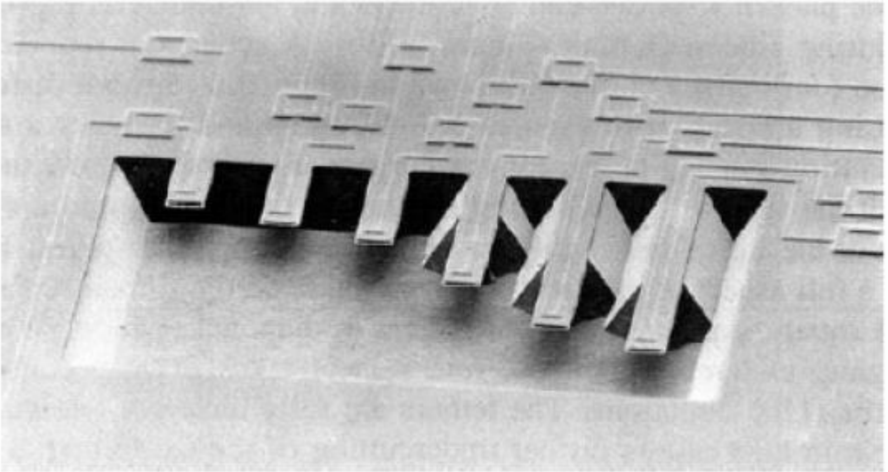

Boundary of
rectangular pit
[110]
Undercut
Regions
Masking Layer
[100]
Cross Section

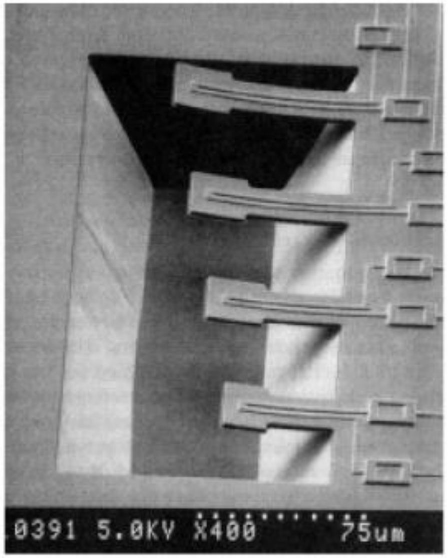

Acc.V Spot Magn Det WD Exp 5 µm
20.9 kV 3.9 4233x SE 14.3 7931 Si 001 RIE+KOH nr 8 retro

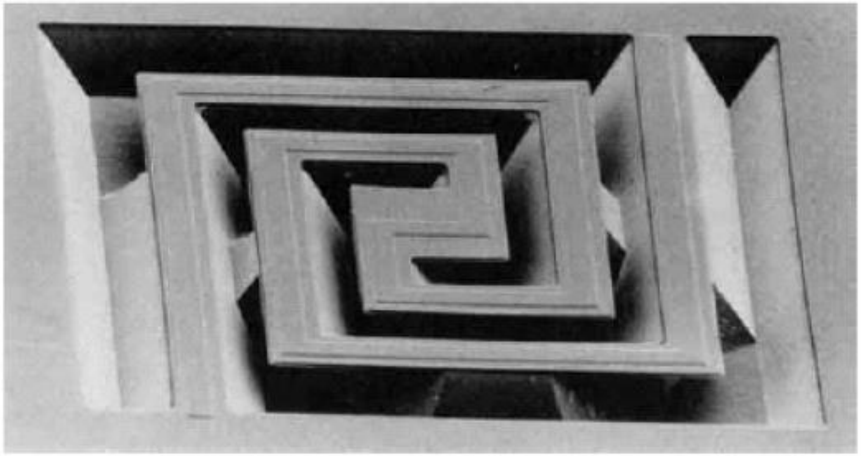

Acc.V Spot Magn Det WD Exp 20 µm
20.9 kV 3.9 1058x SE 14.3 7930 Si 001 RIE+KOH nr 8 retro

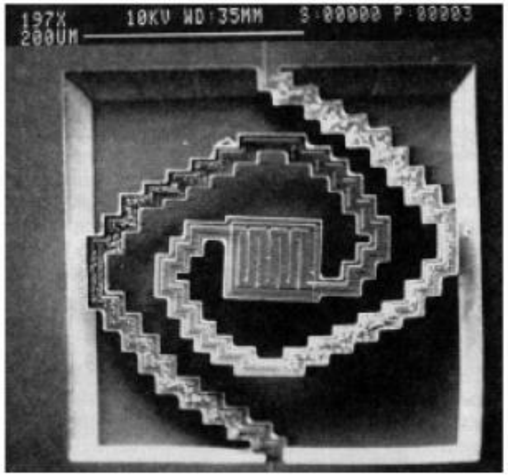

[110]
[100]
Masking Layer
[110] Silicon
Cross Section
[110]
Convex corners are rapidly undercut
[110]
[100]
Cross Section

Bulk Micromachining

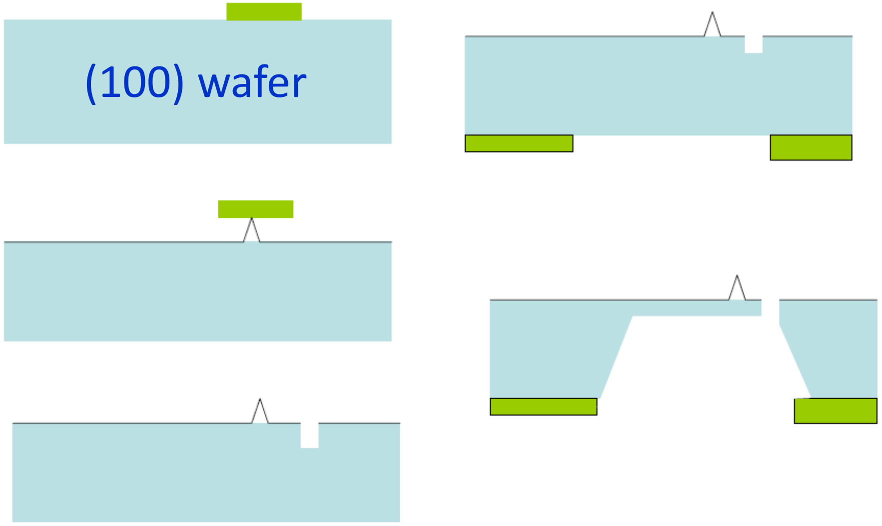


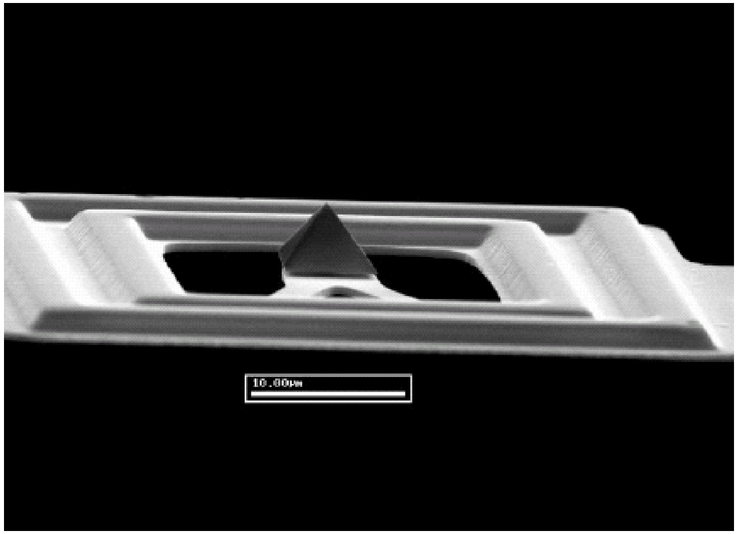


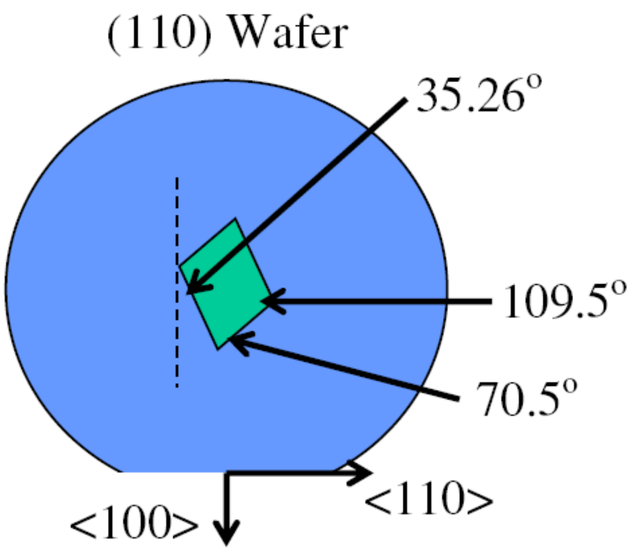


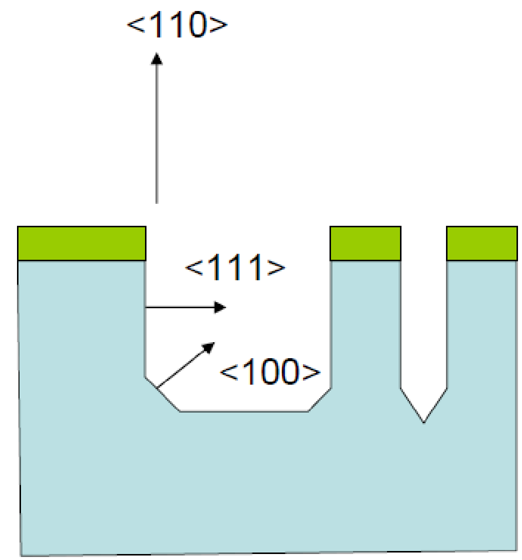


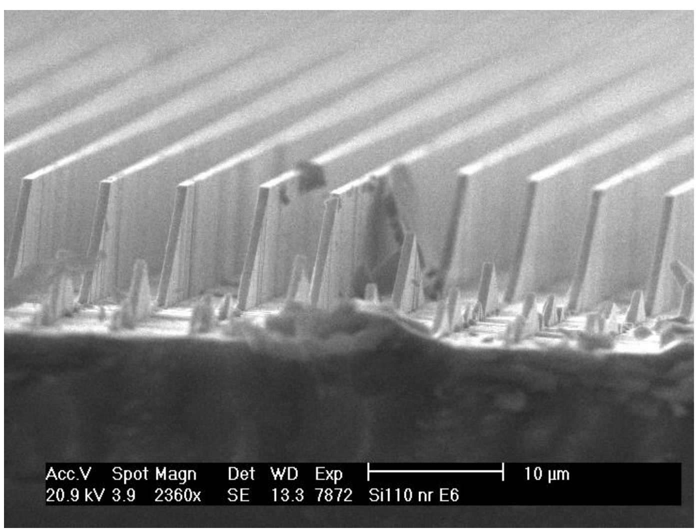
AFM (atomic force microscope) tips

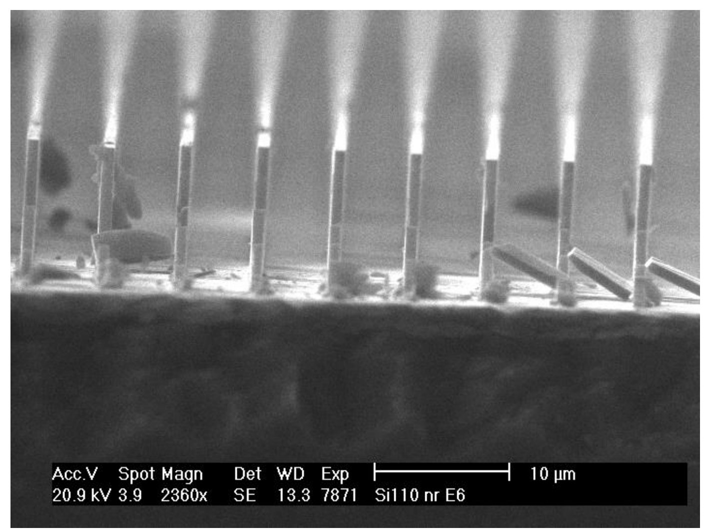


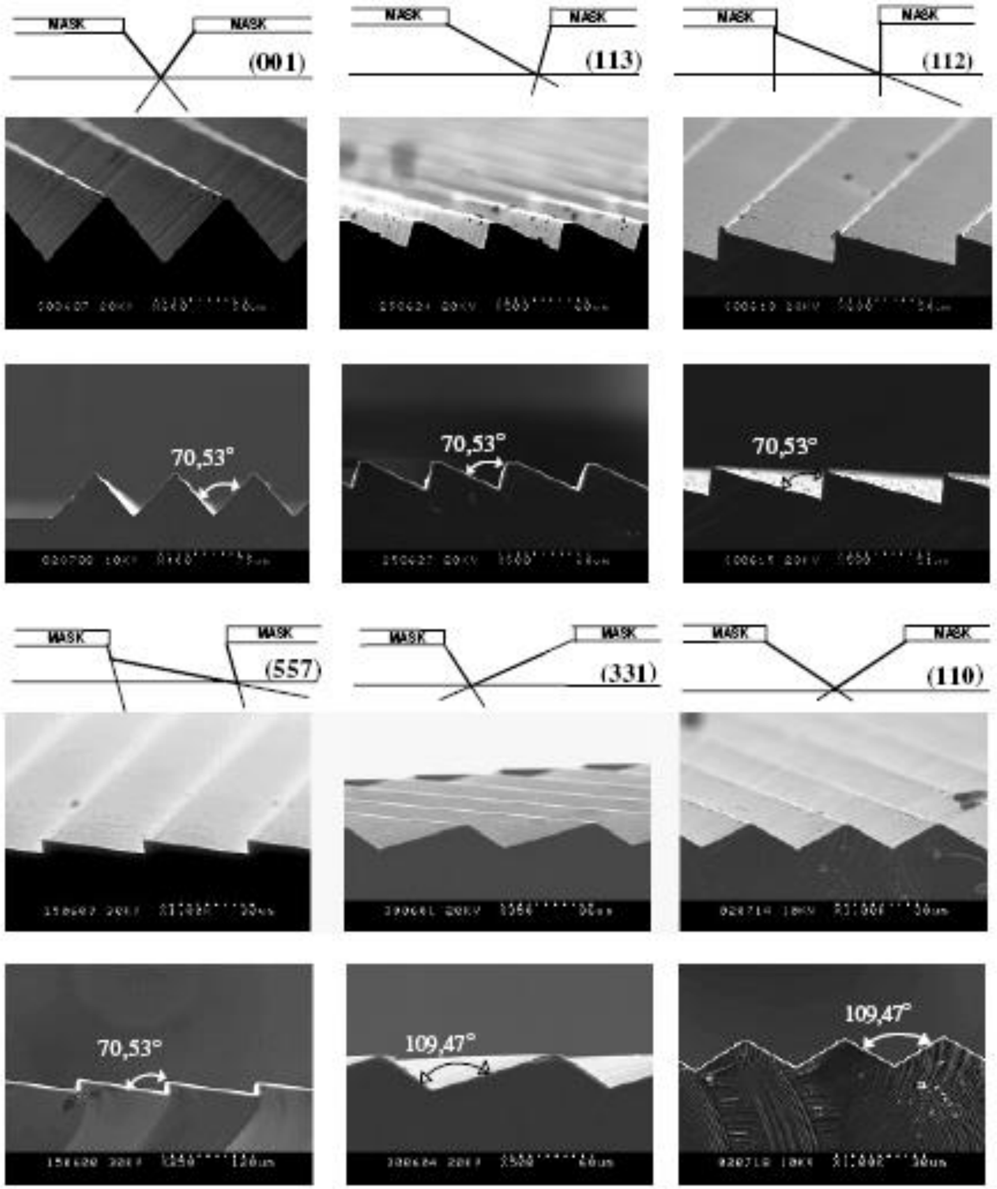


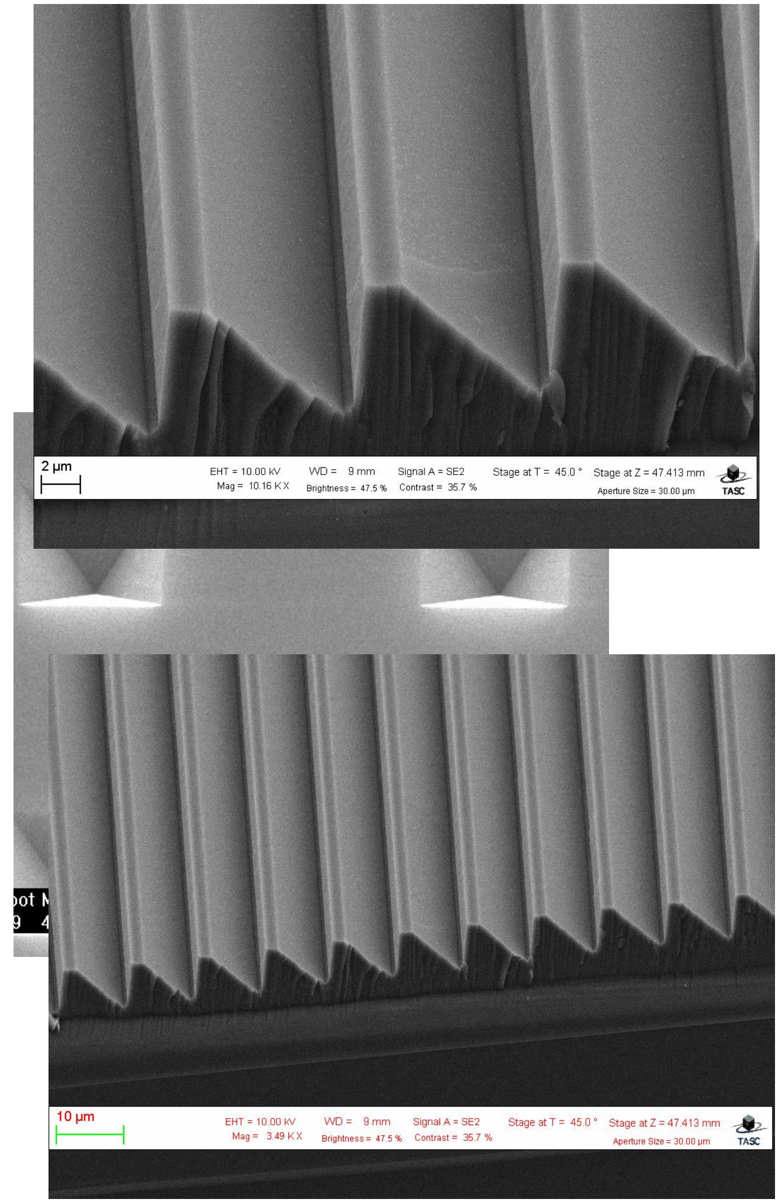

(110) Wafer
35.26°
109.5°
70.5°
<100>
<110>


<110>
<111>
<100>


Acc.V Spot Magn Det WD Exp 10 µm
20.9 kV 3.9 2360x SE 13.3 7872 Si110 nr E6


Acc.V Spot Magn Det WD Exp 10 µm
20.9 kV 3.9 2360x SE 13.3 7871 Si110 nr E6


MASK
(001)
(113)
(112)
70,53°
70,53°
70,53°
MASK
(557)
(331)
(110)
70,53°
109,47°
109,47°


2 µm
EHT = 10.00 kV
Mag = 10.16 K X
WD = 9 mm
Brightness = 47.5 %
Signal A = SE2
Contrast = 35.7 %
Stage at T = 45.0 °
Stage at Z = 47.413 mm
Aperture Size = 30.00 µm
TASC
10 µm
EHT = 10.00 kV
Mag = 3.49 K X
WD = 9 mm
Brightness = 47.5 %
Signal A = SE2
Contrast = 35.7 %
Stage at T = 45.0 °
Stage at Z = 47.413 mm
Aperture Size = 30.00 µm
TASC