

*Lecture 19, 20:*

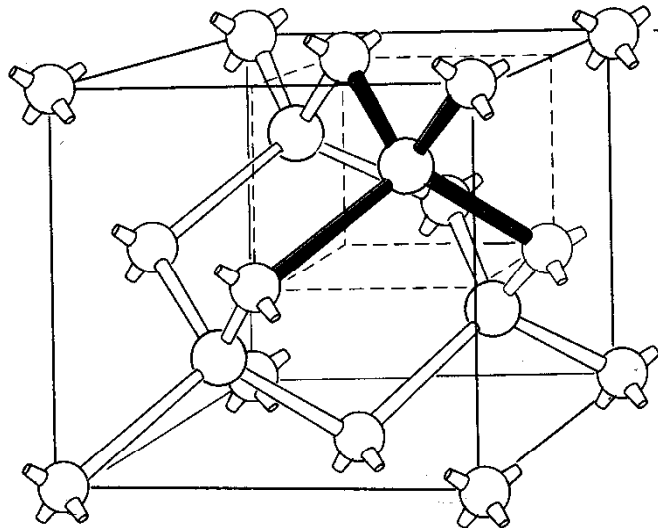
# Silicon Wet Etching

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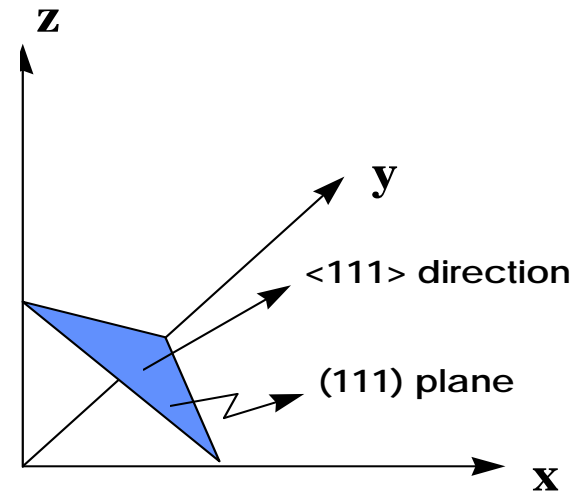
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Seoul National University  
Nano/Micro Systems & Controls Laboratory

# Silicon Crystallography (1)



Si crystalline structure



- Miller indices
  - $(i\ j\ k)$  : a specific crystal plane or face
  - $\{i\ j\ k\}$  : a family of equivalent planes
  - $[i\ j\ k]$  : a specific direction of a unit vector
  - $\langle i\ j\ k \rangle$  : a family of equivalent directions



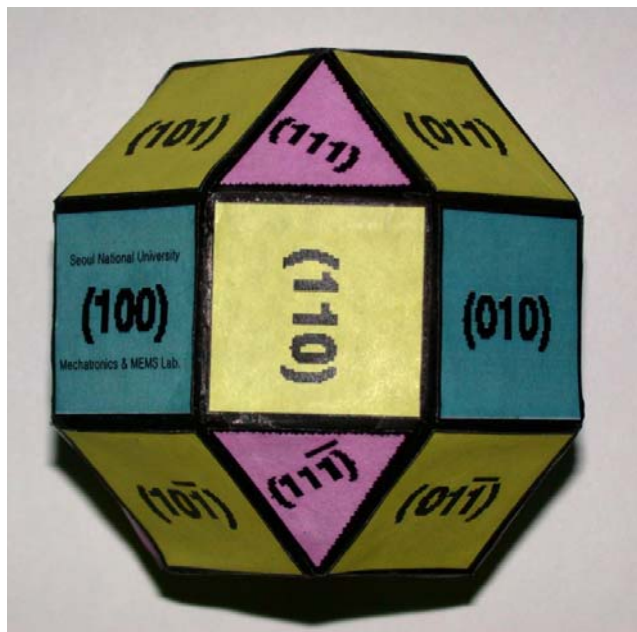
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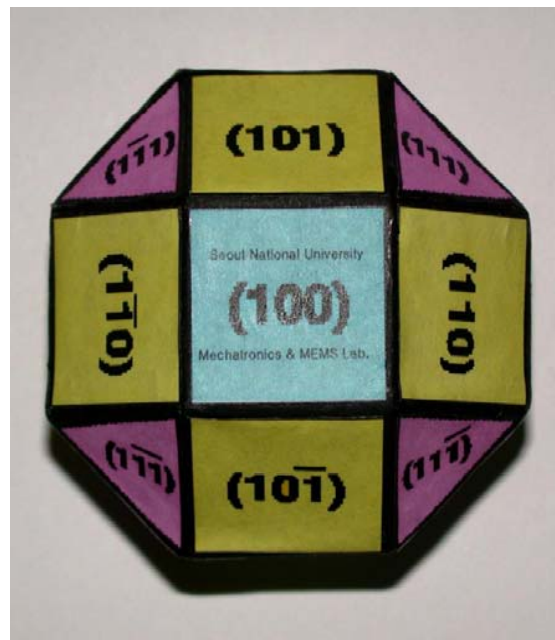
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# Silicon Crystallography (2)

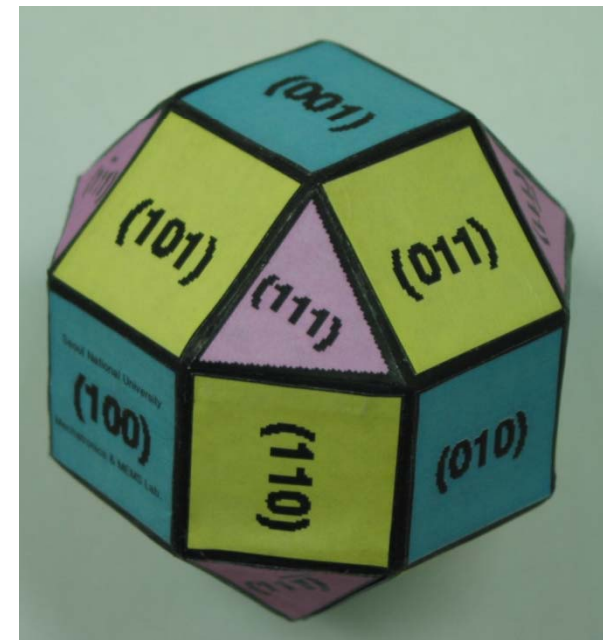
(110) silicon



(100) silicon



(111) silicon

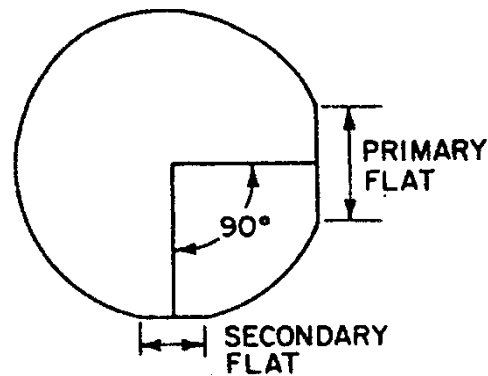
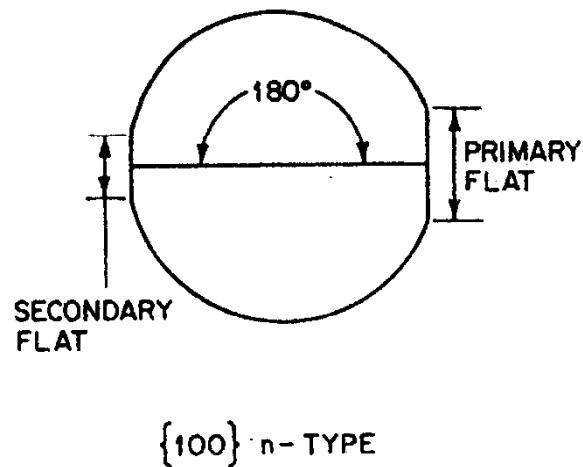
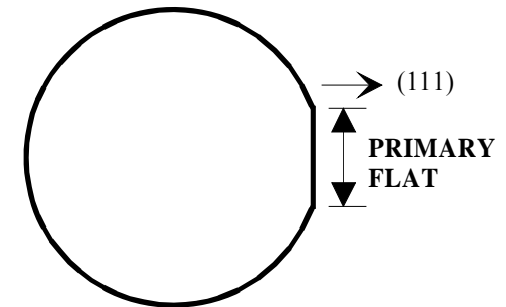
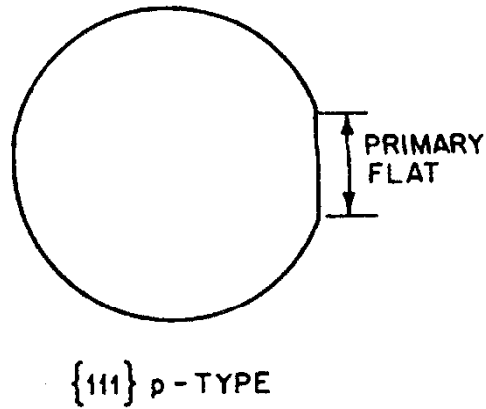
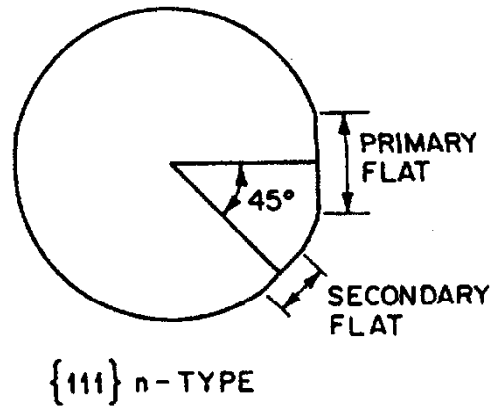


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# Wafer Type



(110) wafer secondary flat is different from company to company



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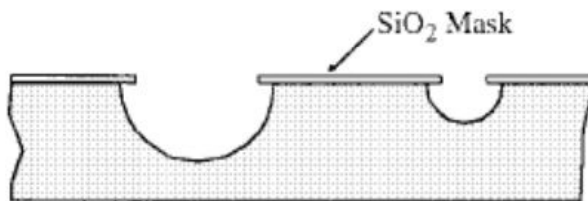
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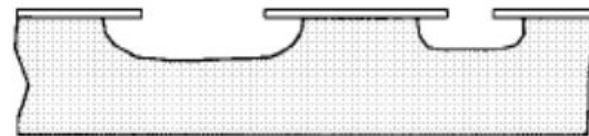
# Isotropic Wet Etching (1)

- Si isotropic etching by HNA
  - HNA: **H**ydrofluoric acid + **N**itric acid + **A**cetic acid
  - Isotropic etchant
  - $\text{Si} + \text{HNO}_3 + 6\text{HF} \rightarrow \text{H}_2\text{SiF}_6 + \text{HNO}_2 + \text{H}_2\text{O} + \text{H}_2$
  - $\text{HNO}_3$ : oxidize silicon
  - HF: F ion forms the soluble compound,  $\text{H}_2\text{SiF}_6$
  - $\text{CH}_3\text{COOH}$ : Prevent dissociation of  $\text{HNO}_3$  into  $\text{NO}_3$  or  $\text{NO}_2$   
→ thereby allowing formation of the species directly responsible for the oxidation of Si:  $\text{N}_2\text{O}_4 \leftrightarrow 2\text{NO}_2$
  - Drawback: Poor selectivity over  $\text{SiO}_2$

ISOTROPIC WET ETCHING: AGITATION



ISOTROPIC WET ETCHING: NO AGITATION



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# Isotropic Wet Etching (2)

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- Electrochemical reaction in HNA etching

- Injection of holes into Si to form  $\text{Si}^{2+}$



- Reaction of hydrated Si to form  $\text{SiO}_2$



- Dissolution of  $\text{SiO}_2$  and formation of water soluble product



Overall reaction is,



Which can be rewritten,

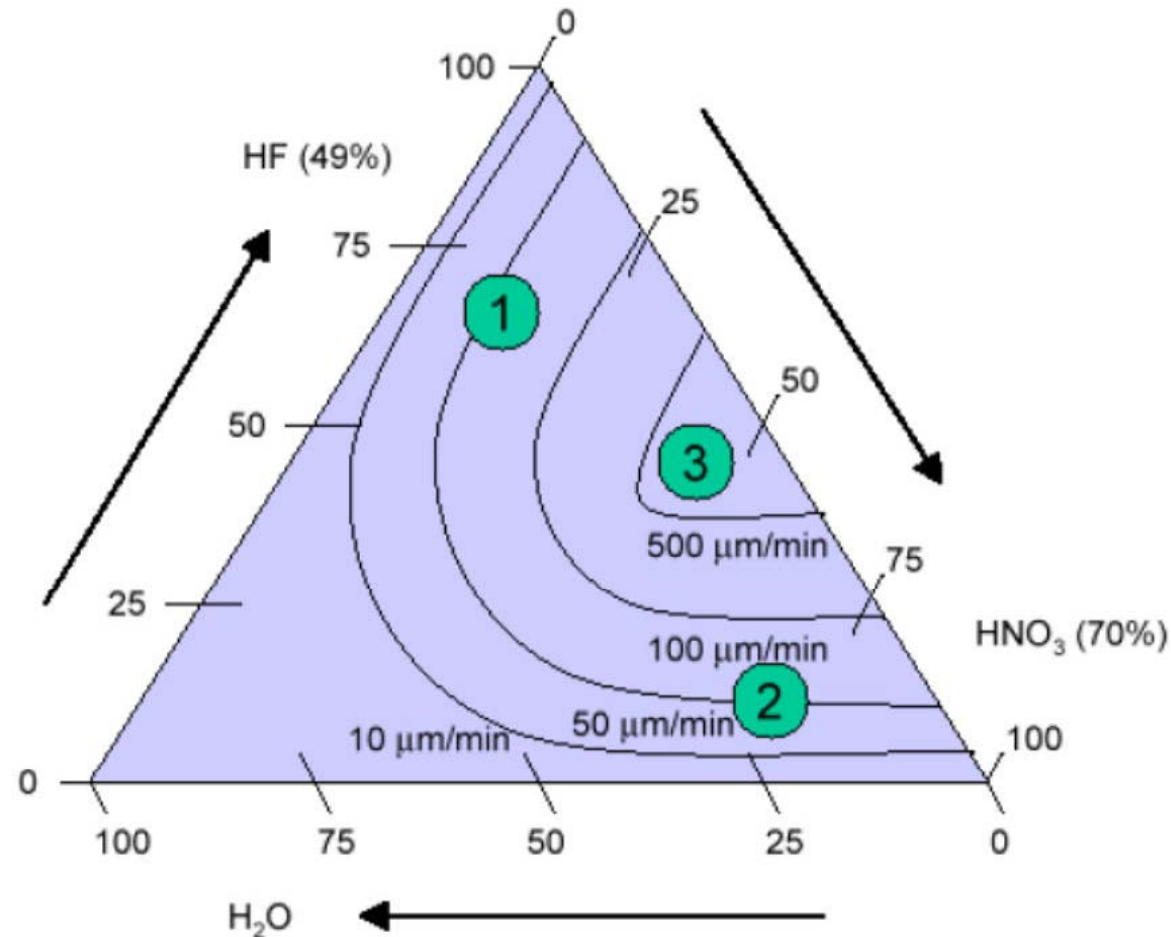


→ Etching is “Charge-transfer-driven process”



# Isotropic Wet Etching (3)

- Isoetch contours



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# Isotropic Wet Etching (4)

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- Region (1)
  - For high HF concentrations, contours are parallel to the lines of constant  $\text{HNO}_3$ , therefore the etch rate is controlled by  $\text{HNO}_3$  in this region
  - Leaves little residual oxide
- Region (2)
  - For high  $\text{HNO}_3$  concentrations contours are parallel to the lines of constant HF, therefore the etch rate is controlled by HF in this region
  - Leaves a residual 300~500 nm of oxide
- Region (3)
  - Initially not very sensitive to the amount of  $\text{H}_2\text{O}$ , then etch rate falls of sharply for 1:1 HF: $\text{HNO}_3$  ratio



# Isotropic Wet Etching (5)

Etchant (Diluent)	Reagent Quantities	Temp. °C	Etch Rate (μm/min)	(100)/(111) Etch Ratio	Dopant Dependence	Masking Films (etch rate)
HF	10 ml				$\leq 10^{17} \text{ cm}^{-3}$ n or p reduces etch rate $\approx 150\times$	
HNO <sub>3</sub>	30 ml	22	0.7 to 3.0	1:1		SiO <sub>2</sub> (30 nm/min)
(water, CH <sub>3</sub> COOH)	80 ml					
HF	25 ml					
HNO <sub>3</sub>	50 ml	22	4	1:1	no dependence	Si <sub>3</sub> N <sub>4</sub>
(water, CH <sub>3</sub> COOH)	25 ml					
HF	9 ml					
HNO <sub>3</sub>	75 ml	22	7	1:1	---	SiO <sub>2</sub> (70 nm/min)
(water, CH <sub>3</sub> COOH)	30 ml					

Table of HNA etchant formulations

Ref. ) Kurt E. Petersen, Proceedings of The IEEE, 70(5), pp. 420-457, 1982



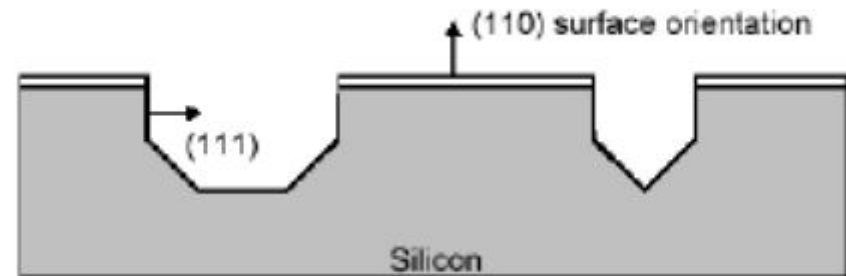
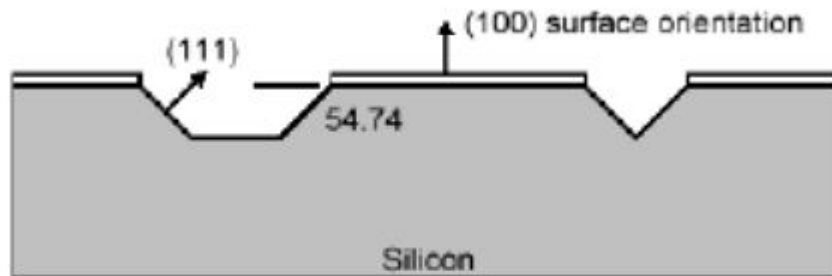
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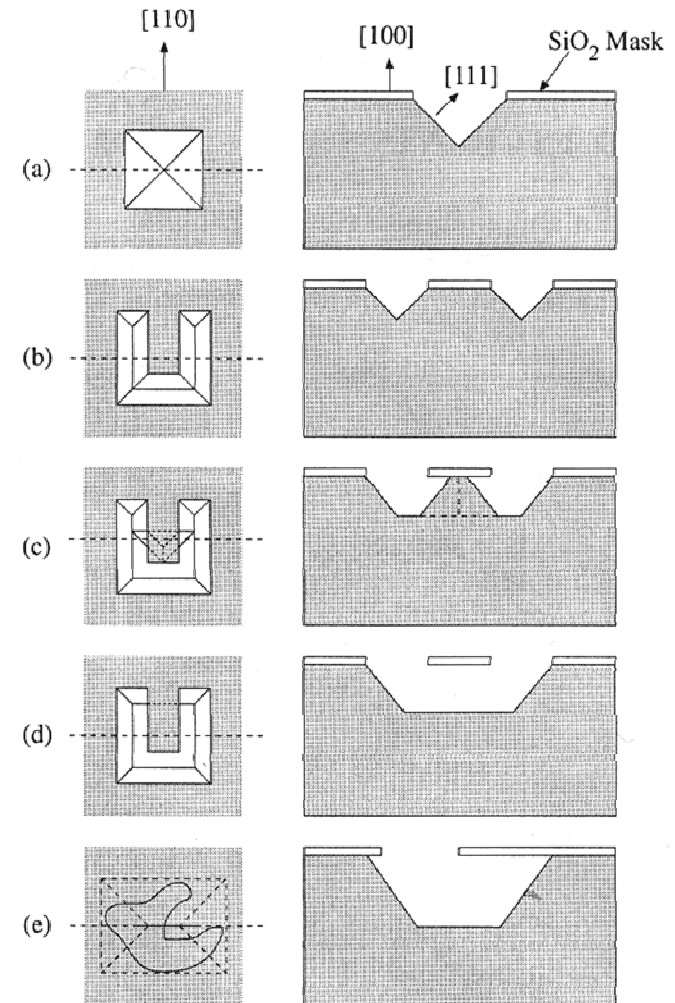
# Anisotropic Wet Etching (1)

- Anisotropic wet etching
  - Anisotropic etchants etch much faster in one direction than in another
    - Exposing the slowest etching crystal planes over time
    - (111) planes have the slowest etch rate
  - Several solutions: Alkaline OH (KOH, NaOH), TMAH, EDP
  - Etching at concave corners on (100), stop at (111) intersections, convex corners are undercut

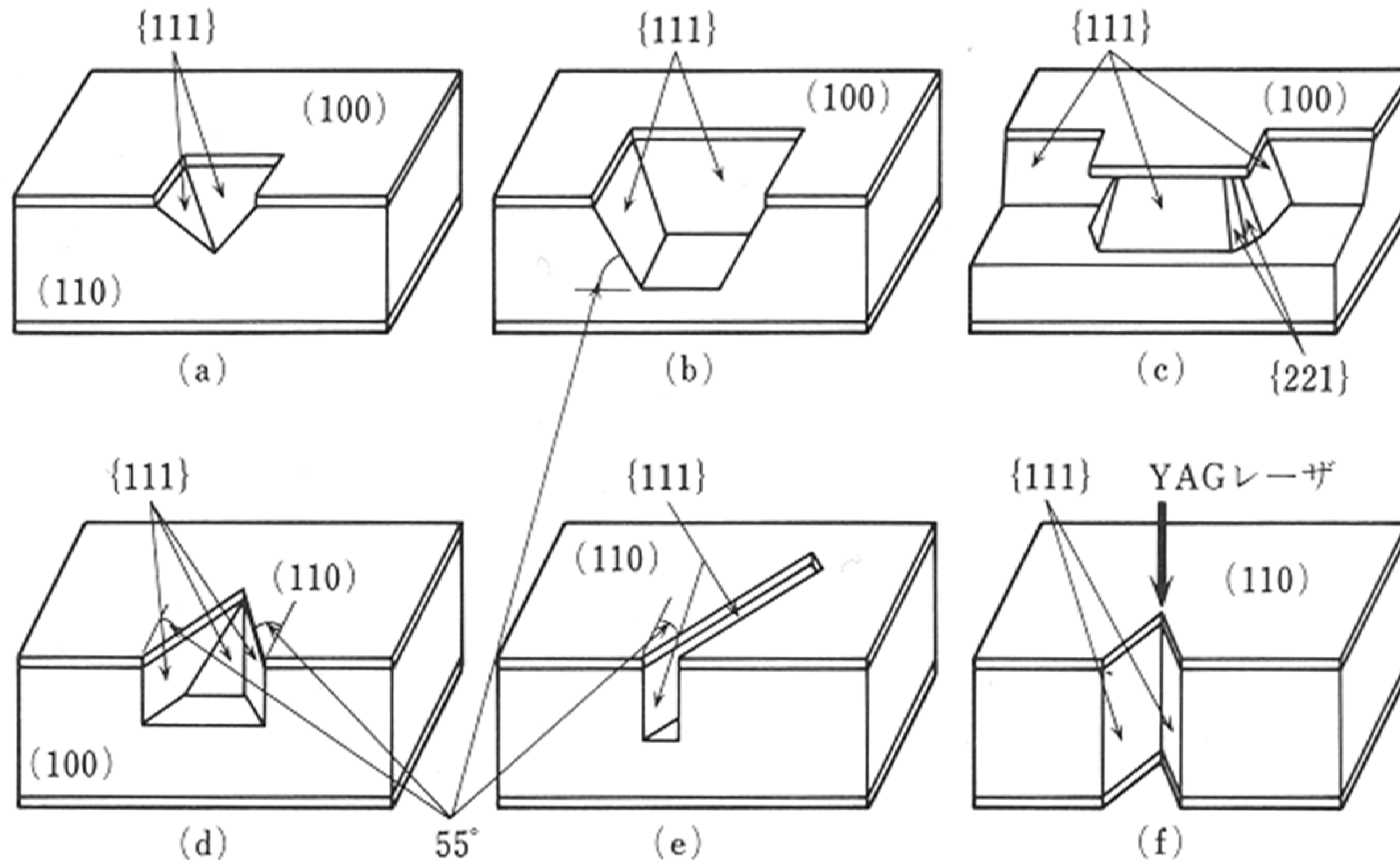


# Anisotropic Wet Etching (2)

- Examples of anisotropic etching
  - typical pyramidal pit bounded by (111) planes, etched into (100) silicon with an anisotropic etch through a square hole in an oxide mask
  - cantilever mask pattern with a slow convex undercut rate
  - the same mask pattern can result in a substantial degree of undercutting using an etchant with a fast convex undercut rate such as EDP
  - further etching of (c) produces a cantilever beam suspended over pit
  - illustration of the fact that anisotropic etch undercutting converges to predictable shapes after a sufficiently long time



# Anisotropic Wet Etching (3)



Silicon anisotropic wet etching of (100) and (110) silicon



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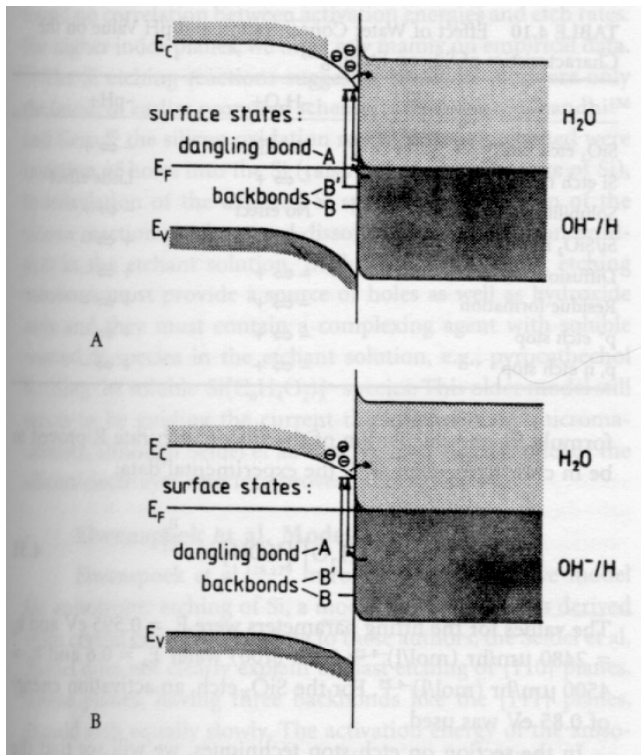
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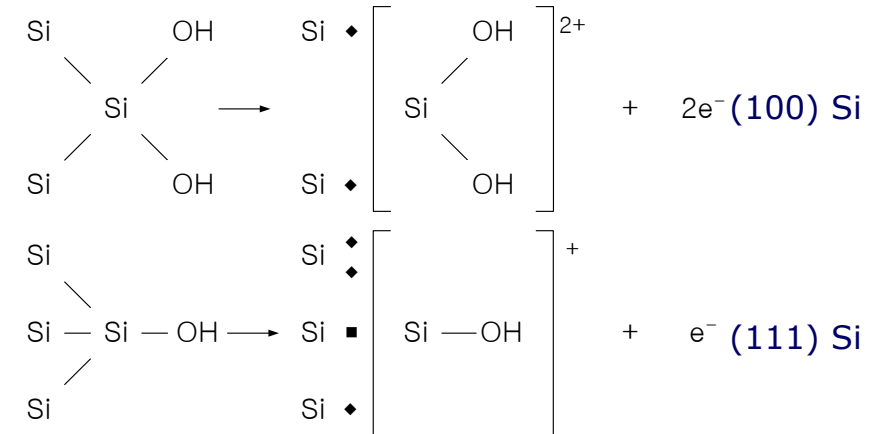
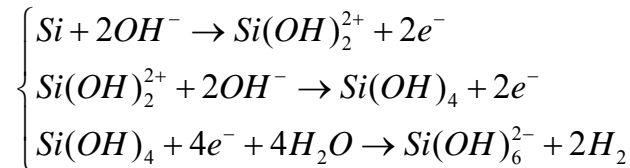
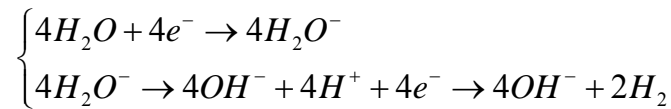


# Anisotropic Wet Etching Mechanism (1)

- H. Seidel et al.
  - Band model of the silicon/electrolyte interface for moderately doped Si



Band model of the Si/electrolyte interface  
(A) p-type Si, (B) n-type Si



Ref.) H. Seidel, et al., J. Electrochem. Soc.,  
vol. 137, no. 11, Nov. 1990



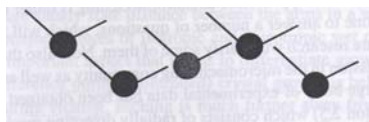
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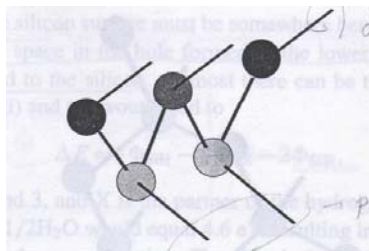
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# Anisotropic Wet Etching Mechanism (2)

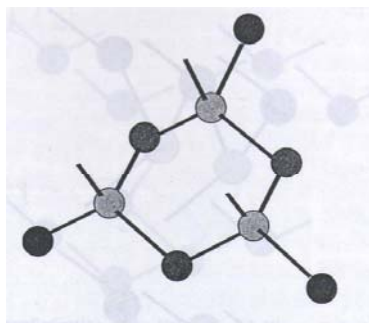
- M. Elwenspoek et al.
  - Explained the etching mechanism by the crystal growth theory
  - {111} plane has slow etch rate ← {111} plane is the smooth face



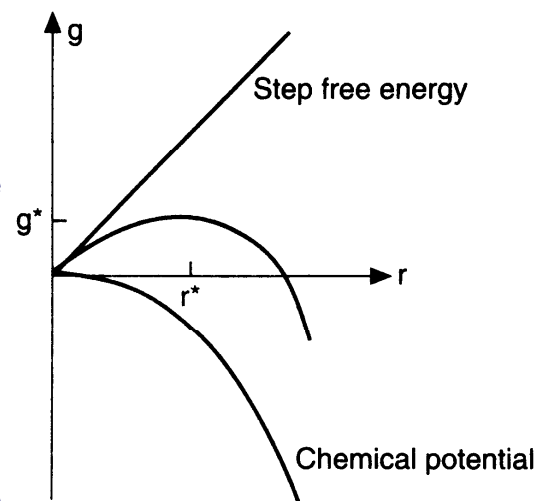
{ 100 } plane



{ 110 } plane



{ 111 } plane



$\Delta\mu$  : the chemical potential difference

$\gamma$  : step free energy

$h$  : the height of the step

$r$  : the radius of the hole or island

$\rho$  : the density of the solid material

$$\Delta G = -\pi r^2 h \rho \Delta\mu + 2\pi r \gamma$$

$$r^* = \frac{\gamma}{h \rho \Delta\mu}$$

$$\Delta G^* = \Delta G(r^*) = \frac{\pi \gamma^2}{h \rho \Delta\mu}$$

Ref.) M. Elwenspoek, and H. V. Jansen, Silicon Micromachining, Cambridge University Press, 1998



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# Si Anisotropic Etchants

	Alkali-OH	EDP(ethylene diamine pyrocatechol)	TMAH (tetramethyl ammonium hydroxide)
Si etch rate $\mu\text{m}/\text{min}$	1 to 2	1 to 30	$\sim 1$
Si roughness	Low	Low	variable <sup>1</sup>
Nitride etch	Low	Low	1 to 10 nm/min
Oxide etch	1 to 10 nm/min	1-80 nm/min	1 nm/min
Al selective	No	No <sup>2</sup>	Yes <sup>3</sup>
Au selective	Yes	Yes	Yes
P++ etch stop ?	Yes	Yes	Yes
Electrochemical stop ?	Yes	Yes	Yes
CMOS compatible ? <sup>4</sup>	No	Yes	Yes
Cost <sup>5</sup>	Low	Moderate	Moderate
Disposal	Easy	Difficult	Moderate
Safety	Moderate	Low	High

1 Varies with wt% TMAH, can be controlled to yield very low roughness.

2 Some formulations do not attack Al, but are not common.

3 With added Si, polysilicic acid or pH control.

4 Defined as 1) allowing wafer to be immersed directly with no special measures and 2) no alkali ions.

5 Includes cost of equipment.



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# Hydroxide Etching of Si

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- Several hydroxides are useful
  - KOH, NaOH, CeOH, RbOH, NH<sub>4</sub>OH, TMAH: (CH<sub>3</sub>)<sub>4</sub>NOH
- Oxidations of silicon by hydroxyls to form a silicate
$$\text{Si} + 2\text{OH}^- + 4\text{h}^+ \rightarrow \text{Si}(\text{OH})_2^{++}$$
- Reduction of wafer
$$2\text{H}_2\text{O} \rightarrow 4\text{OH}^- + 2\text{H}_2 + 4\text{h}^+$$
- Silicate further reacts with hydroxyls to form a water soluble complex
$$\text{Si}(\text{OH})_2^{++} + 4\text{OH}^- \rightarrow \text{SiO}_2(\text{OH})_2^{2-} + 2\text{H}_2\text{O}$$
- Overall redox reaction
$$\text{Si} + 2\text{OH}^- + 4\text{H}_2\text{O} \rightarrow \text{Si}(\text{OH})_2^{++} + 2\text{H}_2 + 4\text{OH}^-$$



# KOH Etching of Si (1)

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- Typical and most used of the hydroxide etches
- Etch rate
  - $\sim 1 \text{ } \mu\text{m/min}$  for (100) Si planes
  - Slow down for boron-doping levels above  $2 \times 10^{19} \text{ cm}^{-3}$
  - $\sim 140 \text{ nm/hr}$  for silicon nitride
  - $\sim 200 \text{ nm/min}$  for oxide
- Anisotropy
$$(111):(110):(100) \approx 1:600:400$$



# KOH Etching of Si (2)

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- Simple hardware
  - Hot plate & stirrer
  - Keep cover or use reflux condenser to keep propanol from evaporating
- Presence of alkali metal (potassium, K) makes this completely incompatible with MOS or CMOS processing
- Comparatively safer and non-toxic



# KOH Etching of Si (3)

- Typical recipe and etch rate of KOH Si etching

Formulation	Temp °C	Etch rate ( $\mu\text{m}/\text{min}$ )	(100)/(111) Etch ratio	Masking films (etch rate)
KOH (44 g) Water, isopropanol (100 ml)	85	1.4	400:1	SiO <sub>2</sub> (1.4 nm/min) Si <sub>3</sub> N <sub>4</sub> (negligible)
KOH (50 g) Water, isopropanol (100 ml)	50	1.0	400:1	SiO <sub>2</sub> (1.4 nm/min) Si <sub>3</sub> N <sub>4</sub> (negligible)



# TMAH Etching of Si (1)

---

- Tetra Methyl Ammonium Hydroxide:  $(\text{CH}_3)_4\text{NOH}$
- Etch rate:  $0.5 \sim 1.5 \text{ } \mu\text{m}/\text{min}$
- Etch rate falls off ten times at  $10^{20} \text{ cm}^{-3}$  boron concentration  
→ B solid solubility in Si:  $2.5 \times 10^{20} \text{ cm}^{-3}$
- Al etch rate  $1 \text{ } \mu\text{m}/\text{min} \rightarrow 1 \text{ nm}/\text{min}$ , when pH 13  $\rightarrow$  pH 12 (for 22 wt% TMAH)
- MOS/CMOS compatible
  - No alkali metals: Li, Na, K, ...
  - Used in positive photoresist developers which do not use choline.
  - Does not significantly etch  $\text{SiO}_2$  or Al! (Bond wire safe!)
- Anisotropy:  $(111):(100) \approx 1:10$  to  $1:35$





# TMAH Etching of Si (2)

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- Hydroxide etches are generally safe and predictable, but they usually involve an alkali metal which makes them incompatible with MOS or CMOS processing.
- Ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) is one hydroxide which is free of alkali metal, but it is really ammonia which is dissolved into water. Heating to  $90^\circ \text{C}$  for etching will rapidly evaporate the ammonia from solution.
- Ballasting the ammonium hydroxide with a less volatile organic solves the problem:
  - Tetramethyl ammonium hydroxide:  $(\text{CH}_3)_4\text{NOH}$
  - Tetraethyl ammonium hydroxide:  $(\text{C}_2\text{H}_5)_4\text{NOH}$



# TMAH Etching of Si (3)

- Selectivity of TMAH etchants

Selectivity of TMAH Etchants for Various Dielectrics versus (100) Silicon			
Dielectric	Selectivity 4 wt% TMAH, 80°C	Selectivity (Si-doped, 13.5g/l), 4 wt% TMAH, 80°C	Selectivity 20 wt% TMAH, 95°C
Thermal Silicon Dioxide	$5.3 \times 10^3$	$34.7 \times 10^3$	$5.2 \times 10^3$
Low-Temperature Oxide (LTO)	$1.3 \times 10^3$	$4.2 \times 10^3$	$2.8 \times 10^3$
PECVD Oxide	$1.4 \times 10^3$	$4.3 \times 10^3$	No value given
LPCVD Silicon Nitride	$24.4 \times 10^3$	$49.3 \times 10^3$	$38 \times 10^3$
PECVD Silicon Nitride	$9.2 \times 10^3$	$18.5 \times 10^3$	$3.6 \times 10^3$



# Ammonium Hydroxide Wet Etching

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- $\text{NH}_4\text{OH}$  (ammonium hydroxide)
- CMOS compatibility
- Several recipes
  - 9.7 wt%  $\text{NH}_4\text{OH}$  in  $\text{H}_2\text{O}$ 
    - (110) silicon etch rate: 0.11um/min at 85 ~ 92 °C
  - 1~18 wt%  $\text{NH}_4\text{OH}$  at 75 °C
    - (100) max. etch rate: 30 um/h
    - Rough surface
- Disadvantage
  - Slow etch rate, hillock formation
  - Rapid evaporative losses of ammonia gas (noxious) when heated



# EDP Etching of Si (1)

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- Ethylene Diamine Pyrocatechol
- Also known as Ethylene diamine-Pyrocatechol-Water (EPW)
- EDP etching is readily masked by  $\text{SiO}_2$ ,  $\text{Si}_3\text{N}_4$ , Au, Cr, Ag, Cu, and Ta  
→ But EDP can etch Al!
- Anisotropy: (111):(100)  $\approx$  1:35
- EDP is very corrosive, very carcinogenic, and never allowed near mainstream electronic microfabrication.
- 50 times slowing of etch rate for  $> 7 \times 10^{19} \text{ cm}^{-3}$  boron doping



# EDP Etching of Si (2)

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- Typical formulation

- 1 L ethylene diamine,  $\text{NH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_2$
- 160 g pyrocatechol,  $\text{C}_6\text{H}_4(\text{OH})_2$
- 6 g pyrazine,  $\text{C}_4\text{H}_4\text{N}_2$
- 133 mL  $\text{H}_2\text{O}$

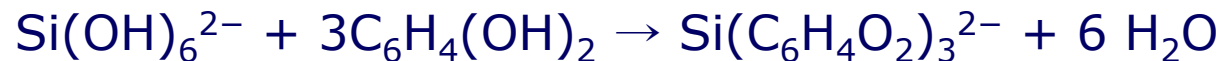
- Ionization of ethylene diamine



- Oxidation of Si and reduction of water



- Chelation of hydrous silica



# EDP Etching of Si (3)

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- Requires reflux condenser to keep volatile ingredients from evaporating.
- Completely incompatible with MOS or CMOS processing!
  - It must be used in a fume collecting bench by itself.
  - It will rust any metal in the nearby vicinity.
  - It leaves brown stains on surfaces that are difficult to remove.
- EDP has a faster etch rate on convex corners than other anisotropic etches
  - It is generally preferred for undercutting cantilevers.
  - It tends to leave a smoother finish than other etches, since faster etching of convex corners produces a polishing action.



# EDP Etching of Si (4)

- Typical recipe and etch rate of KOH Si etching

Formulation	Temp °C	Etch Rate ( $\mu\text{m}/\text{min}$ )	(100)/(111) Etch Ratio	Masking Films (etch rate)
Ethylene diamine (759ml) Pyrocatechol (120g) Water (100ml)	115	0.75	35:1	SiO <sub>2</sub> (0.2 nm/min) Si <sub>3</sub> N <sub>4</sub> (0.1 nm/min) Au, Cr, Ag, Cu, Ta (negligible)
Ethylene diamine (759ml) Pyrocatechol (120g) Water (240ml)	115	1.25	35:1	As above



# Hydrazine Etching of Si

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- Hydrazine ( $\text{N}_2\text{H}_4$ ) + water mixtures
- Anisotropic silicon etchants
- 100 ml  $\text{N}_2\text{H}_4$  in 100 ml water at 100 °C: etch rate 2  $\mu\text{m}/\text{min}$ , no doping dependence, masked with silicon dioxide or aluminum
  - Heavily antimony doped wafer at 70 ~ 120 °C: 0.8 ~ 2  $\mu\text{m}/\text{min}$
  - Moderately doped samples at 70 ~ 120 °C : 1.5 ~ 3.3  $\mu\text{m}/\text{min}$
- Hydrazine is very dangerous
  - A very powerful reducing agent (used for rocket fuel)
  - Flammable liquid
  - Hypergolic:  $\text{N}_2\text{H}_4 + 2\text{H}_2\text{O}_2 \rightarrow \text{N}_2 + 4\text{H}_2\text{O}$  (explosively)
  - Pyrophoric:  $\text{N}_2\text{H}_4 + \text{O}_2 \rightarrow \text{N}_2 + 4\text{H}_2\text{O}$  (explosively)
  - Flash point: 52 °C in air.





# Amine Gallate Etching of Si

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- Much safer than EDP
- Typical recipe
  - 100 g gallic acid
  - 305 mL ethanolamine
  - 140 mL H<sub>2</sub>O
  - 1.3 g pyrazine
  - 0.26 mL FC-129 surfactant
- Anisotropy: (111):(100)  $\approx$  1:50 to 1:100
- Etch rate:  $\sim$ 1.7  $\mu\text{m}/\text{min}$  at 118° C



# Silicon Wet Etchants (1)

Comparison of Example Silicon Etchants							
	HNA (HF+HNO <sub>3</sub> +Acetic Acid)	Alkali-OH	EDP (ethylene diamine pyrochat- echol)	TMAH (tetramethyl- ammonium hydroxide)	XeF <sub>2</sub>	SF <sub>6</sub> Plasma	DRIE (Deep Reactive Ion Etch)
Etch Type	wet	wet	wet	wet	dry <sup>1</sup>	dry	dry
Anisotropic?	no	yes	yes	yes	no	varies	yes
Availability	common	common	moderate	moderate	limited	common	limited
Si Etch Rate μm/min	1 to 3	1 to 2	1 to 30	≈ 1	1 to 3	≈ 1	> 1
Si Roughness	low	low	low	variable <sup>2</sup>	high <sup>3</sup>	variable	low
Nitride Etch	low	low	low	1 to 10 nm/min	?	low	low
Oxide Etch	10 to 30 nm/min	1 to 10 nm/min	1 to 80 nm/min	≈ 1 nm/min	low	low	low
Al Selective	no	no	no <sup>4</sup>	yes <sup>5</sup>	yes	yes	yes
Au Selective	likely	yes	yes	yes	yes	yes	yes
p++ Etch Stop?	no (n slows)	yes	yes	yes	no	no (some dopant effects)	no



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# Silicon Wet Etchants (2)

Comparison of Example Silicon Etchants							
	HNA (HF+HNO <sub>3</sub> +Acetic Acid)	Alkali-OH	EDP (ethylene diamine pyrochat- echol)	TMAH (tetramethyl- ammonium hydroxide)	XeF <sub>2</sub>	SF <sub>6</sub> Plasma	DRIE (Deep Reactive Ion Etch)
Electrochemical Stop?	?	yes	yes	yes	no	no	no
CMOS Compatible? <sup>6</sup>	no	no	yes	yes	yes	yes	yes
Cost <sup>7</sup>	low	low	moderate	moderate	moderate	high	high
Disposal	low	easy	difficult	moderate	N/A	N/A	N/A
Safety	moderate	moderate	low	high	moderate?	high	high

Ref. ) Kurt E. Petersen, Proceedings of The IEEE, 70(5), pp. 420-457, 1982



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# Boron Etch Stop (1)

- Boron etch stop
  - 20 times slowing of etch rate for  $> 10^{20} \text{ cm}^{-3}$  boron doping in KOH
  - 50 times slowing of etch rate for  $> 7 \times 10^{19} \text{ cm}^{-3}$  boron doping in EDP
  - Tensile stress (Boron atoms are smaller than silicon)
  - The extremely high boron concentrations are not compatible with standard CMOS or bipolar techniques

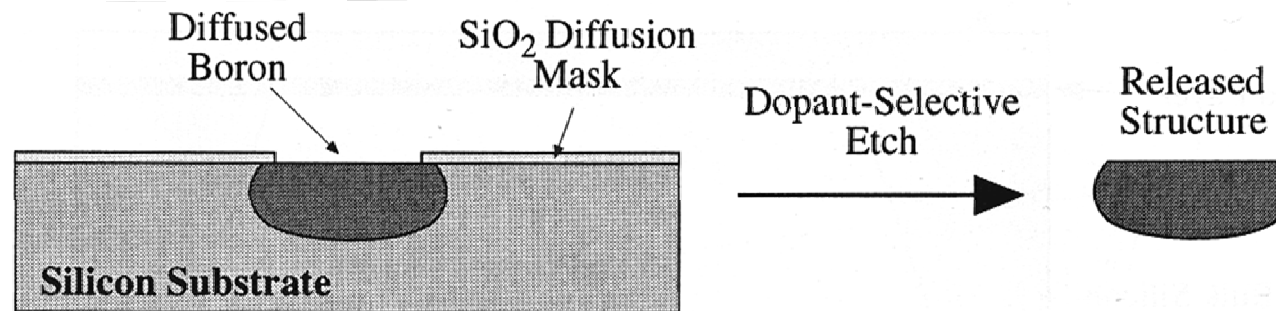


Illustration of the use of heavy boron doping with a dopant-selective etch to form free structures



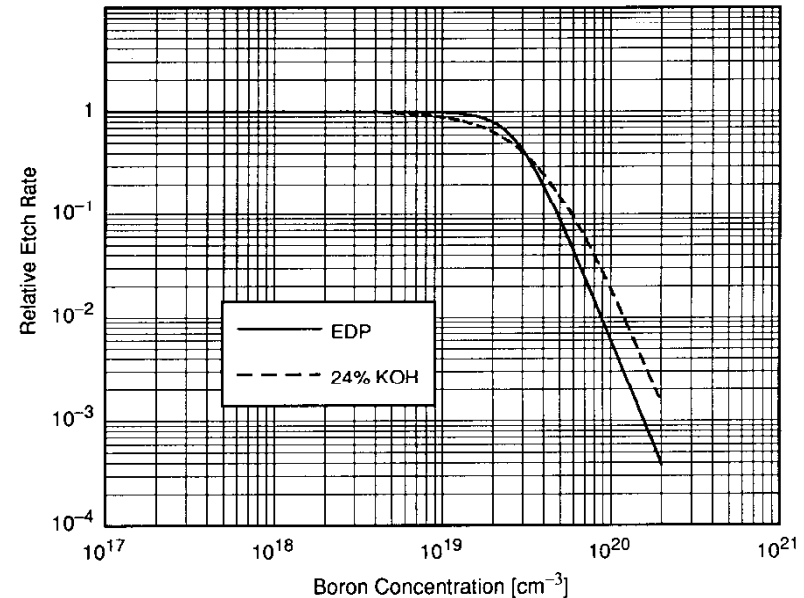
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# Boron Etch Stop (2)

- Boron penetration
  - Excessive Boron doping affects IC.
  - Boron having high diffusion rate penetrates channel and gate oxide of IC.
  - In general IC MEMS, backside of substrate is wet-etched.
  - Extremely high boron doping of backside damages gate of IC, and then can be a representative cause of leak current.



# Electrochemical Etch Stop (1)

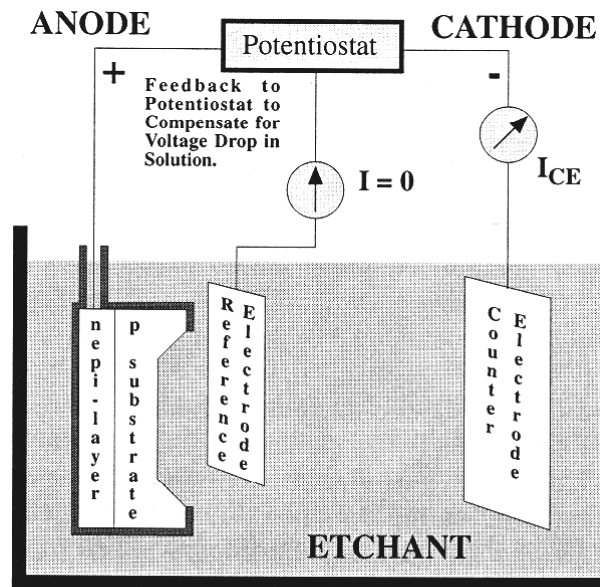
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- Electrochemical wet etching
  - Applying external voltage → Implanting hole → Changing surface to hydroxide
  - Applying voltage through chemical
  - Cathode: Platinum electrode
  - Anode: Silicon
  - Hole is implanted to silicon positively charged → Silicon draws OH-of chemical → Oxidizing
  - HF added to chemical removes oxide of Si surface, then induces etching.
  - Etching effects electro polishing, because surface roughness is low.
  - Nitride or PR are used as etch mask.



# Electrochemical Etch Stop (2)

- Diode junction etch stop
  - P-type Si is etched away in etchants (KOH, EDP, TMAH)
  - Formation of  $\text{SiO}_2$  by anodic oxidation when the etchant reaches the junction
  - Etch-rate drop equivalent to the selectivity over  $\text{SiO}_2$



A standard three-electrode system for diode junction etch stop



# Electrochemical Etch Stop (3)

- Diode junction etch stop mechanism
  - Reverse voltage at Diode → No voltage at P-type silicon
  - Exposure to etchant → Etching
  - N-type is exposed → Making hydroxide → Stop etching
  - Possible to control thickness exactly

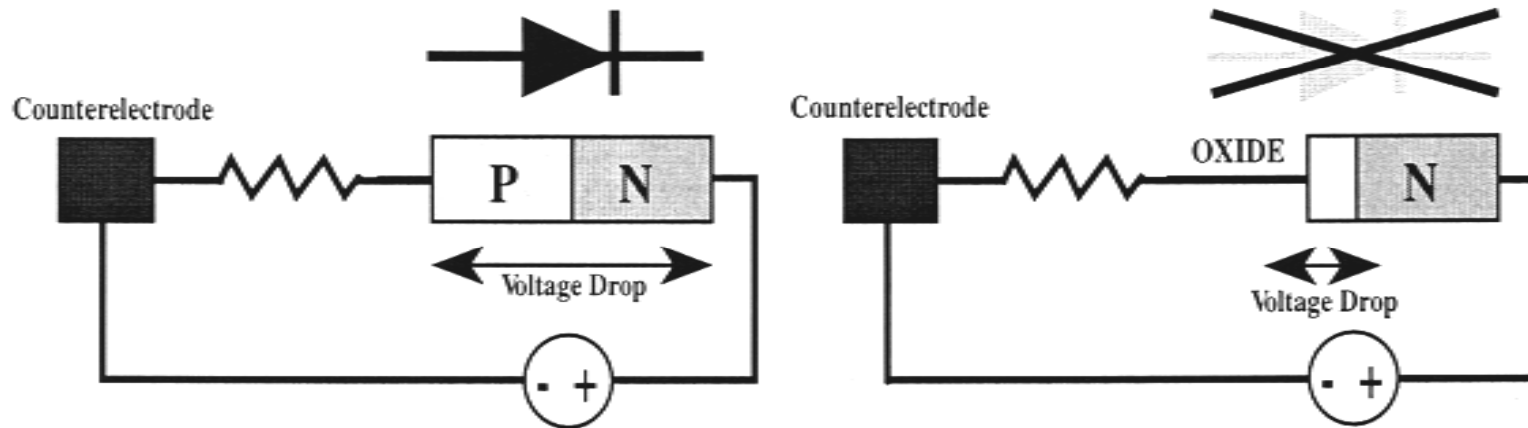


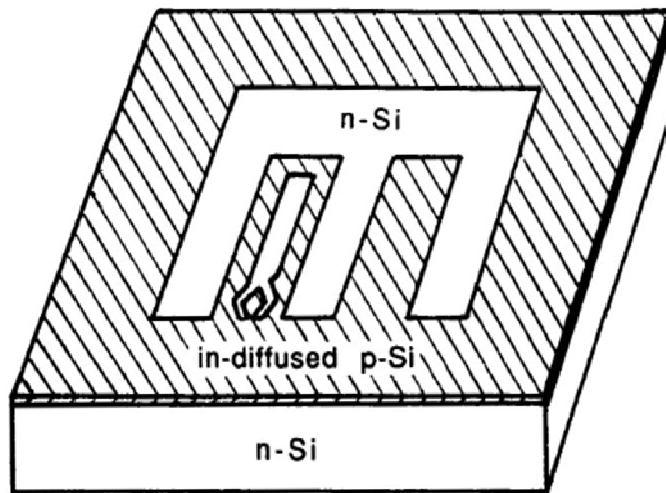
Illustration of diode junction etching



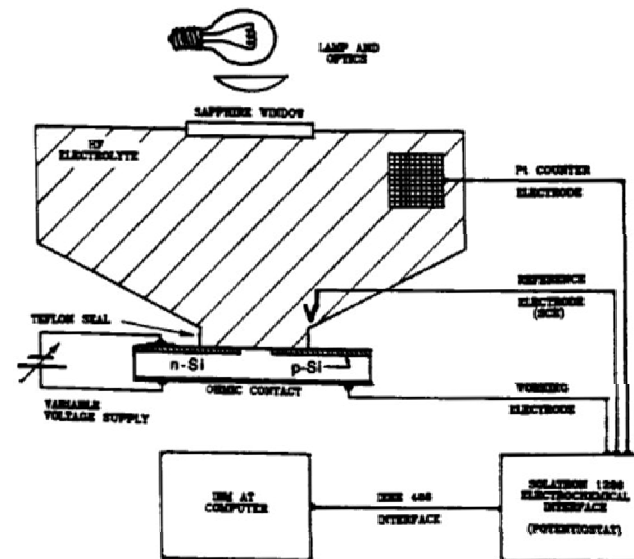


# Electrochemical Etch Stop (4)

- Photo-assisted electrochemical etch stop
  - An n-type silicon region on a wafer may be selectively etched in an HF solution by illustrating and applying a reverse bias across a p-n junction
    - the p-type layer cathodic and the n-type layer anodic



Schematic of the spatial geometry of the indiffused p-Si layer in to n-Si used to form cantilever beam structures



Schematic of the photoelectrochemical etching experimental apparatus



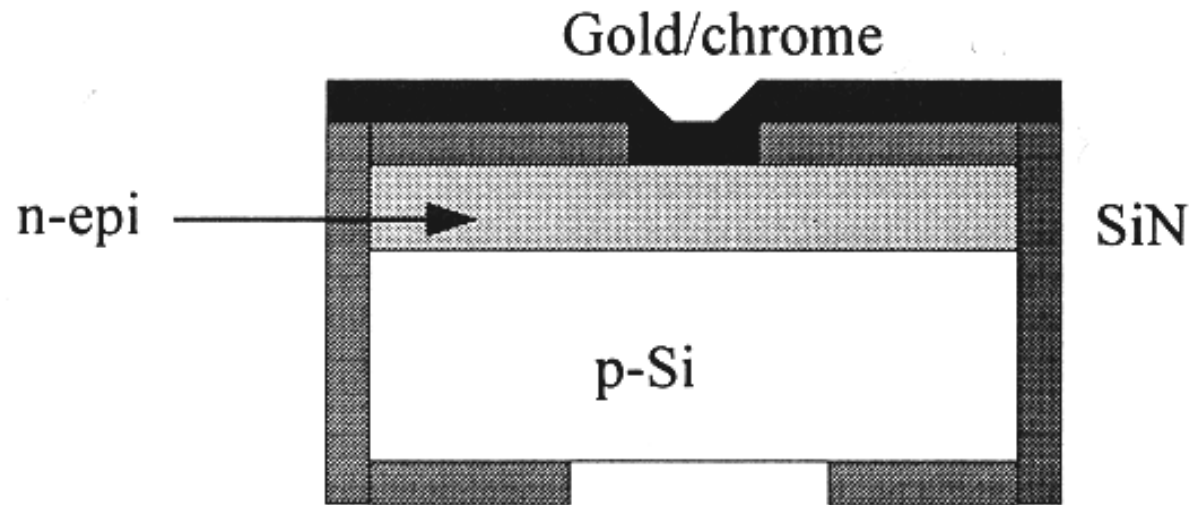
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# Electrochemical Etch Stop (5)

- Electrodeless etch-stop
  - Does not require external contacts or power source
  - The passivation voltage is generated internally in a Au/Cr/n-Si/TMAH cell.
  - The etch stop is effective for both p- and n- type silicon



Test-wafers with SiN on the sides and gold/chrome on the front.



# Wet Etch Mask (1)

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- Mask materials
  - Silicon dioxide
    - Thermal film is the best.
    - CVD films etch 30 % faster
    - Sputter film is poor
  - Silicon nitride
    - CVD films are the best
    - Sputter film is poor
  - Gold, chromium, platinum, silver, copper, tantalum
    - resist against KOH and EDP



# Wet Etch Mask (2)

- Etching Masks: Mask Qualities vs. Etching Properties
  - Mask qualities on etching properties
    - Resolution, CD tolerance, edge sharpness
    - Roughness on vertical sidewall profile
  - Result in selectivity

	<i>Film Mask</i>	<i>E-beam mask</i>
<i>resolution</i>	<i>50 <math>\mu\text{m}</math></i>	<i>1 <math>\mu\text{m}</math></i>
<i>tolerance</i>	<i>7-8 <math>\mu\text{m}</math></i>	<i>0.2 <math>\mu\text{m}</math></i>
<i>cost</i>	<i>25 \$</i>	<i>1400 \$</i>
<i>contrast</i>	<i>bad</i>	<i>excellent</i>
<i>cleaning</i>	<i>No</i>	<i>Yes</i>
<i># of usage</i>	<i>saveral</i>	<i>unlimited if cleaned</i>
<i>hardness</i>	<i>flexible</i>	<i>hard</i>

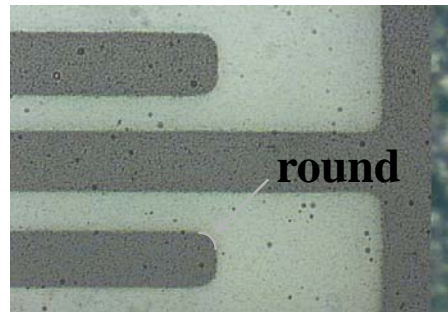


# Wet Etch Mask (3)

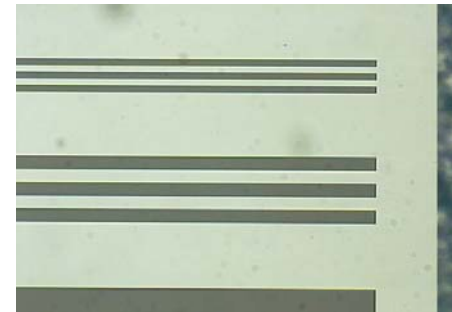
- Etching masks: comparison of mask properties

**Film Mask**

×100

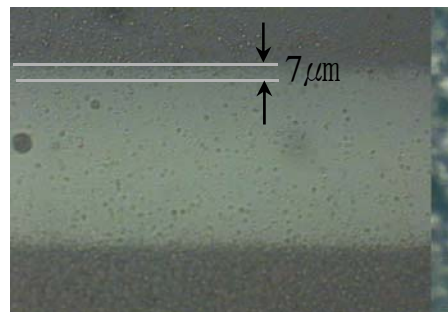


**E-beam Mask**



100  $\mu\text{m}$  width  
50  $\mu\text{m}$  gap

×500



10  $\mu\text{m}$  width  
10  $\mu\text{m}$  gap



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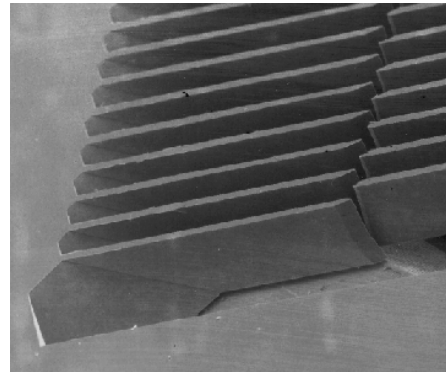
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# Wet Etch Mask (4)

- Etching masks: fabricated structures using different Mask

**Film mask**

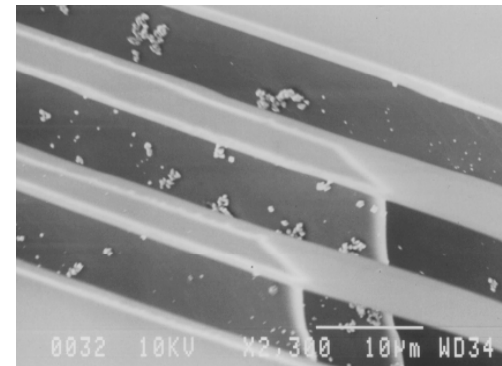


**Layout**      100  $\mu\text{m}$  width  
50  $\mu\text{m}$  gap

**Fabrication**    75  $\mu\text{m}$  width  
75  $\mu\text{m}$  gap

**Selectivity**      45

**E-beam mask**



**Layout**      10  $\mu\text{m}$  width  
10  $\mu\text{m}$  gap

**Fabrication**    8  $\mu\text{m}$  width  
12  $\mu\text{m}$  gap

**Selectivity**      90



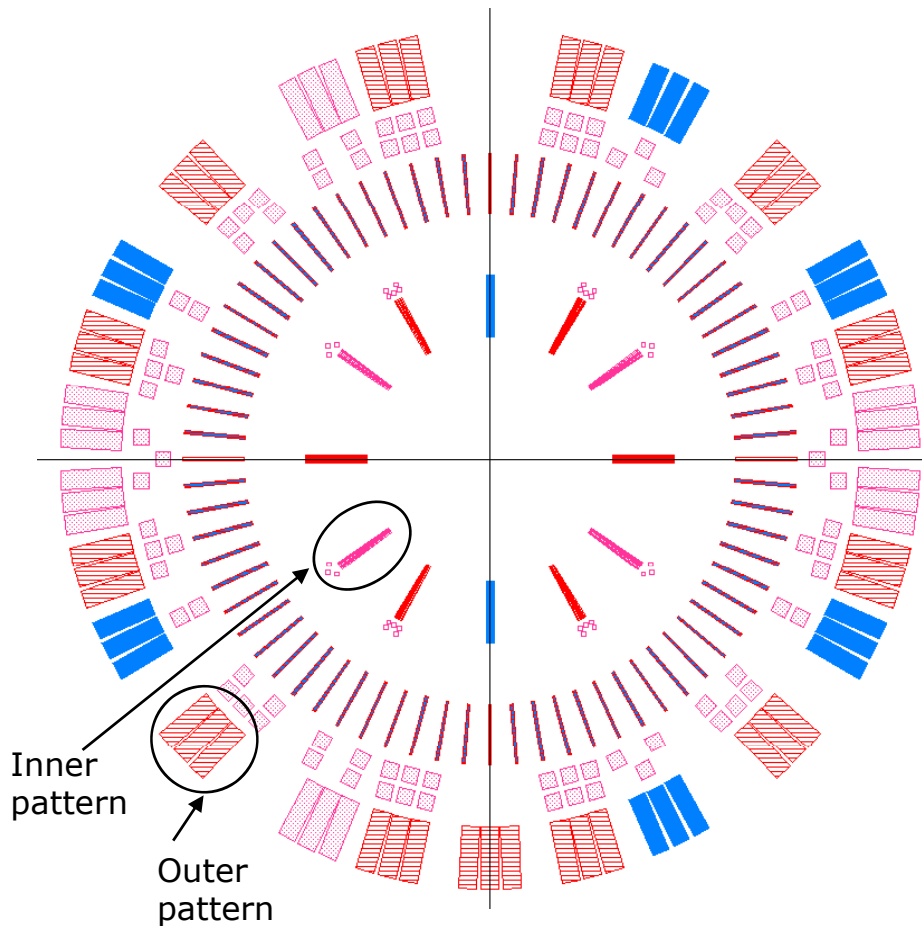
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# Wet Etch Test Pattern (1)

- Wagon wheel pattern mask



- Wagon wheel pattern
  - Size:  $50\text{ }\mu\text{m} \times 400\text{ }\mu\text{m}$
  - Pattern repeated every 5 degree
  - Inner pattern
    - Pattern width  $5\text{ }\mu\text{m}$
    - Observation of slow etch rate
  - Outer pattern
    - Pattern width  $300\text{ }\mu\text{m}$
    - Observation of fast etch rate



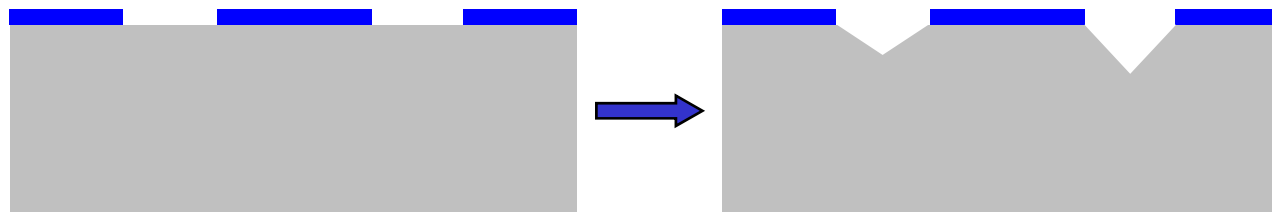
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# Wet Etch Test Pattern (2)

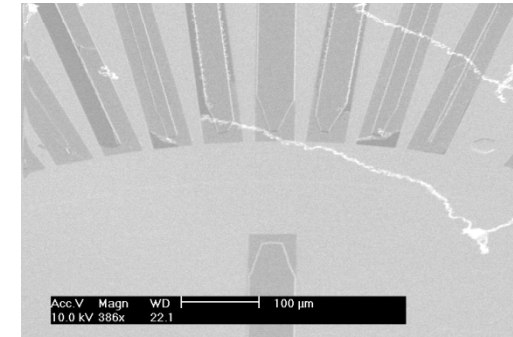
- Patterns defined by only photolithography



Pattern

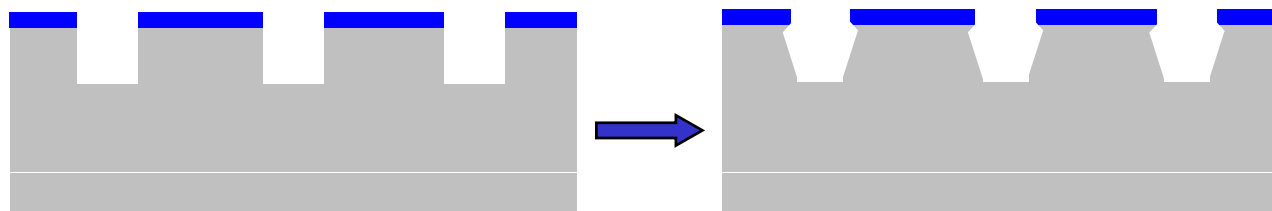
Wet etch

 Oxide  Silicon



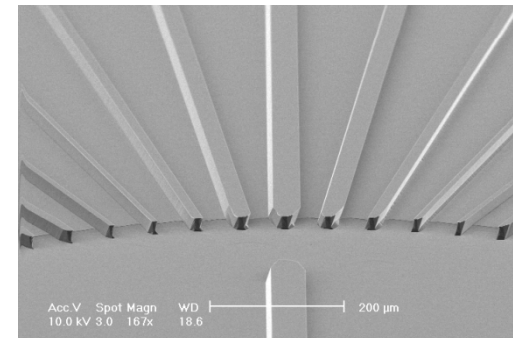
Wet etch result

- Patterns defined by deep Si etch



Pattern

Wet etch



Wet etch result



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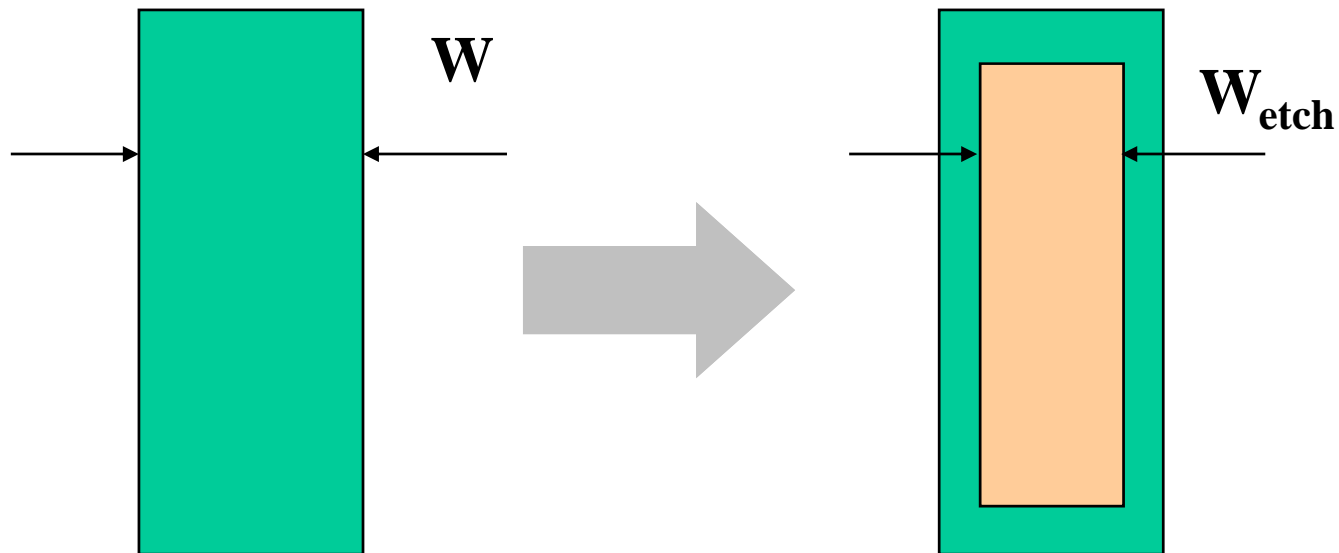
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# Wet Etch Test Pattern (3)

- Wet etch rate inspection



$$\text{Etch rate} = \frac{W - W_{etch}}{2}$$

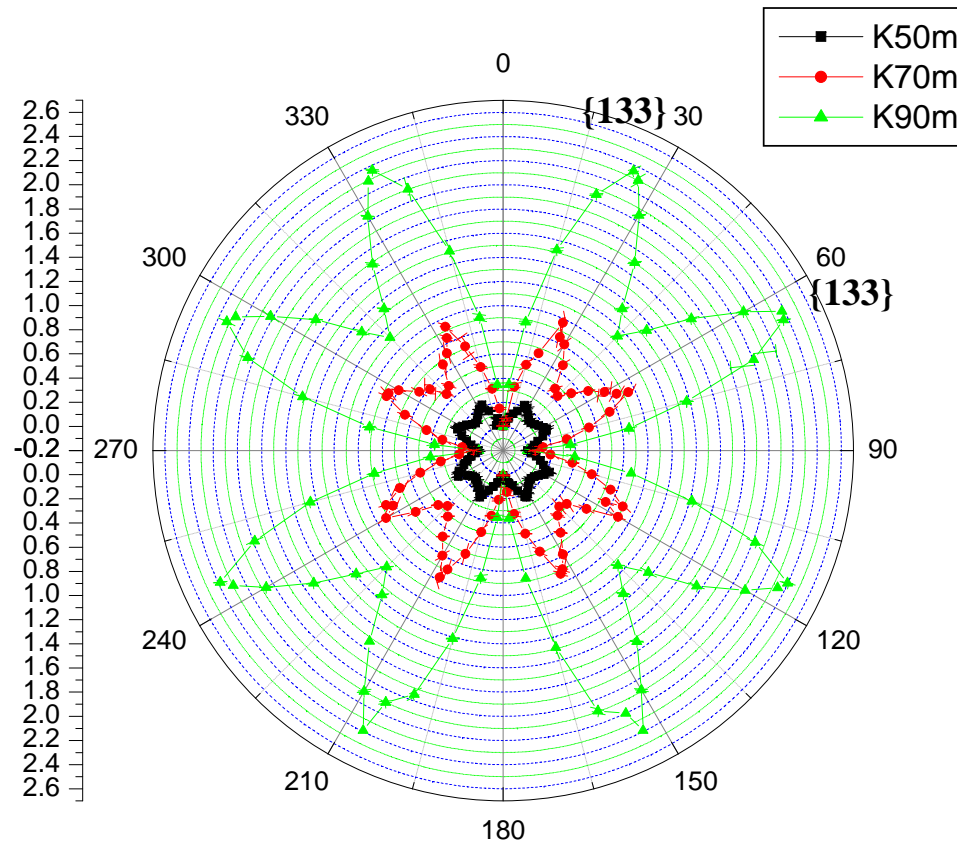


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# (100) Si Wet Etch (1)



40wt % KOH

K50m: 50 °C

K70m: 70 °C

K90m: 90 °C

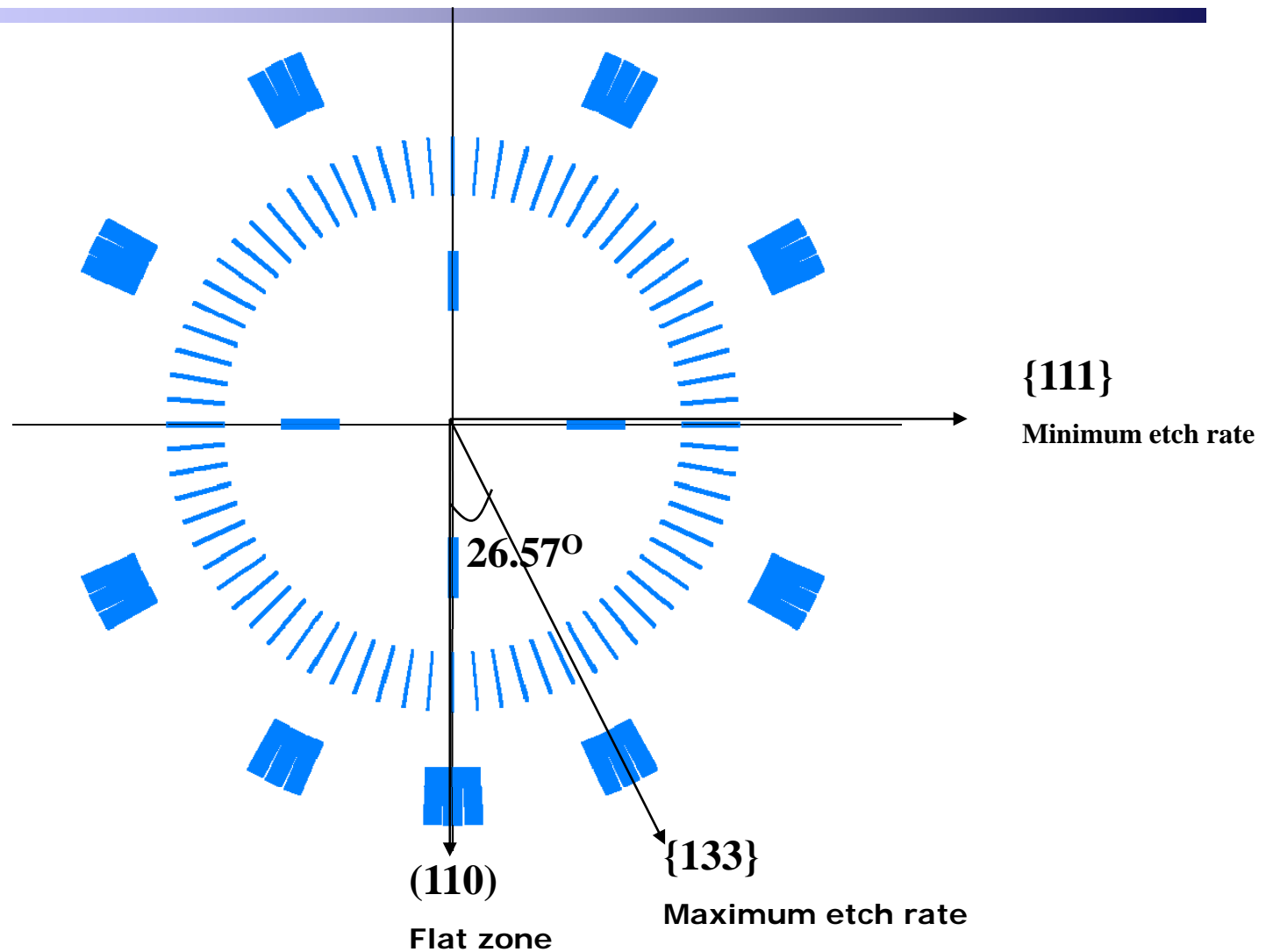


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# (100) Si Wet Etch (2)

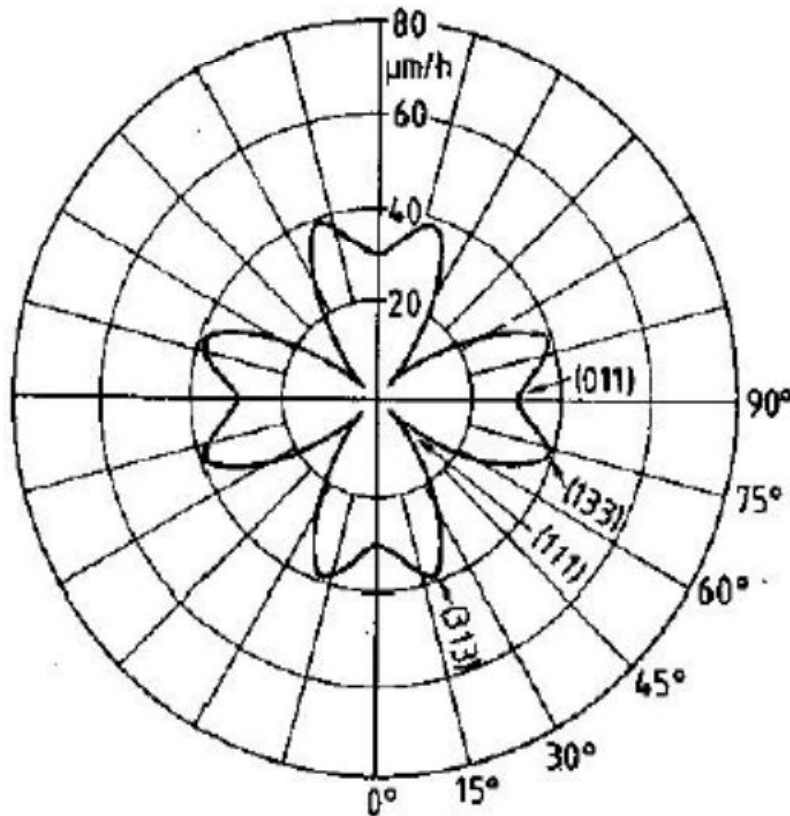


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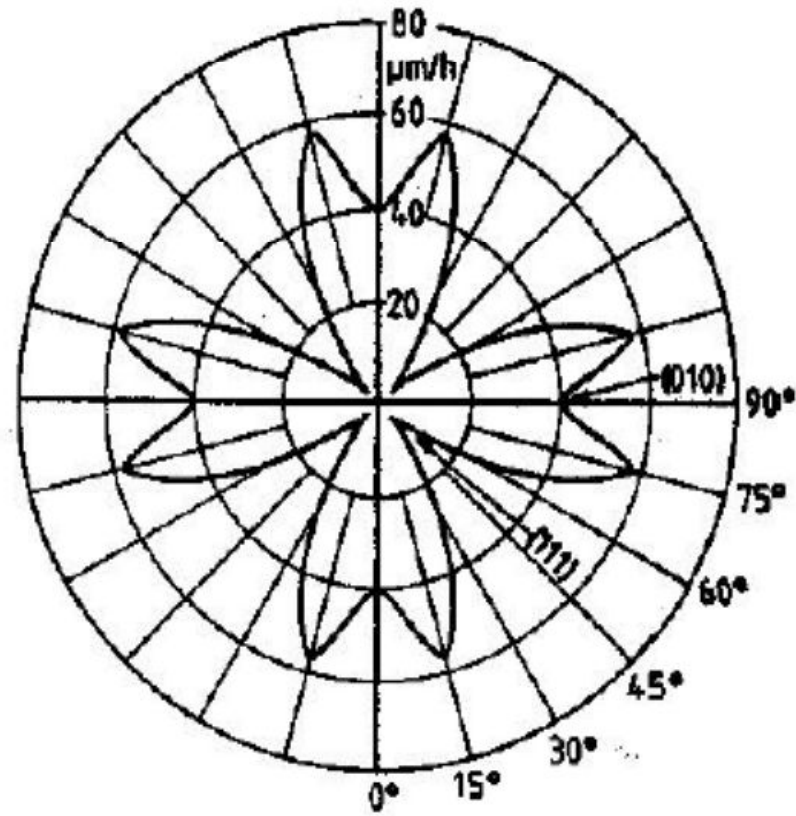
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# (100) Si Wet Etch (3)



EDP solution at 95 °C



KOH solution at 78 °C

Ref.) H. Seidel, *J. of Electrochemical Society*, 137(11), pp. 3613-3632, 1990



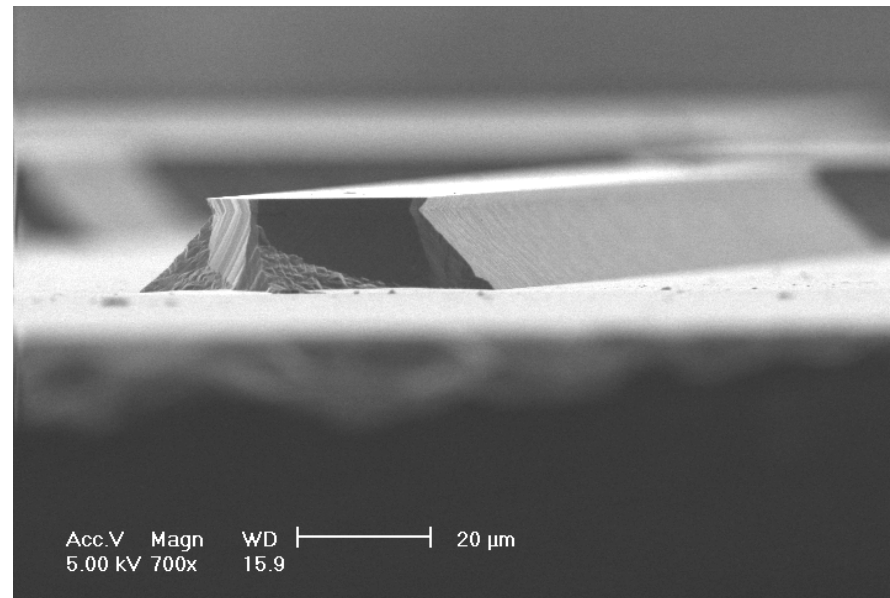
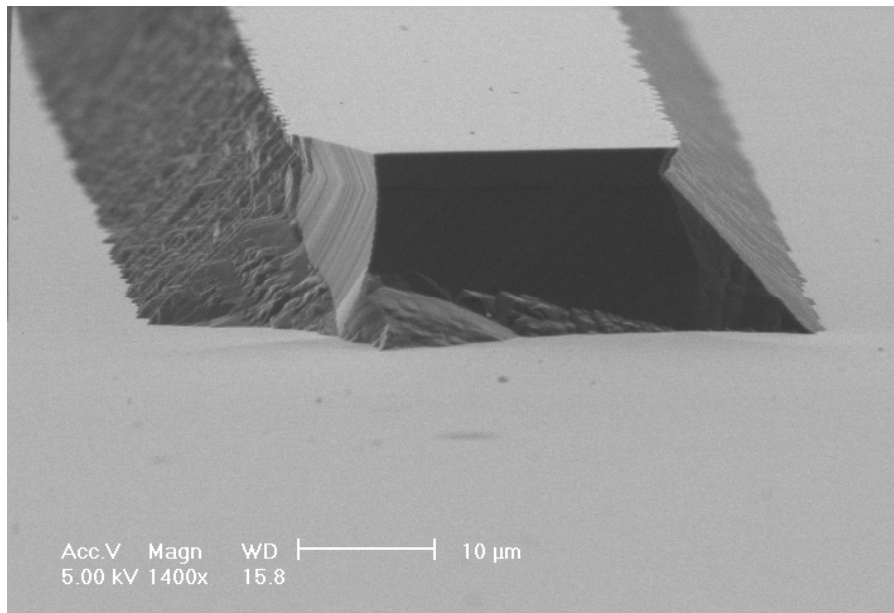
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# (100) Si Wet Etch (4)

- SEM view: (100) wafer, KOH 40%, 50 °C



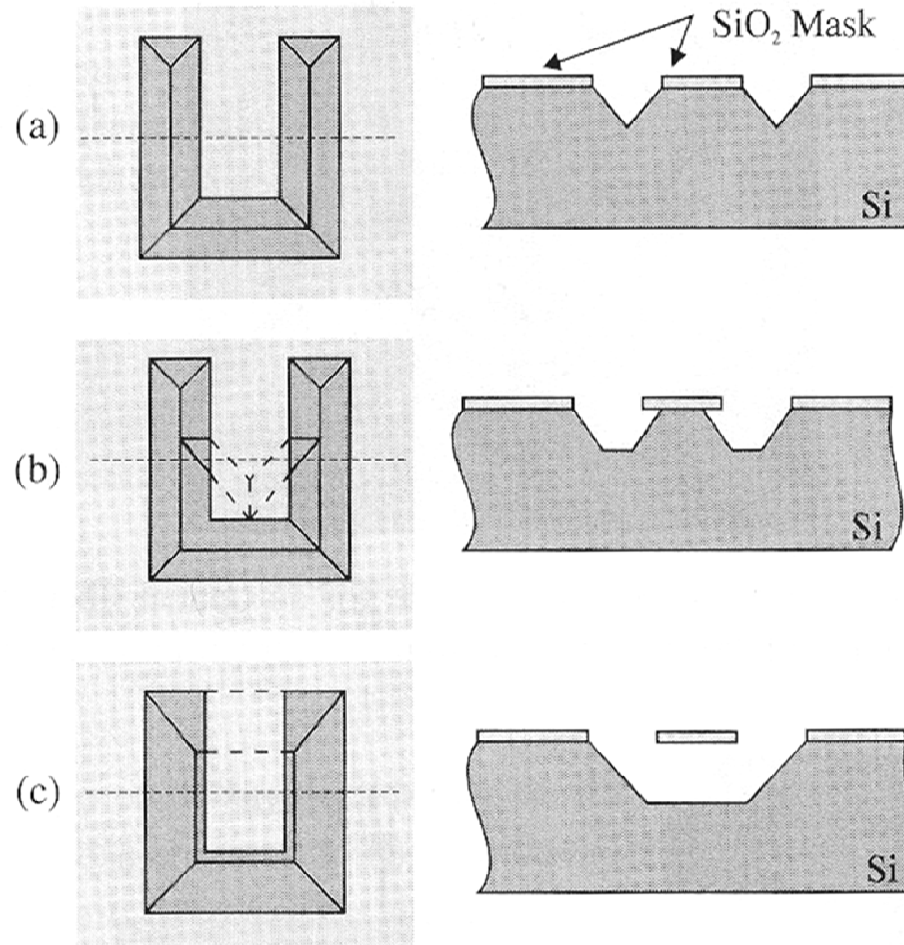
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# (100) Si Wet Etch (5)

- Micromachining of (100) wafer



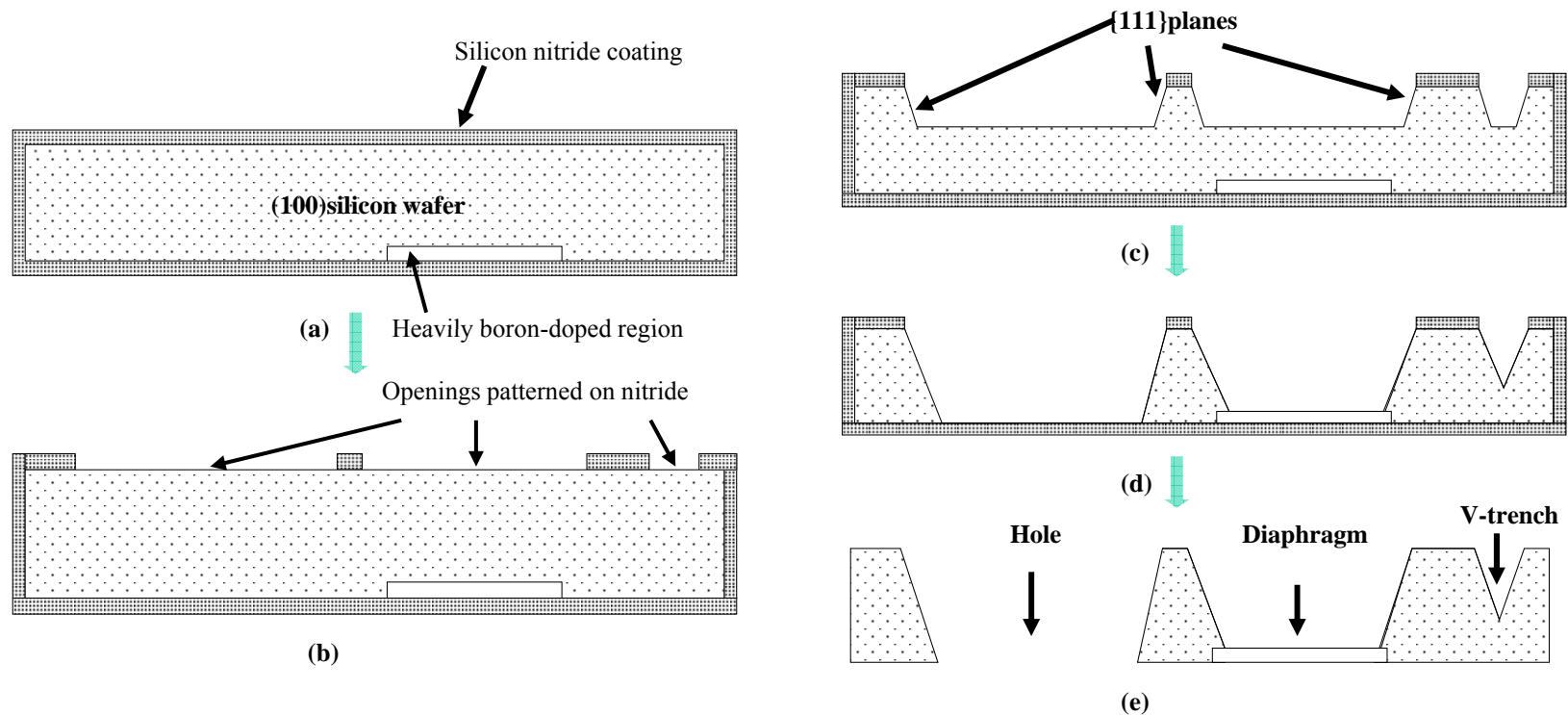
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# (100) Si Wet Etch (6)

- Anisotropic Silicon Etching



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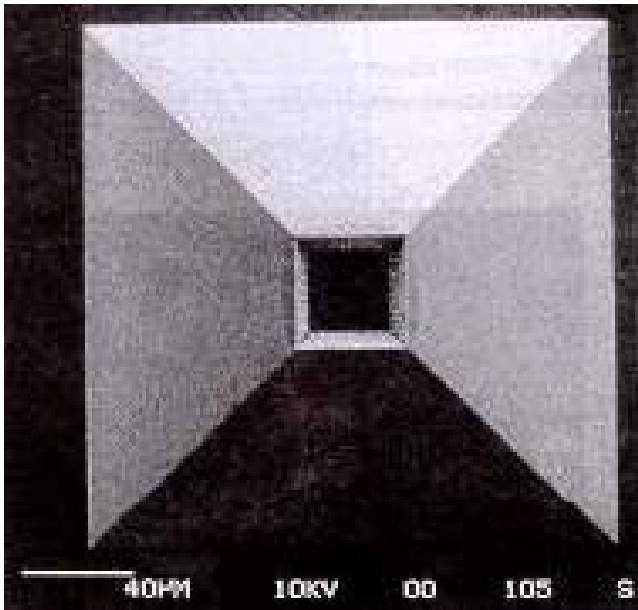
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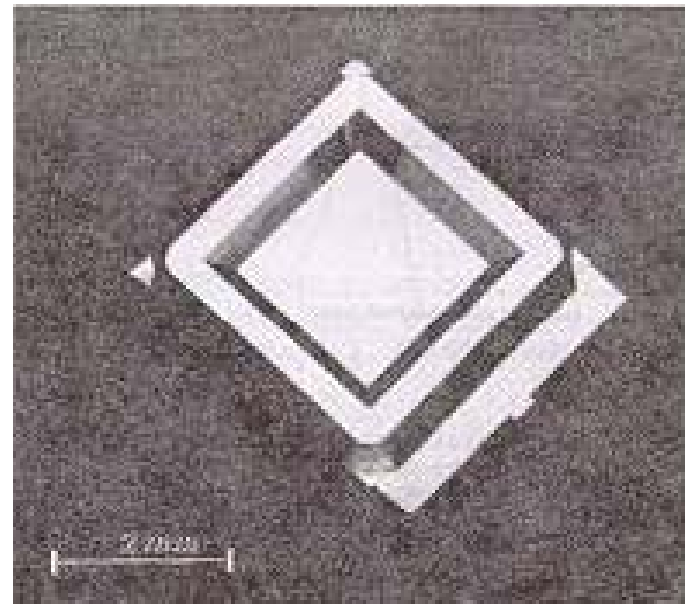


# (100) Si Wet Etch (7)

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Nozzle



Diaphragm



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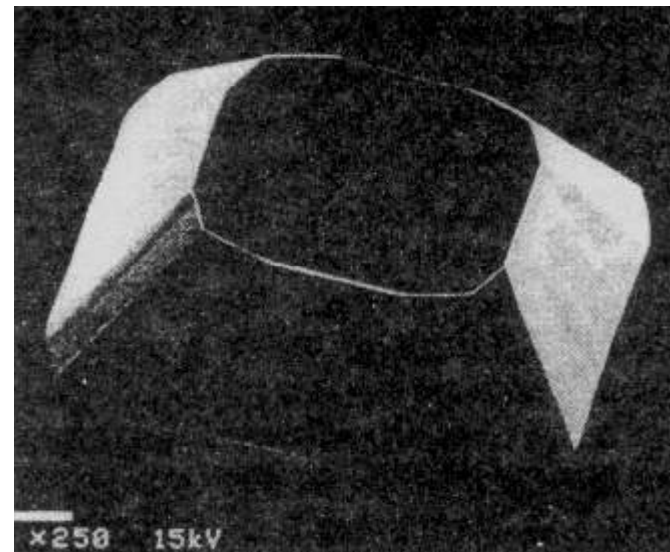
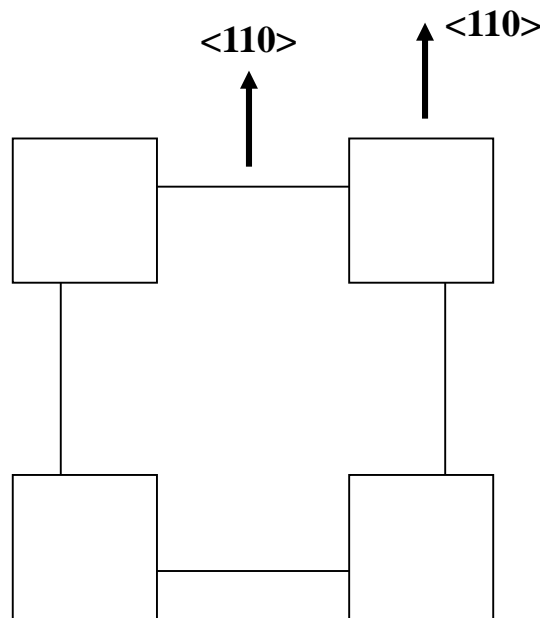
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# (100) Si Wet Etch (8)

- Rectangular corner compensation for mesa structure fabrication
  - Mask layout of compensation pattern for preventing undercut



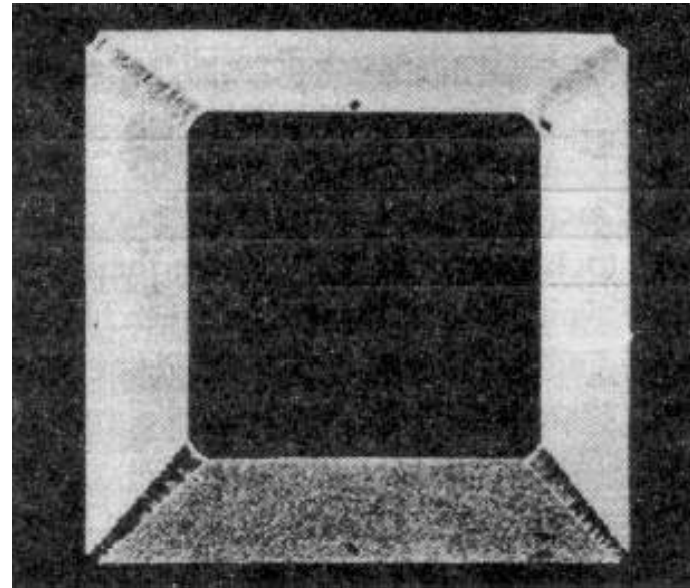
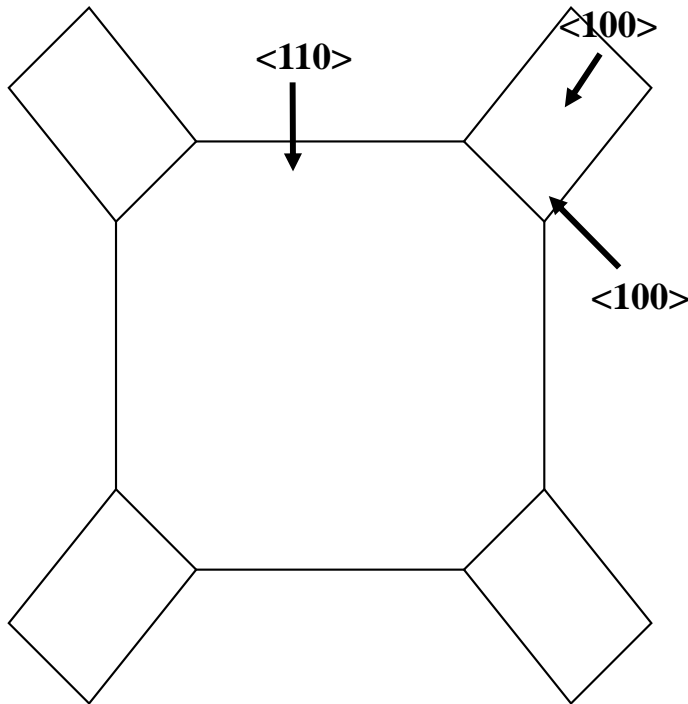
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# (100) Si Wet Etch (9)

- 45° rotated rectangular corner compensation for mesa structure fabrication



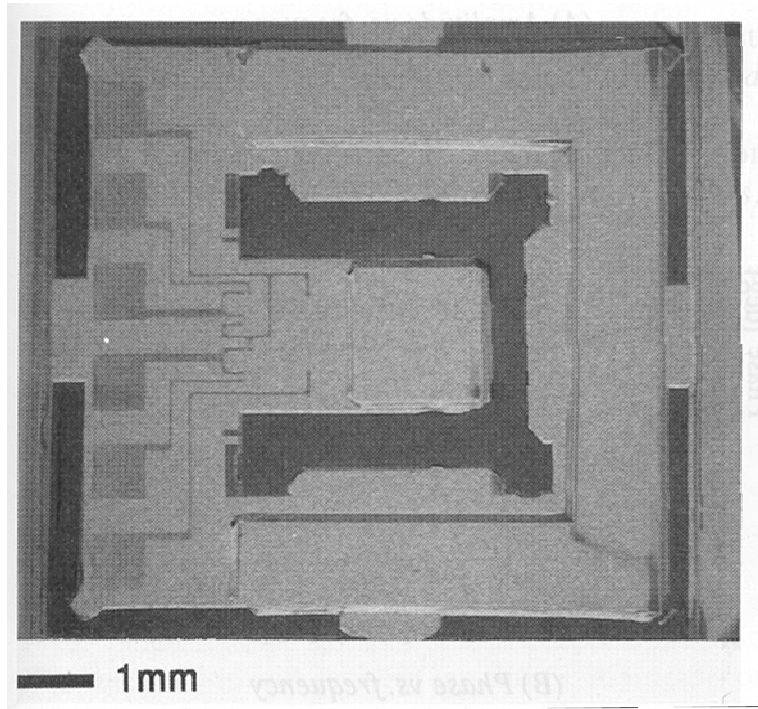
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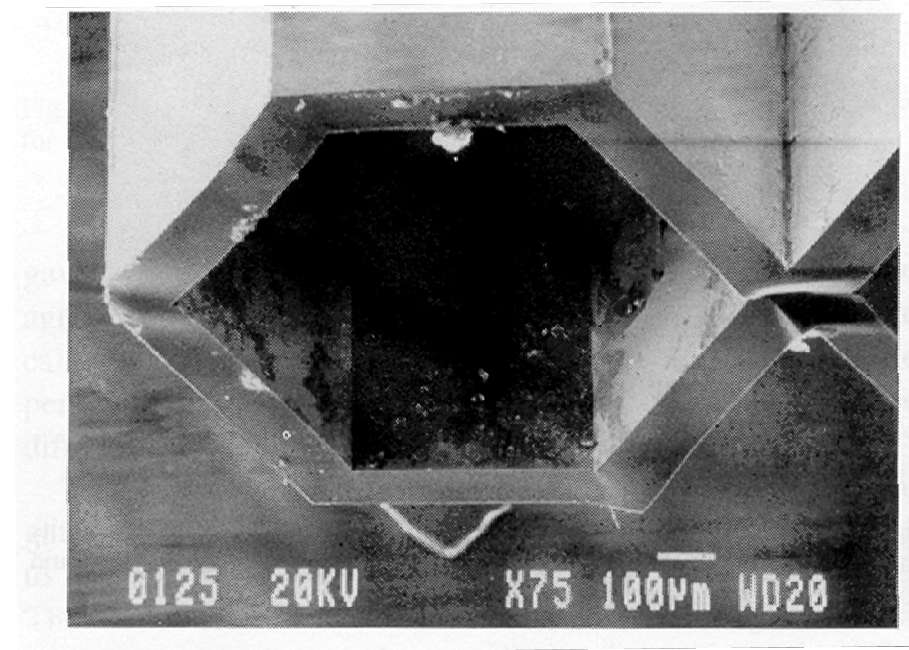
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# (100) Si Wet Etch (10)

- Application examples (1)



Accelerometer



Tube



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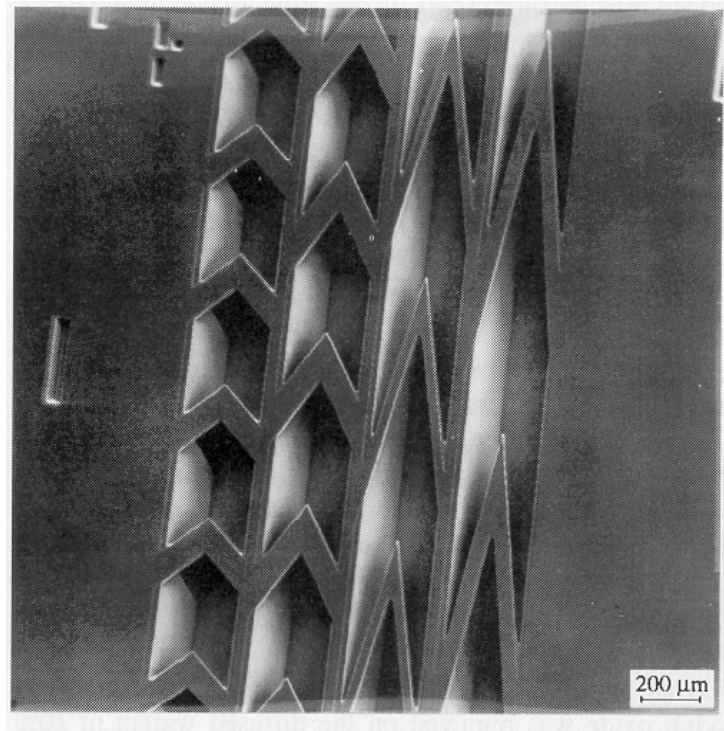
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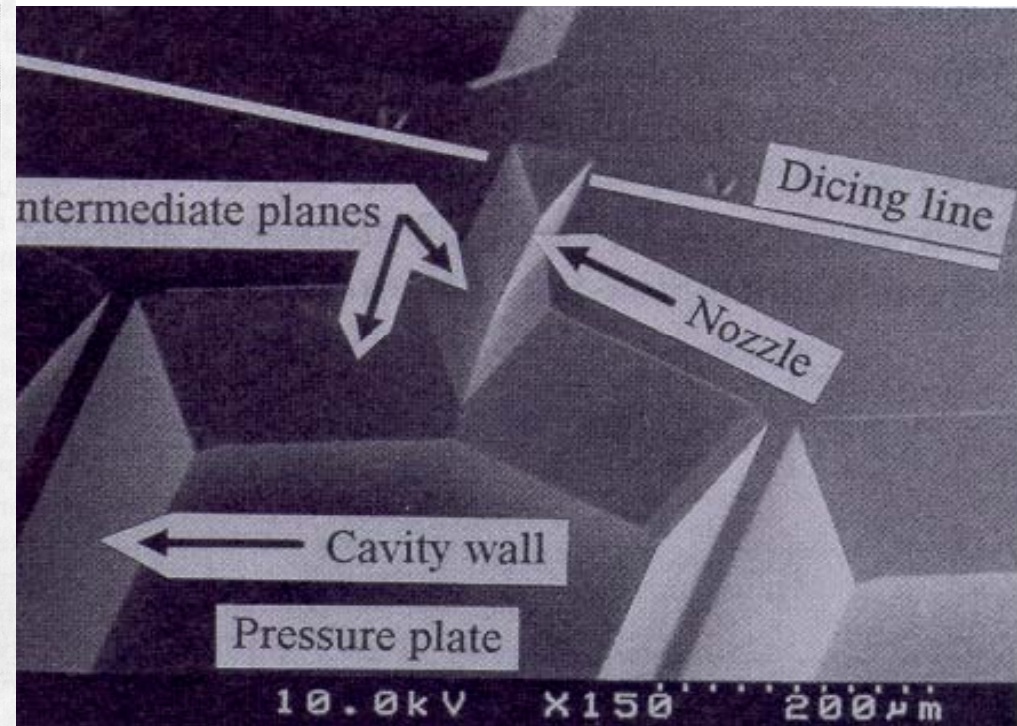


# (100) Si Wet Etch (11)

- Application examples (2)



Holding structure over v-grooves



Ink jet printer nozzle

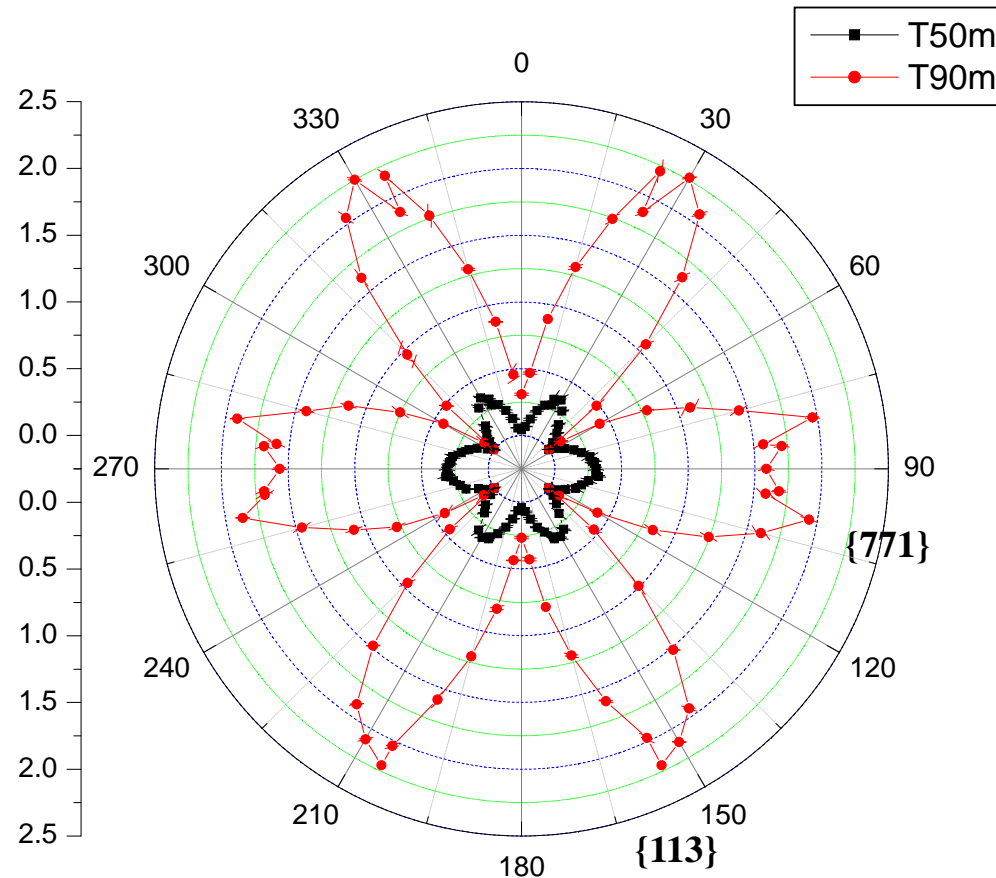


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# (110) Si Wet Etch (1)



40wt % TMAH

T50m: 50 °C

T90m: 90 °C

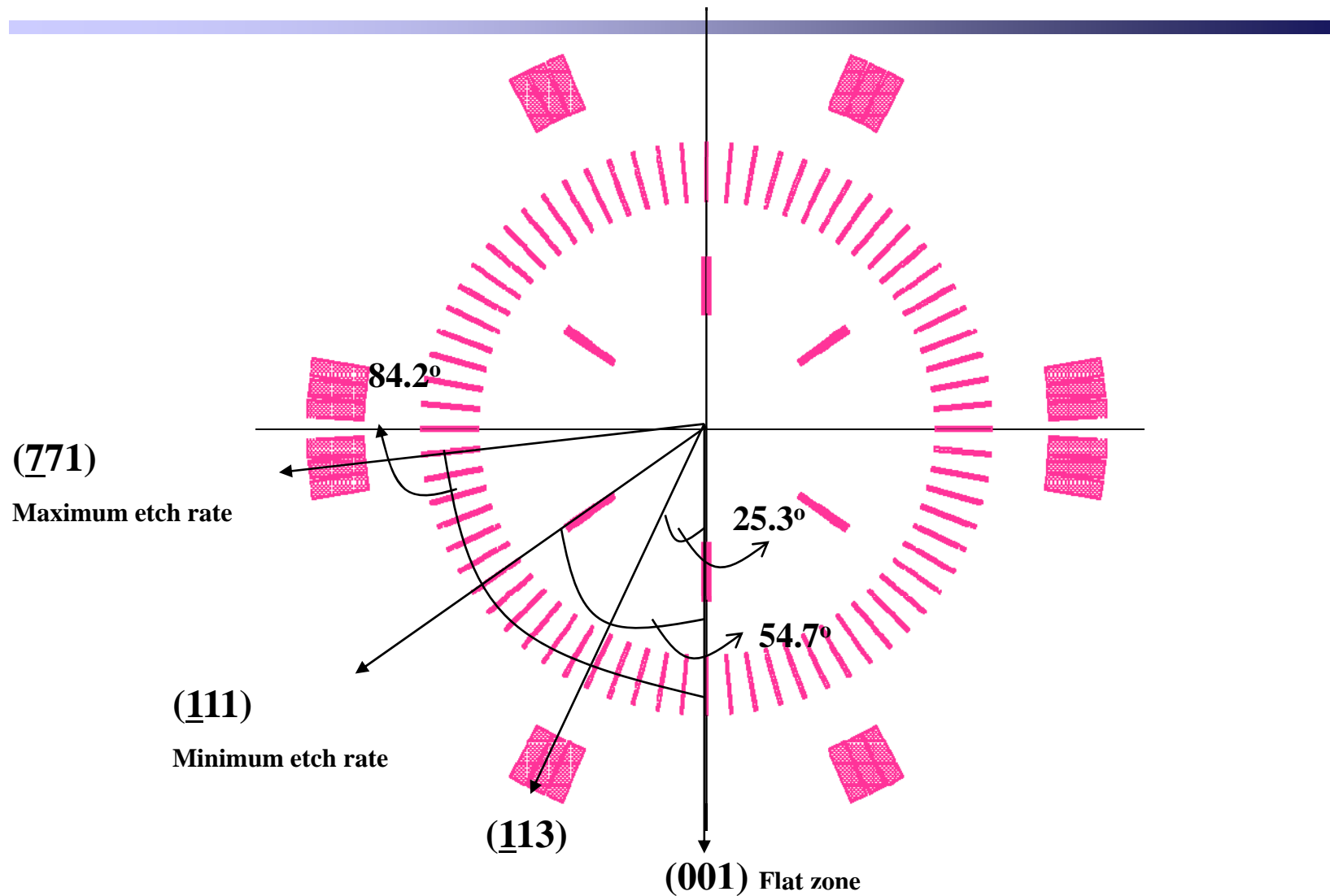


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# (110) Si Wet Etch (2)

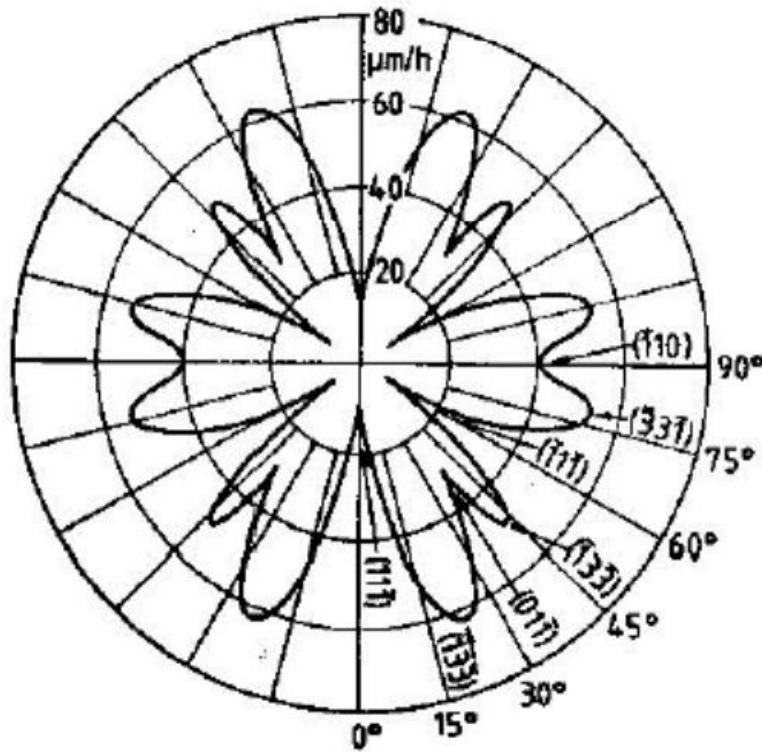


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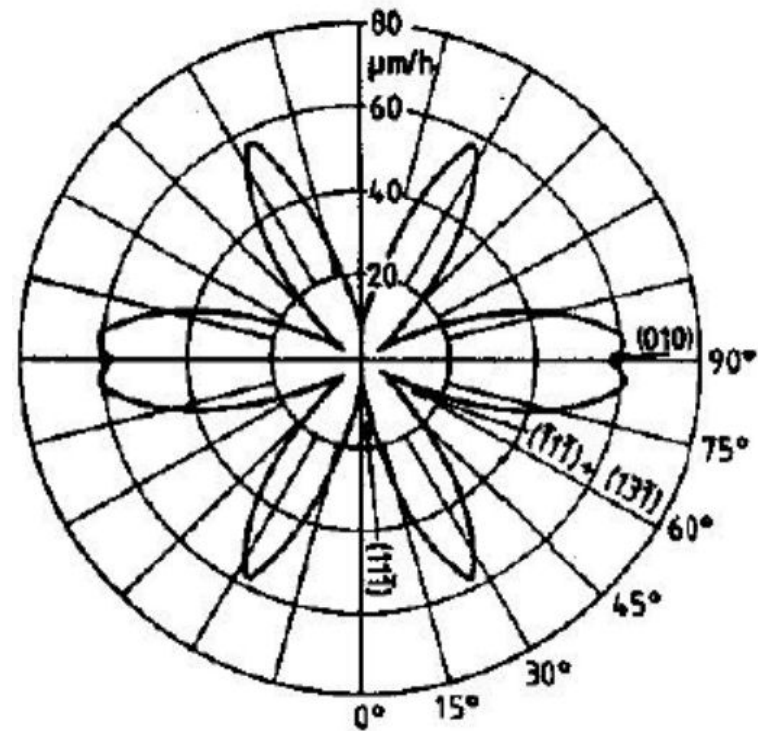
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# (110) Si Wet Etch (3)



EDP solution at 95 °C



KOH solution at 78 °C

Ref.) H. Seidel, *J. of Electrochemical Society*, 137(11), pp. 3613-3632, 1990



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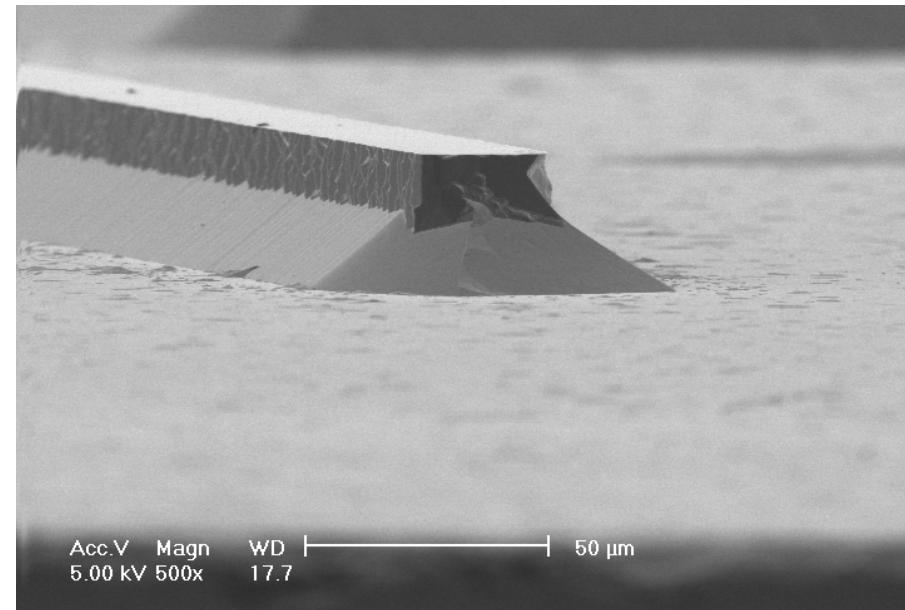
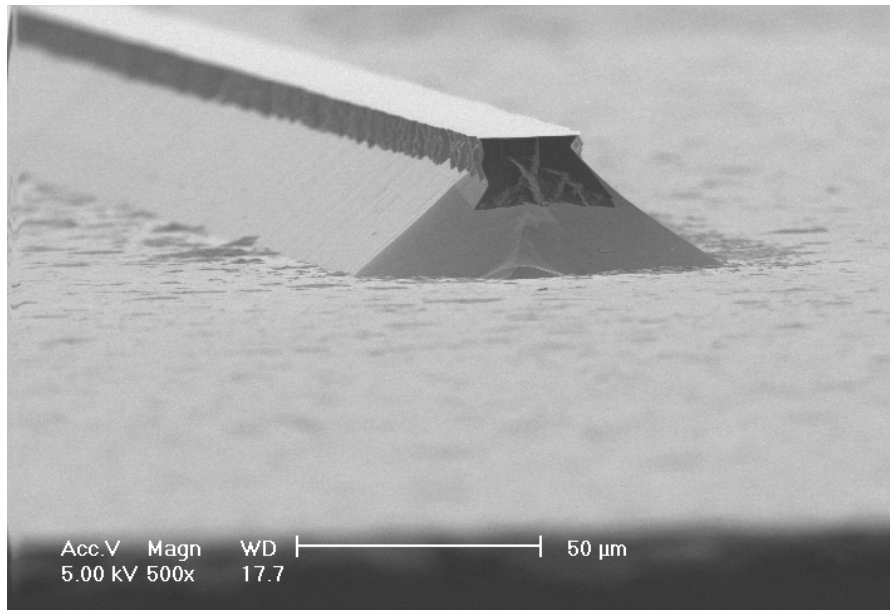
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# (110) Si Wet Etch (4)

- SEM view: (110) wafer, KOH 40%, 50 °C



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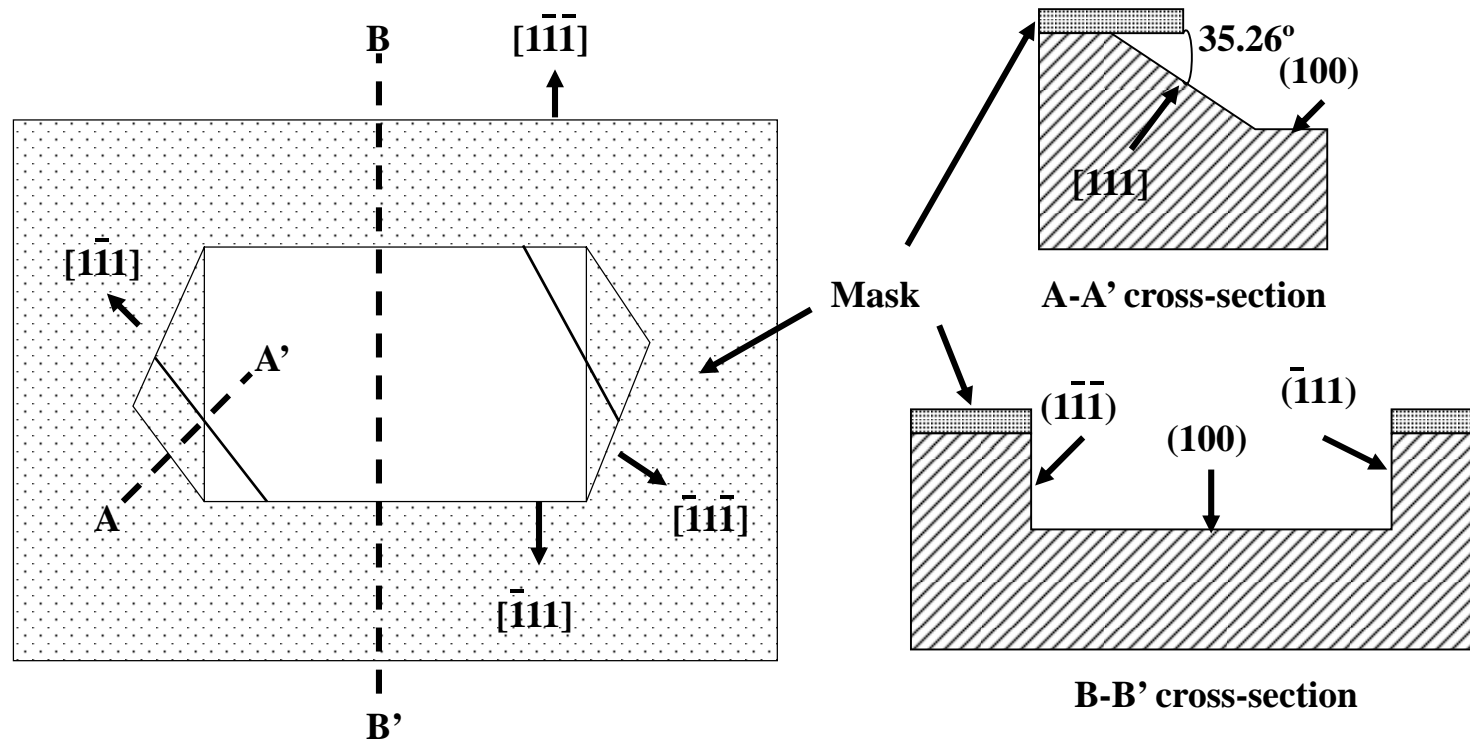
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# (110) Si Wet Etch (5)

- Top and cross-sectional view of wet etched (110) silicon wafer



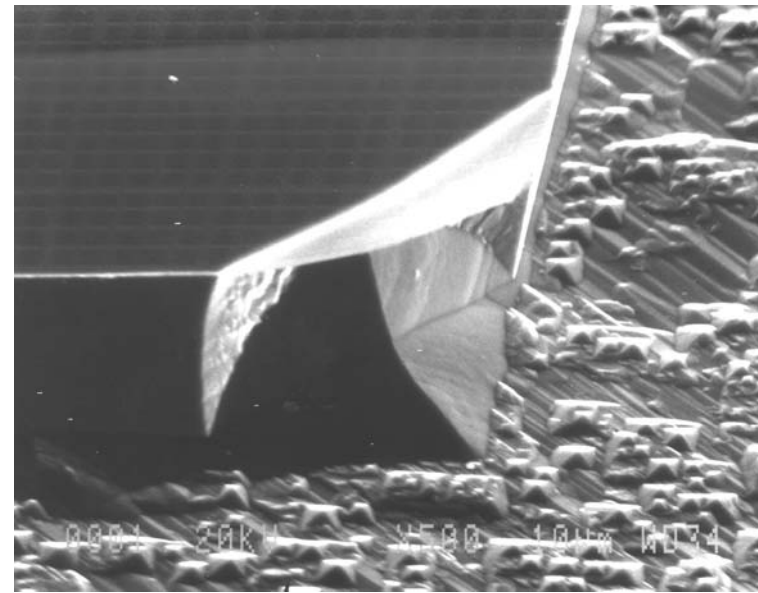
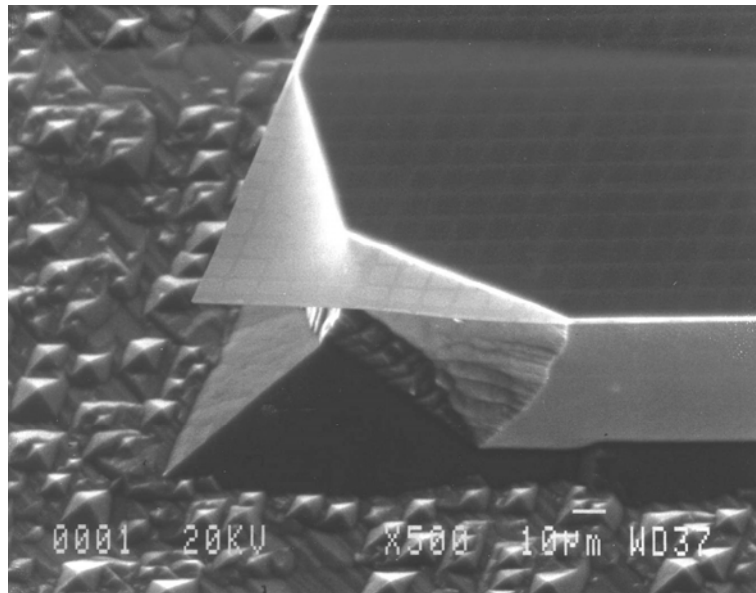
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# (110) Si Wet Etch (6)

- Convex corners
  - The planes that emerge under convex corners are not compatible with the planes that we find in the etch rate minima.
- Acute and obtuse convex corners of parallelogram
  - Need compensation pattern for undercut and residues



(SNU NML)



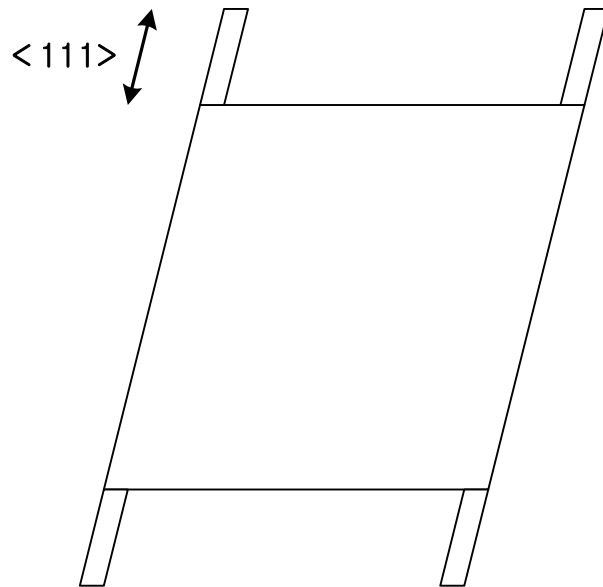
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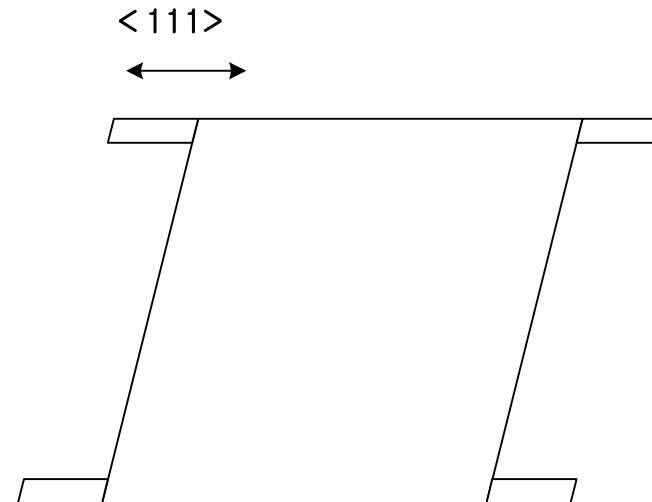
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# (110) Si Wet Etch (7)

- Compensation pattern design using  $\langle 111 \rangle$  beam



$\langle 111 \rangle$  direction compensation  
beams oblique to the wafer flat

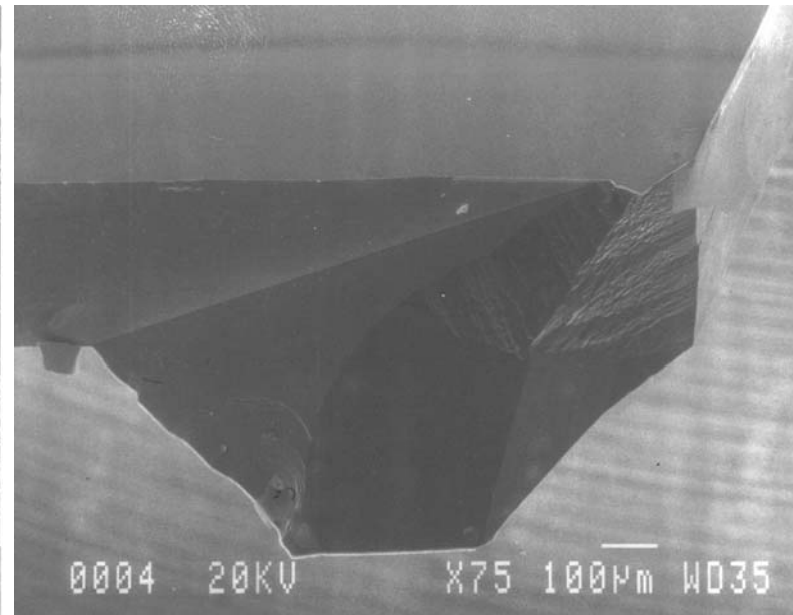
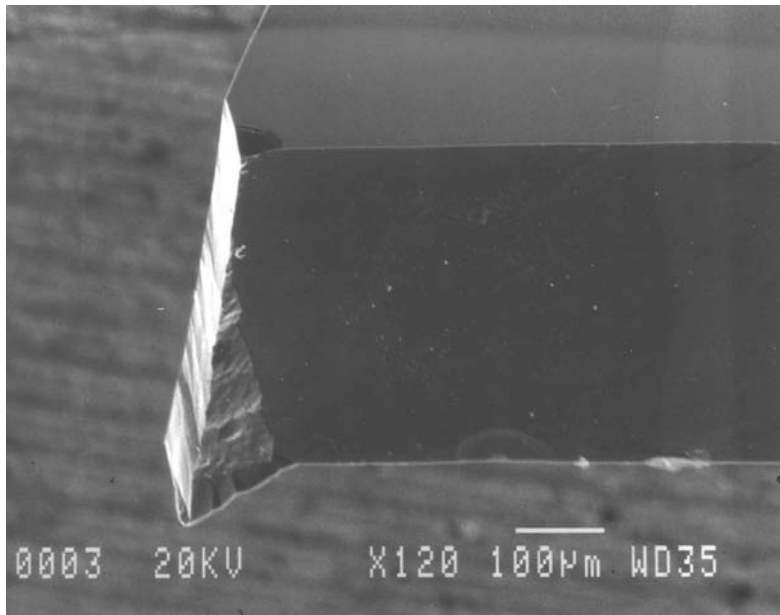


$\langle 111 \rangle$  direction compensation  
beams oblique to the wafer flat



# (110) Si Wet Etch (8)

- Compensation results
  - Good compensation effects on acute corners
  - Need other compensation pattern on convex corners



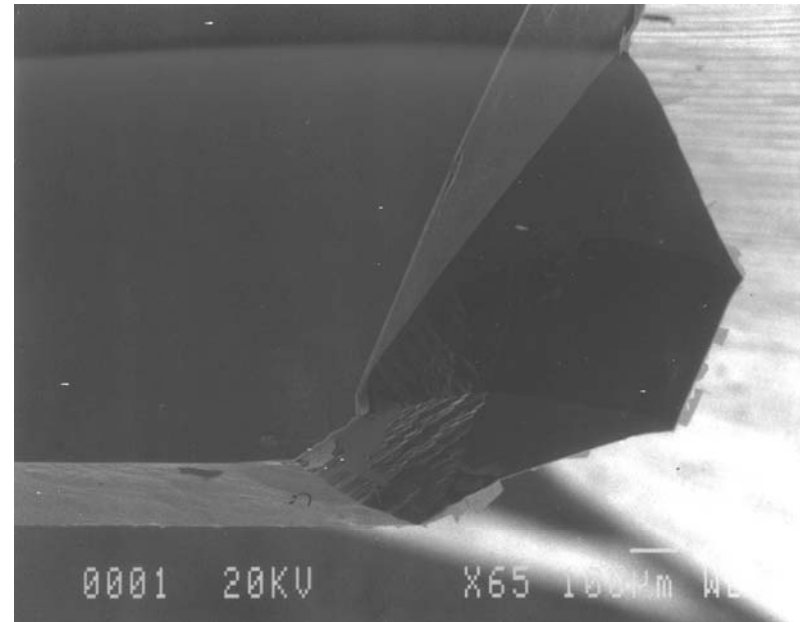
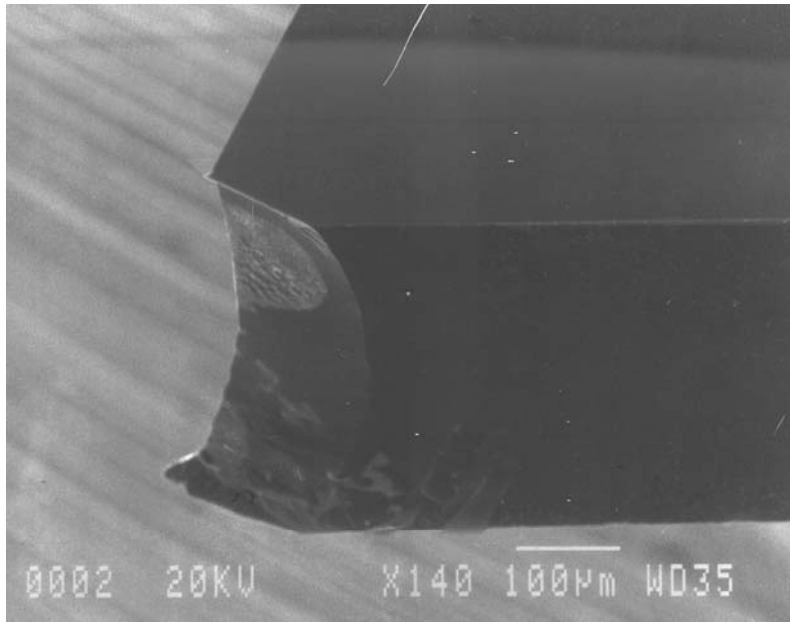
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# (110) Si Wet Etch (9)

- Compensation results
  - Good compensation effects on acute corners
  - Need other compensation pattern on convex corners



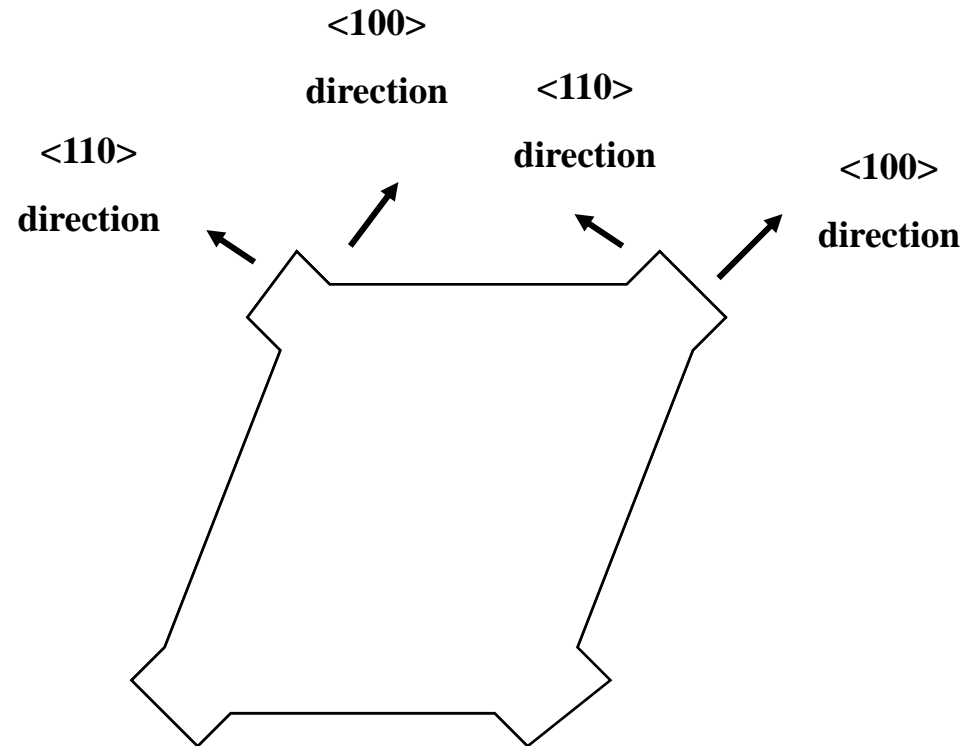
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# (110) Si Wet Etch (10)

- Rectangular compensation pattern design



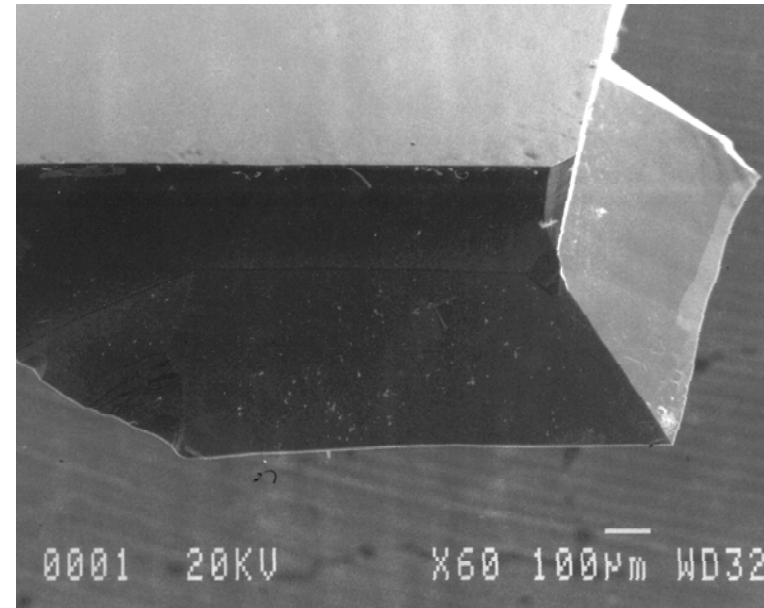
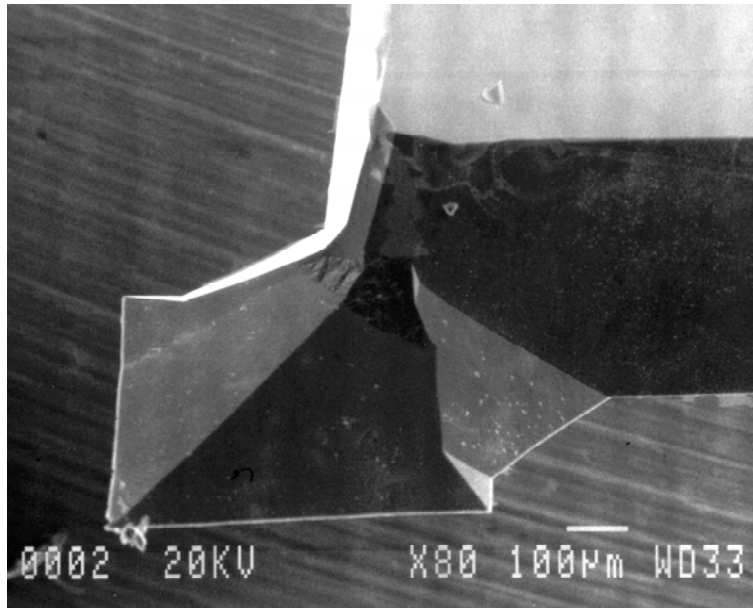
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# (110) Si Wet Etch (11)

- Compensation results
  - Large residues remain



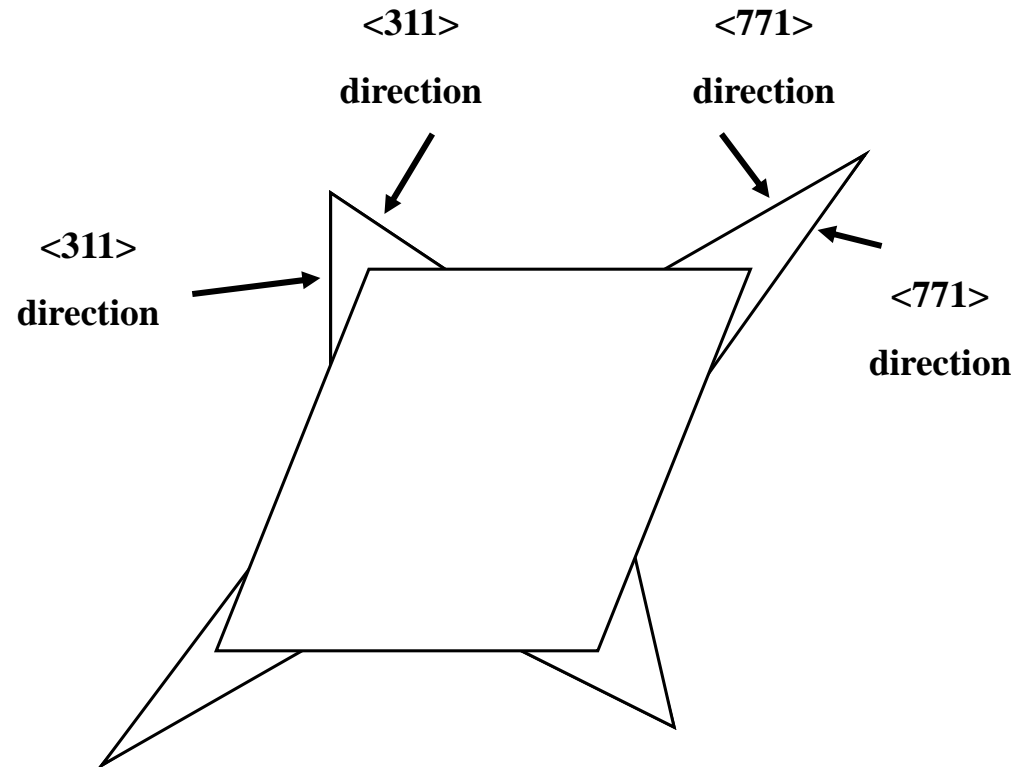
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# (110) Si Wet Etch (12)

- Triangular compensation pattern design



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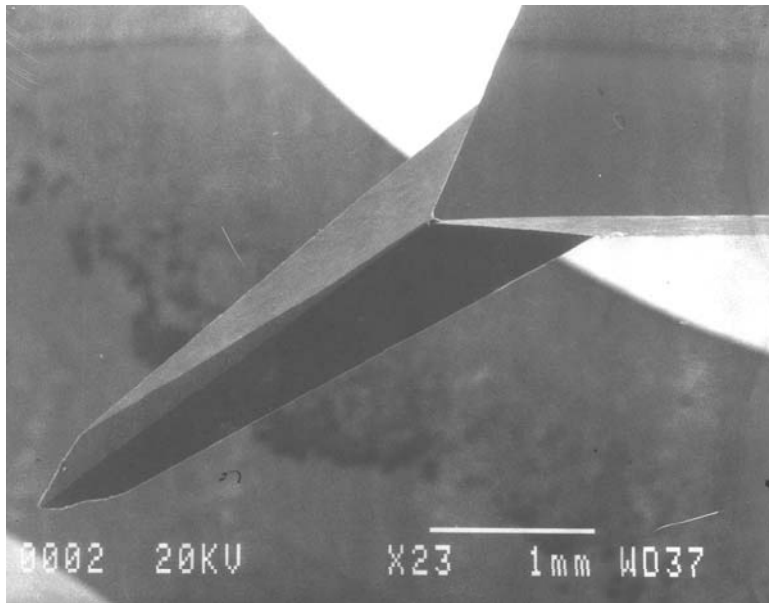
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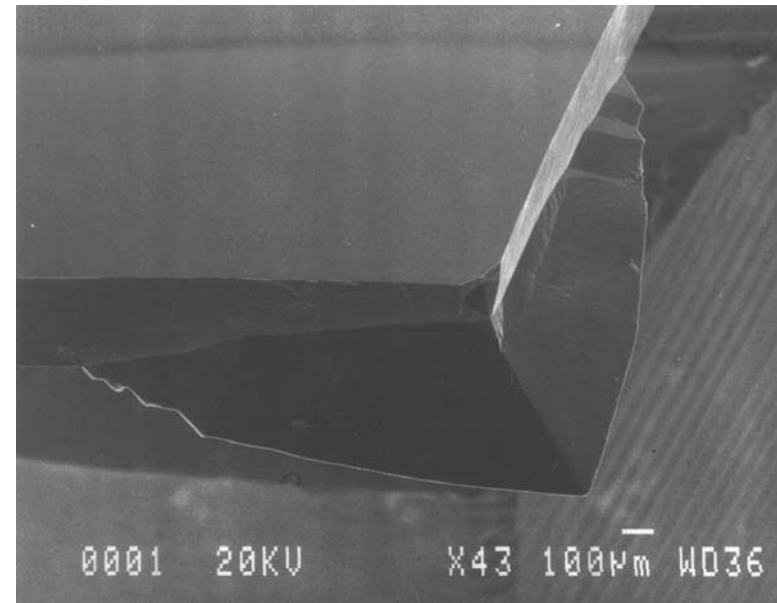


# (110) Si Wet Etch (13)

- Compensation results
  - Very large unwanted residues at the bottom
  - Features sharp corners at the top of the structures



Etch front place : 311



Etch front place : 771



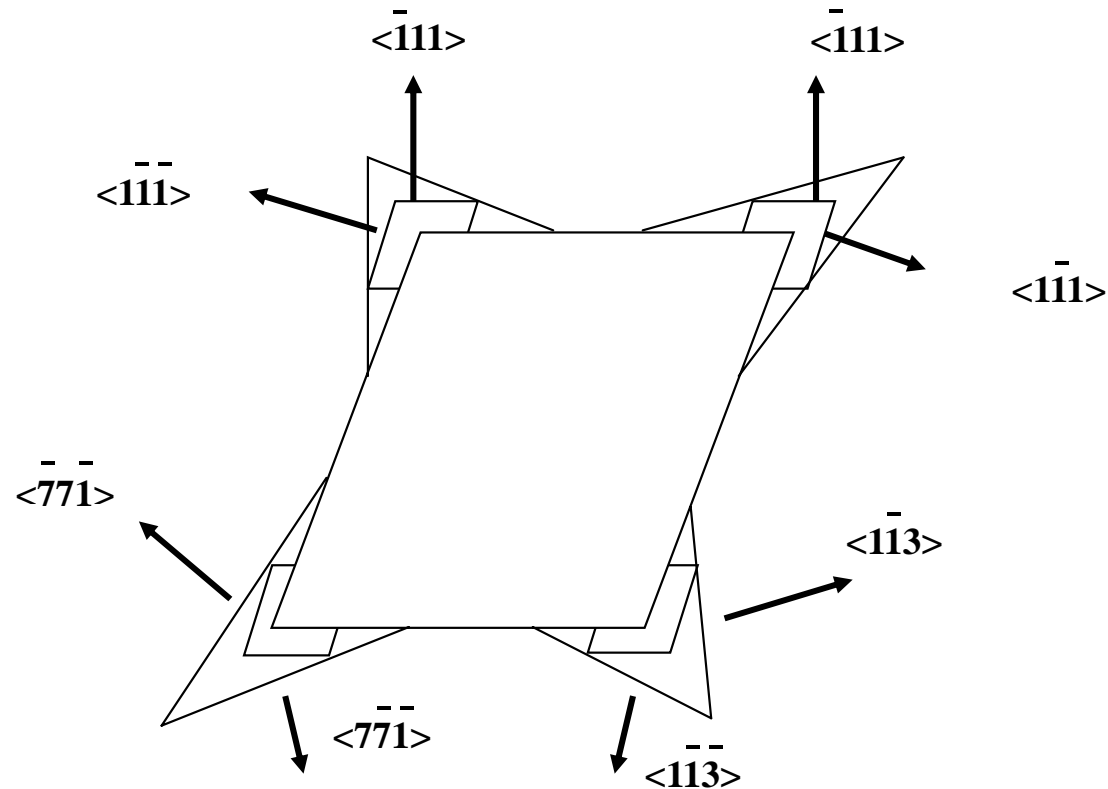
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# (110) Si Wet Etch (14)

- Rhombic compensation pattern design



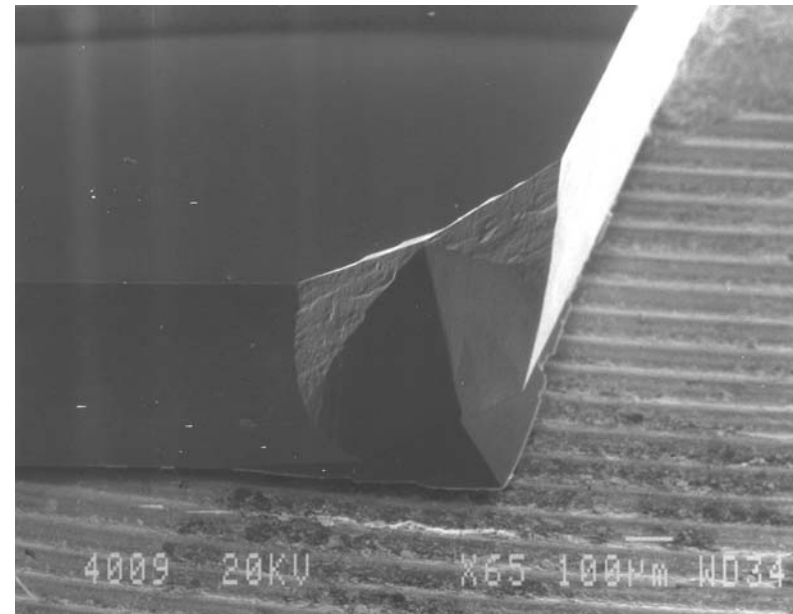
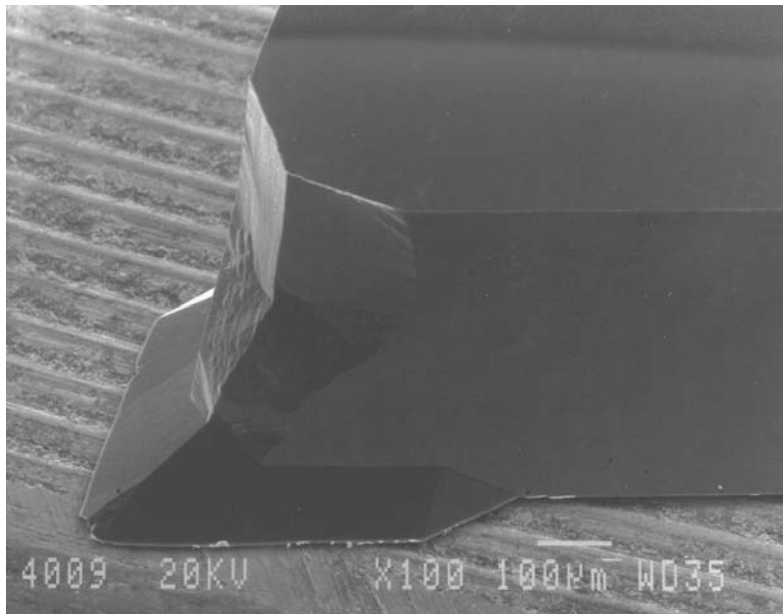
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# (110) Si Wet Etch (15)

- Compensation results
  - Good compensation effects on both corners
  - Very small unwanted residues at the bottom
  - Features relatively sharp corners at the top



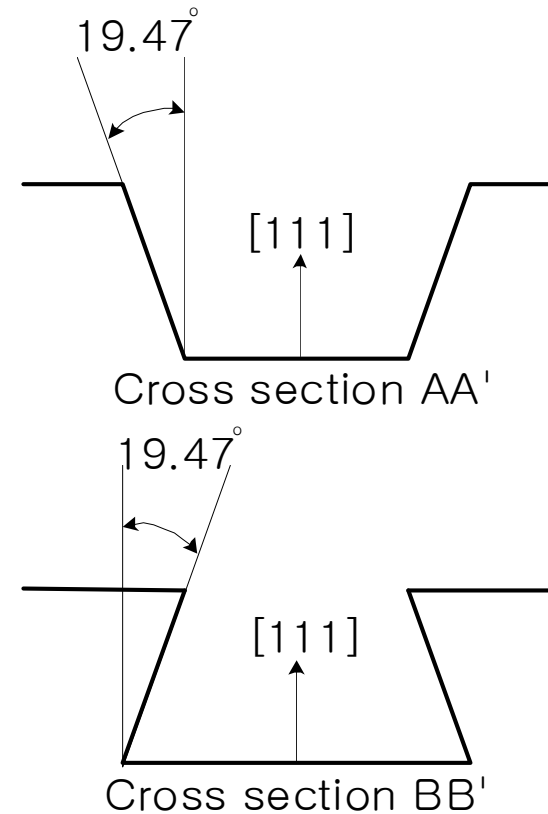
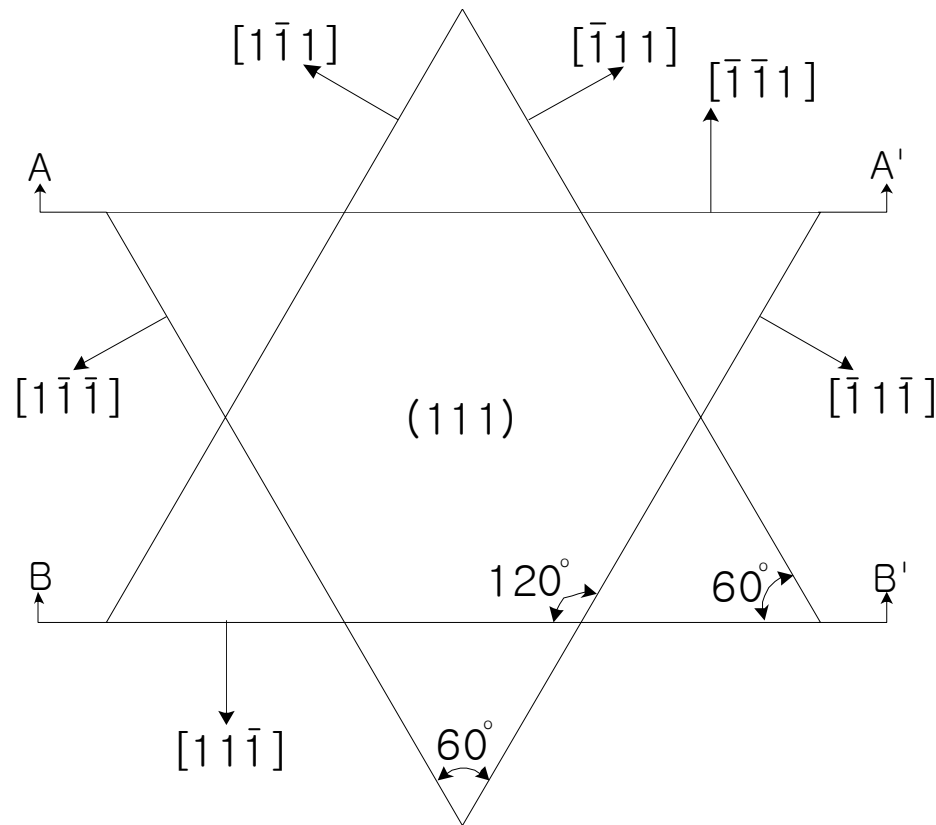
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# (111) Si Wet Etch (1)

- Crystallography of Si (111)

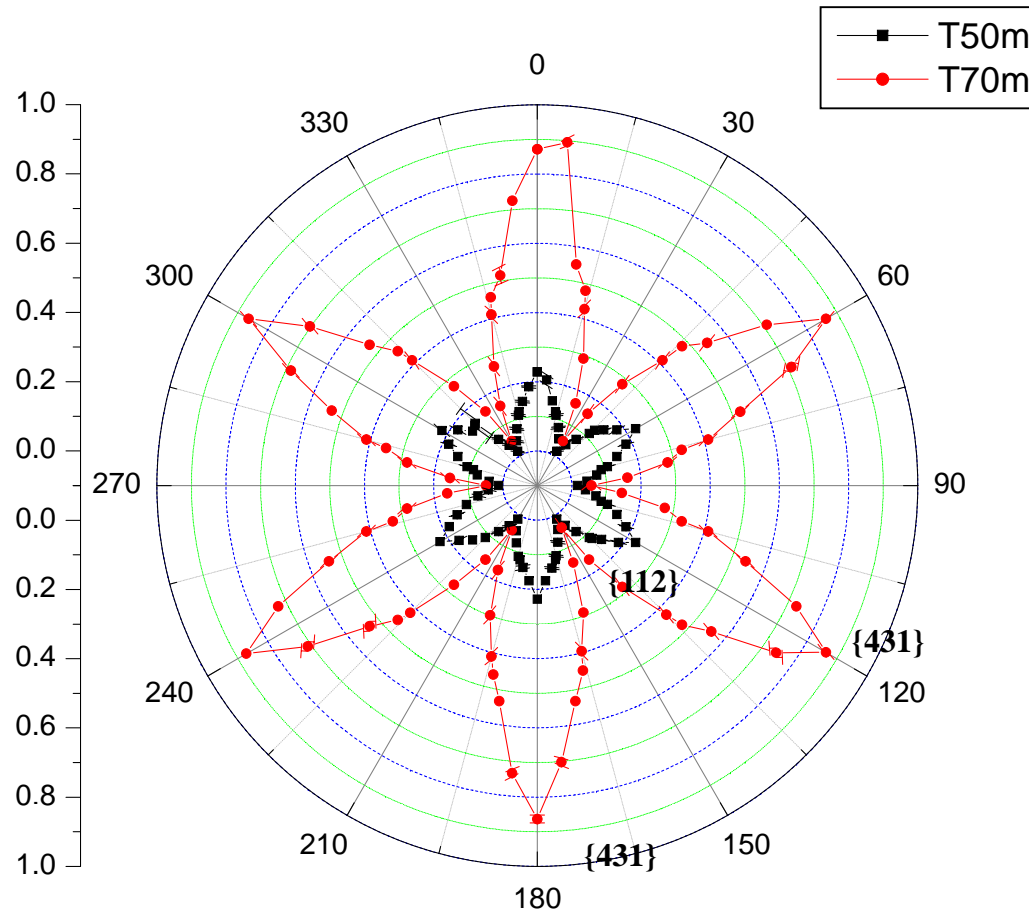


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# (111) Si Wet Etch (2)



40wt % KOH

T50m: 50 °C

T70m: 70 °C

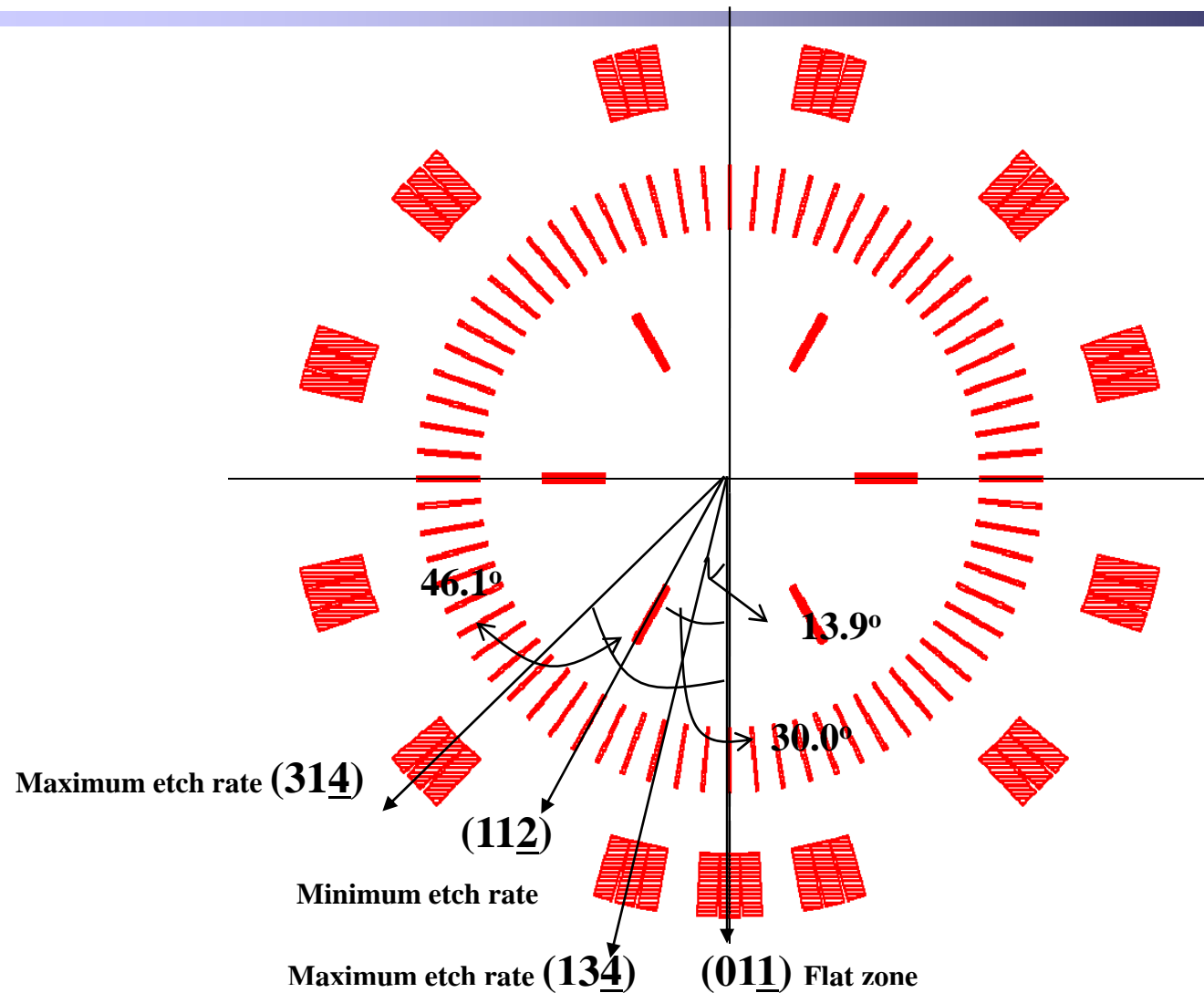


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# (111) Si Wet Etch (3)

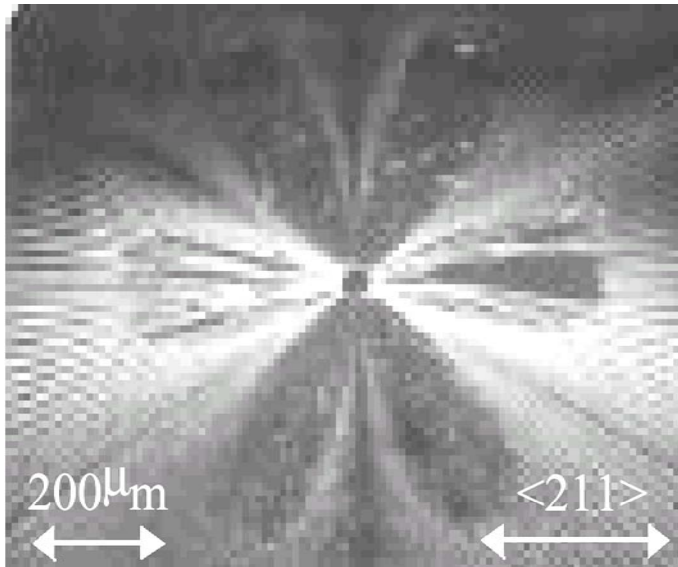


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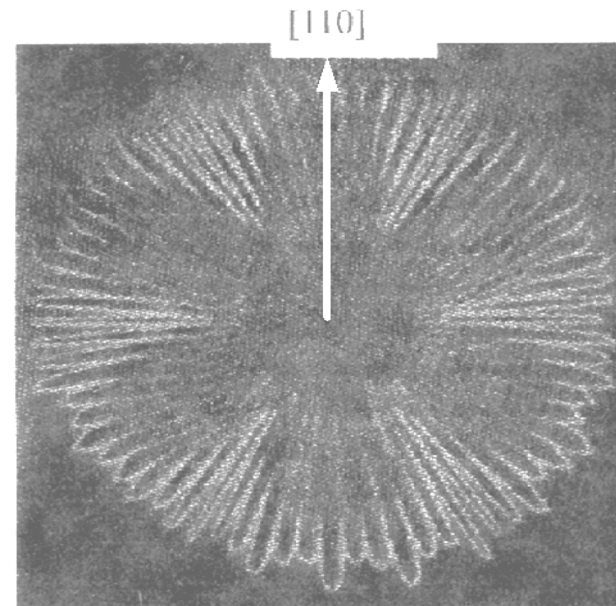
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# (111) Si Wet Etch (4)



22 wt% TMAH at 80°C

Ref) M. Sekimura, MEMS99, 1999



KOH at 80°C

Ref) B.C.S. Chou, C-N. Chen, and J-S. Shie,  
Sensors and Actuators A, vol. 75, 1999



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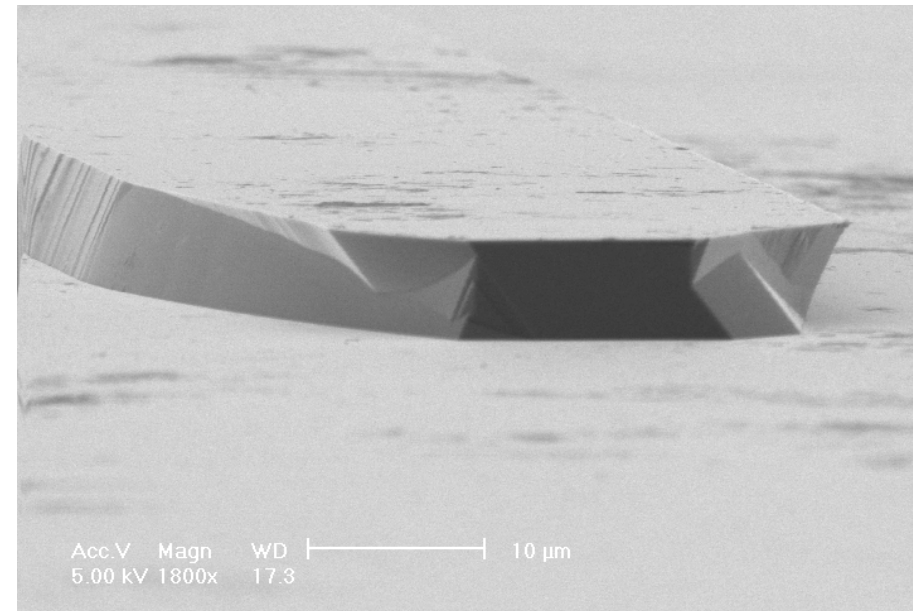
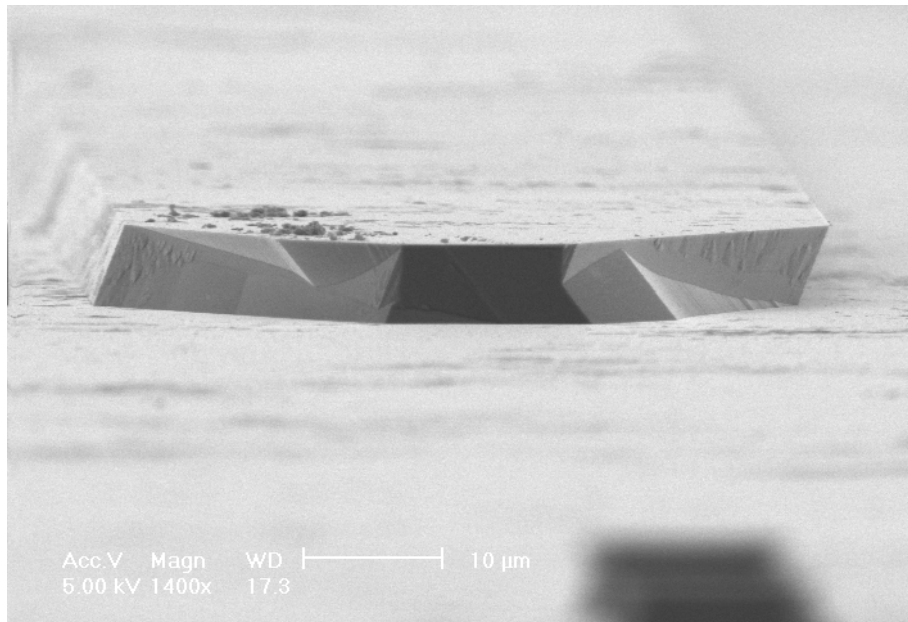
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# (111) Si Wet Etch (5)

- SEM view: (111) wafer, TMAH 10%, 50°C



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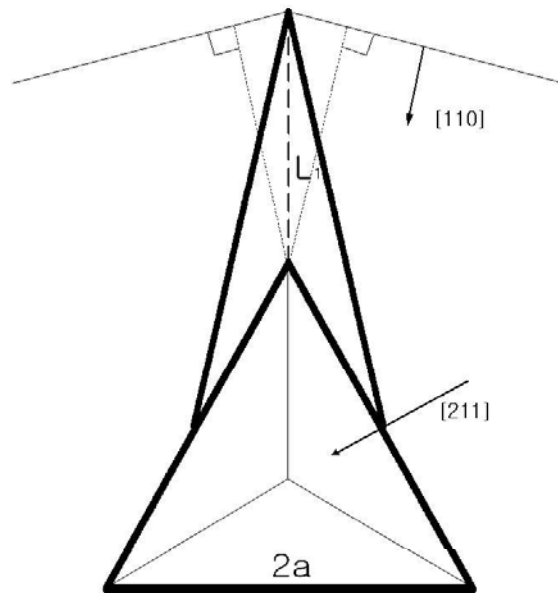
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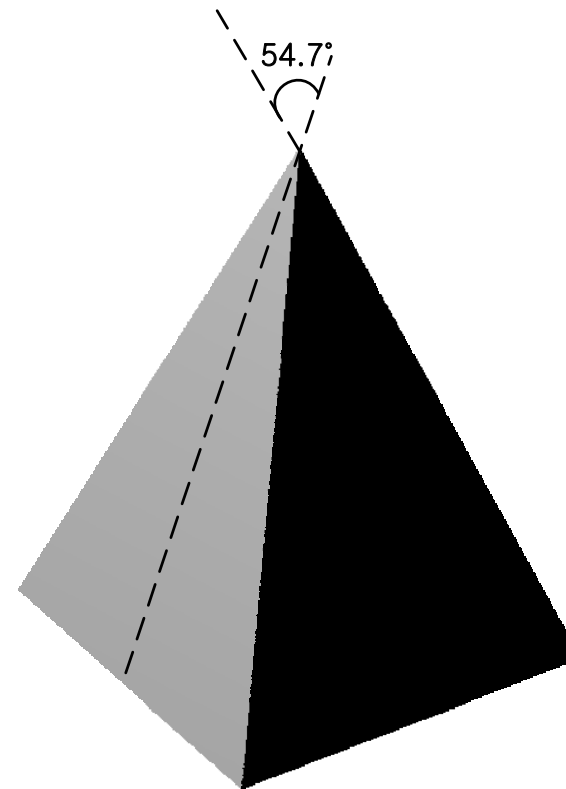


# (111) Si Wet Etch Application (1)

- 3 {111}-faceted tip
  - Very sharp tip with  $54.7^\circ$
  - Convex compensation design



$$L_1 = \frac{2}{3} a \sin 70.53^\circ \frac{R_{110}}{R_{211}}$$



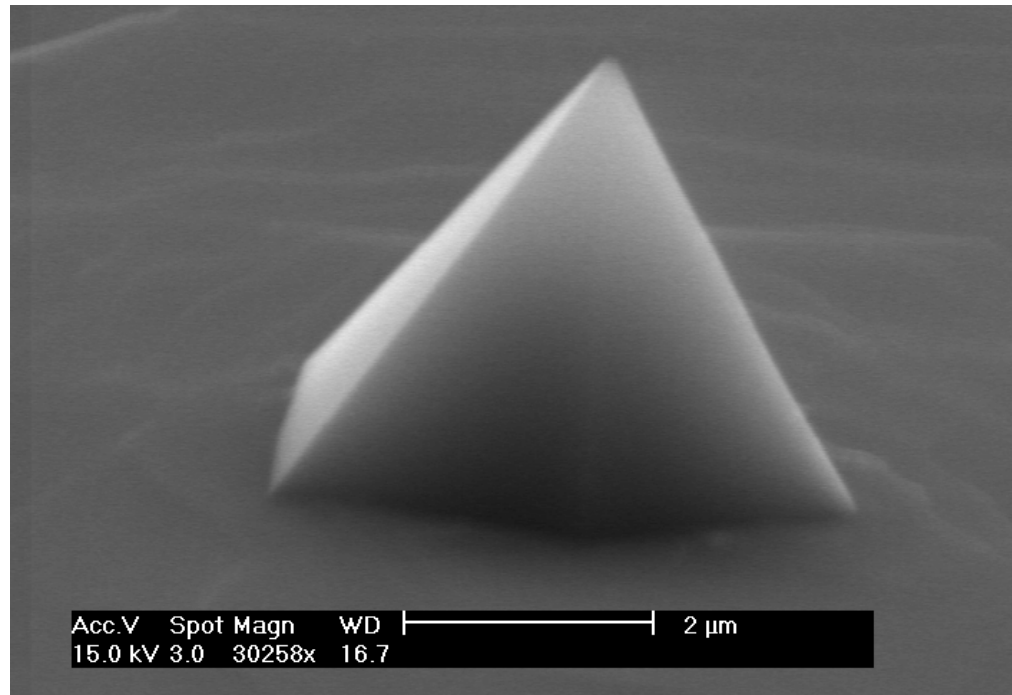
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# (111) Si Wet Etch Application (2)

- 3 {111}-faceted tip (composed of  $(\bar{1}11), (1\bar{1}1), (11\bar{1})$  )
  - Wet etch time: 3 min
  - Tip height: 5  $\mu\text{m}$



3 {111}-faceted tip



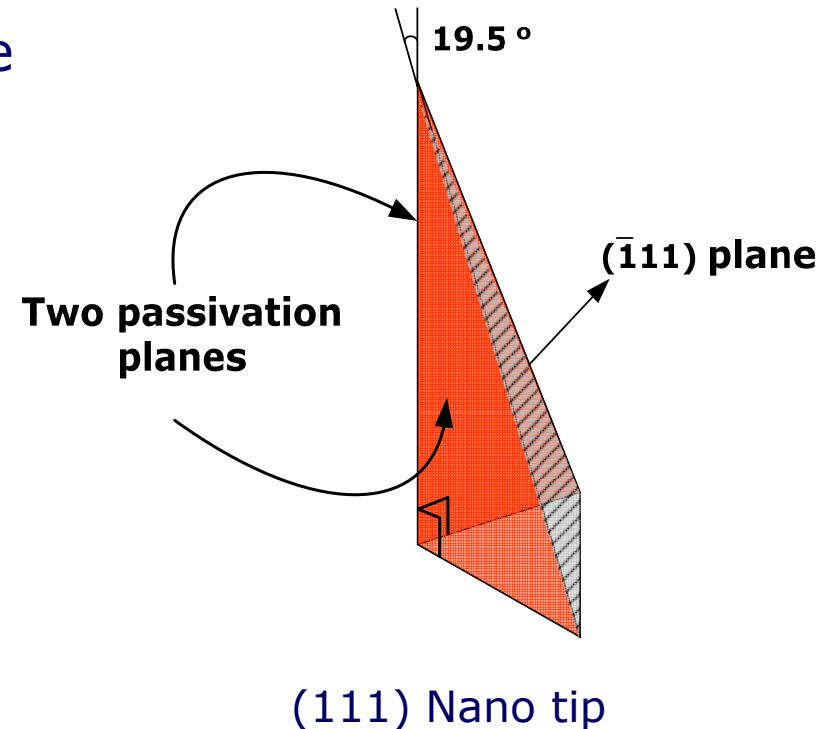
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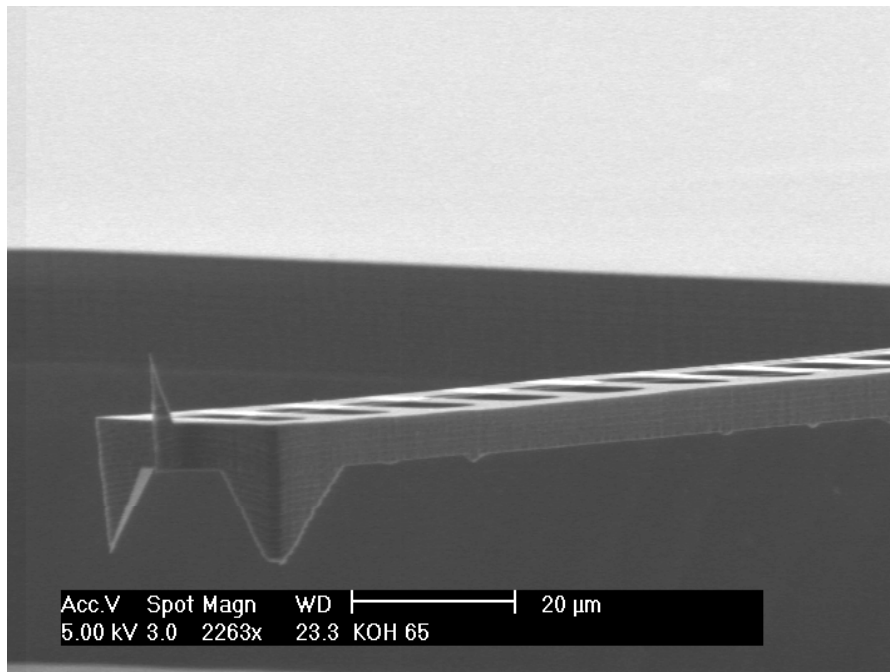
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# (111) Si Wet Etch Application (3)

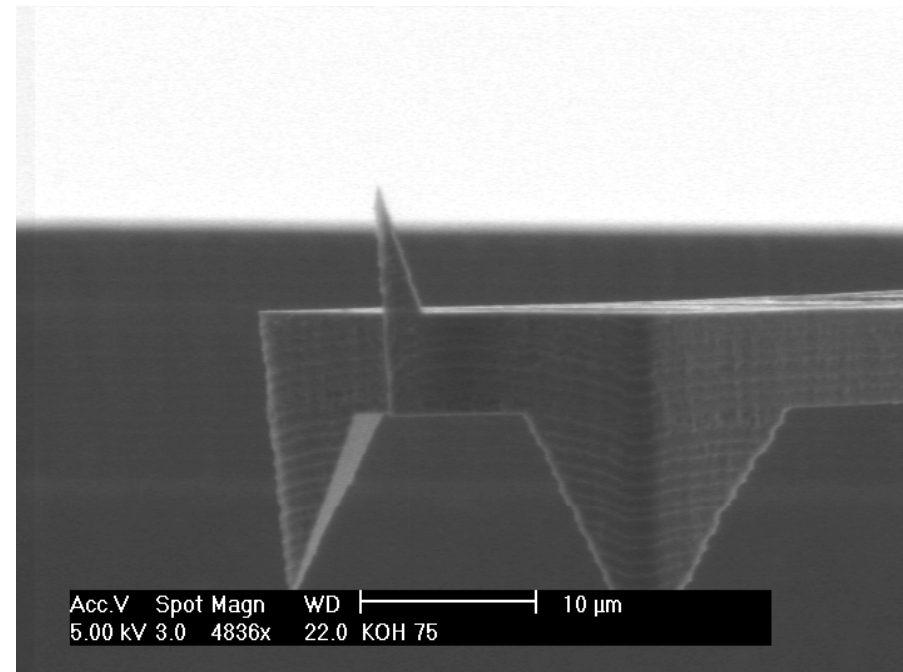
- (111) Nano tip
  - Consist of single (111) plane and two passivation planes
- Advantages
  - Tip sharpness
    - Ultra-sharp cone angle
    - High-aspect ratio nano tip
  - Stable wet etch properties
    - Wet etch time
    - Wet etch conditions



# (111) Si Wet Etch Application (4)



Single nano tip



Tip height: 10 μm

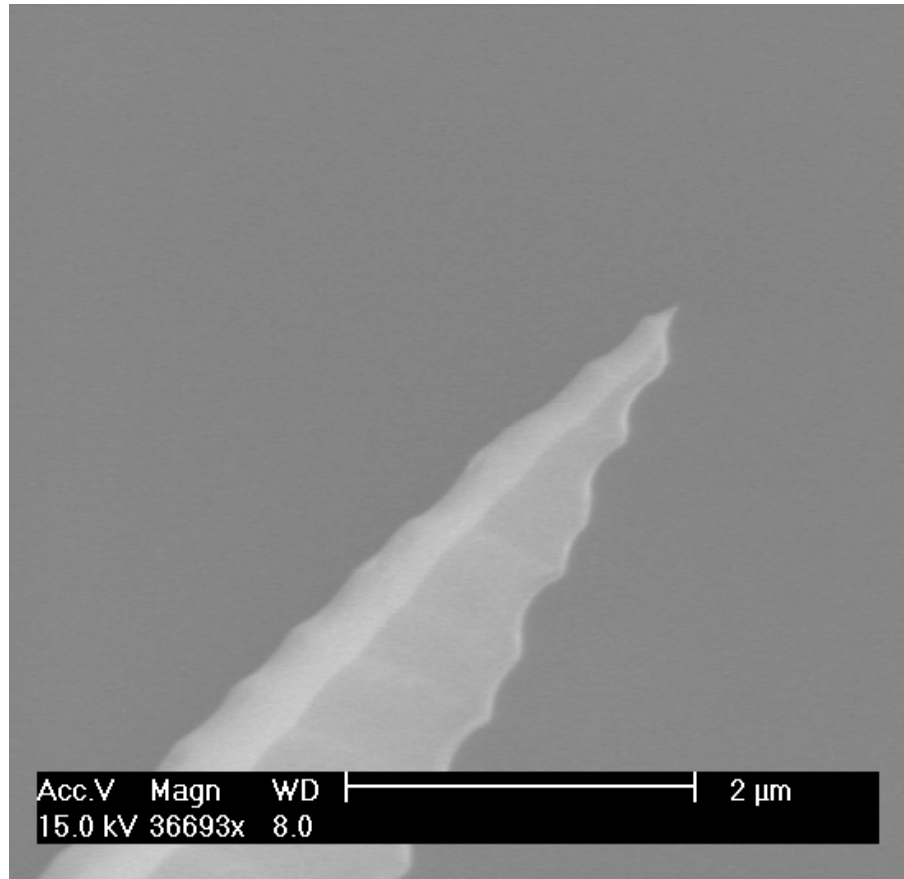


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# (111) Si Wet Etch Application (5)



- Specification of nano tip
  - Cantilever
    - Thickness: 8 μm
    - Length: 250 μm
    - Width: 30 μm
    - Pitch: 200 μm
  - Nano tip
    - Height: 10 μm
    - Aspect ratio: 3:1
    - Tip radius: 10 nm
    - Total cone angle: 19.5°



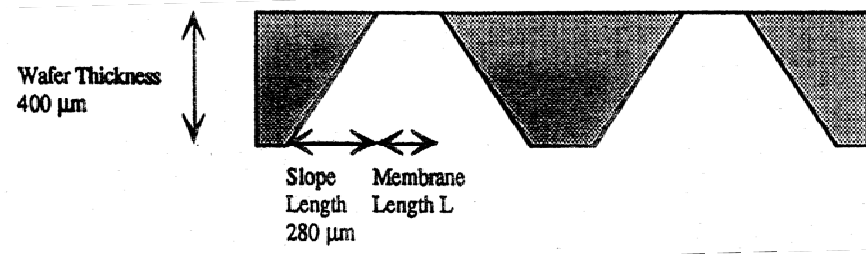
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# Limitation of Wet Etch

- Processing yield: dependent with etch stop method
  - Time etch stop is simple but not reliable
  - Electrochemical etch stop is reliable but complex
- Limited Geometry Freedom (Crystal-direction Dependence)
- Extensive Real Estate Consumption & Large Dimension



- Corner Compensation
- However, for nozzles & grooves, proven mass production method (e.g. injector nozzles, ink jet printer nozzles, pressure sensors, ...)



# Reference

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- K. R. Williams, and R. S. Muller, "Etch Rate for Micromachining Processing," *Microelectromechanical Systems, Journal of*, Vol. 5, No. 4, pp. 256-269, 1996
- K. R. Williams, K. Gupta, and M. Wasilik, "Etch rates for micromachining processing-Part II," *Microelectromechanical Systems, Journal of*, Vol. 12, No. 6, pp. 761-778, 2003
- S. Lee, S. Park, and D. Cho, "The Surface/Bulk Micromachining (SBM) process: anew method for fabricating released microelectromechanical systems in single crystal silicon," *J. Microelectromechanical Syst.*, to appear Sept. 1999
- Kim, B. and Cho, D., "Aqueous KOH Etching of (110) Silicon- Etch Characteristics and Compensation Methods for Convex Corners," *J. of Electrochemical Society*, 145(7), pp. 2499-2507, July 1998
- H. Seidel, "Anisotropic Etching of Crystalline Silicon in Alkaline Solution," *J. of Electrochemical Society*, 137(11), pp. 3613-3632, Nov. 1990



# Reference

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- Kurt E. Petersen, "Silicon as a Mechanical Material," Proceedings of The IEEE, 70(5), pp. 420-457, May 1982
- Melissa A. Hines, "Understanding the Evolution of Silicon Surface Morphology during Aqueous Etching," Sensors and Materials, 13(5), pp. 247-258, 2001
- Paik S., "Characteristics of (111)-oriented Silicon in Aqueous TMAH and its Applications ", MS Thesis, Seoul National University, 2001.
- Marc J. Madou, "Fundamentals of MICROFABICATION 2<sup>nd</sup> edition," CRC Press, 1997.
- J. D. Lee, "Silicon Integrated Circuit microfabrication technology 2<sup>nd</sup> edition," Daeyoungsa, 1997.
- Gregory T. A. Kovacs, "Micromachined Transducers Sourcebook 1<sup>st</sup> edition," McGraw-Hill Science/Engineering/Math, 1998.
- S.M. Sze, "Semiconductor sensors," JOHN WILEY & SONS, INC., 1994

