Wet etching classroom slides

Micro and Nanofabrication

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Isotropic etching of Si

- Hydrofluoric acid + nitric acid + acetic acid bath ('HNA' bath)

$$HF + HNO_3 + CH_3\ COOH\ (A)$$

for Si etching

What is the role of these 3 compounds?

Chemical reactions

- Overall reaction

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$$2NO_2 \rightarrow 2NO_2^- + 2h^+$$

$$2NO_2^- + 2H^+ \rightarrow 2HNO_2$$

$$2h^+ + Si \rightarrow Si^{2+}$$

Chemical reactions

- Si^{2+} combines with OH^-

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

- Generation of SiO_2 with release of H_2O

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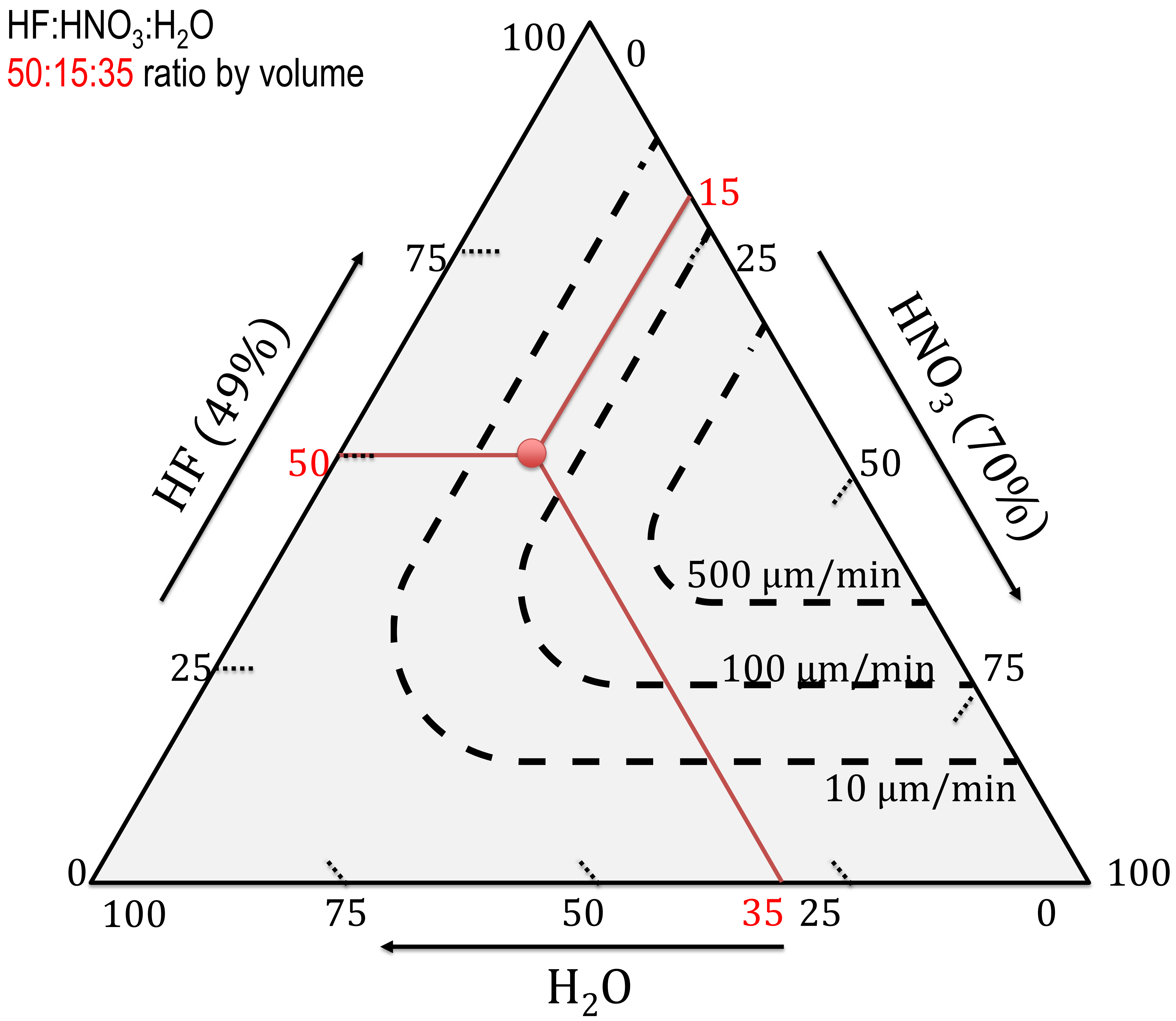
- Next follows the dissolution of the oxide by HF

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

H_2SiF_6 is called fluorosilisic acid. Why an acid?

- Acetic acid ($CH_3\ COOH$) is a diluting agent (also water can be used)

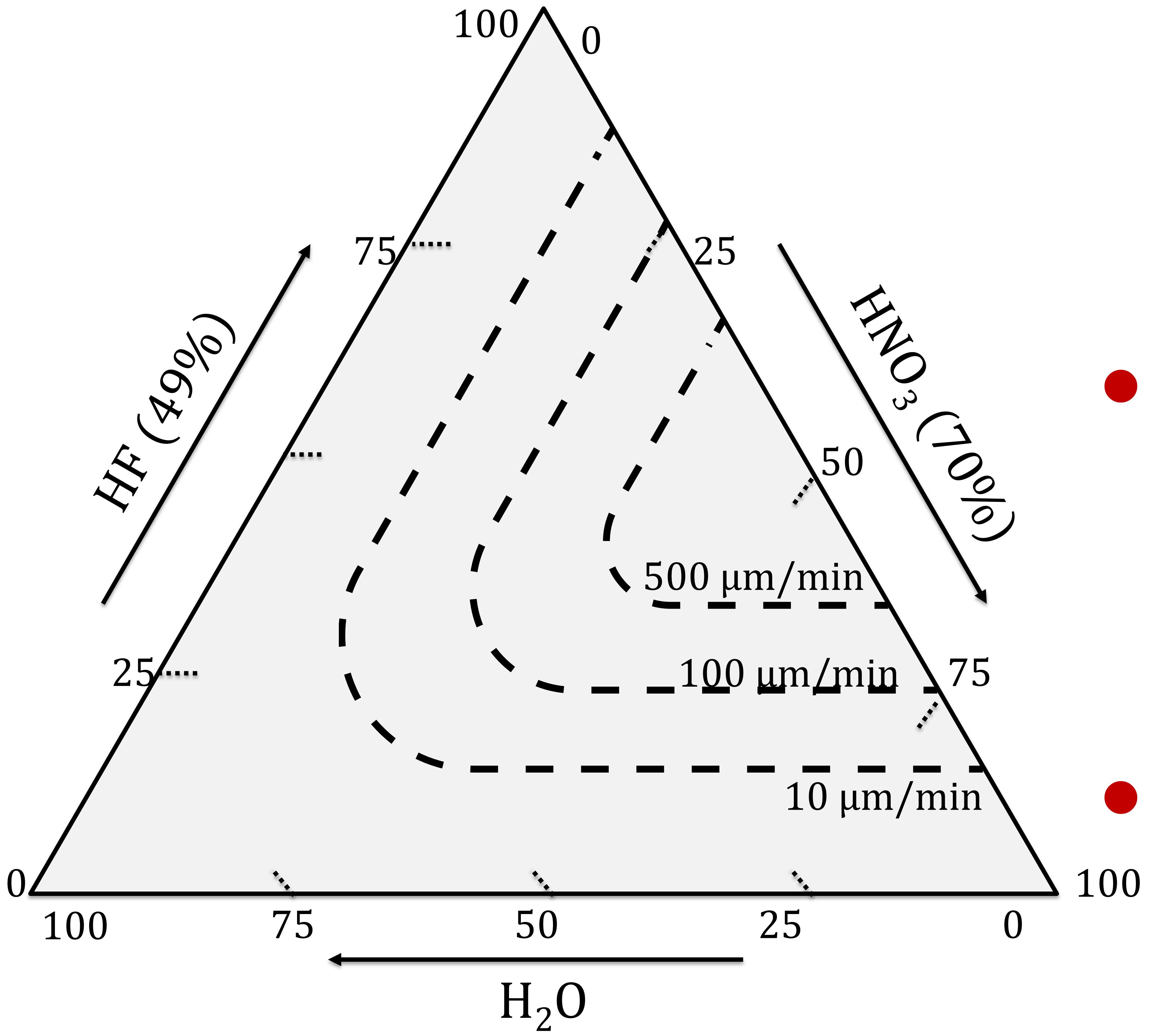
Ternary diagram for HNA bath



Why is ‘pure’ HF only 49%?

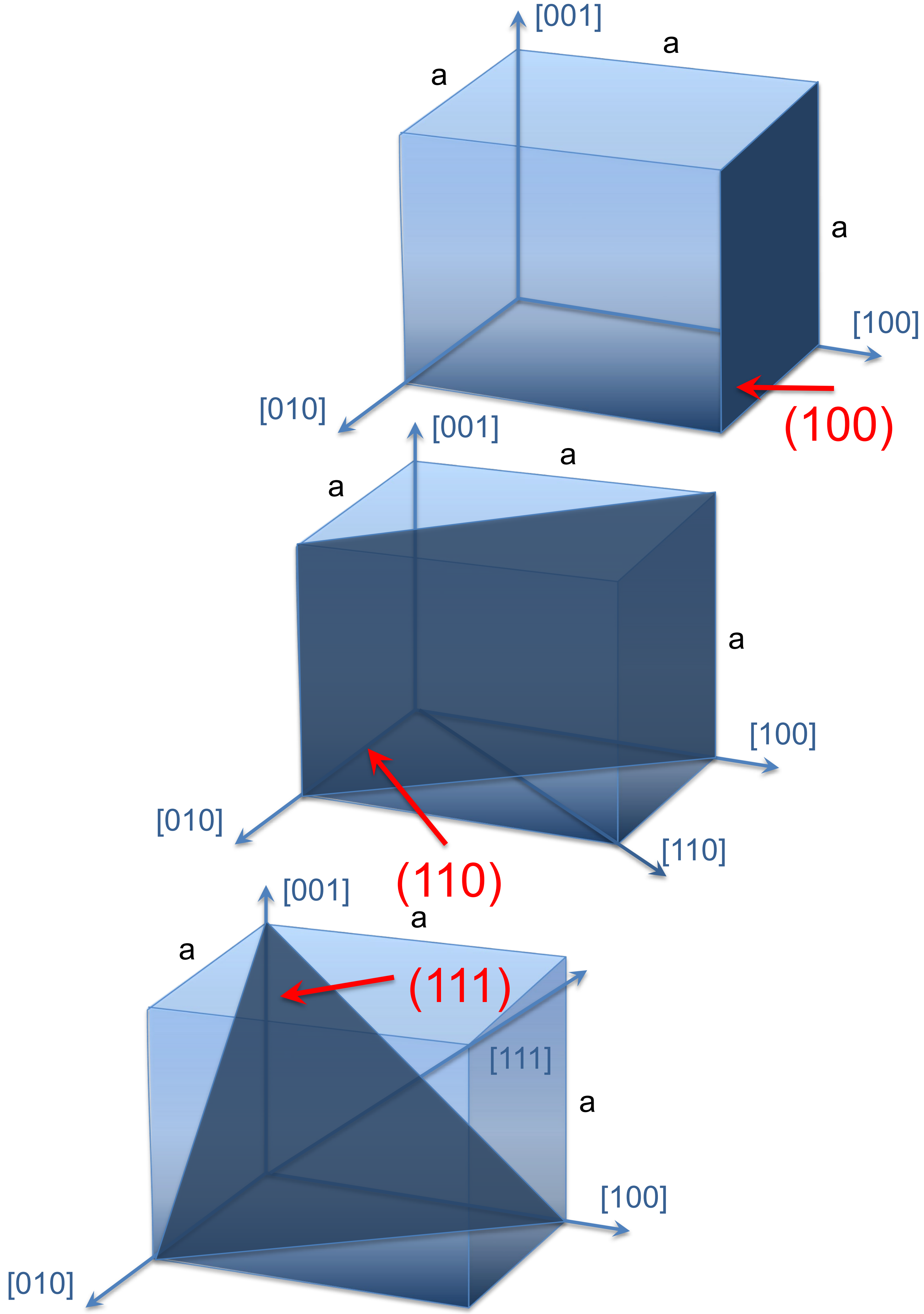
- The concentration of the three basic components HF, HNO_3, and H_2O, are plotted along one of the axes
- A point in the triangle corresponds to a unique composition of the bath
- One can attribute to each point a physical property of the bath with that respective composition, e.g. the etching rate
- Iso-etch curves can be plotted

Iso-etch curves



- For high HF concentration, the iso-etch curves are parallel to the lines of constant HNO_3 and HNO_3 controls the etching rate (oxidation process is limiting)
- For high HNO_3 concentration, the iso-etch curves are parallel to the lines of constant HF and HF controls the etching rate (removal of the oxide is limiting)
- Maximum etch rate when HNO_3 and HF are equilibrated and when H_2O concentration is low

Si crystal planes



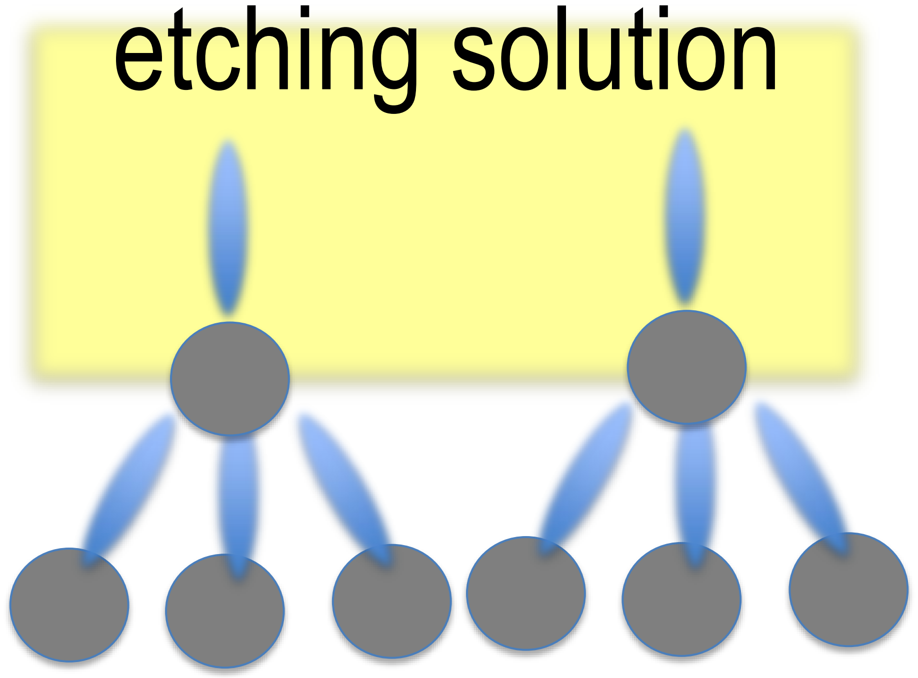
- As planes are characterized by vectors (of the reciprocal lattice), the angle between two planes can be calculated using the vector in-product

$$\boldsymbol{A} \cdot \boldsymbol{B} = |\boldsymbol{A}|\,|\boldsymbol{B}| \cos\varphi$$

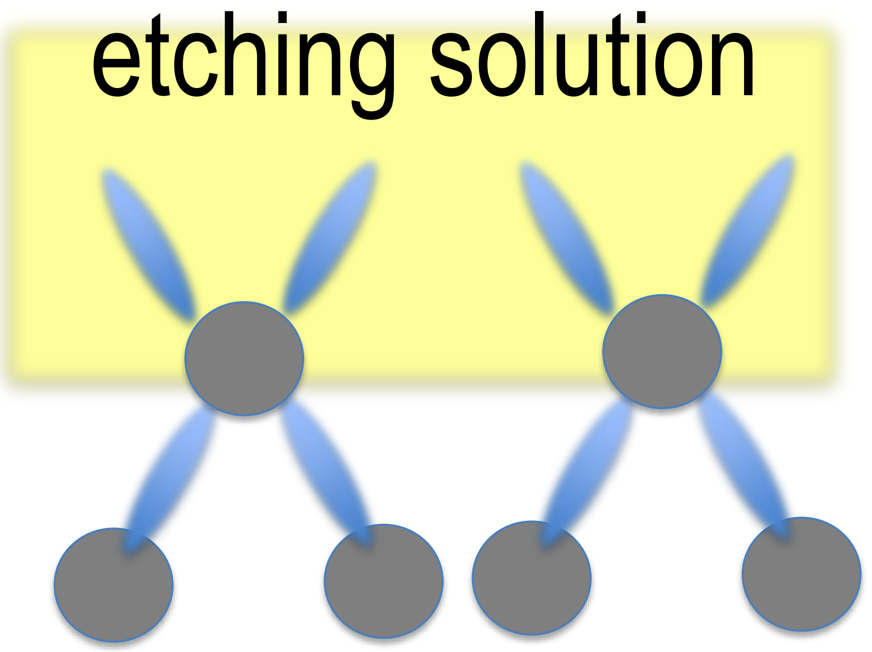
- Example: angle φ between the planes (111) and (001) is

$$\arccos\left\{\frac{(111)\cdot(001)}{|(111)| \times |(001)|}\right\} = \arccos\left\{\frac{1}{\sqrt{3} \times 1}\right\} = 54.74^\circ$$

Origin of etching anisotropy in alkaline bath like KOH



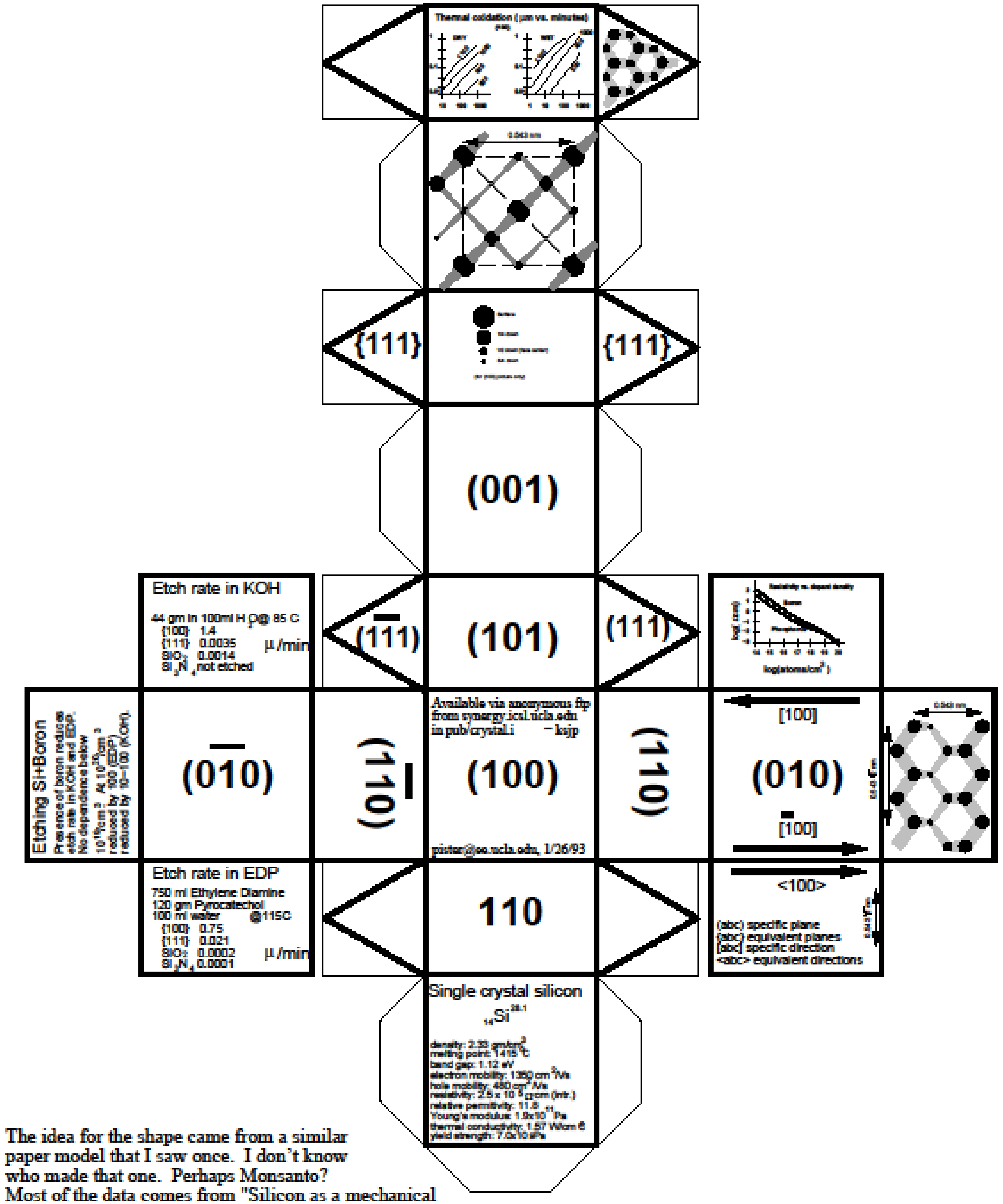
Si atom in (111) plane has 3 backbonds and 1 dangling bond



Si atom in (100) plane has 2 backbonds and 2 dangling bonds

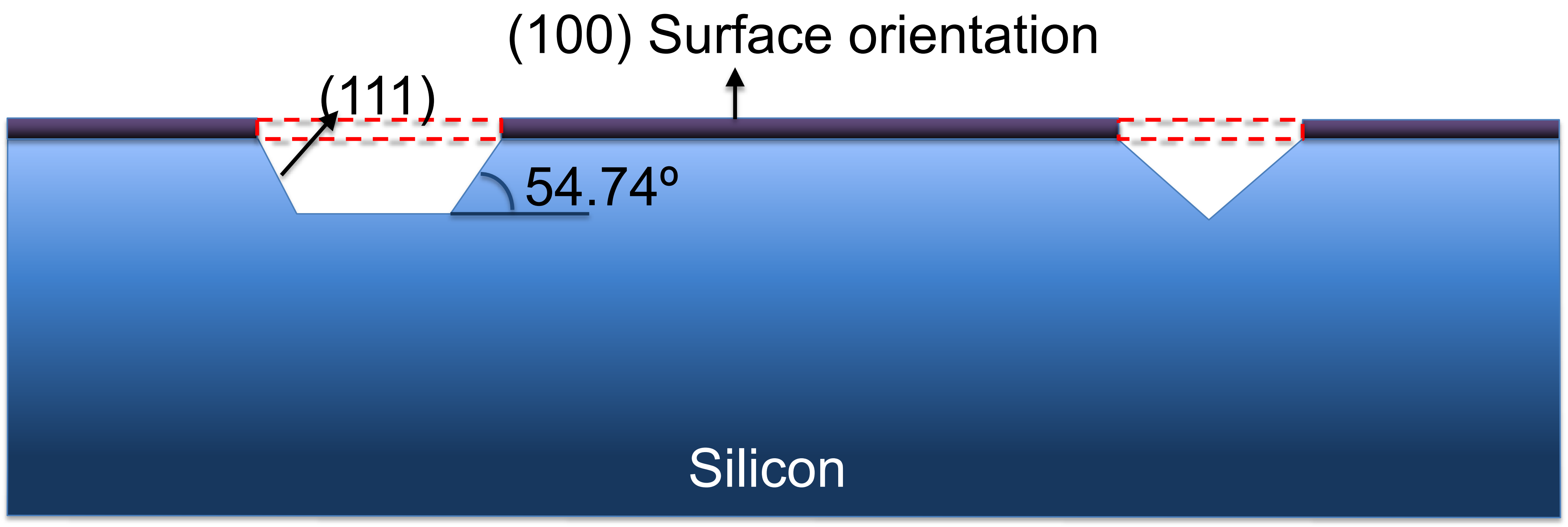
- A Si atom located in a certain plane is differently ‘anchored’ to the back of the substrate and has a different number of dangling bonds that are in contact with the etching solution
- This can give rise to plane-dependent etching rates
- Example: a (111) plane will etch much slower than a (100) plane in an alkaline etching bath

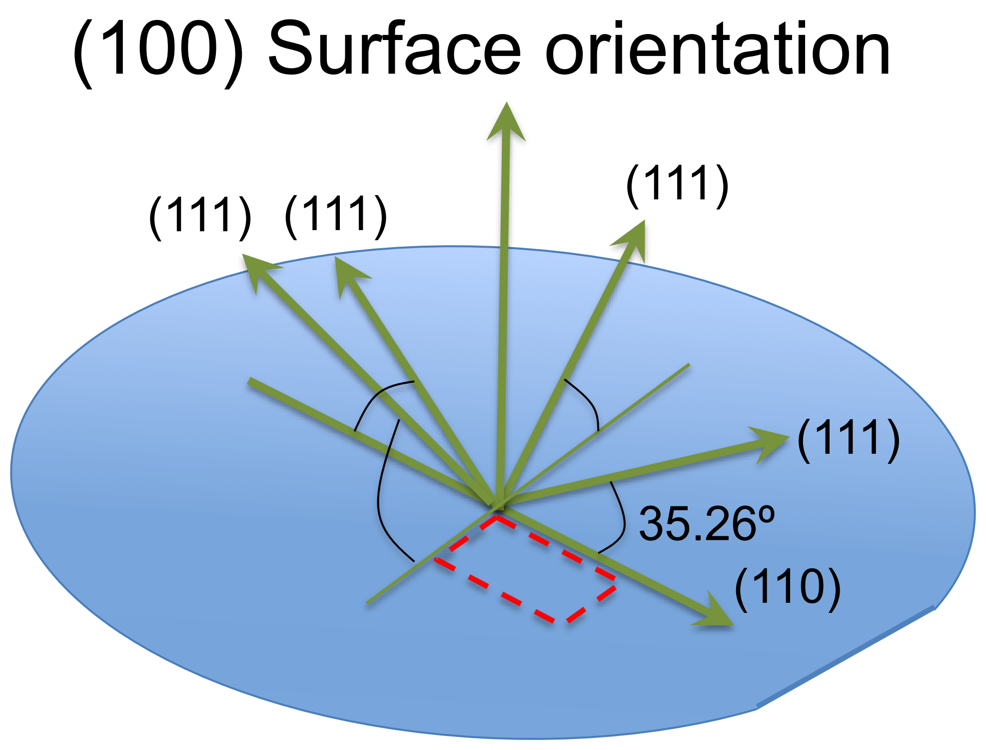
Why an acid bath gives isotropic etching, while an alkaline bath gives anisotropic etching?



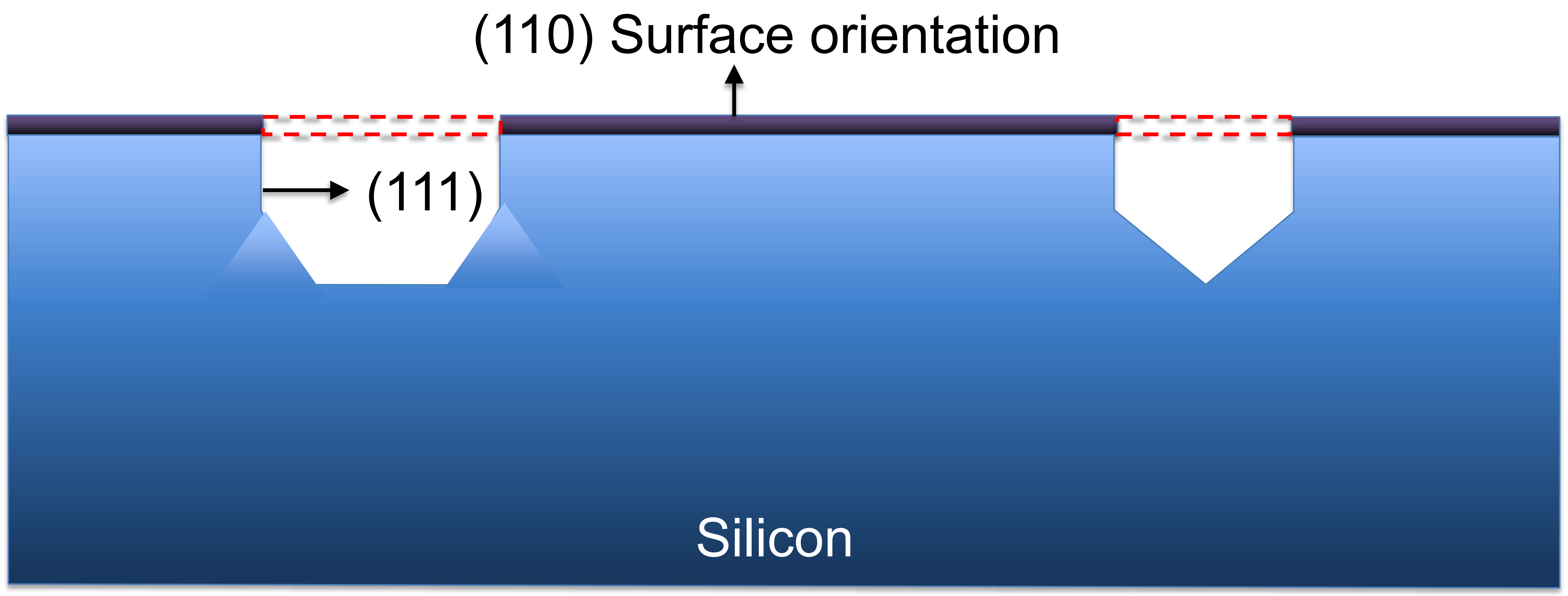
The idea for the shape came from a similar paper model that I saw once. I don't know who made that one. Perhaps Monsanto?
Most of the data comes from "Silicon as a mechanical Material", by Peterson (Proc.IEEE, v70n5, 1982, pp.420–457).
Other data from "VLSI Technology", edited by Sze (McGraw–Hill) and "Solid State Electronic Devices", by Streetman (Prentice–Hall).

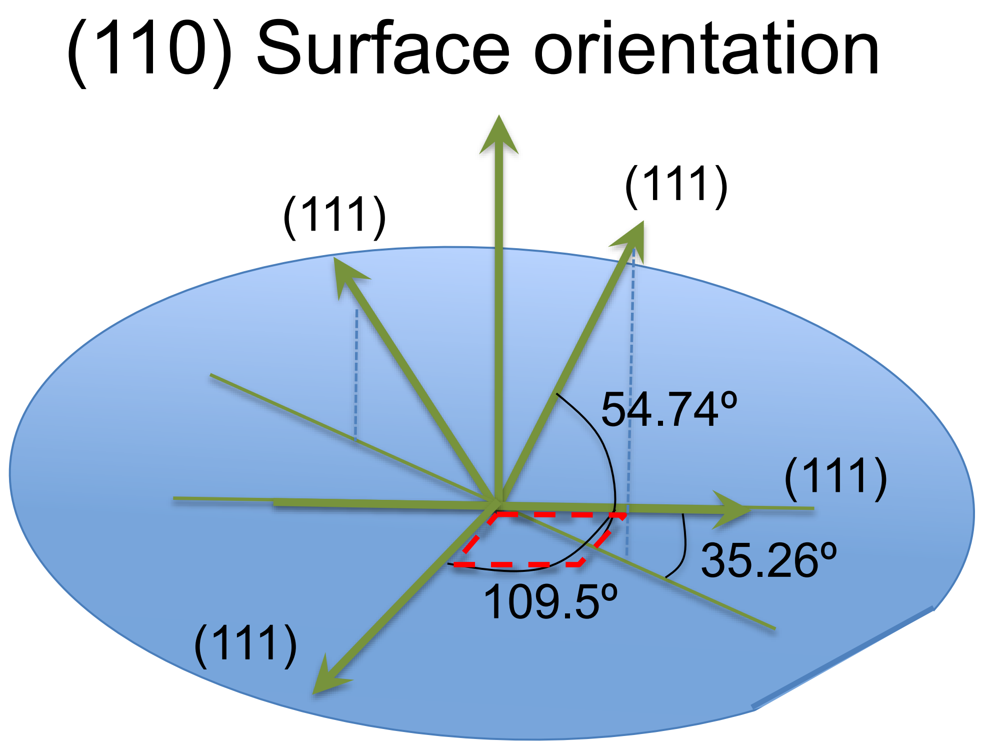
Anisotropic etching profiles



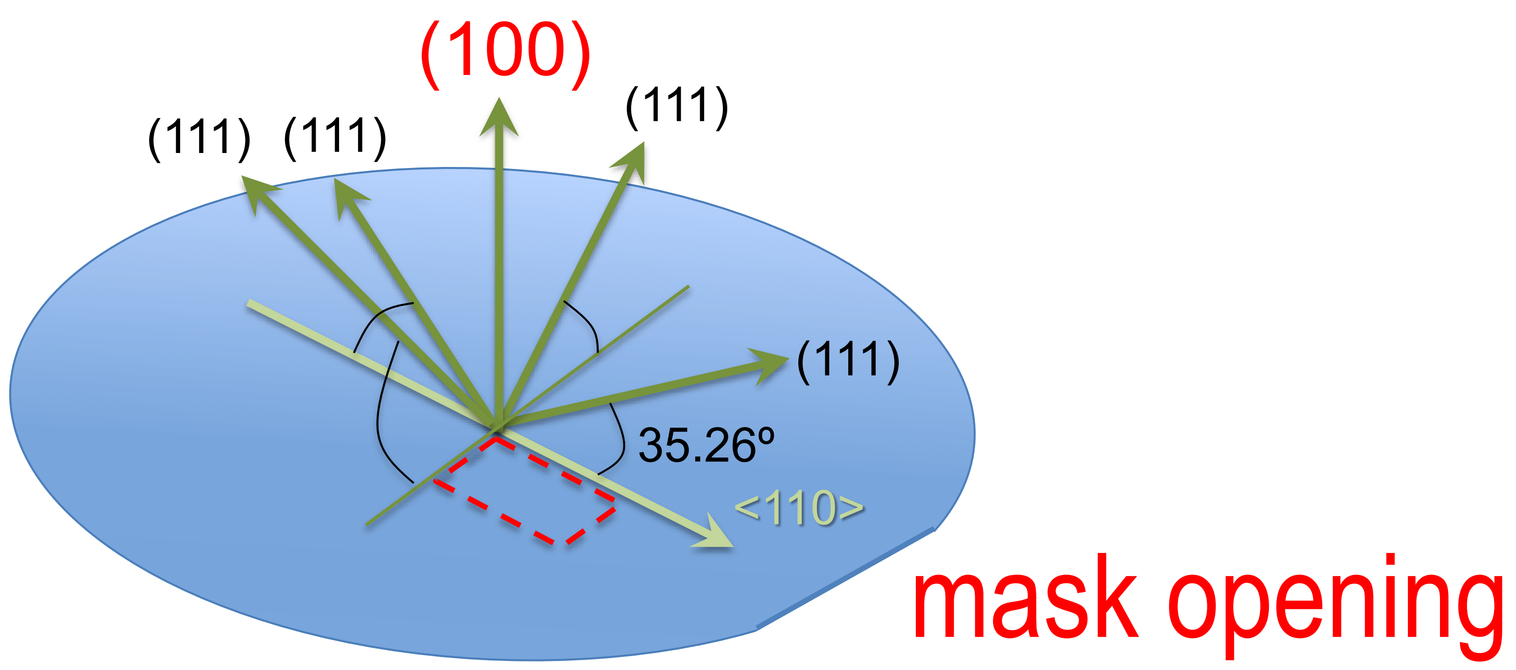


mask openings

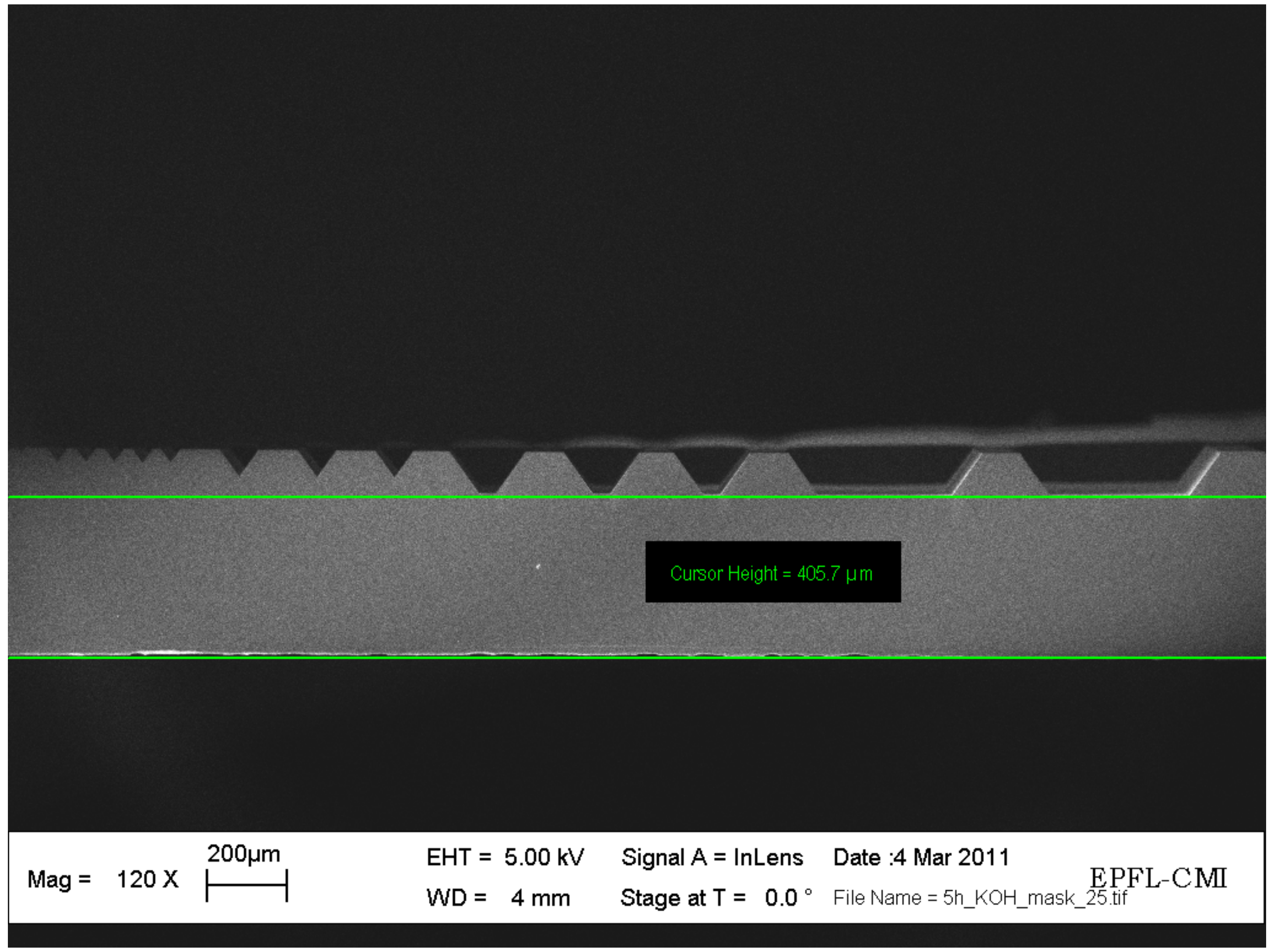




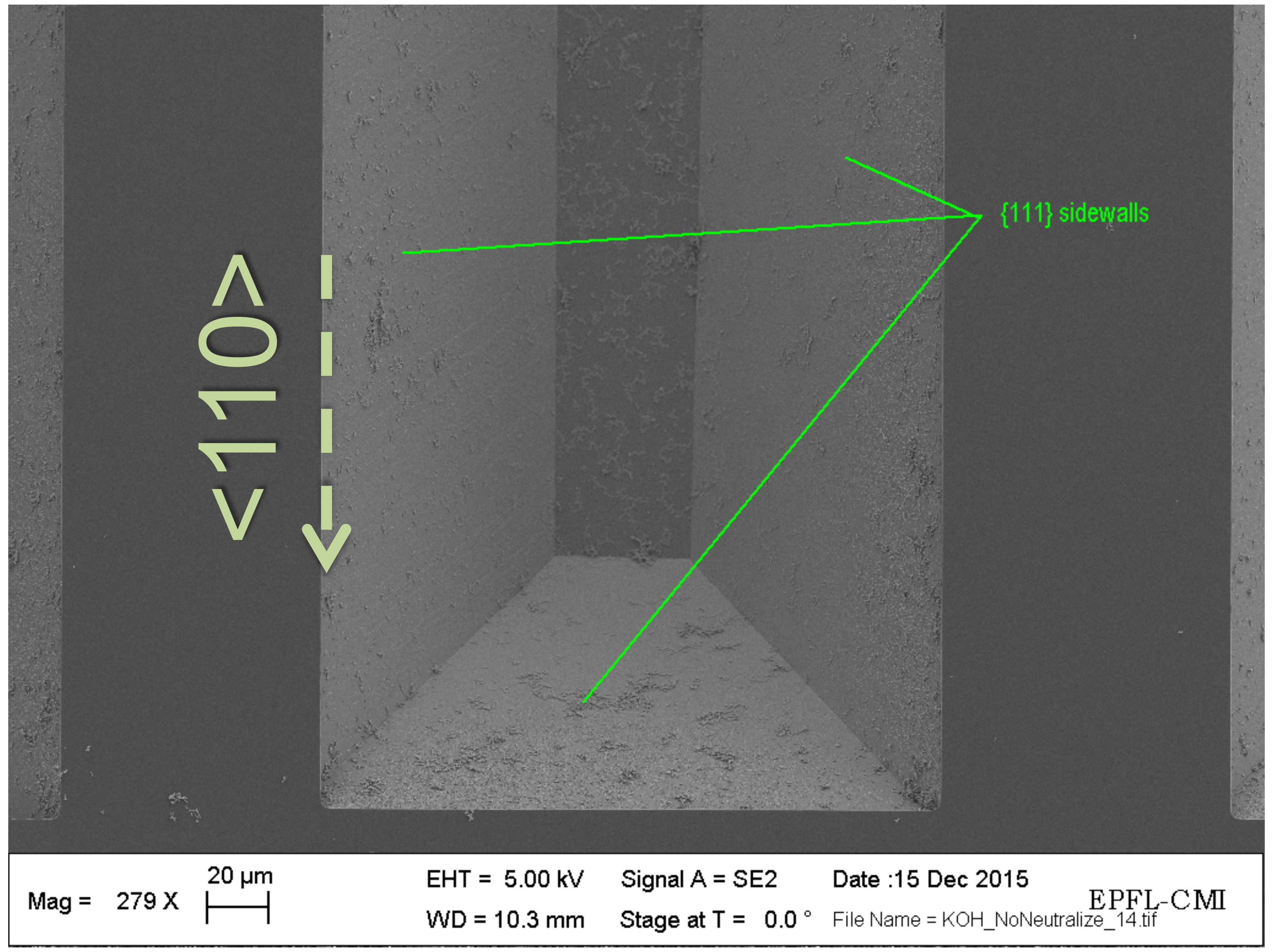
Bulk micromachining



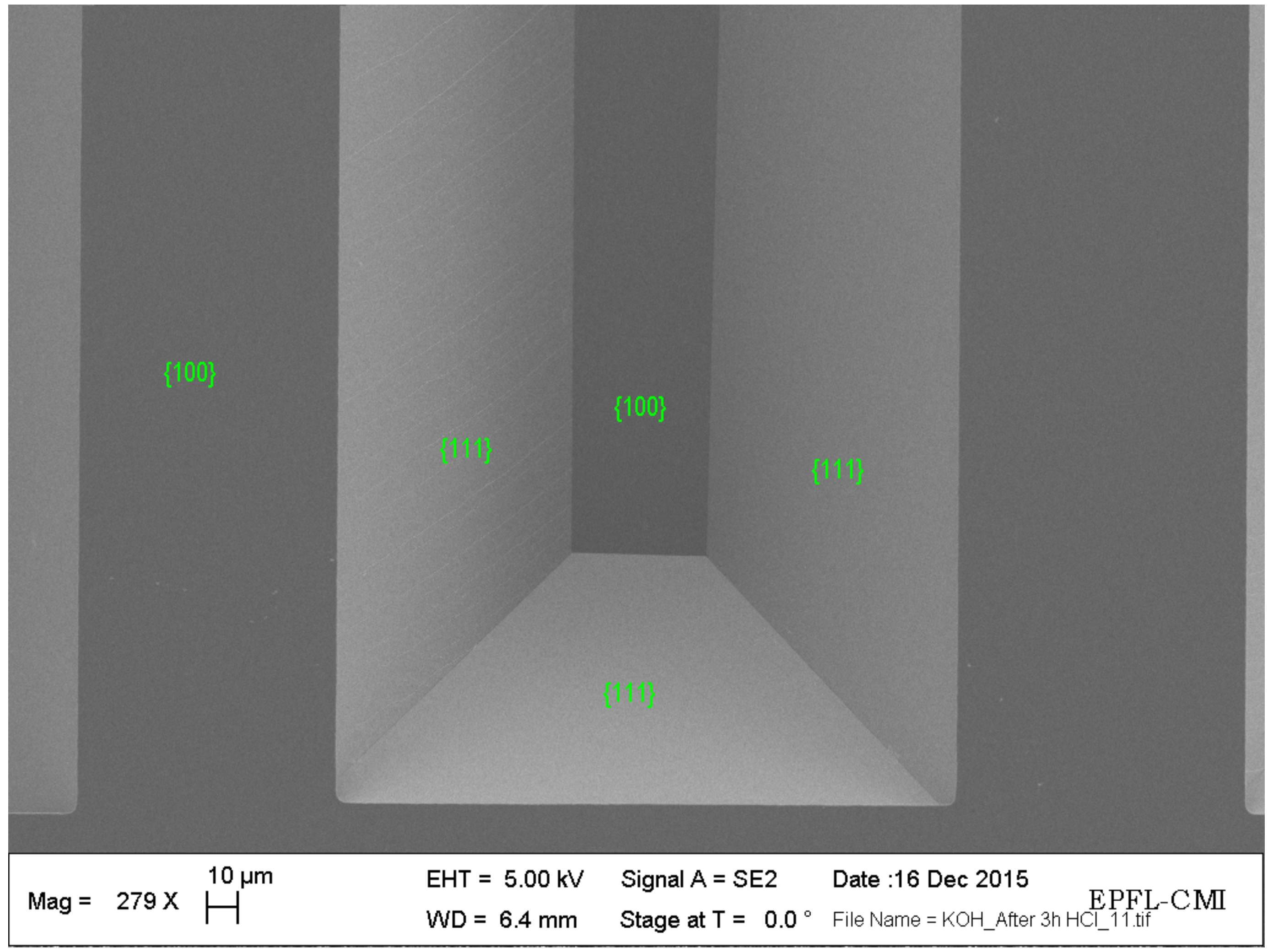
KOH etching of a (100) wafer with rectangular mask oriented along the in-plane <110> direction



K salt deposition



After neutralisation with HCl



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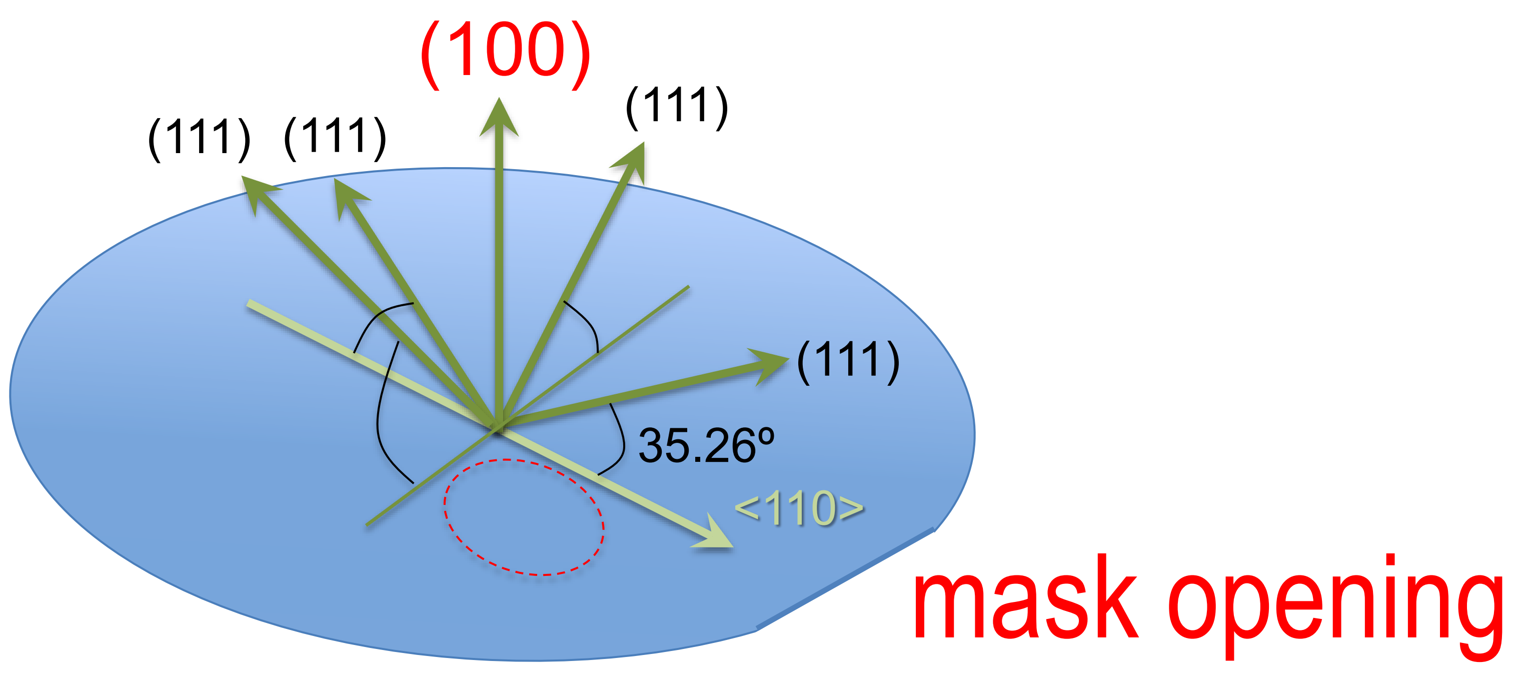
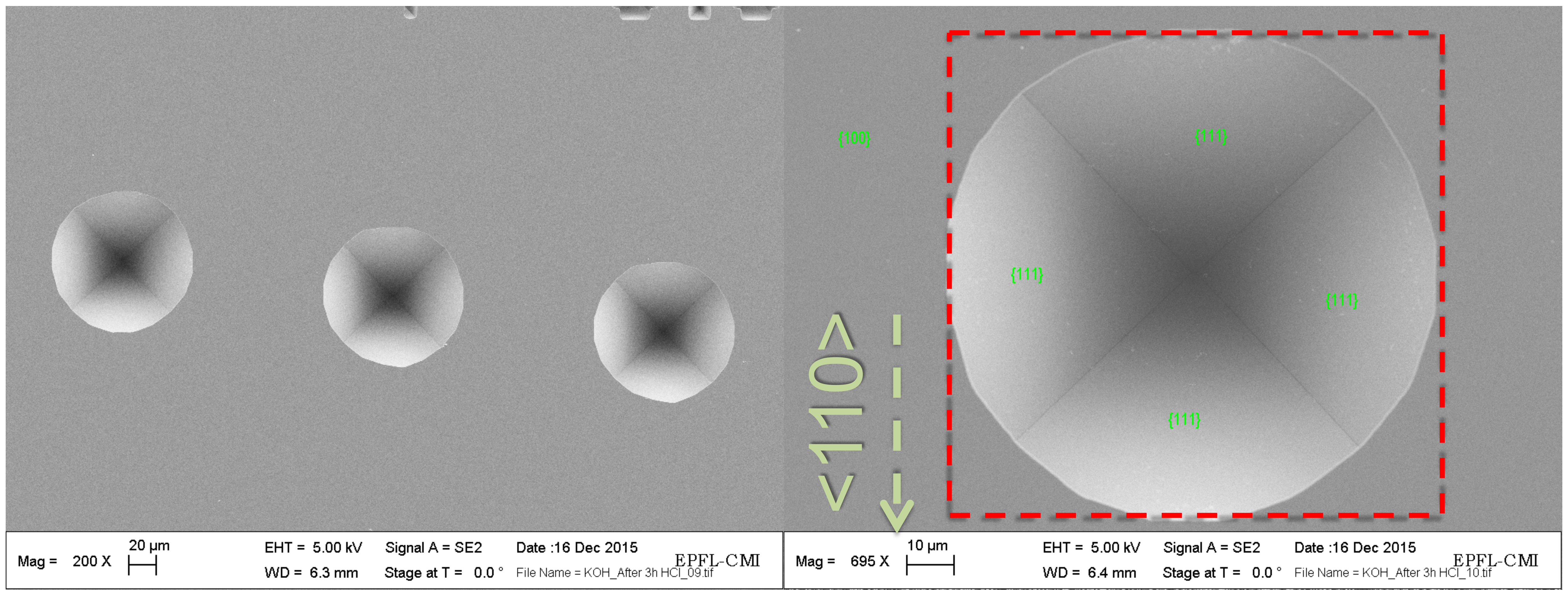
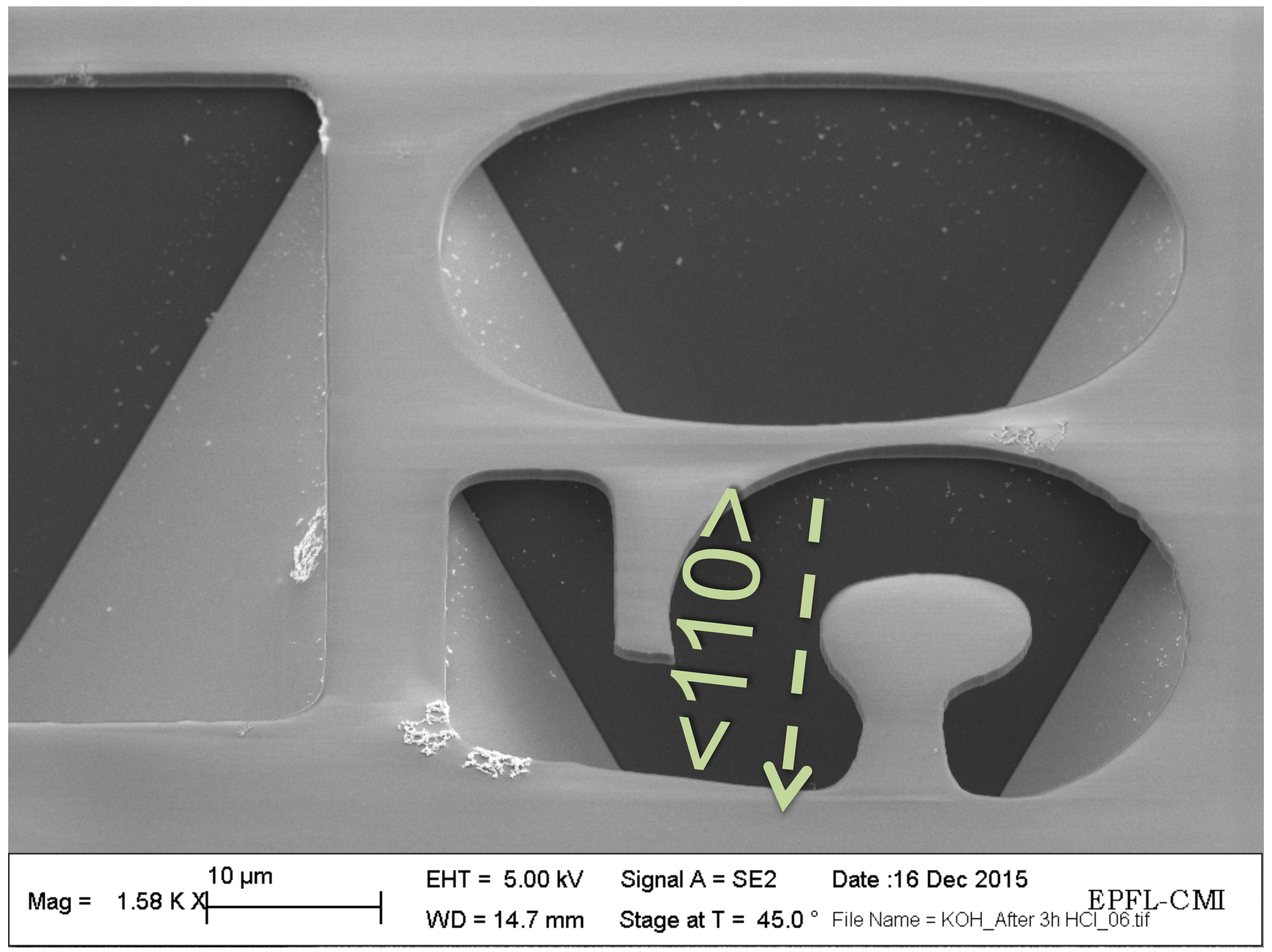


Why is there a pyramidal hole etched?

KOH etching of (100) wafers with arbitrary mask →underetching of the mask and formation of inverted pyramids or 'roofs'





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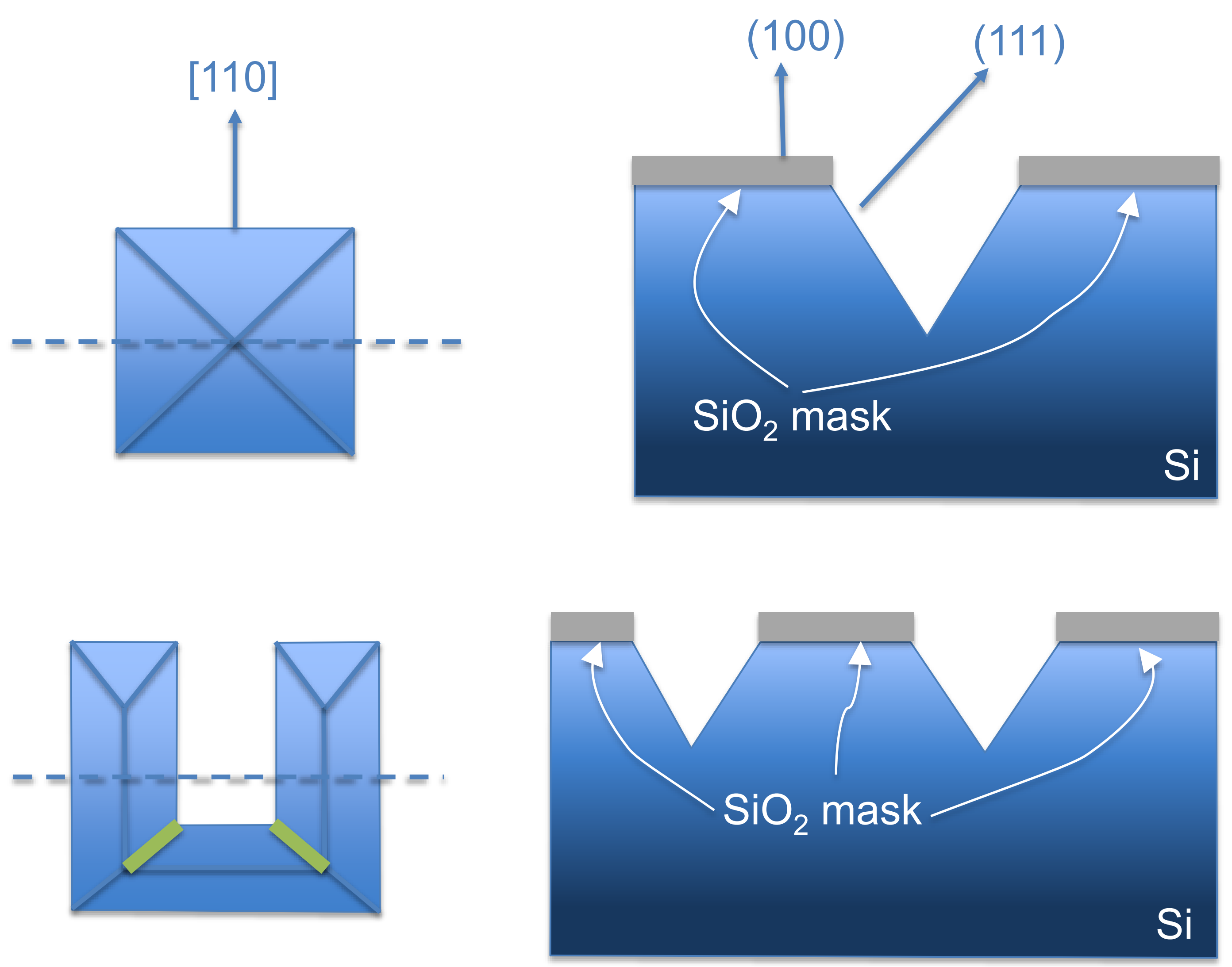
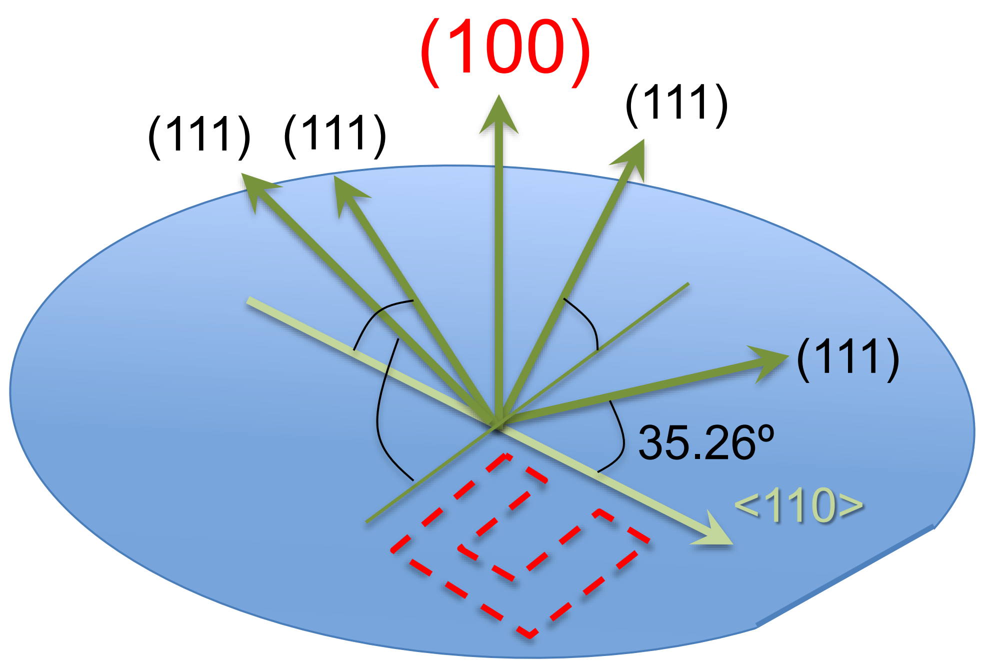


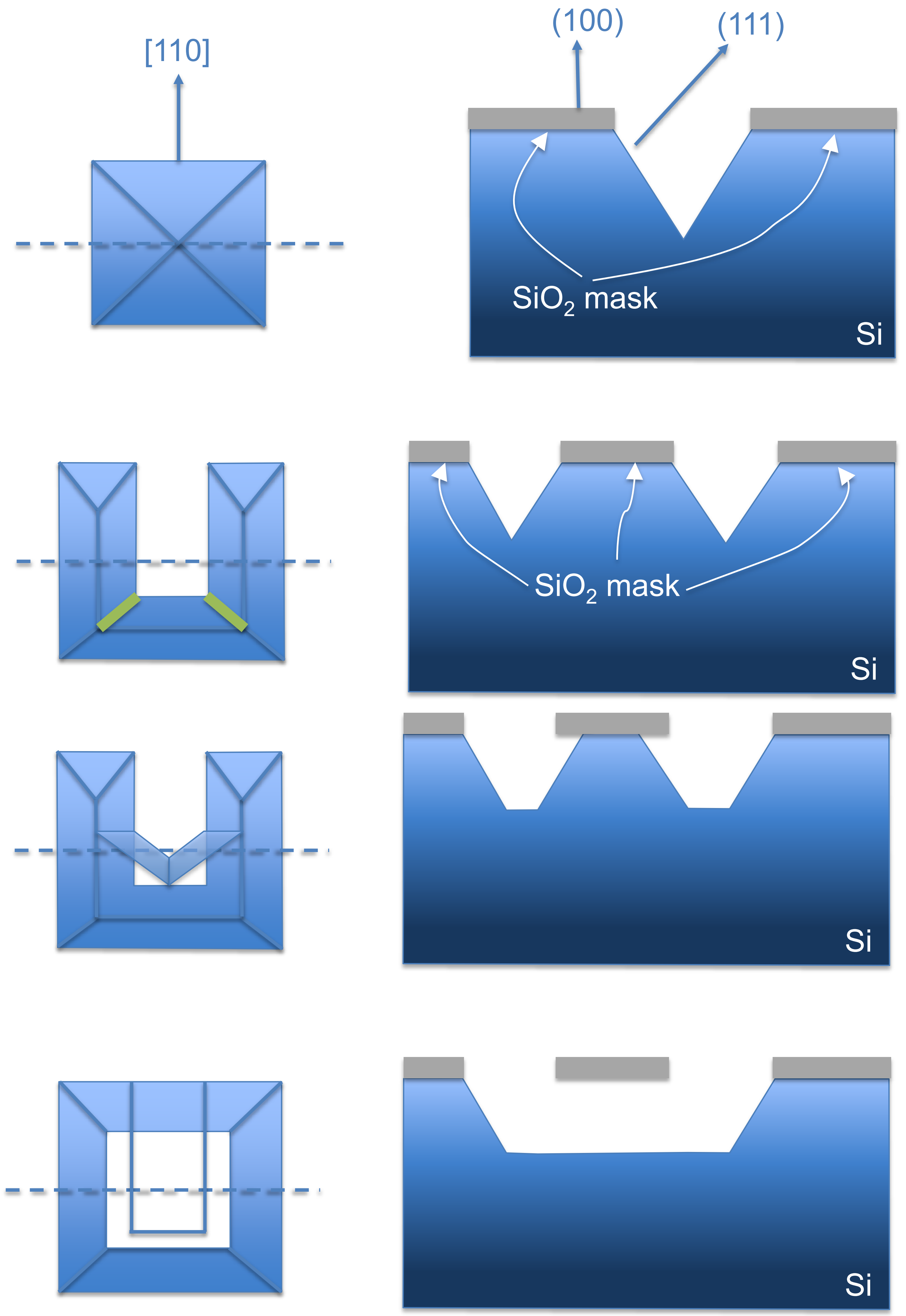
weakly bonded Si atoms

KOH etching of (100) wafer with U-shaped mask

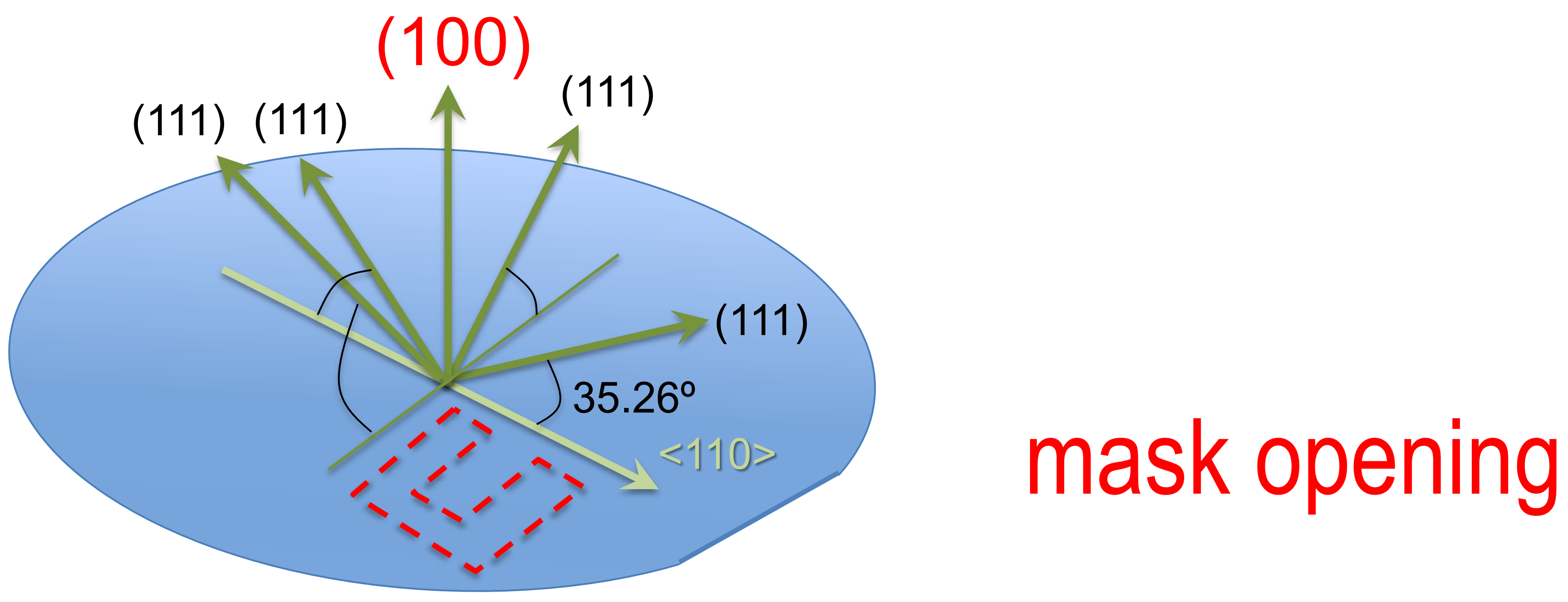


mask opening

Bulk micromachining



KOH etching of (100) wafer with U-shaped mask → underetching of the mask and formation of inverted pyramids or 'roofs' with suspended mask beams



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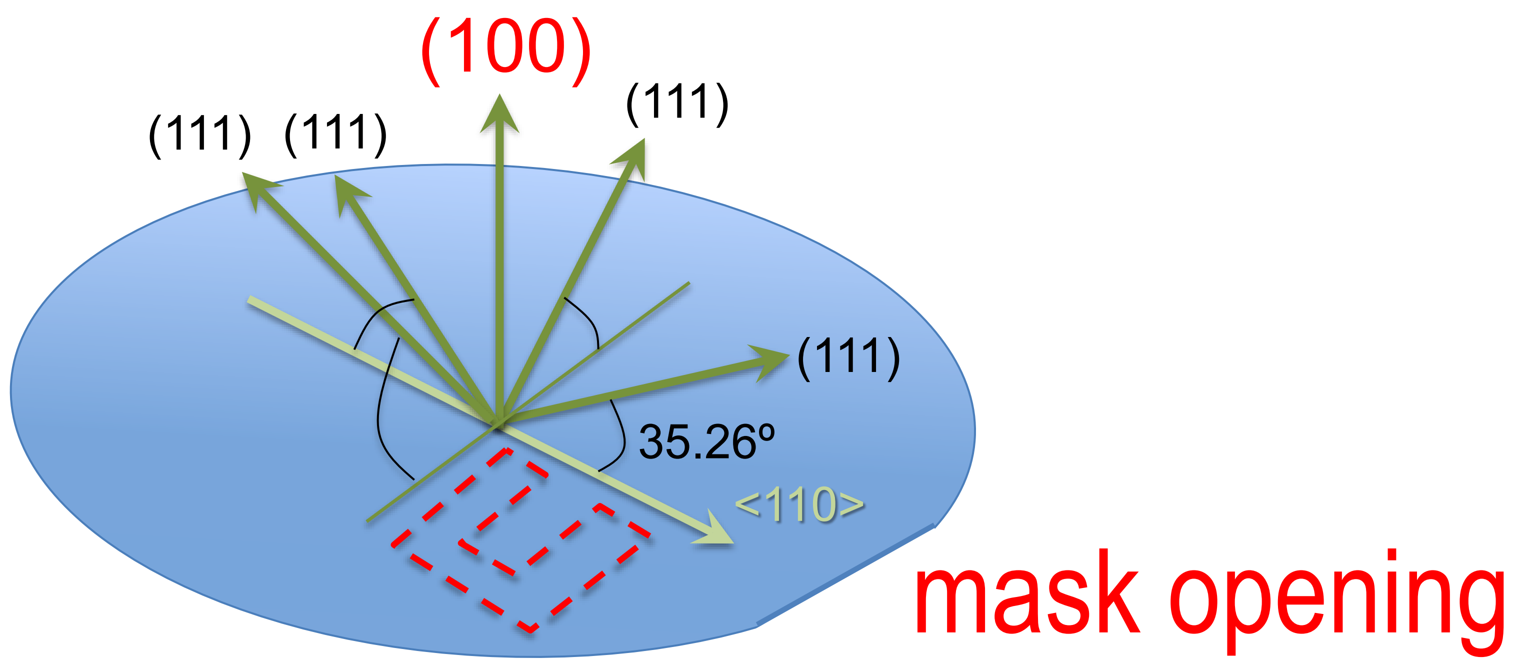
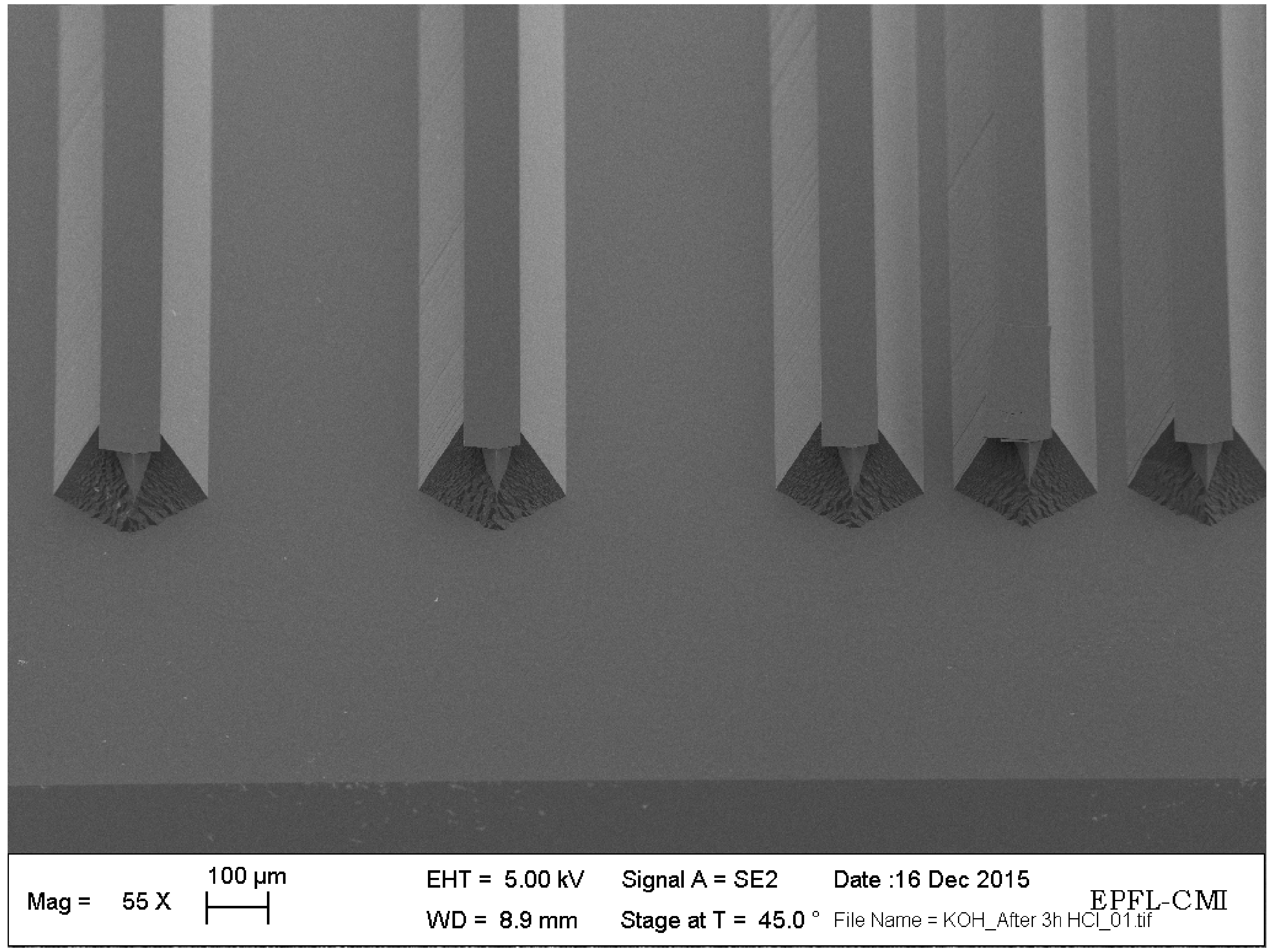
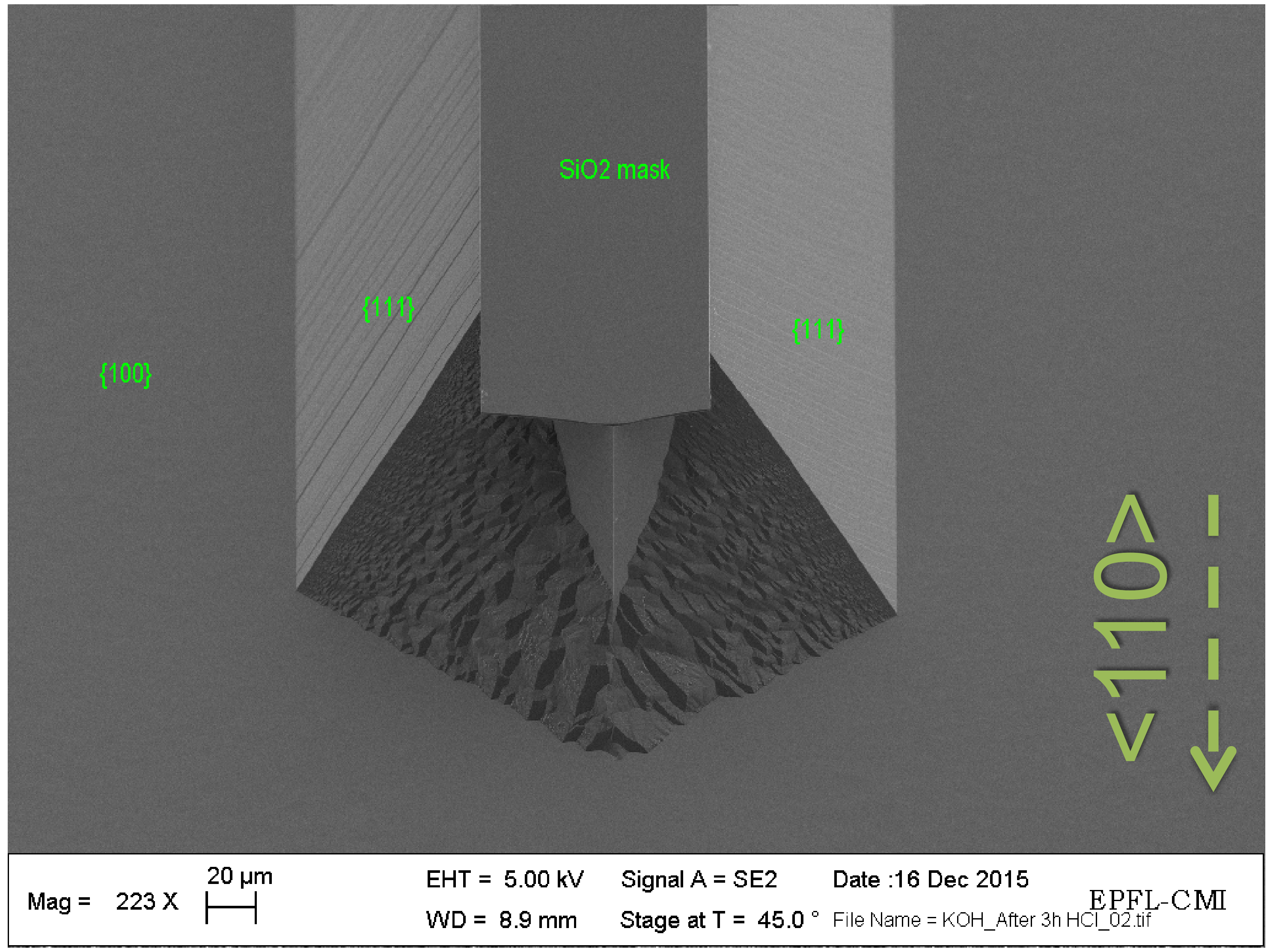
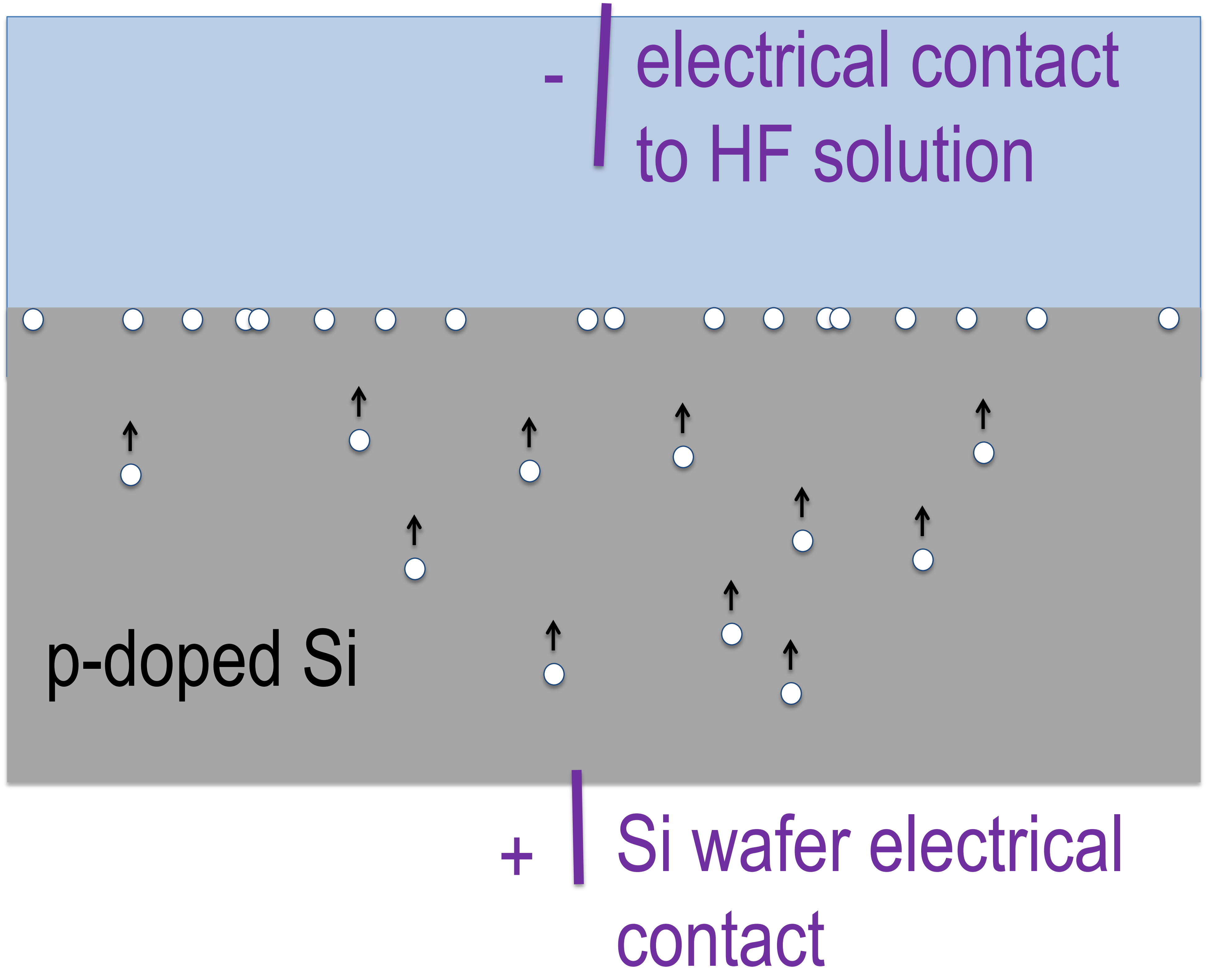


KOH etching of (100) wafer with U-shape type mask →underetching of the mask and formation of suspended mask (SiO_2) beams



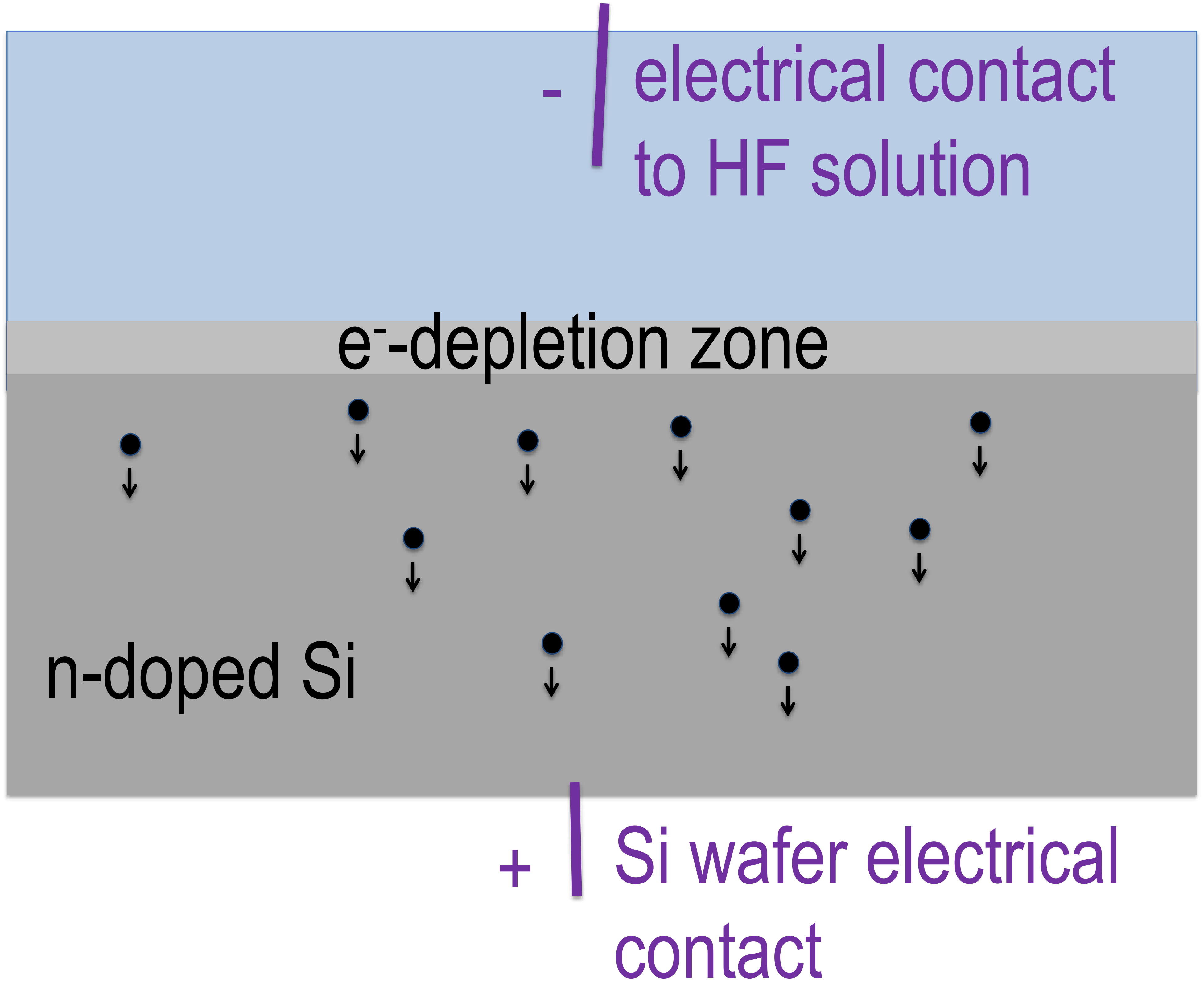


Isotropic etching of p-doped Si with electrical bias



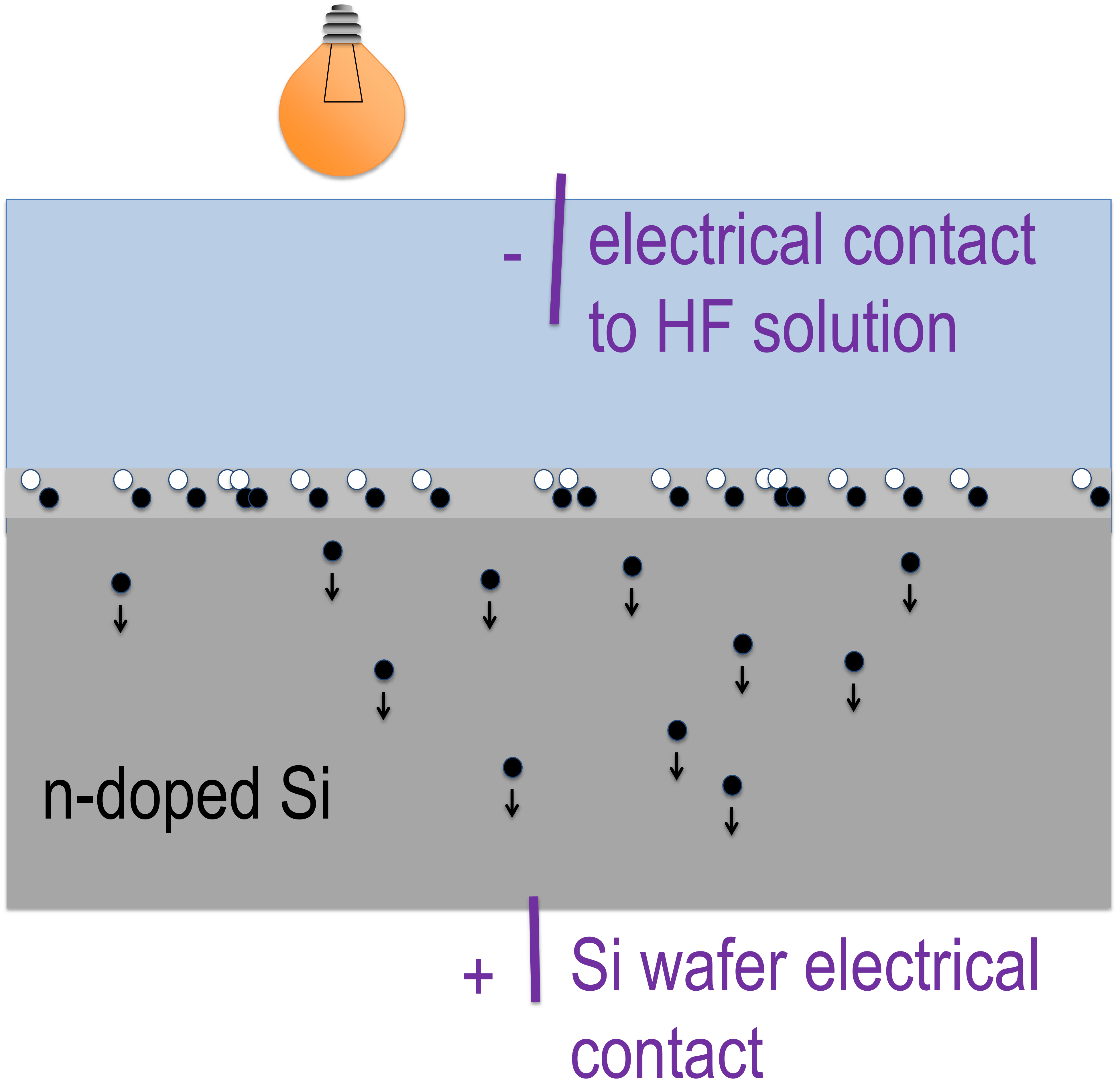
- A high temperature aggressive chemical etching process can be replaced by an electrochemical procedure utilising a milder solution, thus allowing a simple photoresist mask to be employed
- Oxidation can be promoted by a positive voltage bias applied to the p-Si causing an accumulation of holes h^+ in the Si at the Si/electrolyte surface
- No need for HNO_3, 5% HF solution can be used for etching

Situation of n-doped Si with electrical bias



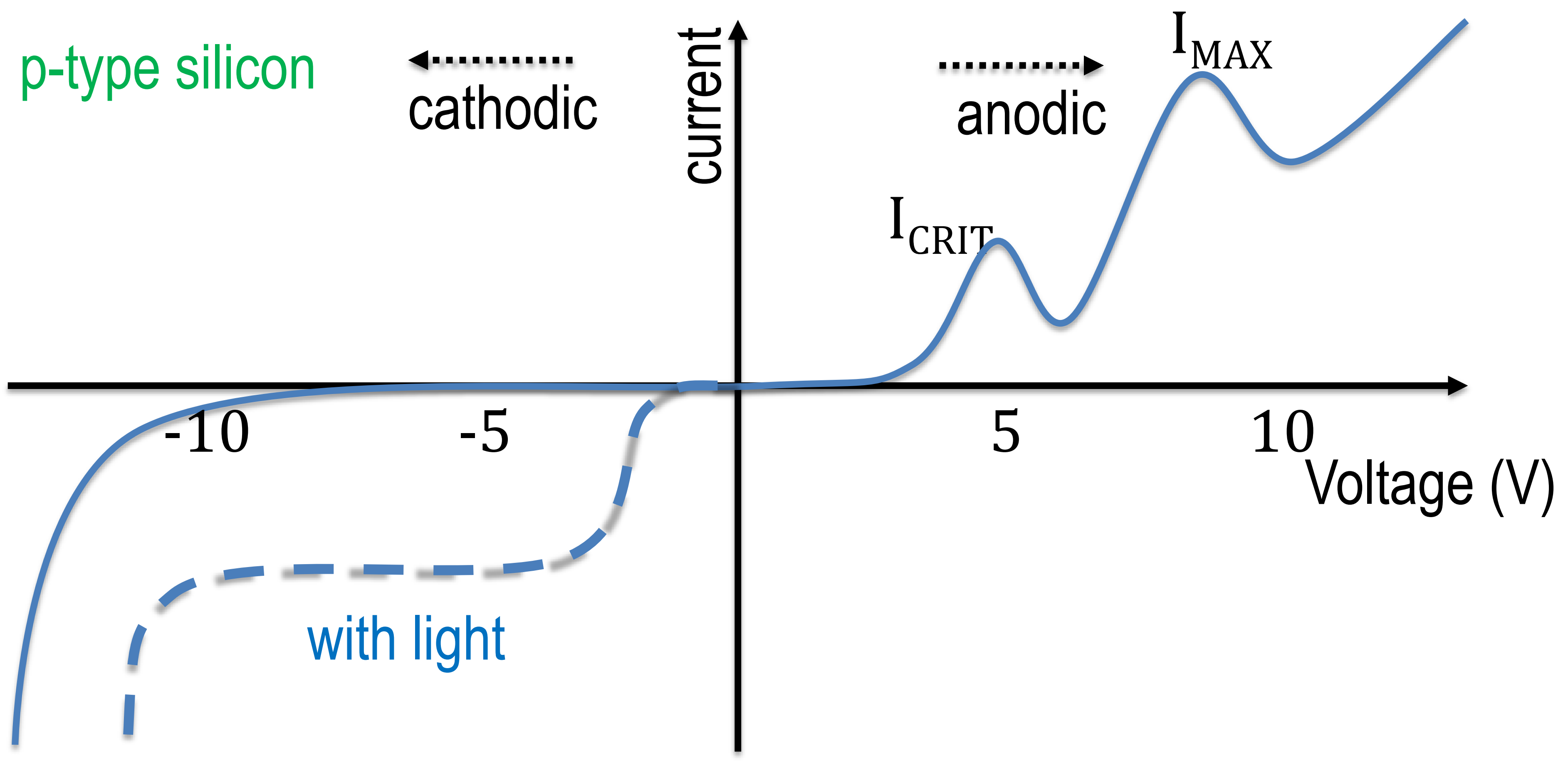
- Applying a positive voltage bias to an n-Si wafer causes a depletion of electrons e^- in the Si at the Si/electrolyte interface
- No etching occurs, except when the voltage is so high that electrical breakdown occurs, transporting h^+ to the interface

Etching n-doped Si with electrical bias and light



- Applying a positive voltage bias to the n-Si causes a depletion of electrons e^- in the Si at the Si/electrolyte surface
- Applying light generates e^- - h^+ pairs in the depletion region
- Electrons e^- are transported to the positive voltage
- Holes h^+ at the surface promote oxidation
- Etching occurs

Current-voltage characteristics



Negative voltage: hydrogen generation

Positive voltage: Si etching

(after Levy-Clement, Electrochem. Acta 37, 877 (1992))

- At i_{MAX} and higher, bright electro-polishing occurs. HF is depleted at the surface and a high concentration of holes builds up at the interface
- Positive voltage: Si etching
- Negative voltage: hydrogen generation
- At i_{CRIT}, there is partial dissolution of Si. This leads to formation of rough and porous Si. Condition: low current densities, i.e. limiting the oxidation of Si due to hole deficiency

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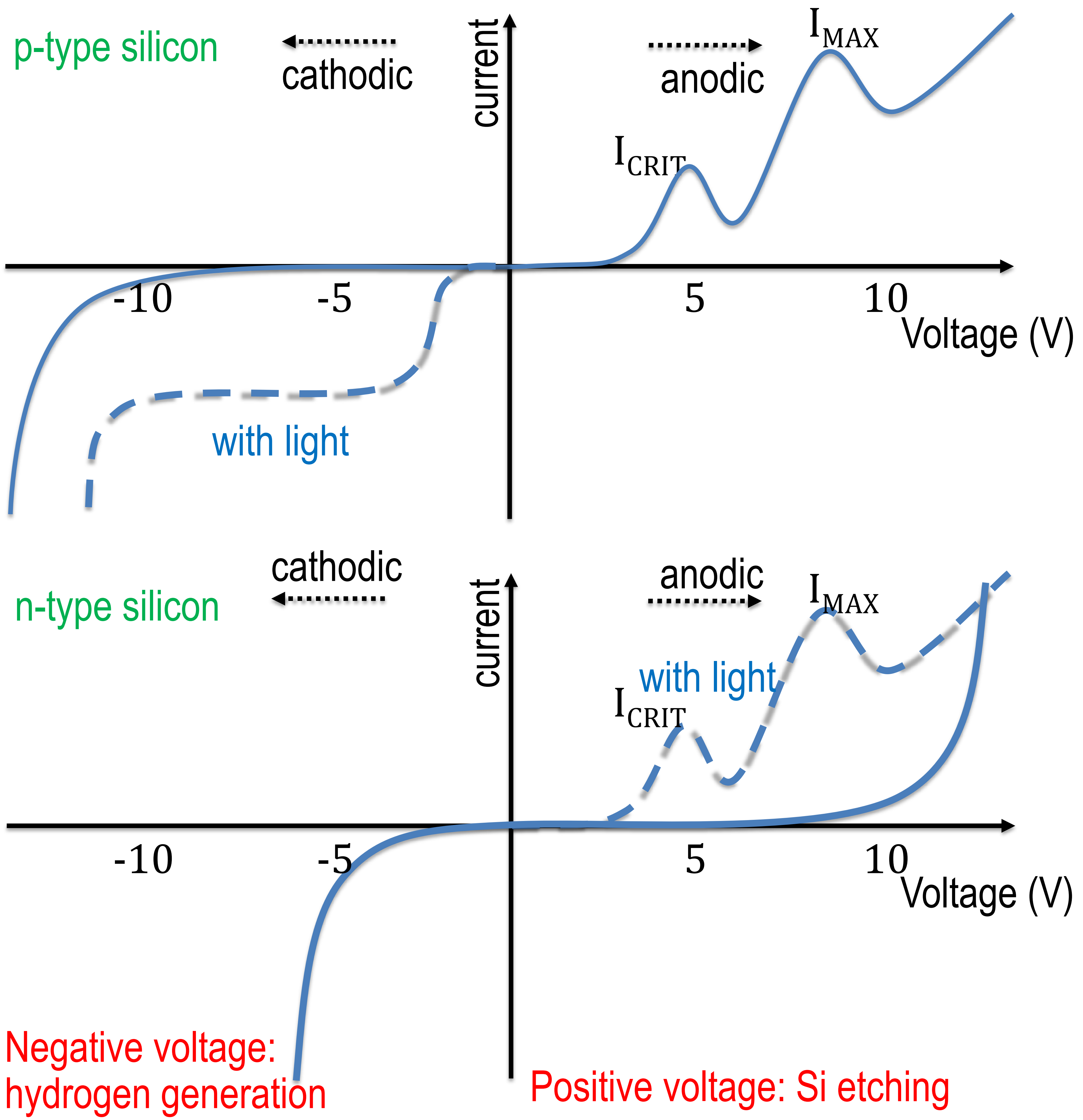

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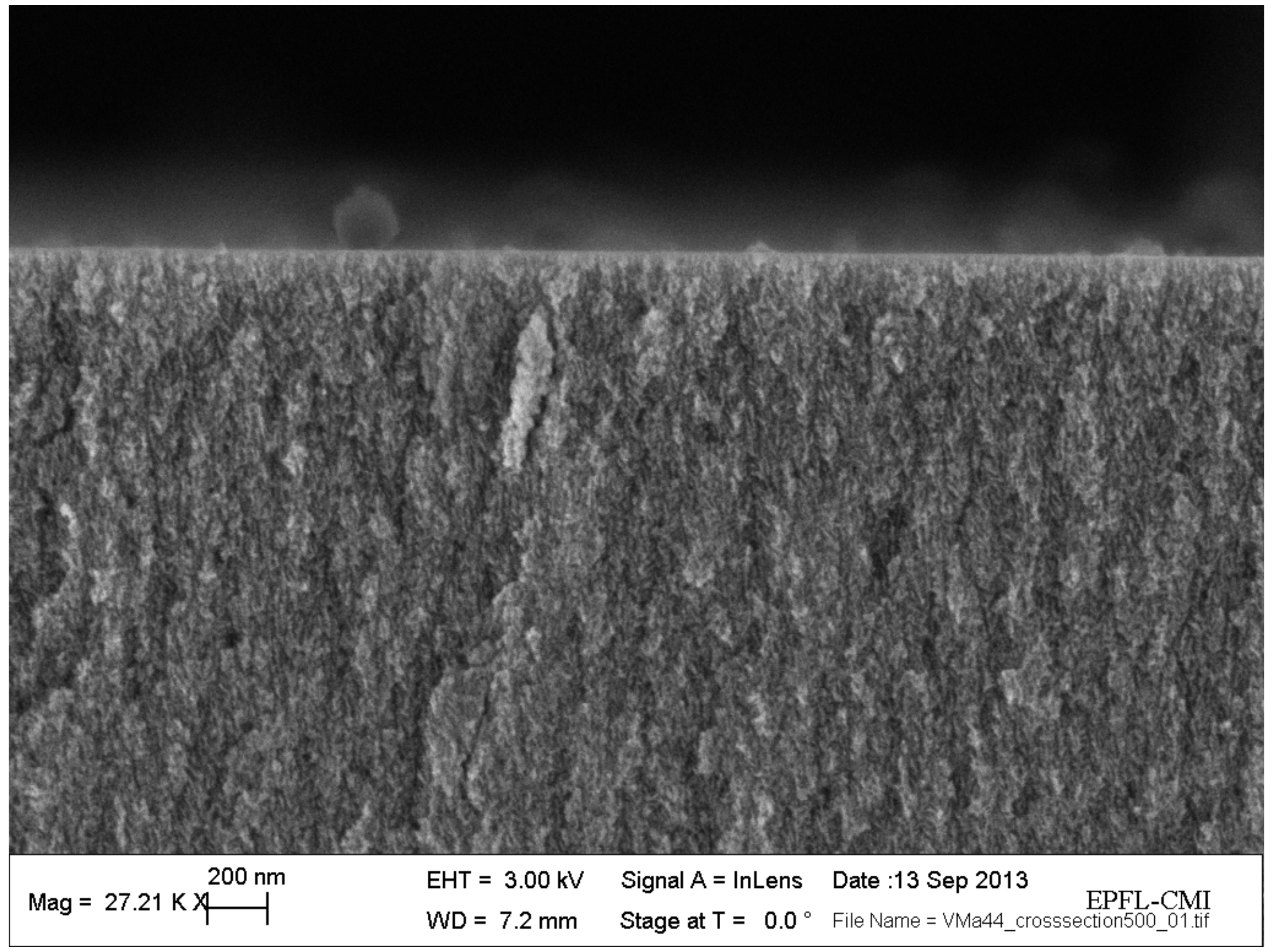
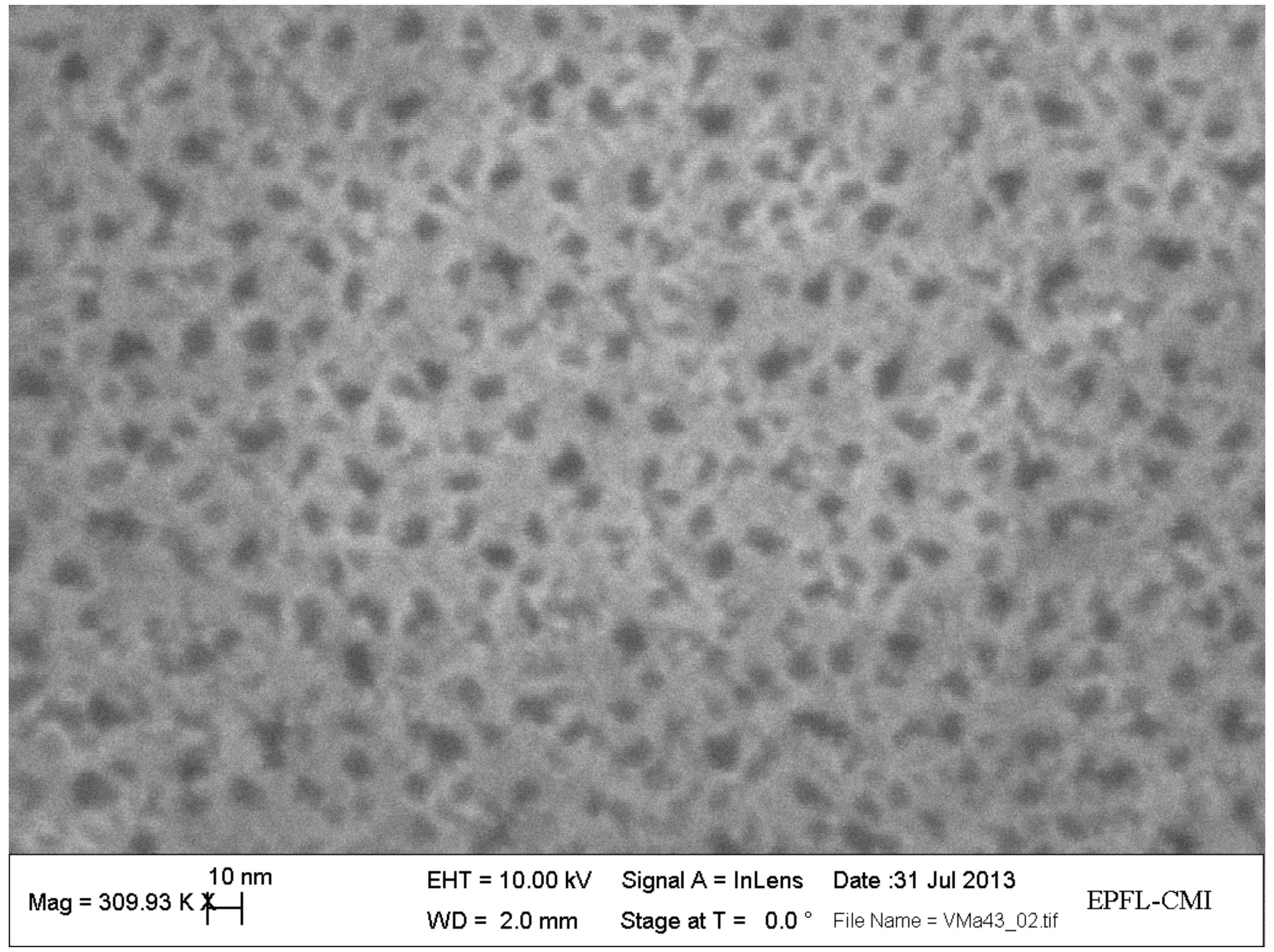
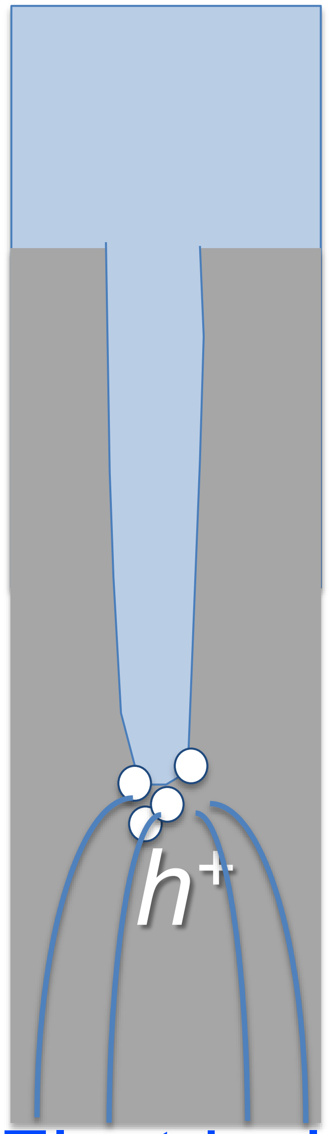
Porous n-type Si







Electrical field lines

- Pore sizes in diameter from 2 nm to 10 μm are possible
- Very high-aspect ratio (250) pores maintained over several mm distance
- For currents below i_{MAX}, a dense network of fine holes forms: microporous Si (pore size 2-20 nm)
- Macropores (size up to 10 μm) have been reported for n-type Si under high anodic voltage(>10 V) and low current density
- Macropore formation is a self-adjusting mechanism with holes h^+ kept on a pore tip by the electrical field