Principles of Micro- and Nanofabrication for Electronic and Photonic Devices

Etching 刻蚀

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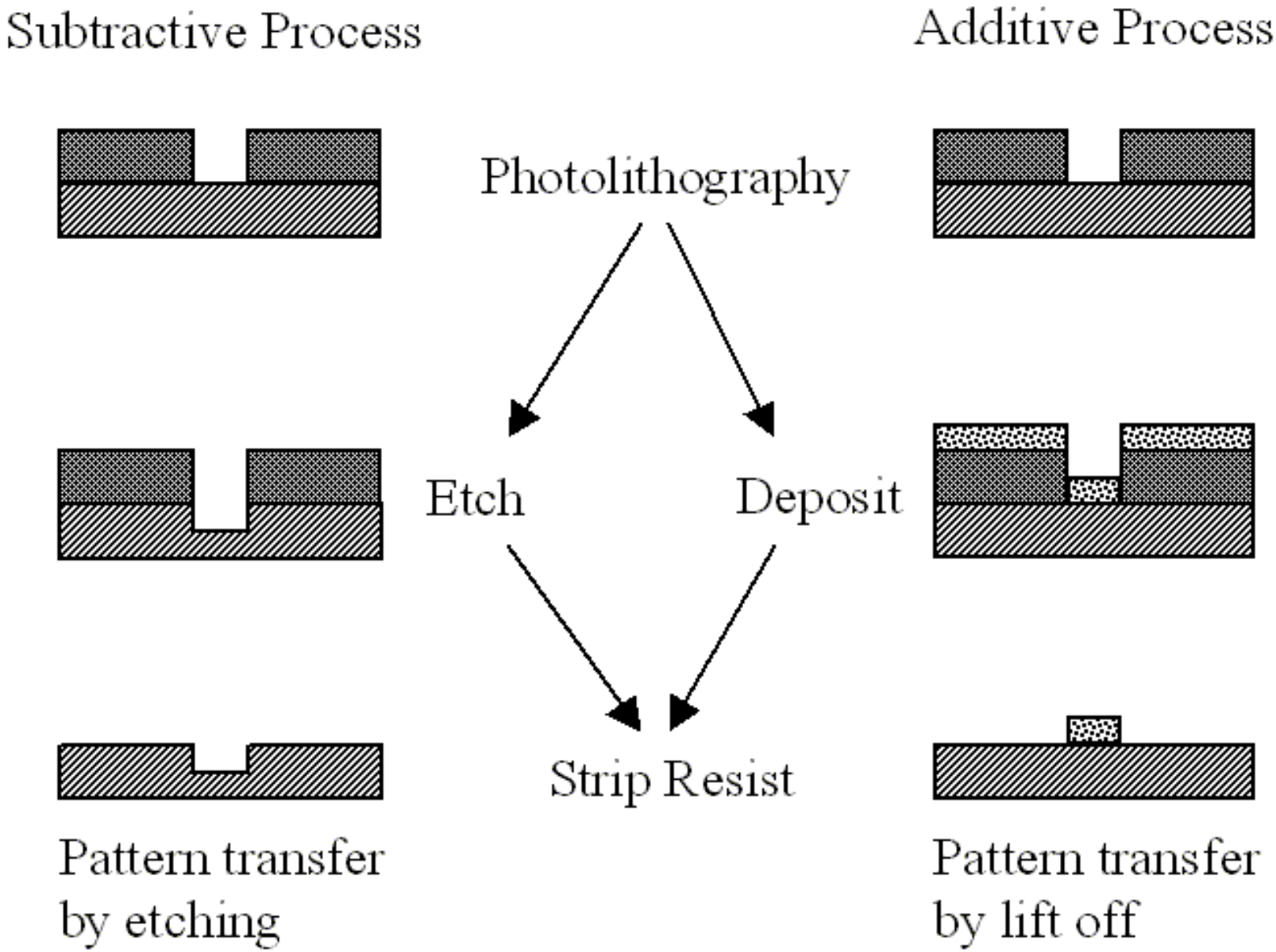
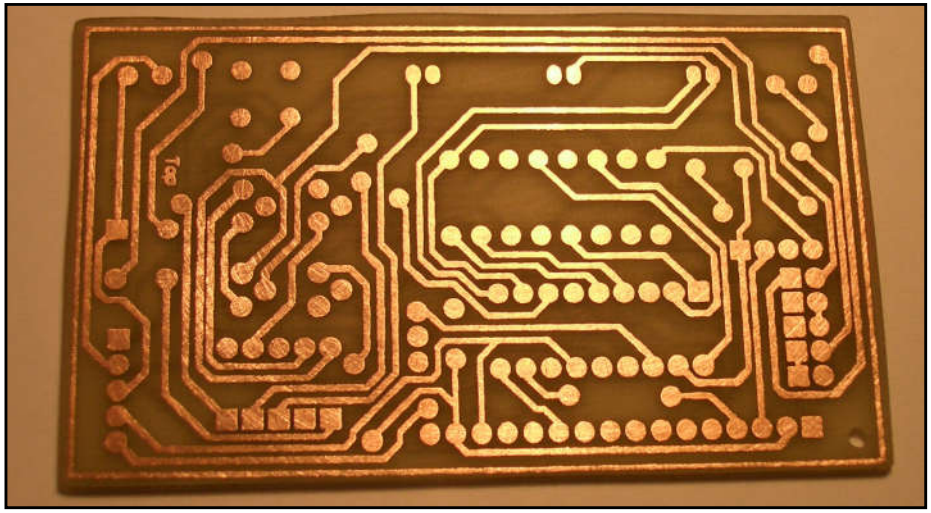
Pattern Formation



Etching vs. Corrosion

Etching (刻蚀)



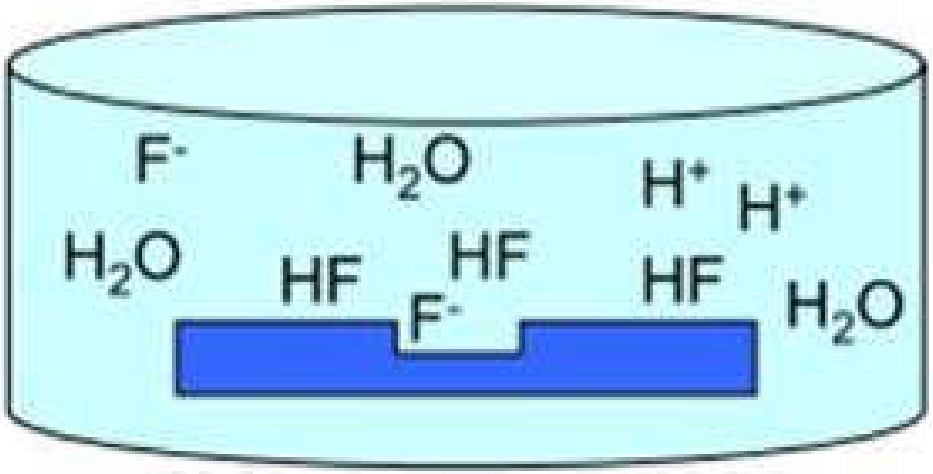
wanted

Corrosion (腐蚀)

unwanted

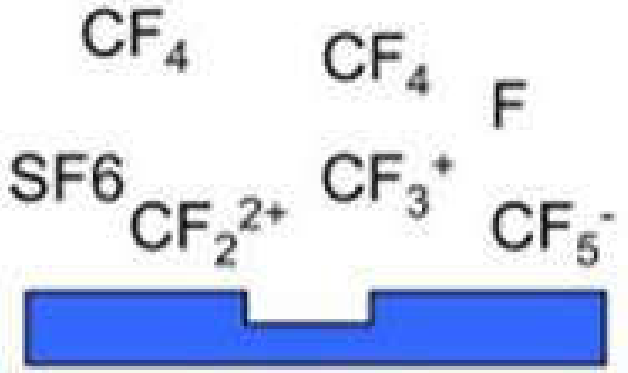
Wet vs. Dry

liquid source



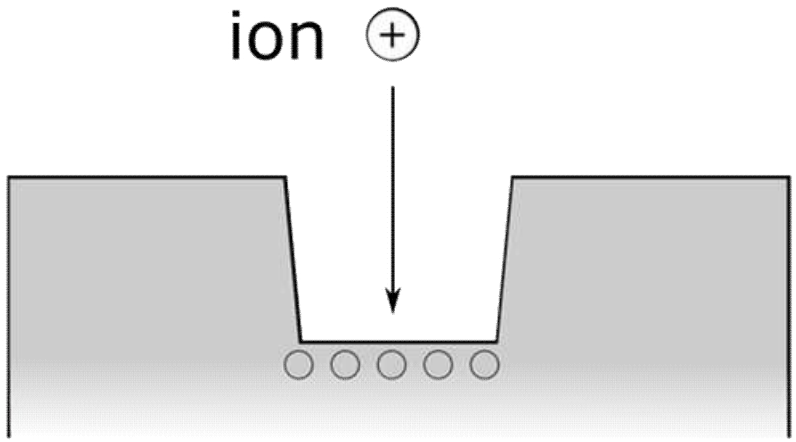
Wet Etch

gas source

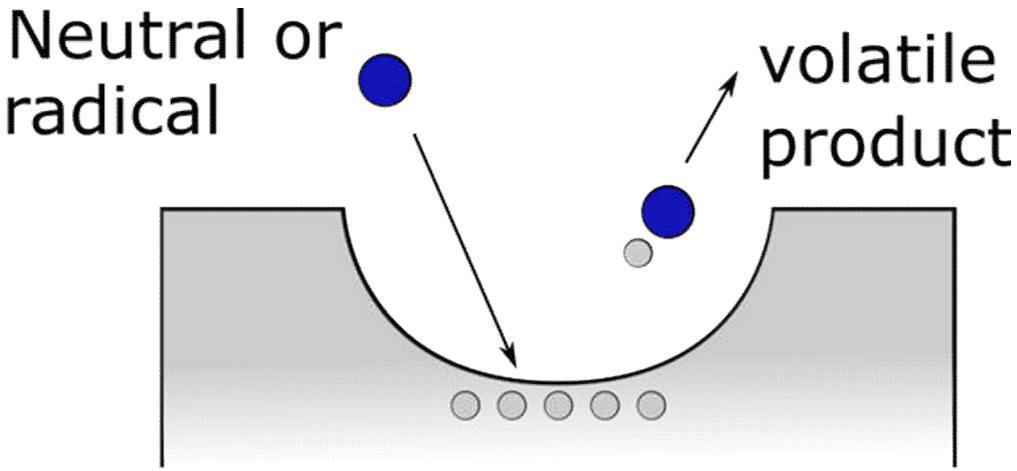


Dry Etch

Chemical vs. Physical



Physical etching
(sputtering)

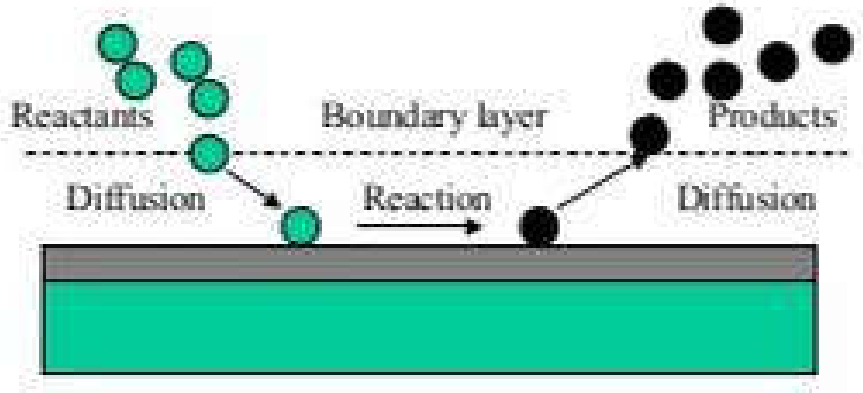


Chemical Etching

Etching

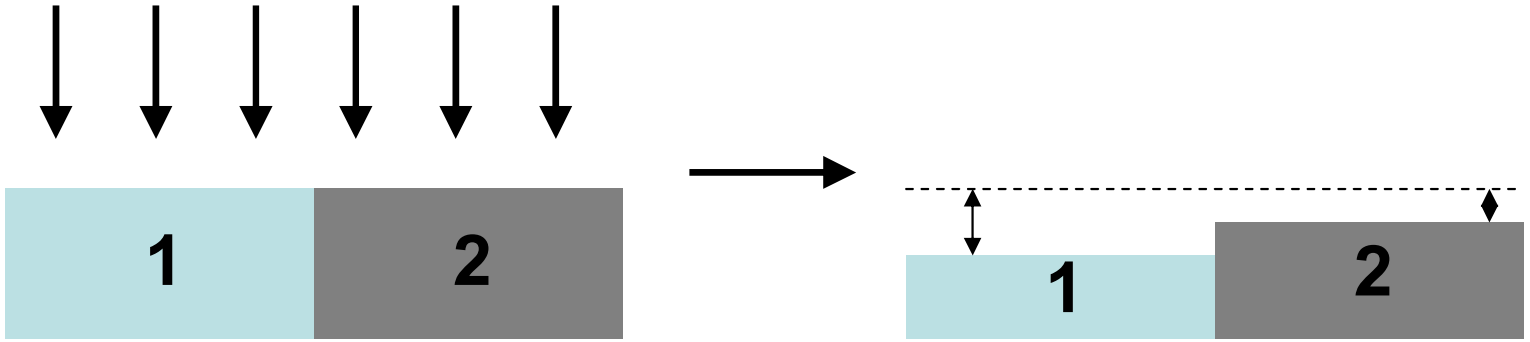
- **Process Parameters**
  - Time
  - Temperature
  - Etchant type
  - Etchant concentration
  - Mask type
  - ...
- **Control Parameters**
  - Etch rate
  - Selectivity
  - Anisotropy
  - Uniformity
  - ...

diffusion - reaction - diffusion

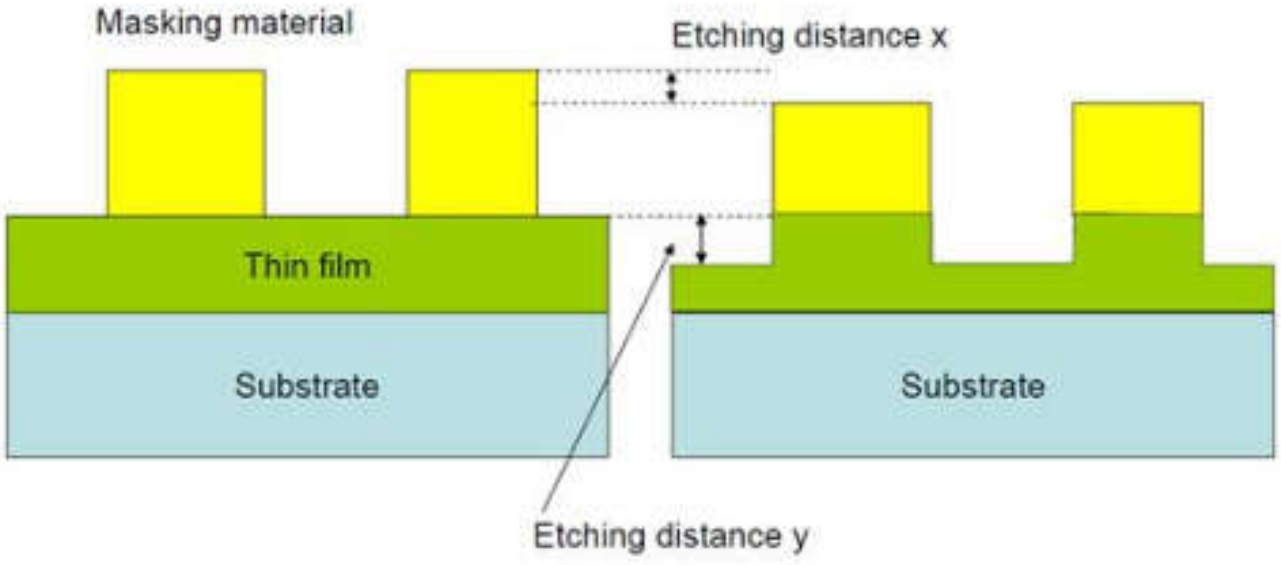


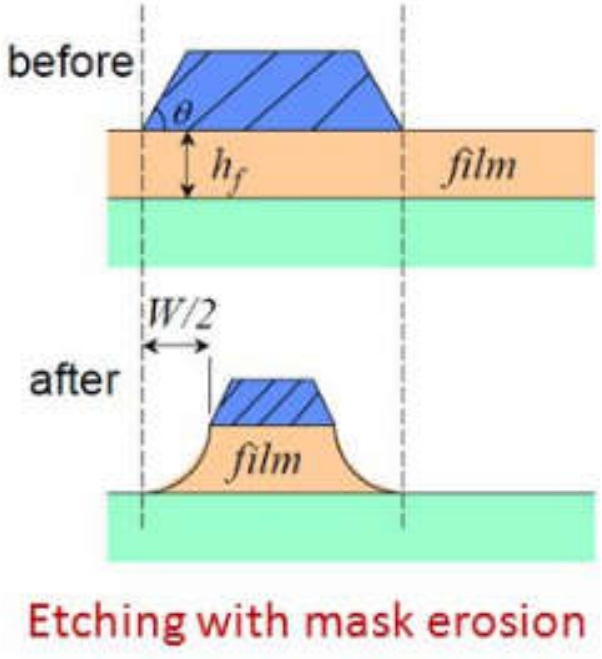
- chemical reactions occur
- products should be disposable

Selectivity



$$S_{12} = \frac{R_1}{R_2}$$





Etching with mask erosion

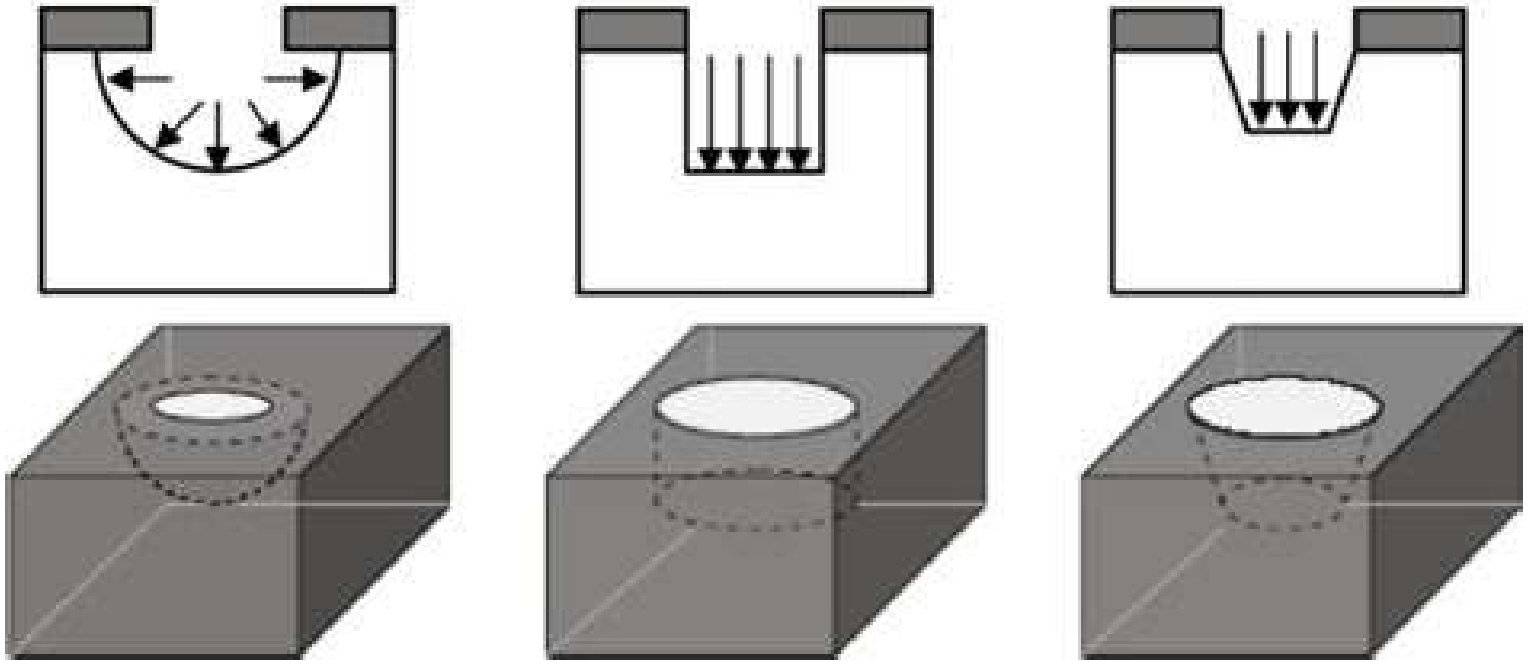
Selectivity - Example

- SiO_2 / Si wet etch by HF solution
  - very large selectivity $S_{SiO2/Si}$ ~ infinity
- SiO_2 / Si dry etch by CF_4 plasma
  - selectivity $S_{SiO2/Si}$ ~ 10

Anisotropy (各向异性)

degree of anisotropy

$$A = 1 - \frac{R_{lateral}}{R_{vertical}}$$



isotropic
A = 0

fully anisotropic
A = 1

anisotropic
0 < A < 1

Isotropic vs. Anisotropic

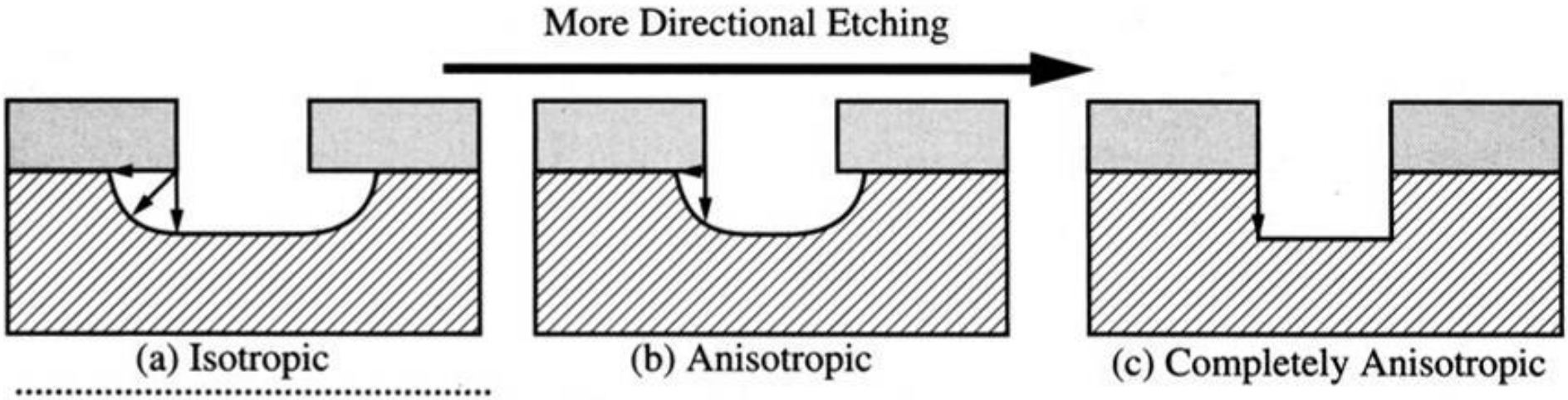
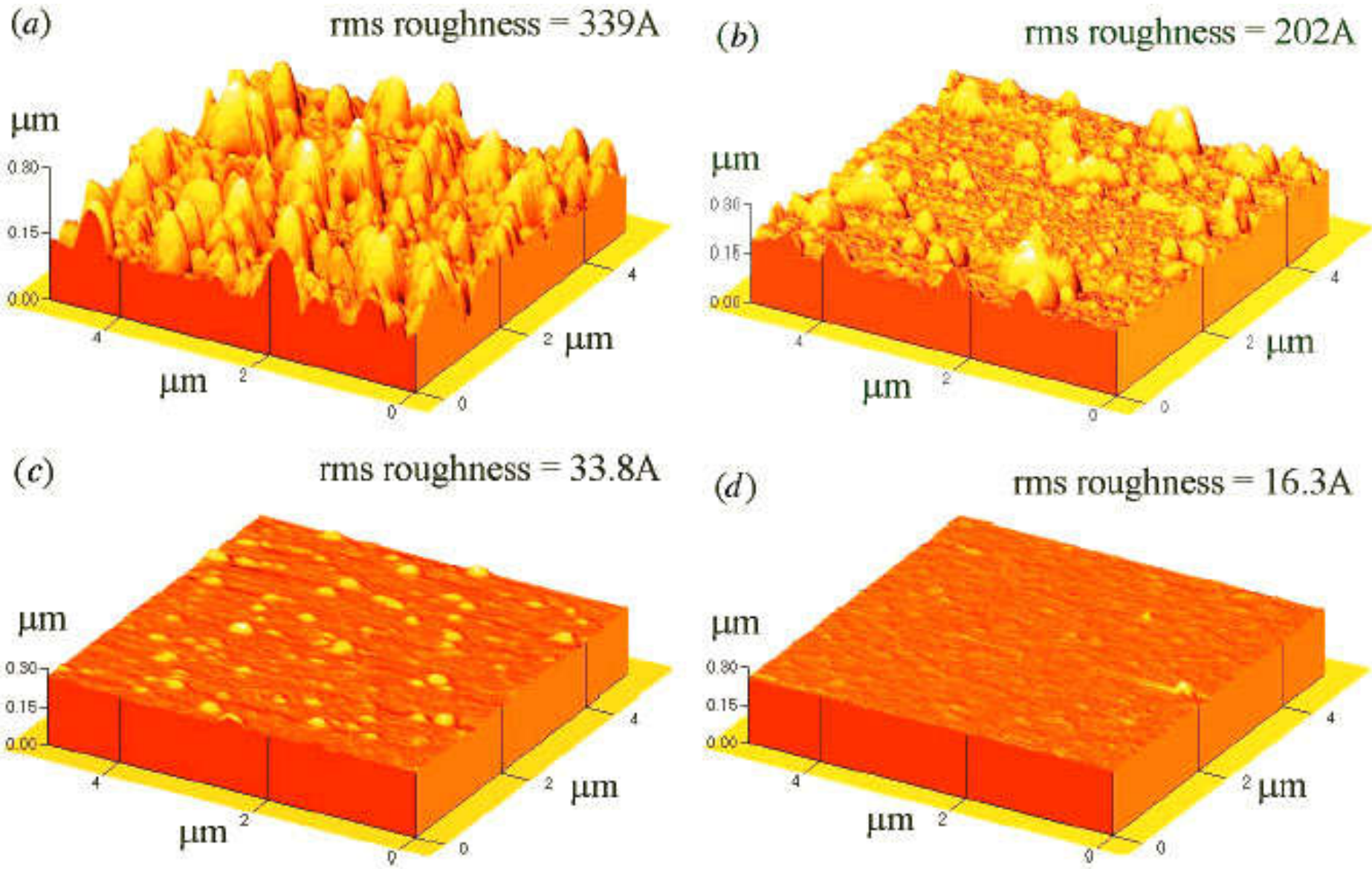


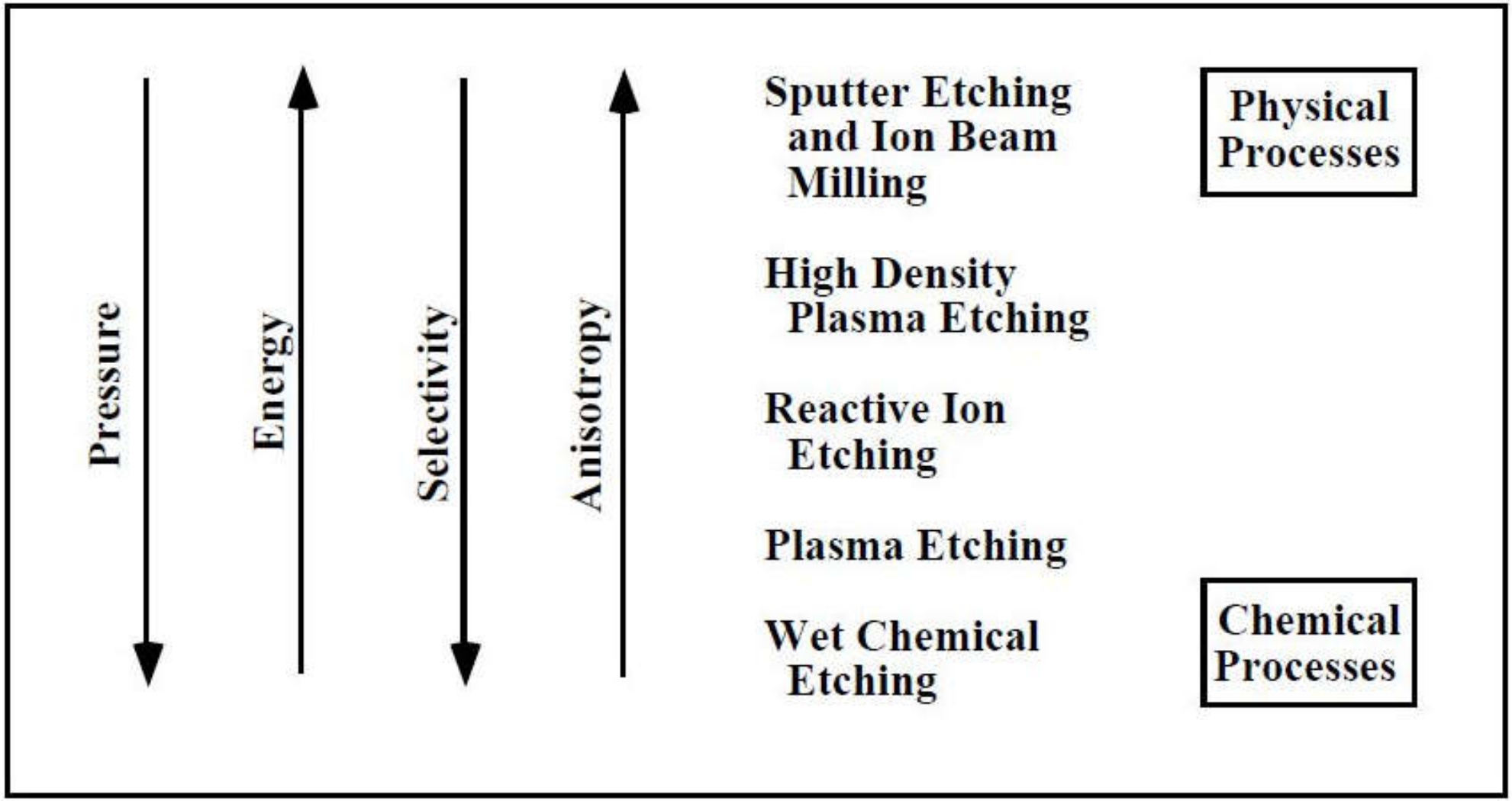
Figure 10–3 Etch profiles for different degrees of anisotropic, or directional, etching: (a) purely isotropic etching; (b) anisotropic etching; (c) completely anisotropic etching.

chemical → **physical**

Uniformity


(a)
rms roughness = 339A
(b)
rms roughness = 202A
(c)
rms roughness = 33.8A
(d)
rms roughness = 16.3A
μm
0.30
0.15
0.00
4
2
0
μm

Trends of Etching



Etching Methods

- Wet Etching 湿法刻蚀
- Dry Etching 干法刻蚀
- CMP and other methods

References

- **Wet Etching Recipes**

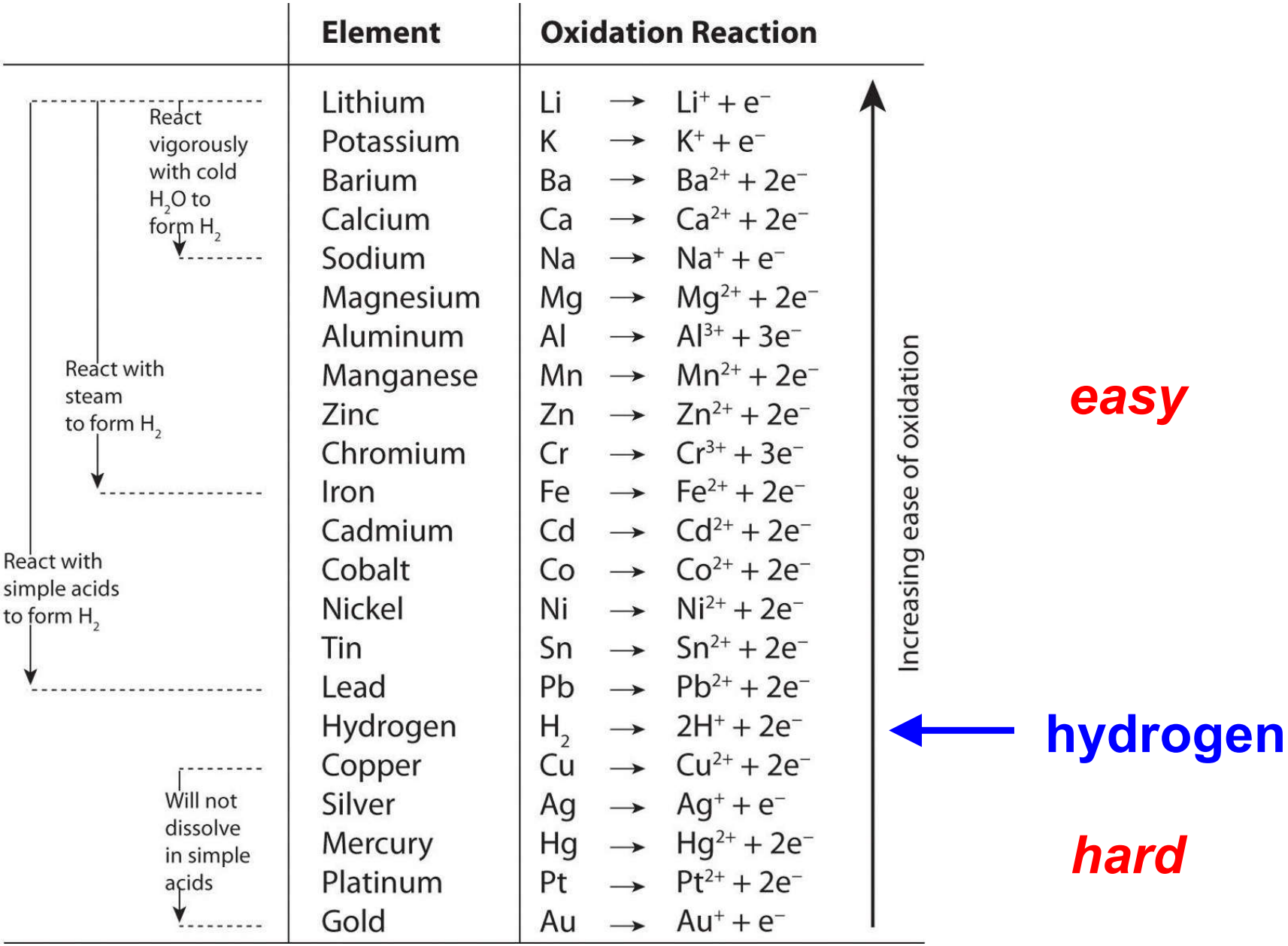
  http://ieeexplore.ieee.org/iel4/84/11954/00546406.pdf
  http://ieeexplore.ieee.org/iel4/84/11954/01257354.pdf

  https://cleanroom.byu.edu/chemical_etching.html

- **Guide to references on III-V semiconductor chemical etching**

http://www.sciencedirect.com/science/article/pii/S0927796X00000279

Metal Dissolution in Acids



Metal Dissolution in Acids

Strong Acids + Strong Oxidants

Piranha $H_2SO_4 : H_2O_2 = 3:1$

dissolves most metals and organics

Aqua Regia (王水) HCl : HNO3 = 3:1

even dissolves Au, Pt

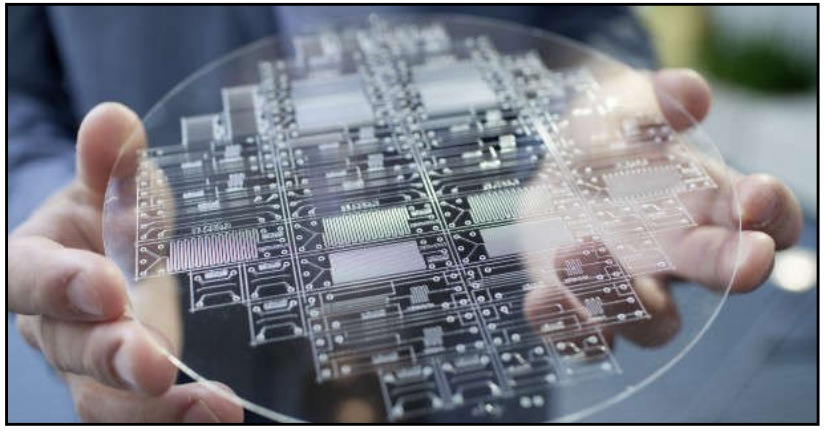
However, difficult to obtain ideal selectivity ...

SiO_2 etching

- Alkali (NaOH, etc) slowly etches SiO_2
  - $SiO_2 + 2NaOH = Na_2SiO_3 + H_2O$
- HF strongly etches SiO_2
  - $SiO_2 + 6HF = H_2SiF_6 + 2H_2O$

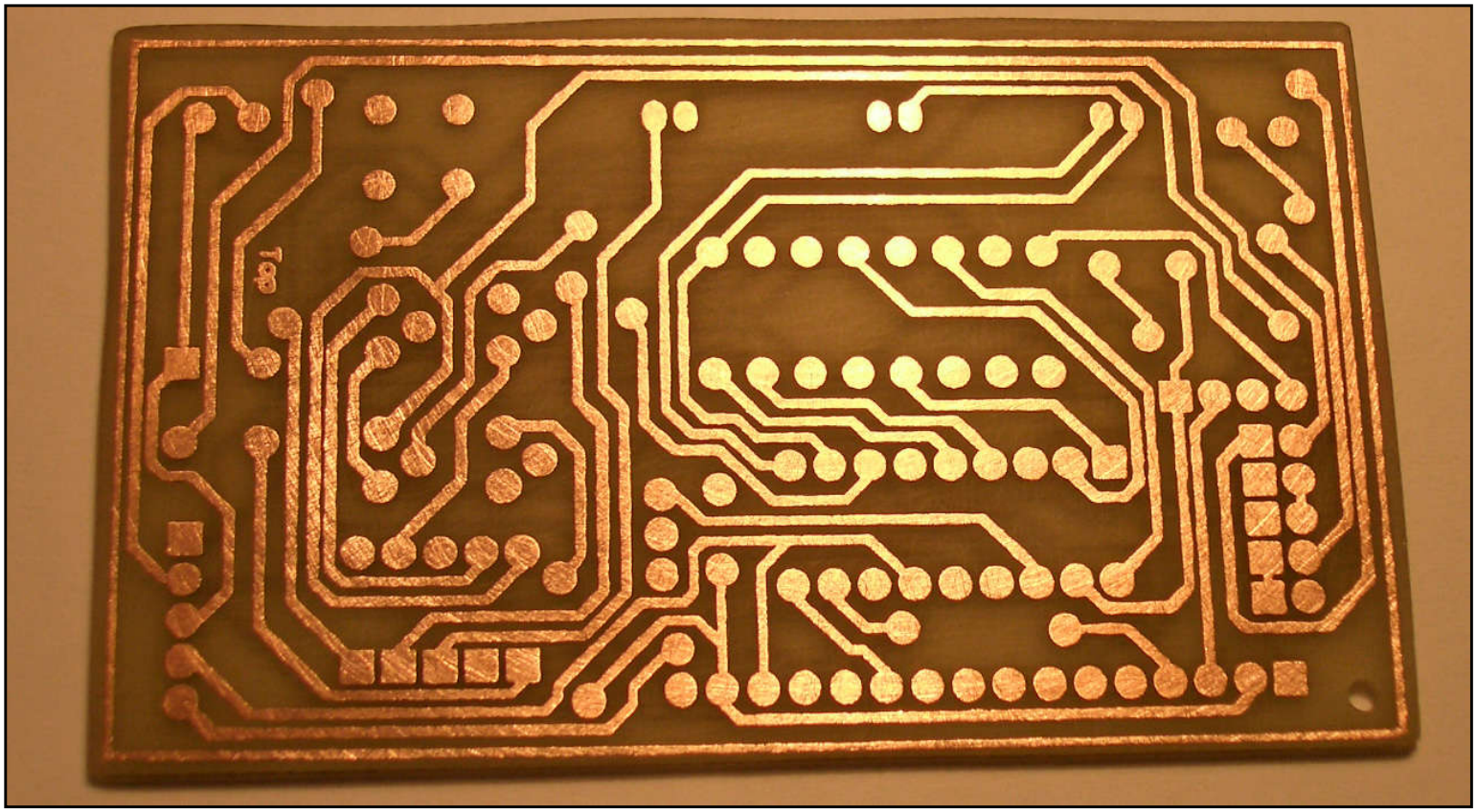
glass art by HF etch

- Buffered HF (BHF/BOE)
  - $HF + NH_4F$
  - lower etch rate
  - safer for use

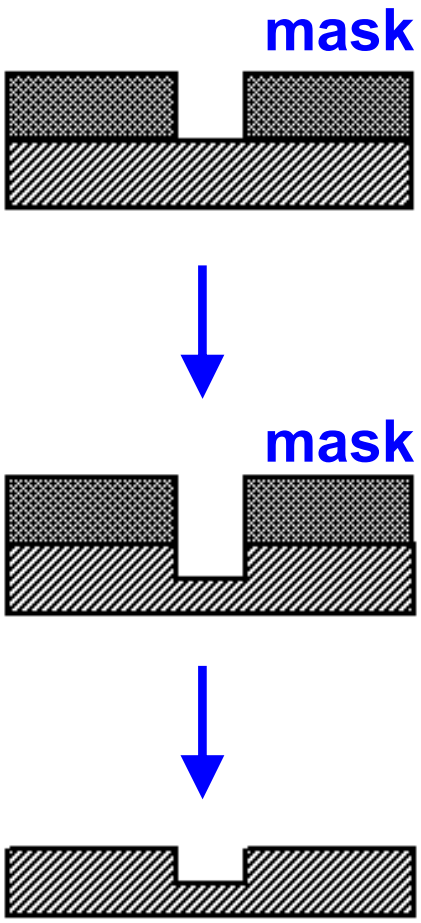


Cu etching

- $Cu + 2FeCl_3 = CuCl_2 + 2FeCl_2$



Selectivity for Wet Etch

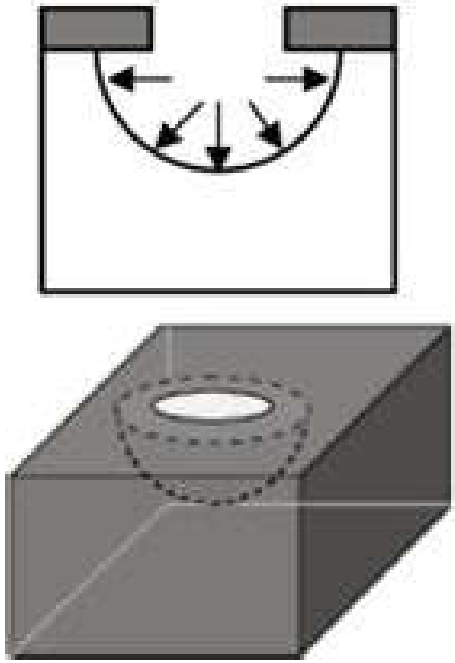


Films	Etchant	Mask
SiO_2	HF	PR
Si	KOH	Si_3N_4
GaAs	H_3PO_4 + H_2O_2	PR
GaP	KOH + $K_3[Fe(CN)_6]$	SiO_2
Cu	$FeCl_3$	PR
Au	KI + I_2	PR

most wet etch recipes are isotropic, except KOH etch for Si

Isotropy for Wet Etch

- Wet etch is usually isotropic
- Exceptions
  - some etching for single crystals
  - KOH etch Si

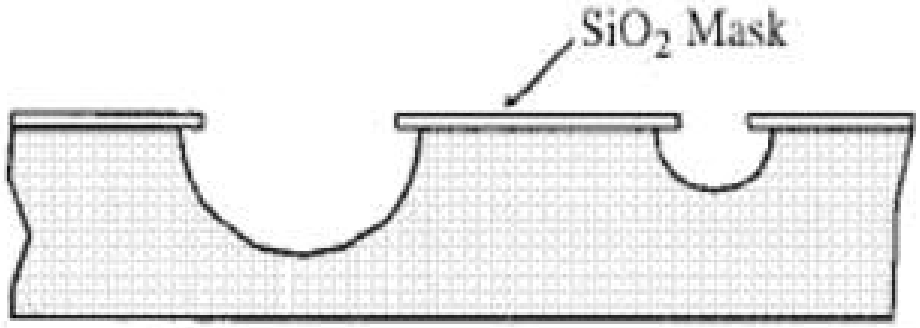


isotropic
A = 0

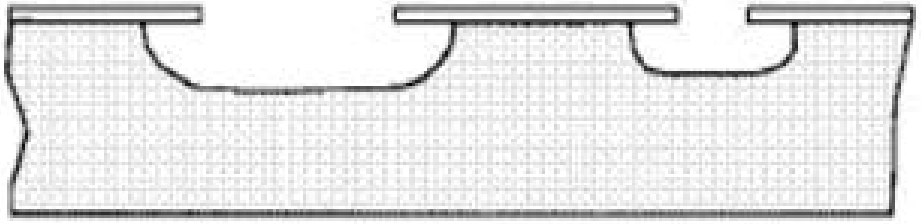
Si etching

- HNO_3 + HF
  - isotropic etch

Isotropic wet etching: Agitation



Isotropic wet etching: No Agitation

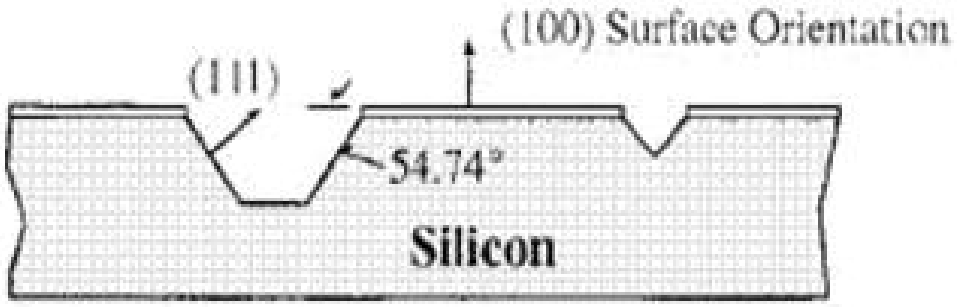


Si etching

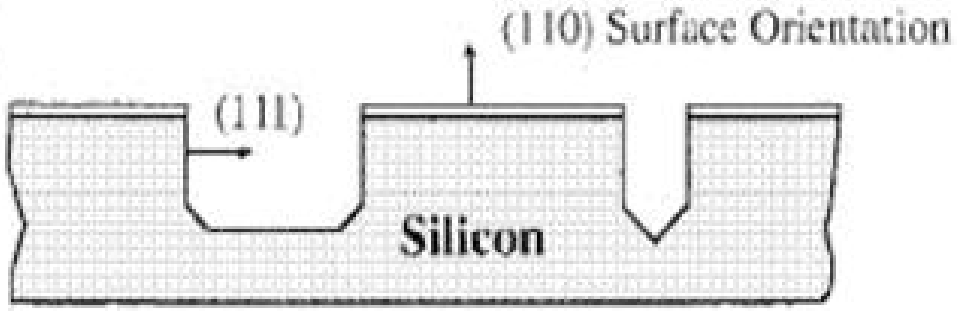
- KOH
  - anisotropic etch
  - etch rate (111):(110):(100) ~ 1:600:400
  - mask: SiO_2, Si_3N_4, Cr/Au, ...

Q: why?

Anisotropic wet etching: (100)



Anisotropic wet etching: (110)

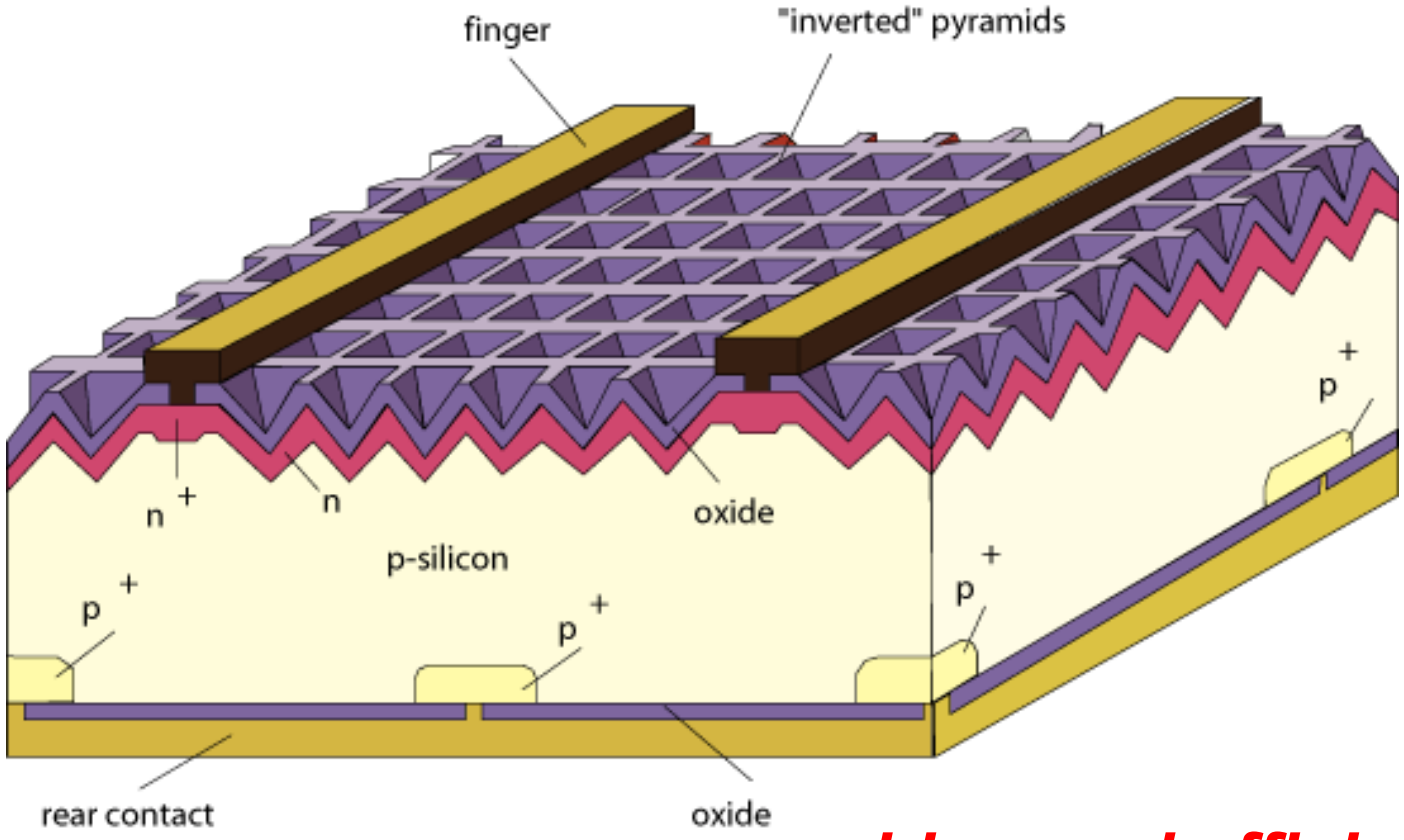


- Other chemistries
  - TMAH: Tetramethyl ammonium hydroxide
  - EDP: Ethylene diamine pyrochatecol

Si etching

- **Single Crystalline Si Solar Cells**
  - **KOH anisotropic etch**

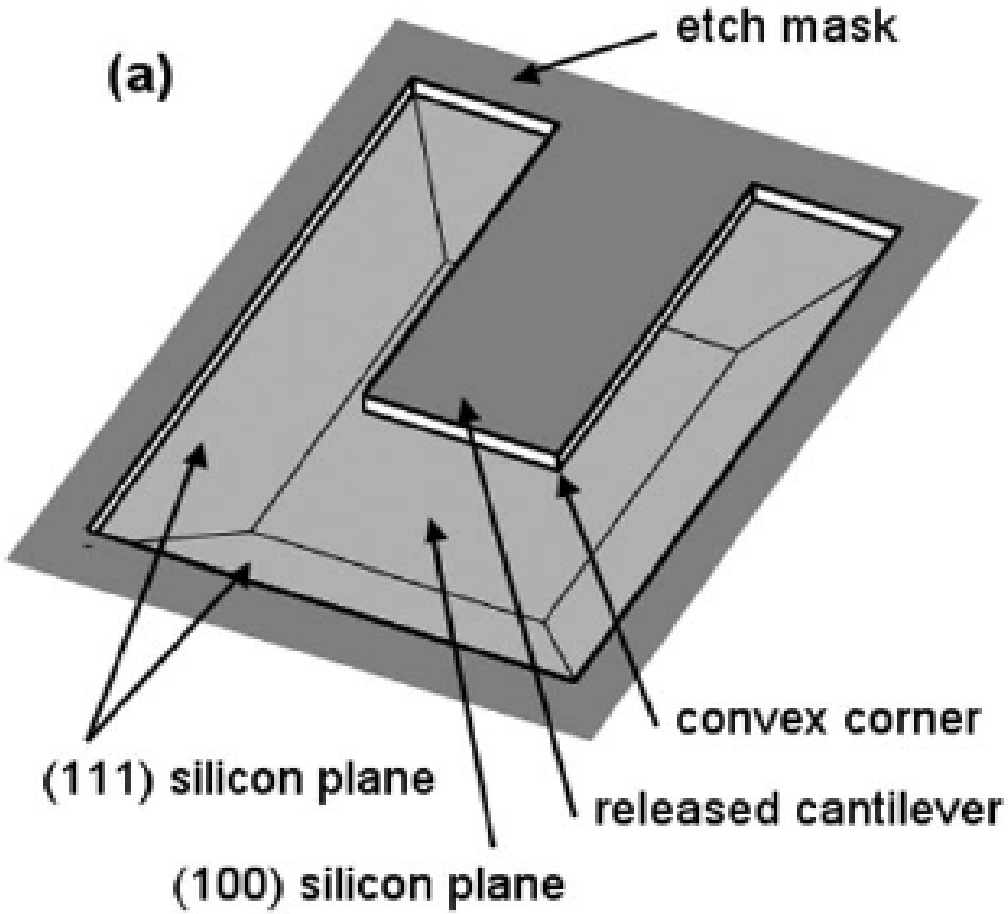
optical trapping and antireflection

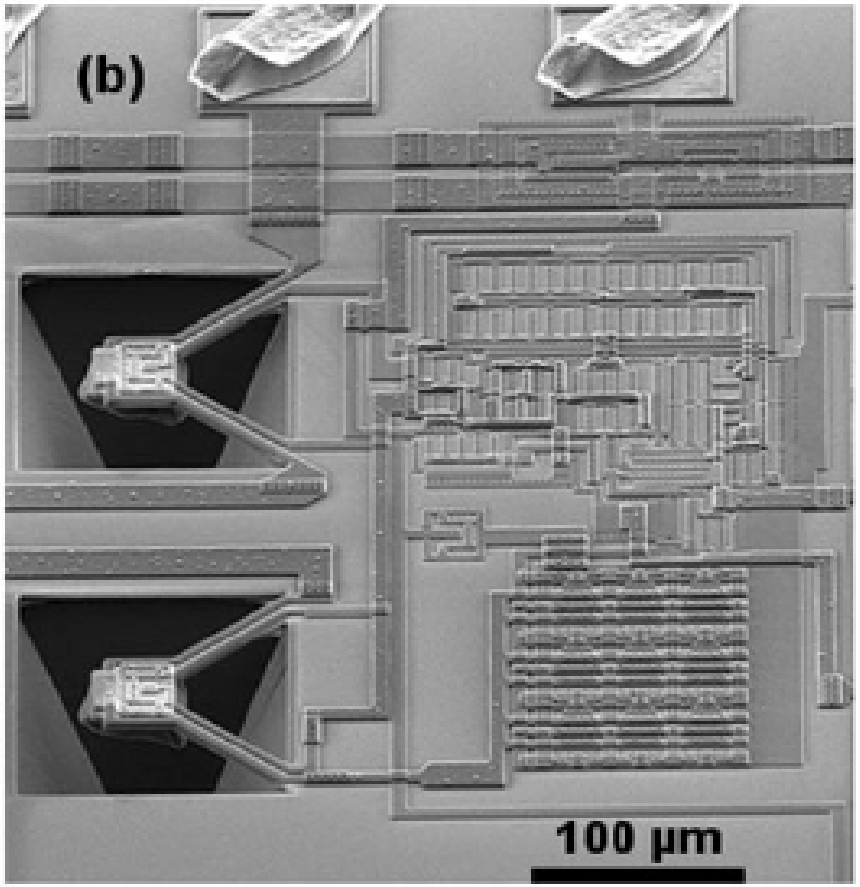


world record efficiency: 26%

Si etching

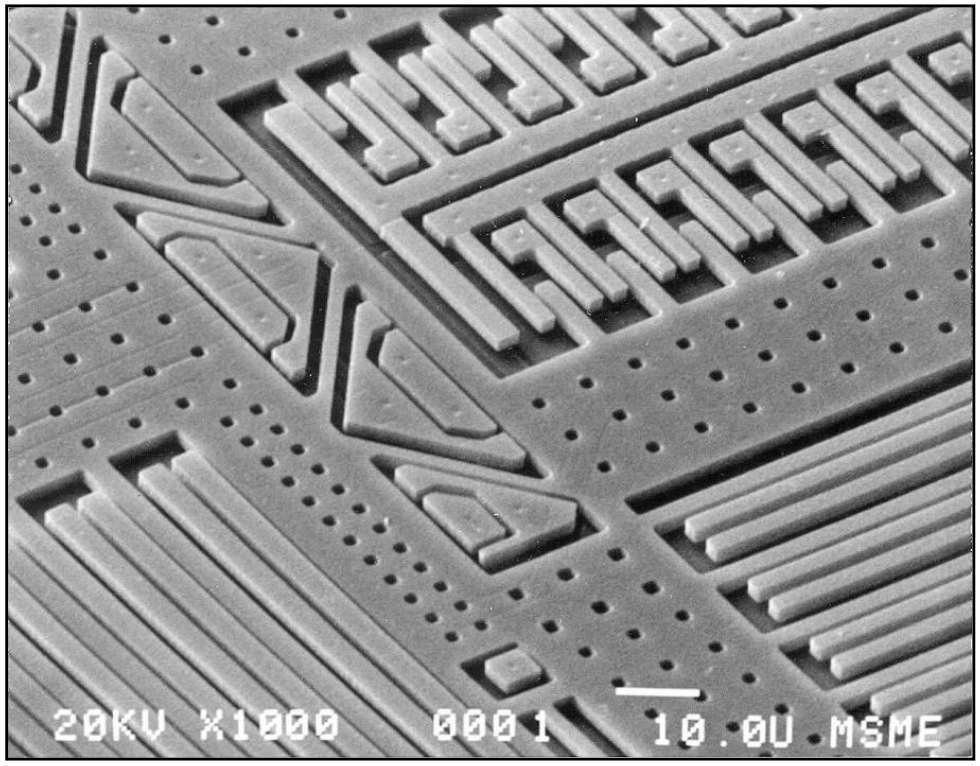
- **Si cantilever beam**
  - **KOH anisotropic etch**





Si etching

- **Micro-Electro-Mechanical Systems (MEMS)**

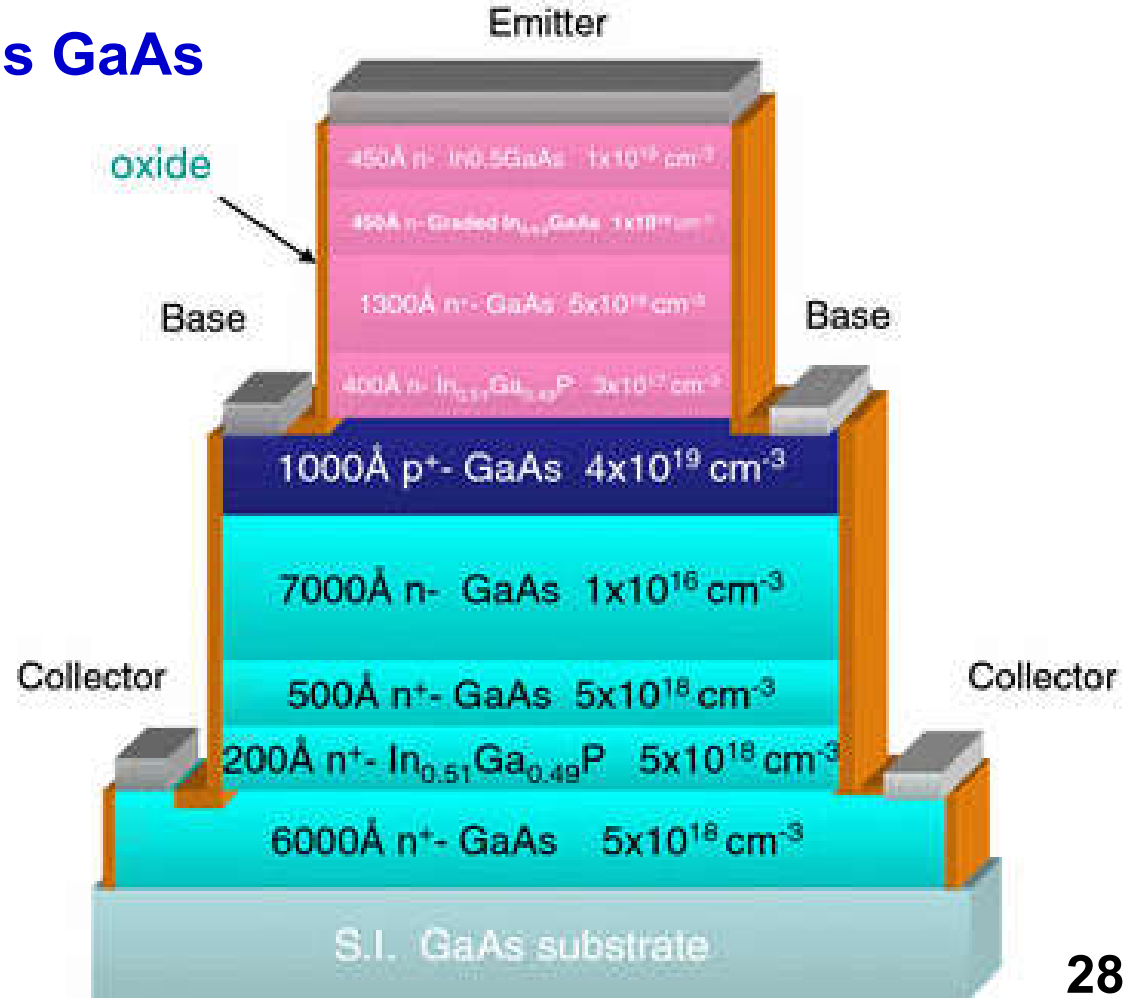


III-V etching

- GaAs, AlGaAs, InGaAs
  - $H_3PO_4 + H_2O_2$
  - $NH_4OH + H_2O_2$
- AlGaAs
  - when Al > 70%, HF and HCl etch
- InP, InGaP, InAlP
  - HCl
- GaN, InGaN
  - no reliable wet etchants ...

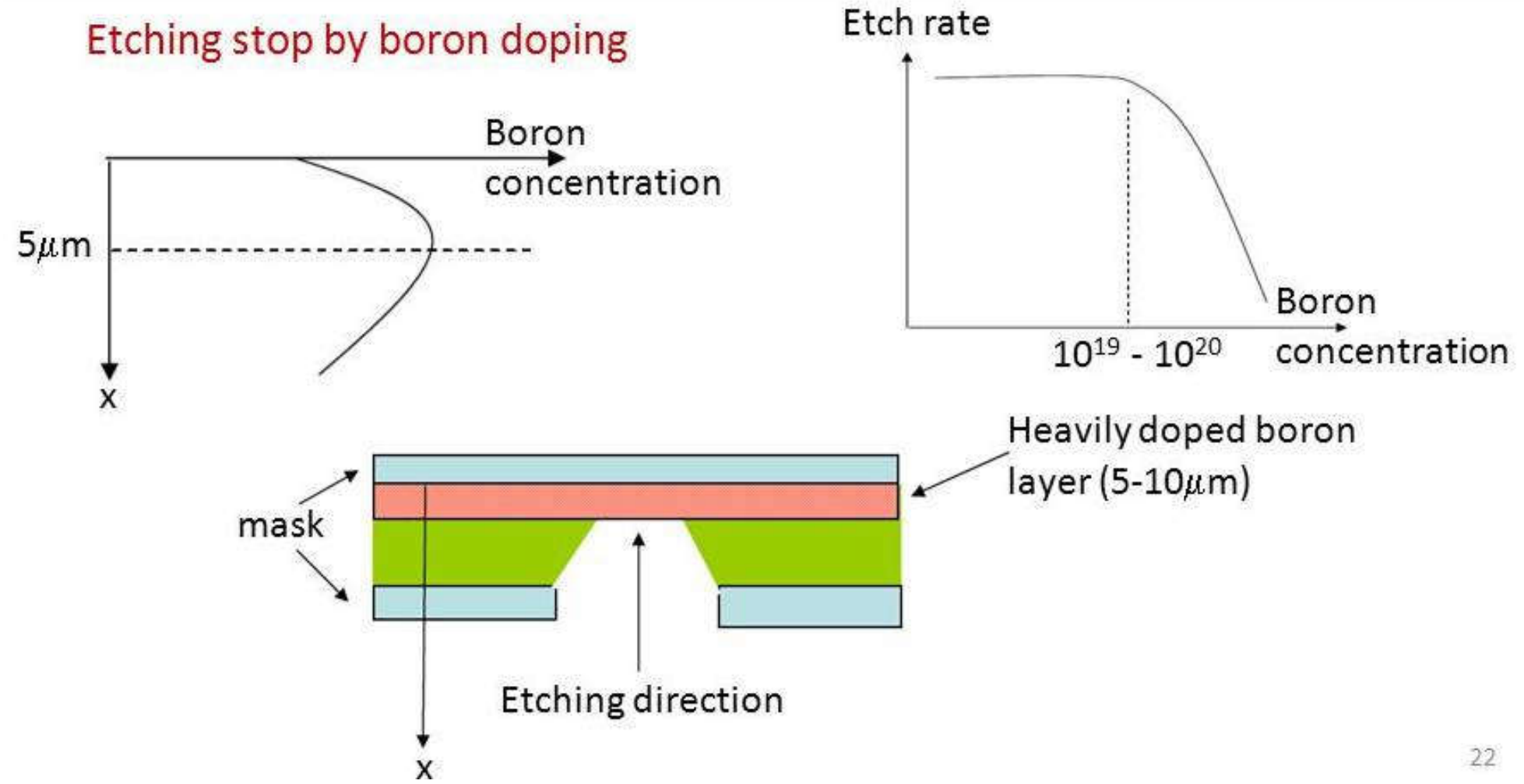
Etch Stops

- **InGaP / GaAs**
  - **lattice matched epitaxy**
  - **$H_3PO_4 + H_2O_2$ only etches GaAs**
  - **HCl only etches InGaP**



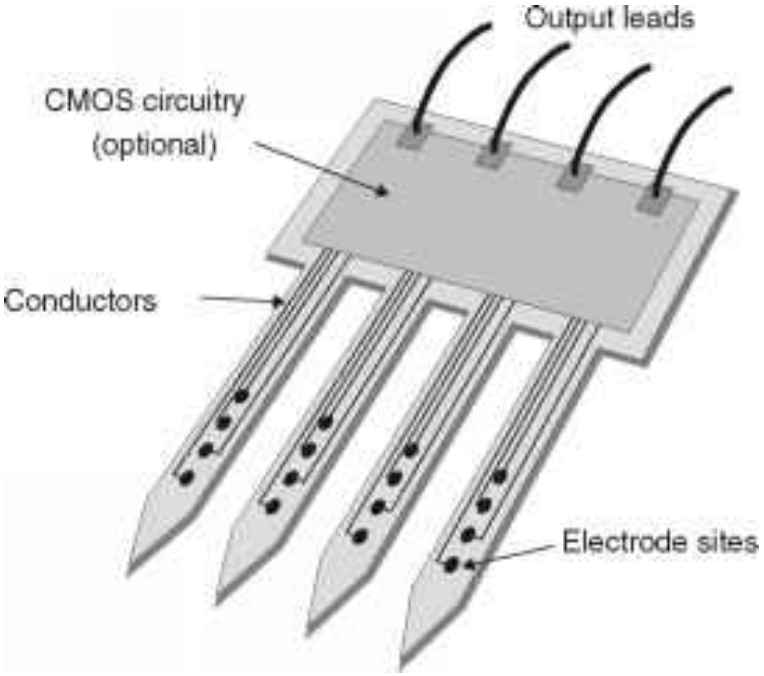
Etch Stops

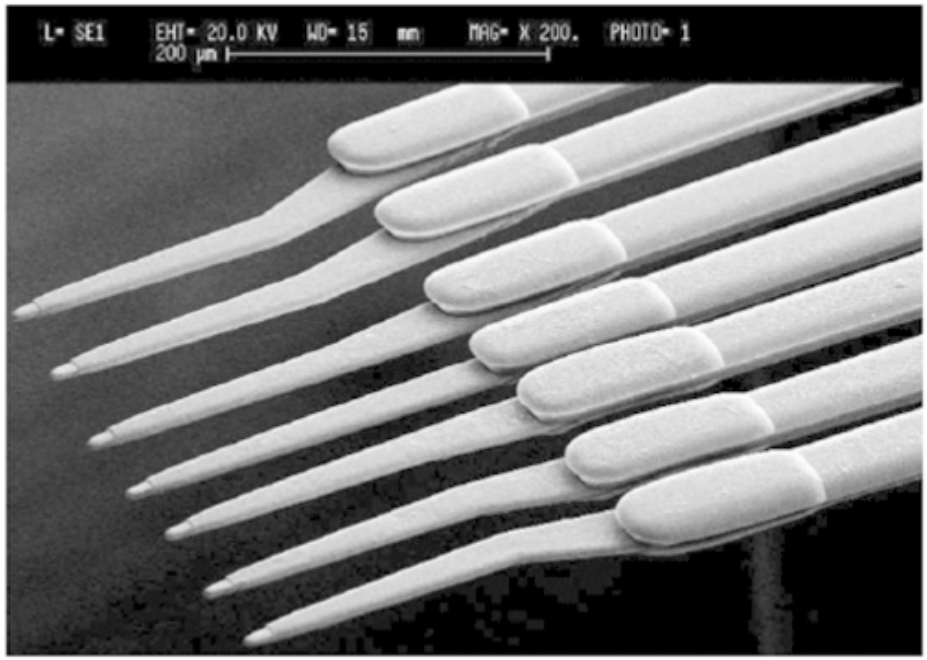
- highly p-dope Si is resistant to KOH



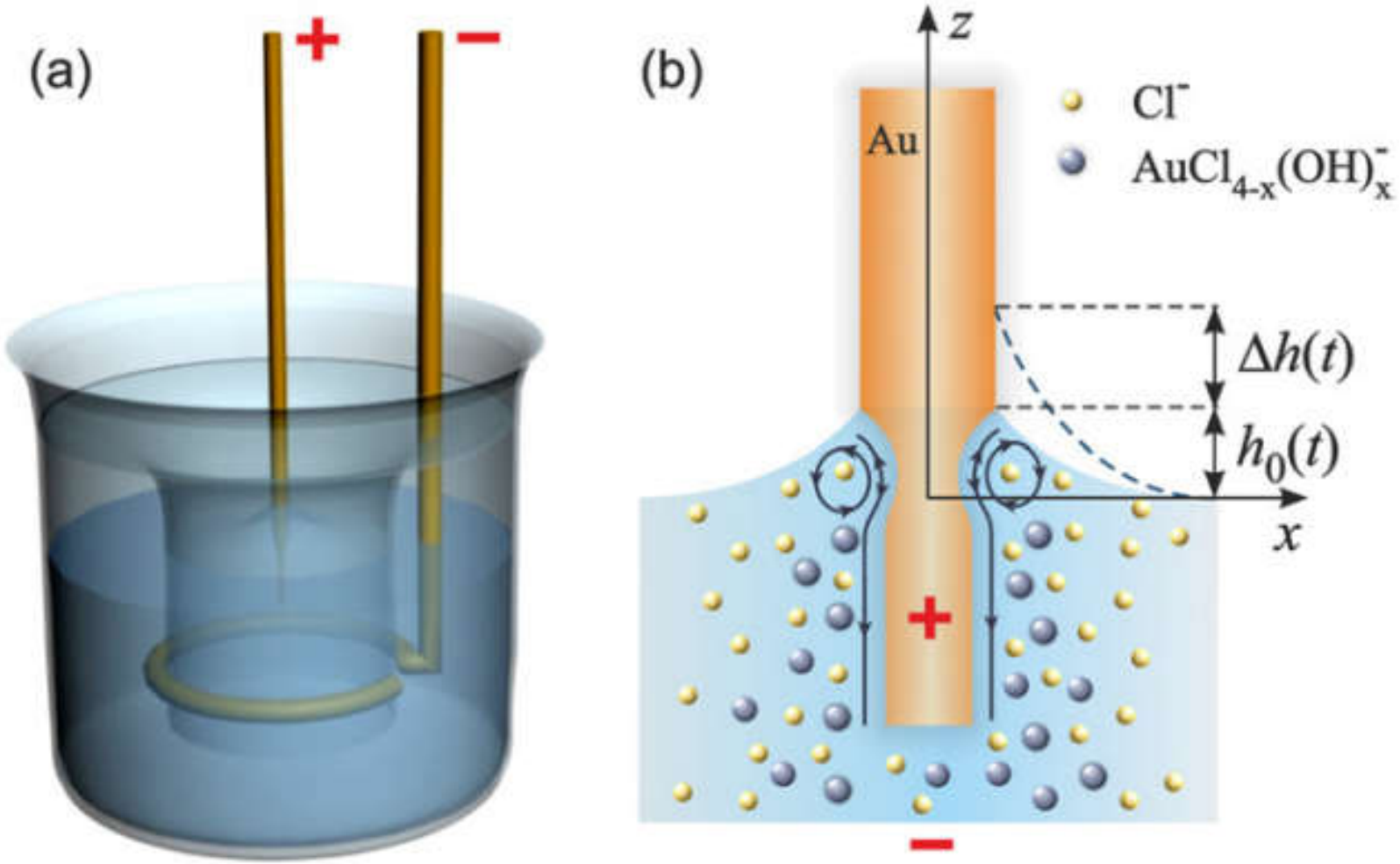
Etch Stops

- **Silicon based 'Michigan Probe' for neuroscience**

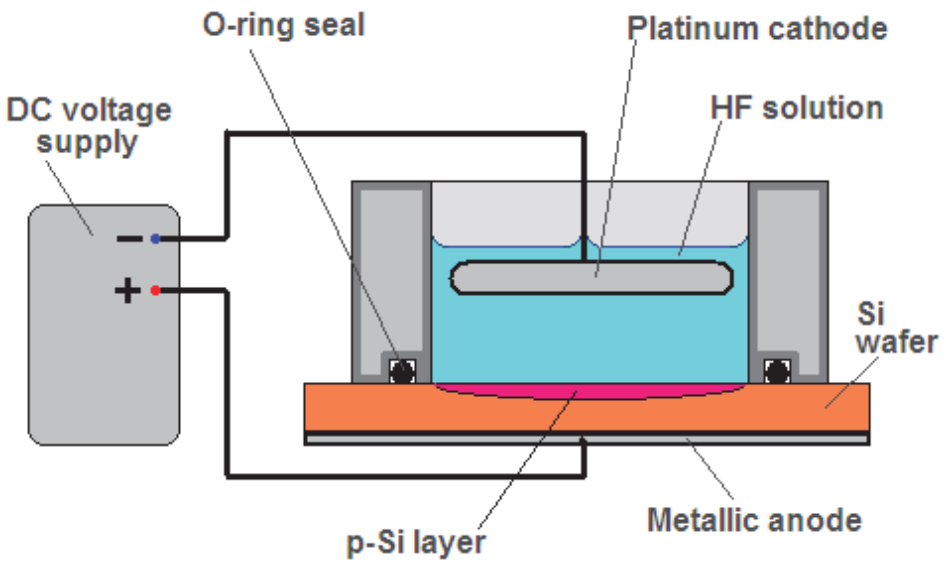


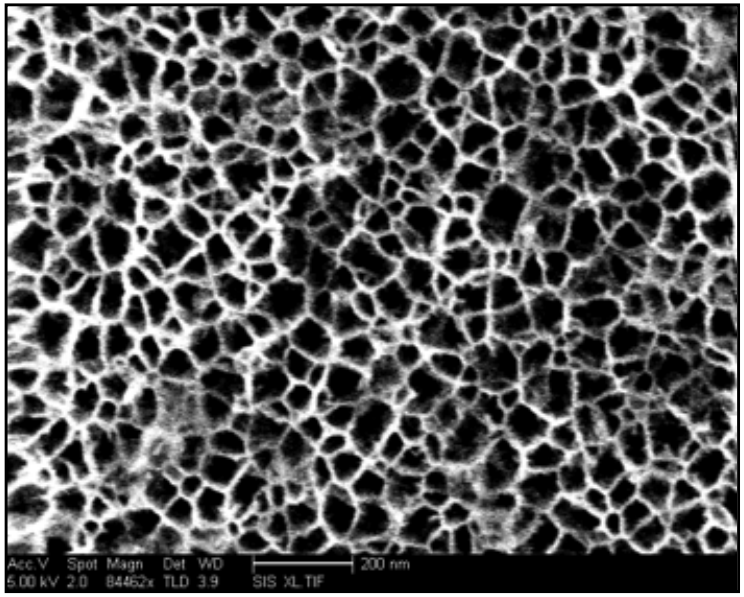


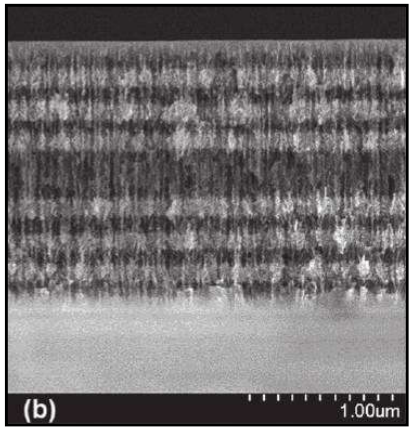
Electrochemical Etch

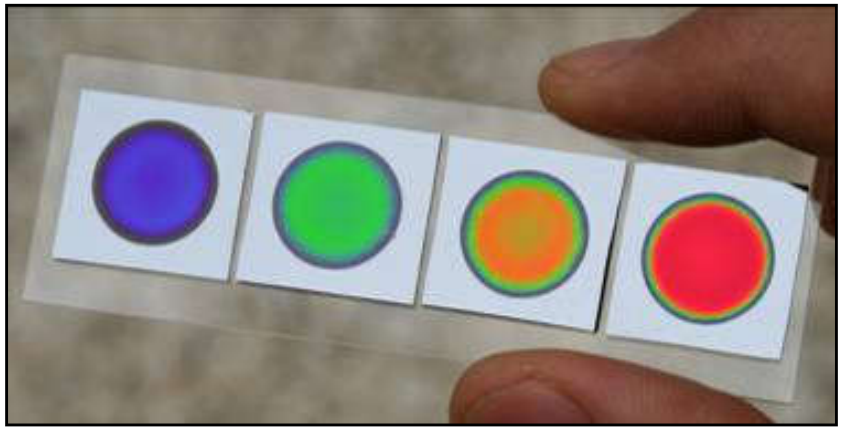


Anodization (阳极氧化) - Porous Si

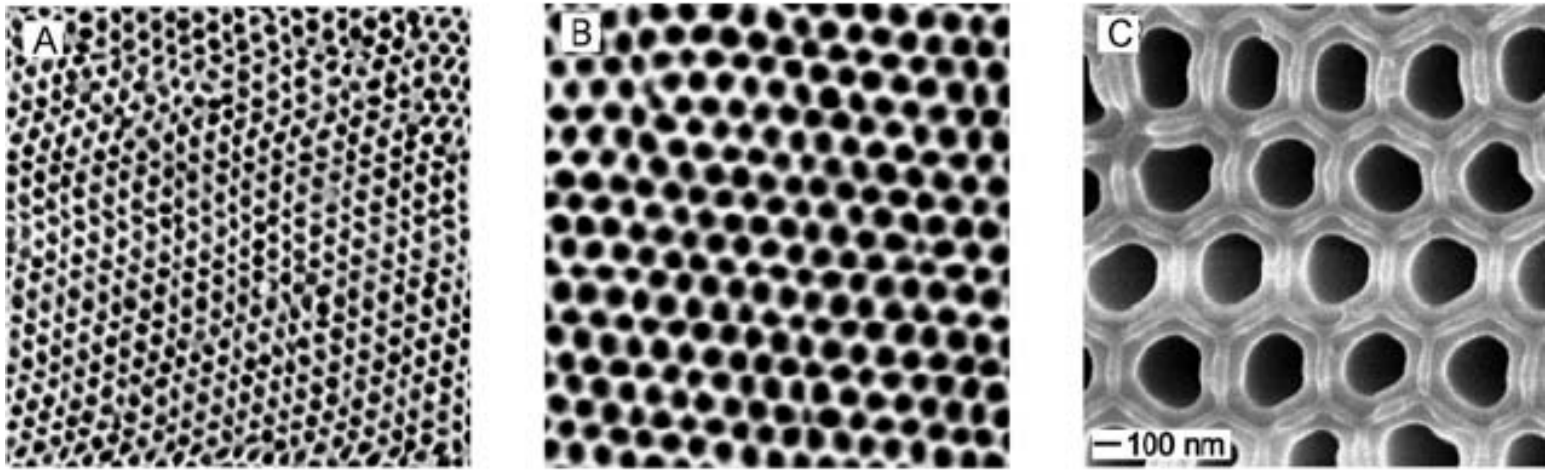


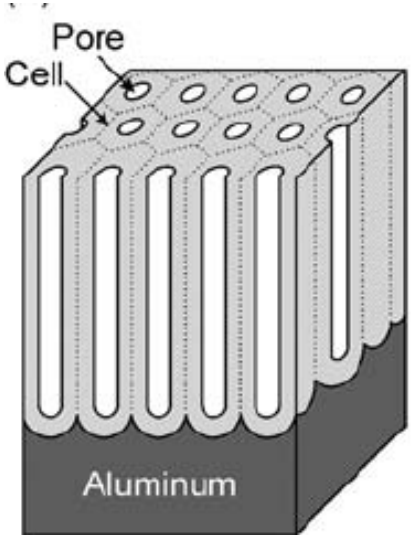


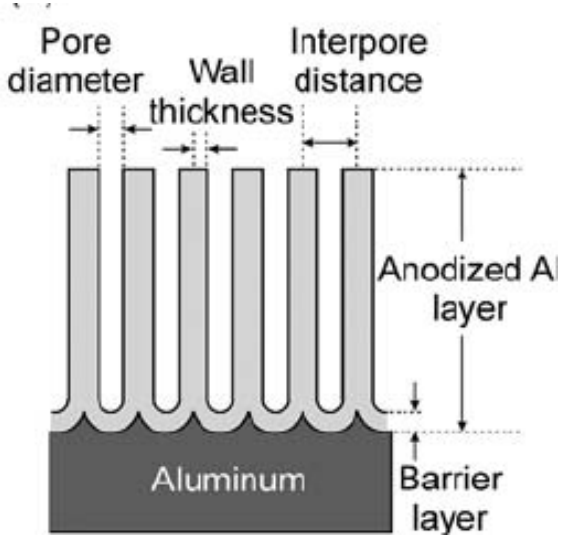


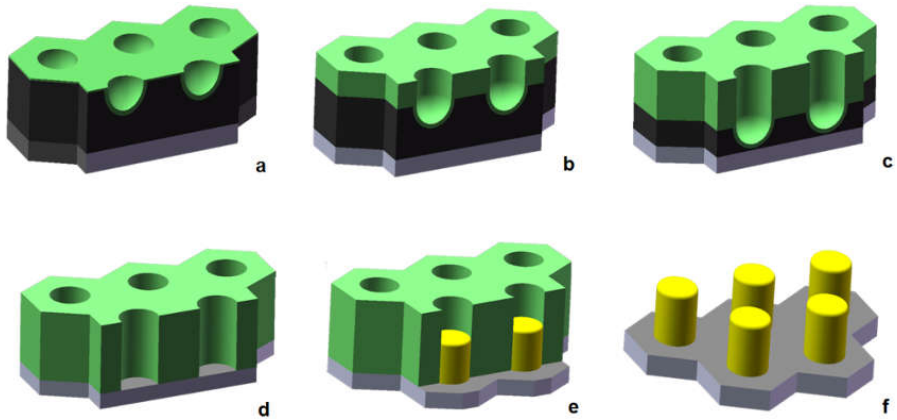


Anodization - Porous Al_2O_3



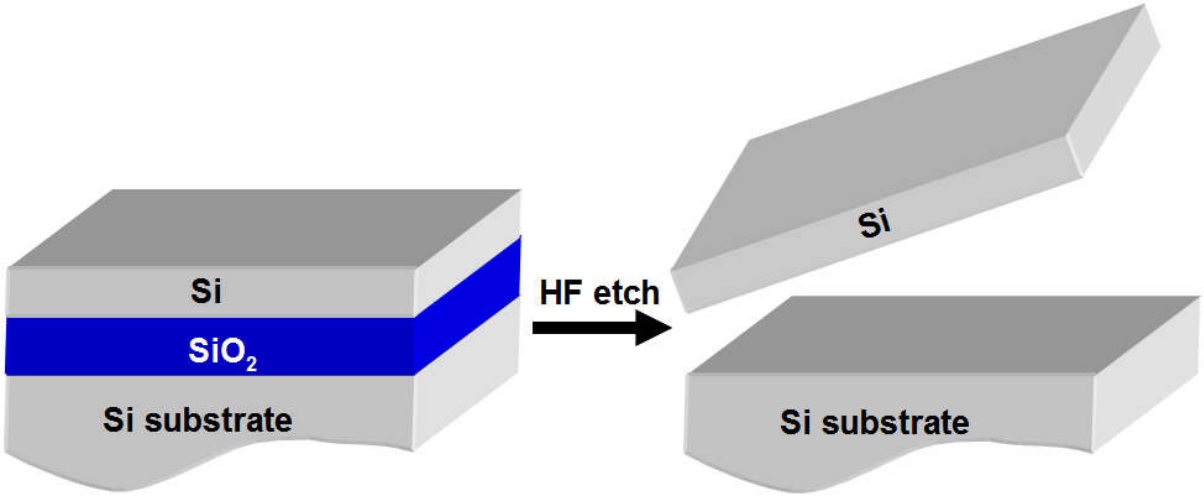


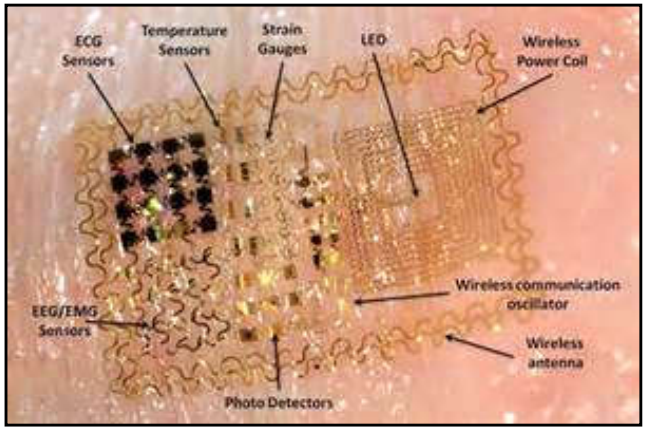




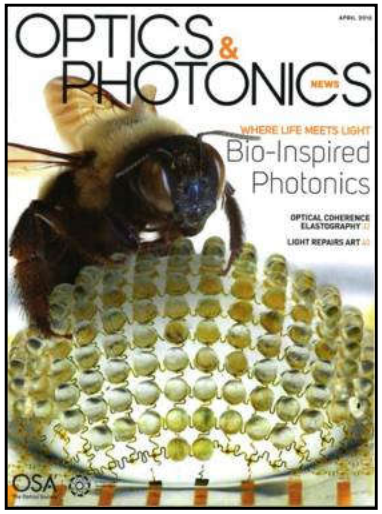
H. Masuda and K. Fukuda, *Science* **268,** 1466 (1995)

Thin-Film Si from SOI wafers





human eyes



compound eyes

'epidermal' electronics

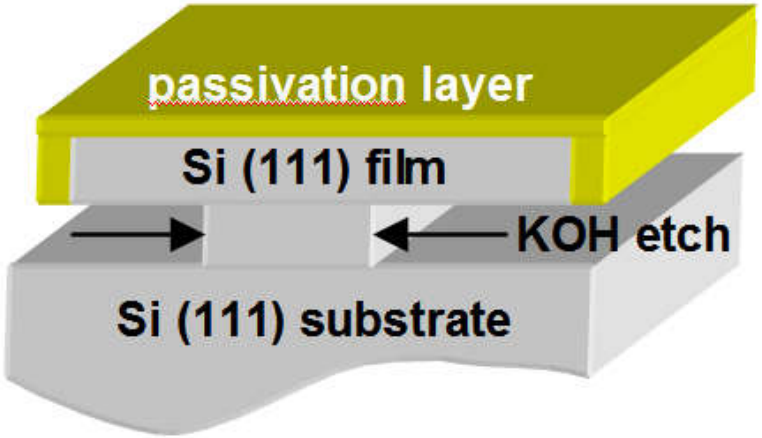
H. C. Ho, *et al.*, *Nature* **454,** 748 (2008)

Y. M. Song, *et al.*, *Nature* **497,** 95 (2013)

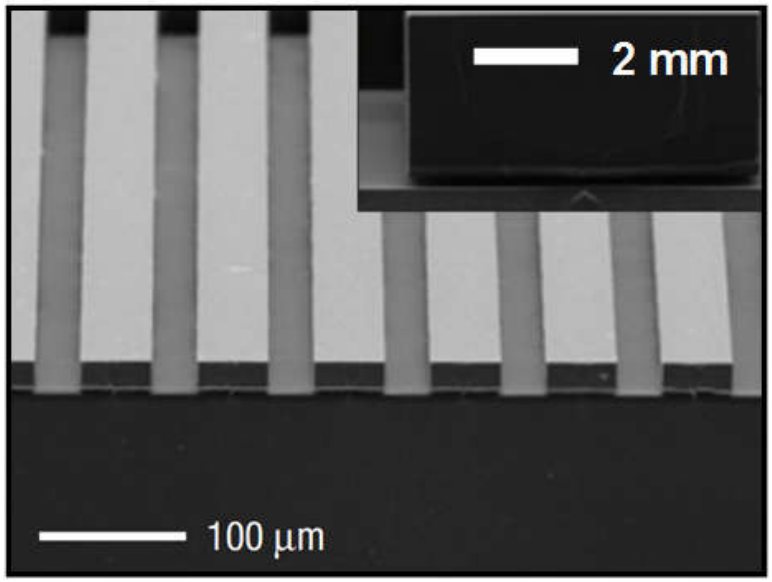
D. Kim, *et al.*, *Science* **333,** 838 (2011)

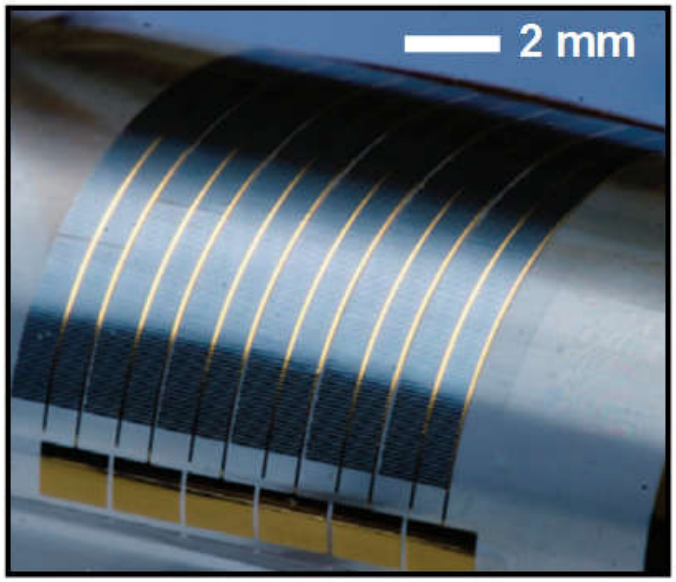
Thin-Film Si from Si (111)

KOH etches faster for Si (100) than (111)



- Thin-film Si solar cells
  - High efficiency (Single Crystal)
  - Flexible
  - Low cost (wafer reuse)

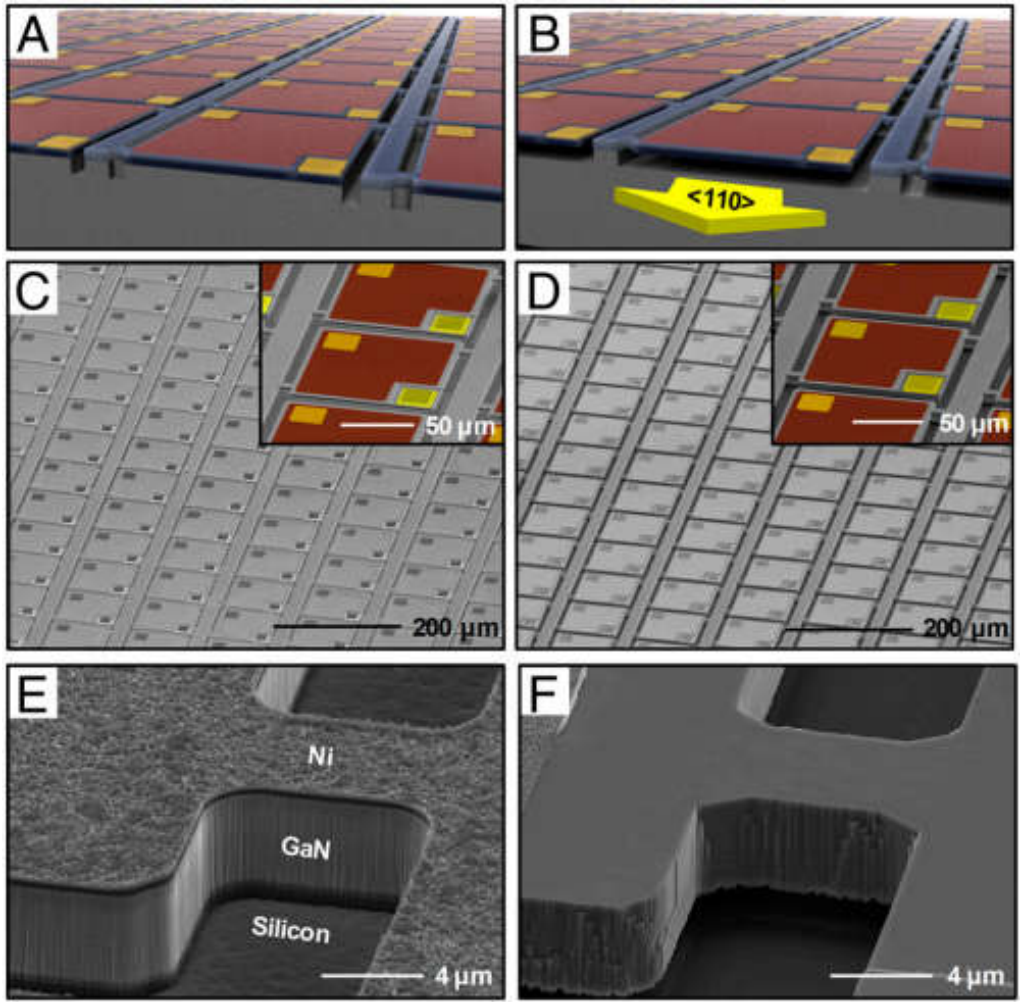


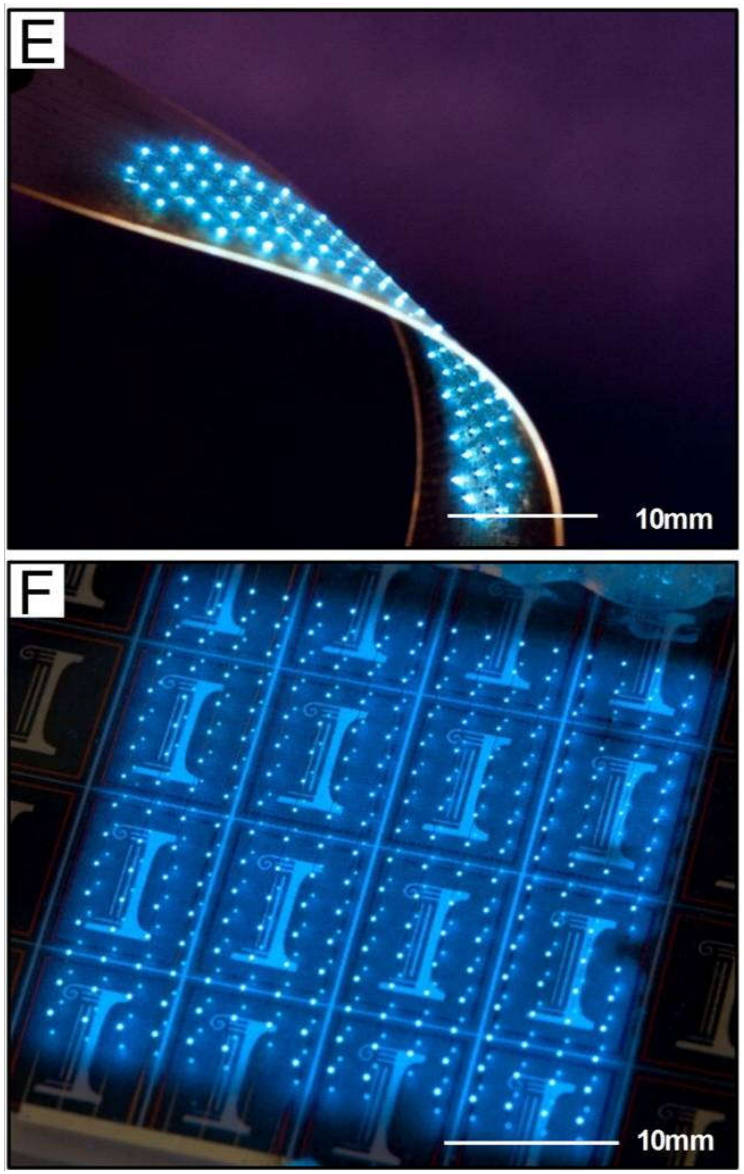


J. Yoon, *et al.*, *Nature Mater.* **7,** 907 (2008)

GaN on Si (111)

KOH etches faster for Si (100) than (111)

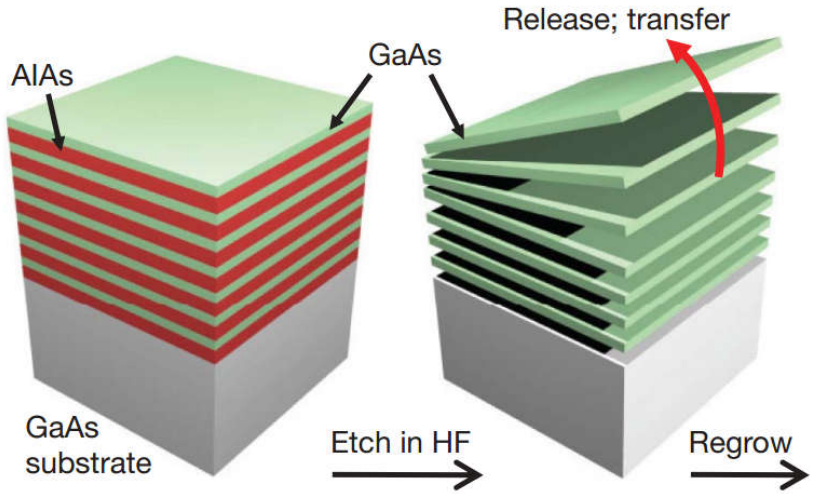


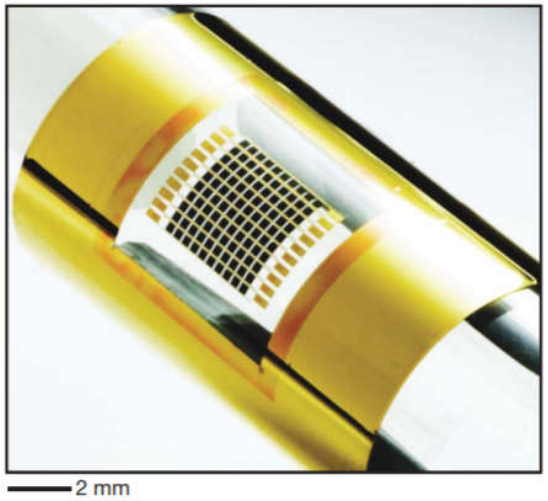


H. Kim, *et al.*, *Proc. Natl. Acad. Sci.* **108,** 10023 (2011)

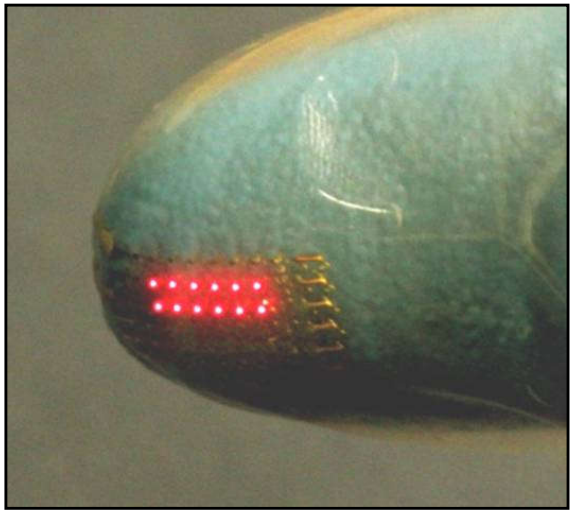
GaAs Device Liftoff

- GaAs and AlAs
  - lattice matched growth
  - AlAs is selectively etched by HF
- flexible III-V devices

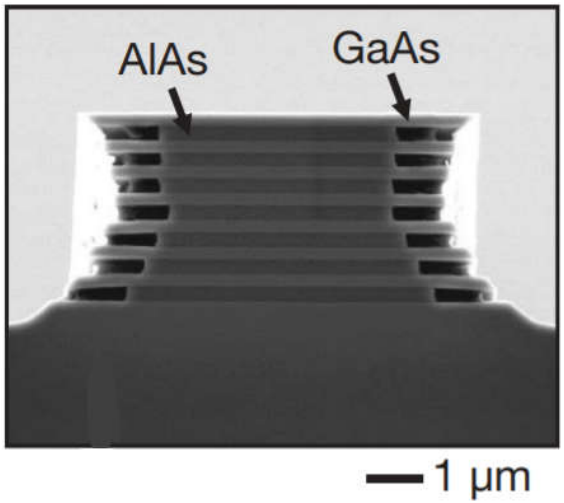




solar cells



LED



S. I. Park, *et al.*, *Science* **325,** 977 (2009)
J. Yoon, *et al.*, *Nature* **465,** 329 (2010)

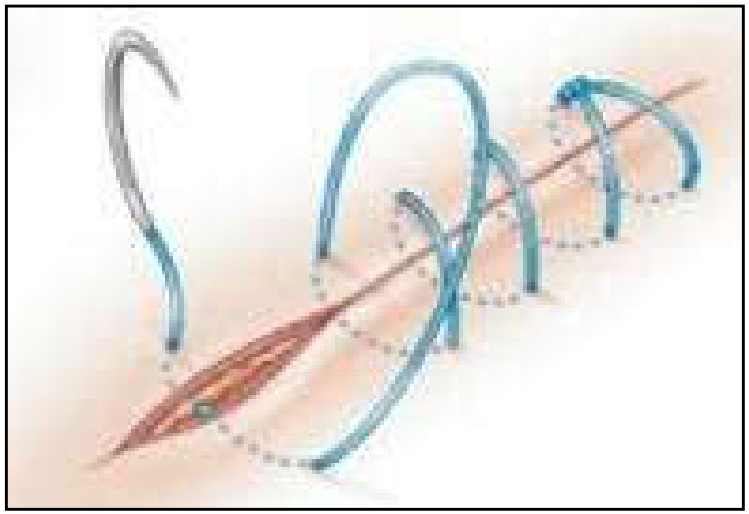
Epitaxy Liftoff

Materials	Sacrificial layers	Substrates	Release methods
Si	SiO_2	Si	HF wet etch
Si (111)	-	Si (111)	KOH wet etch
Ge	SiO_2	Si	HF wet etch
SiC	SiO_2	Si	HF wet etch
GaAs / InGaP	AlAs	GaAs	HF / HCl wet etch
GaAs / InGaP	InAlP	GaAs	HCl wet etch
InGaAs / InP	InGaAs	InP	$FeCl_3$ wet etch
GaN	ZnO	sapphire	HCl wet etch
GaN	-	Si (111)	KOH wet etch
InAs	InGaSb	GaSb	NH_4OH wet etch

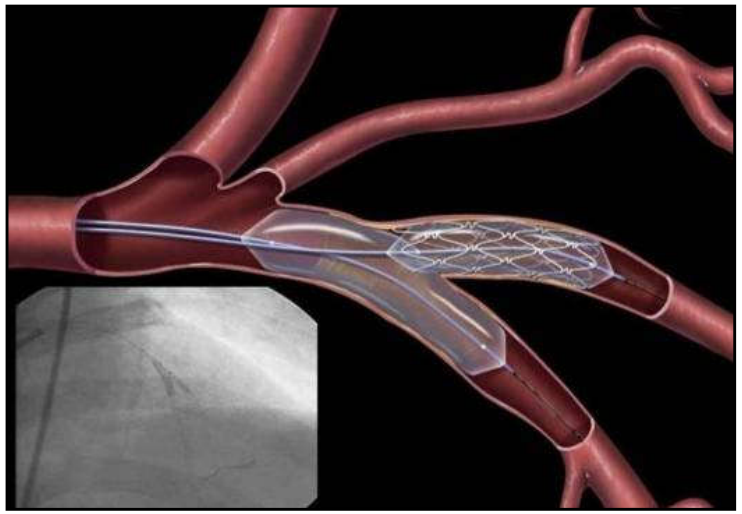
H. Xu, *et al.*, *Adv. Mater.* **30**, 1800156 (2018)

Bio-degradable Materials

Materials that can be dissolved in the body.



Biodegradable Suture



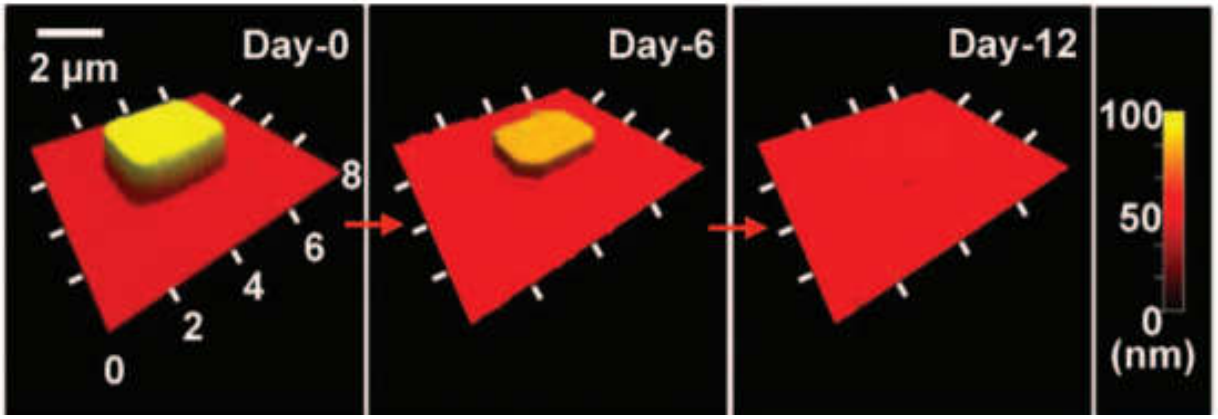
Cardiovascular Stent

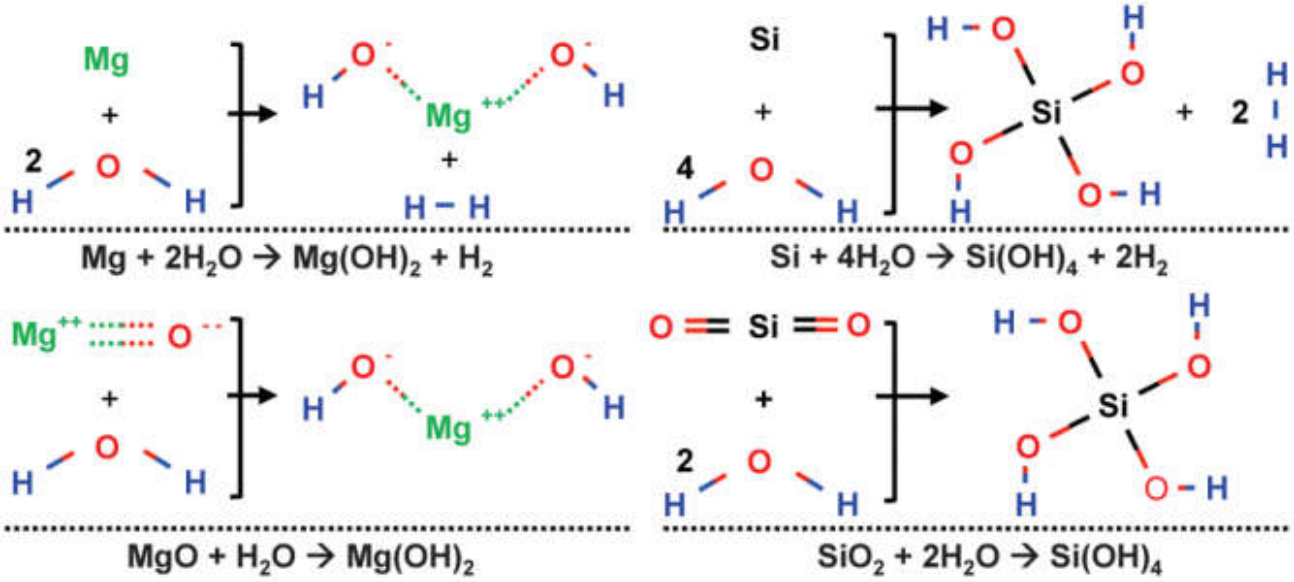
Bone Scaffold

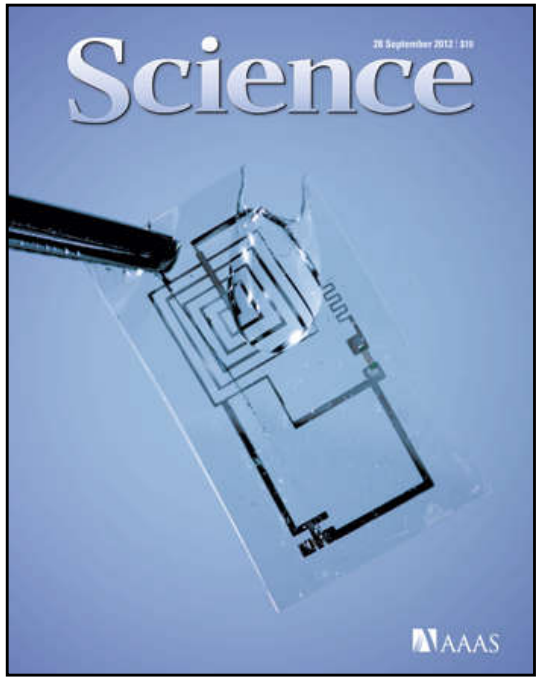
- **Biocompatible and Degradable Materials**
  - **Organic:** PLGA, PLA, silk, ...
  - **Metals:** Mg, Ca, Zn, Fe, ...
  - ***Semiconductors:*** *Si, Ge, ...*

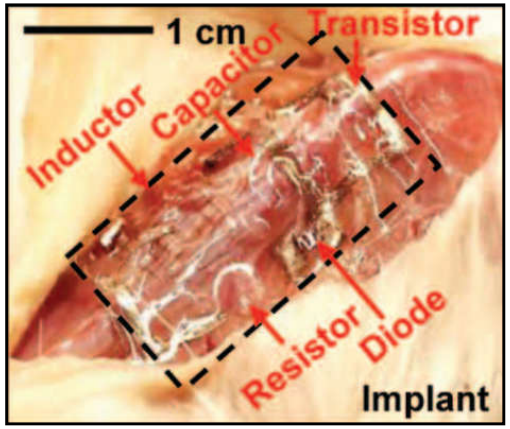
Bio-degradable Electronics

Si devices that can be dissolved by body fluids.









S. Hwang, *et al.*, *Science* **337**, 1640 (2012)

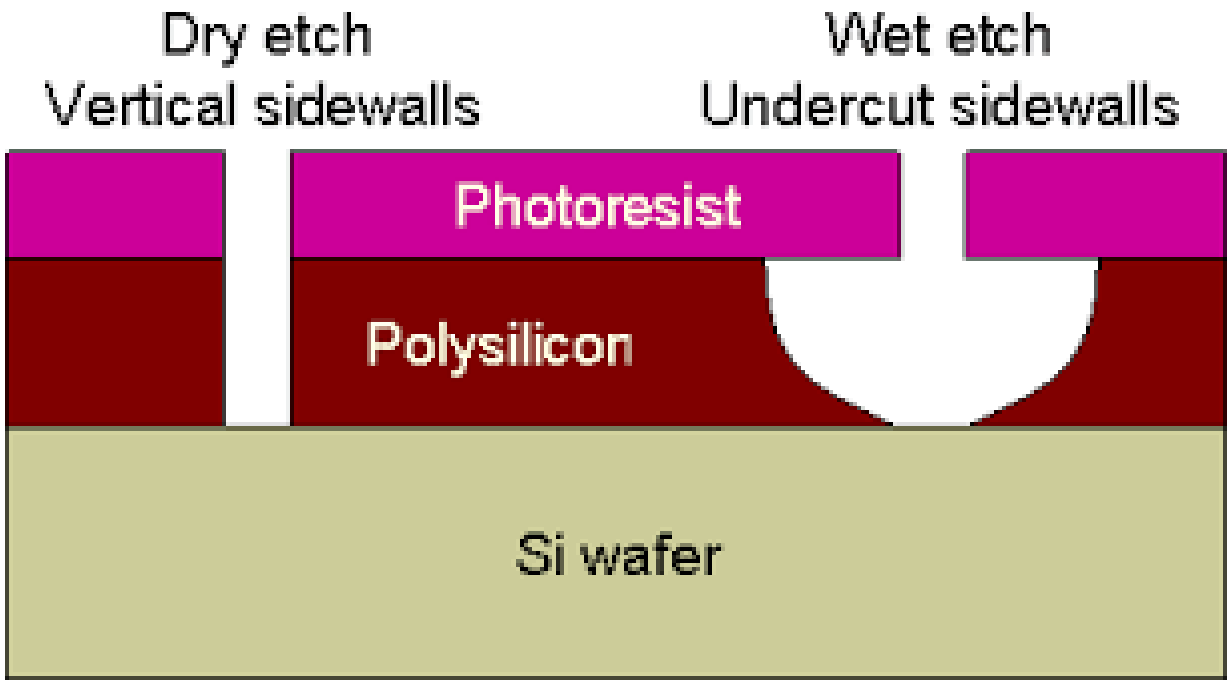
Video

Etching Methods

- Wet Etching 湿法刻蚀
- Dry Etching 干法刻蚀
- CMP and other methods

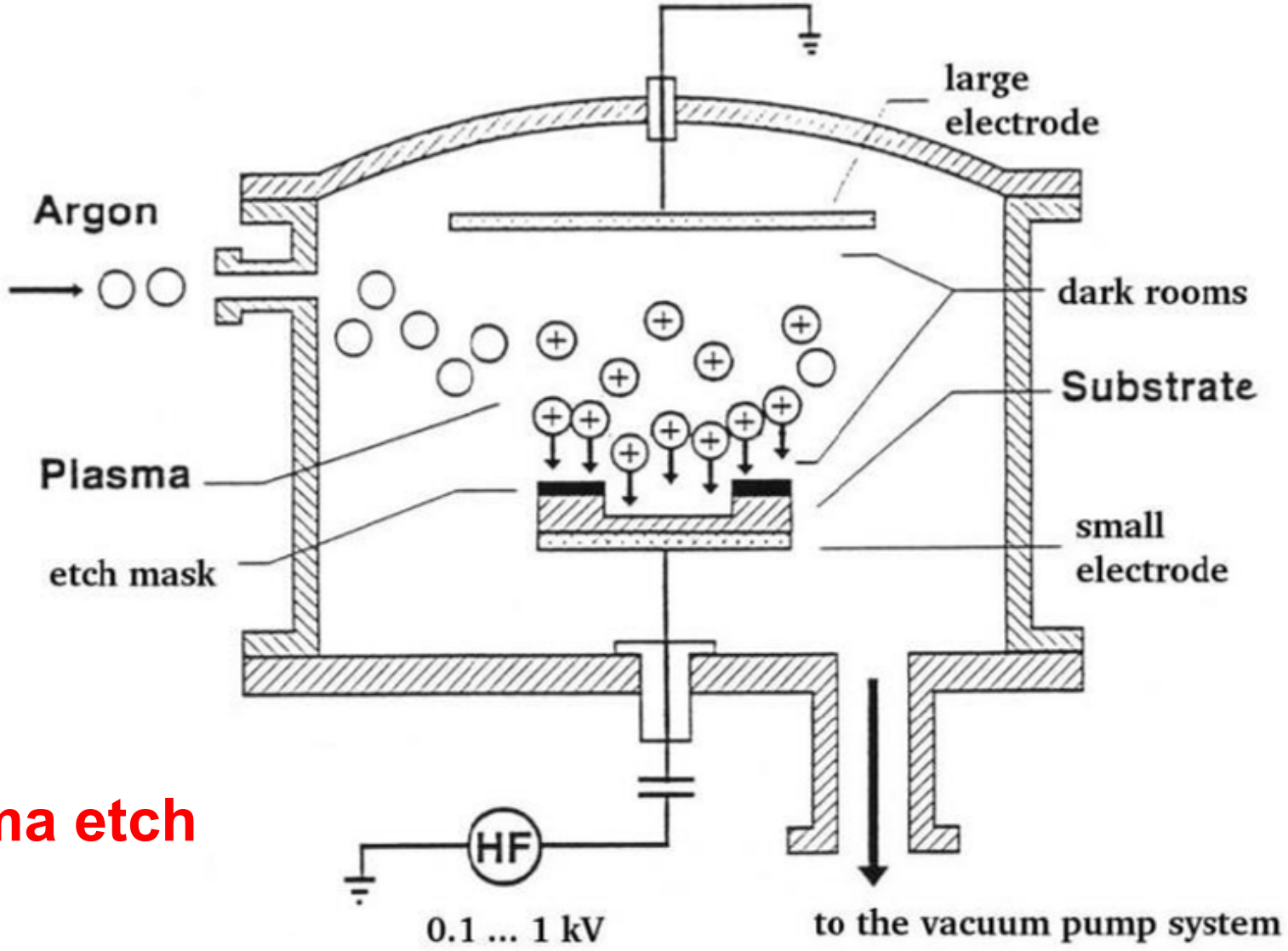
Challenges for Wet Etching

- **Most wet etching processes are chemical, isotropic**



- **For features < 3 μm, dry etching has much better resolution**

Dry Etching

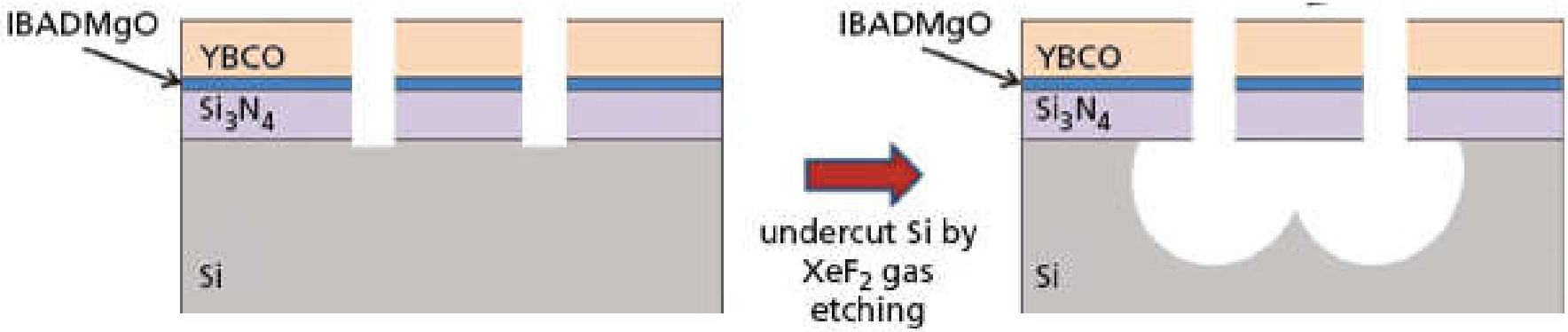


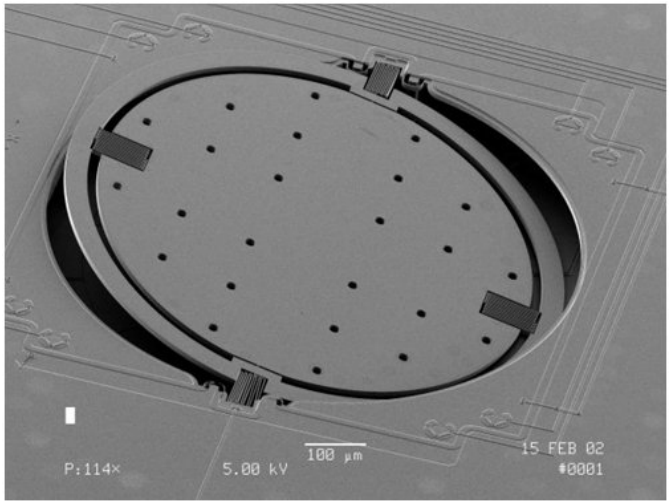
plasma etch

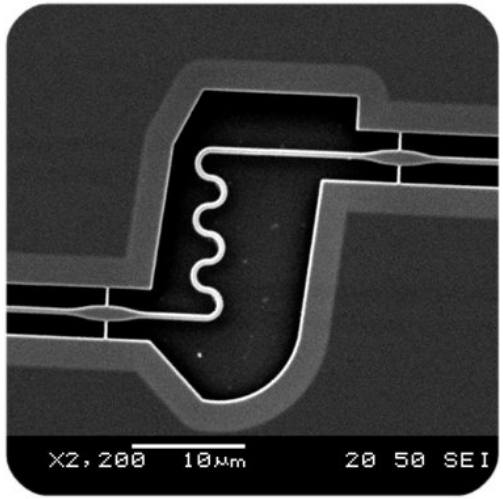
Dry Etch without Plasma

- $2XeF_2$ (g) + Si (g) = 2Xe (g) + SiF_4 (g)
  - very isotropic and selective

SiF_4 boiling point 4 °C

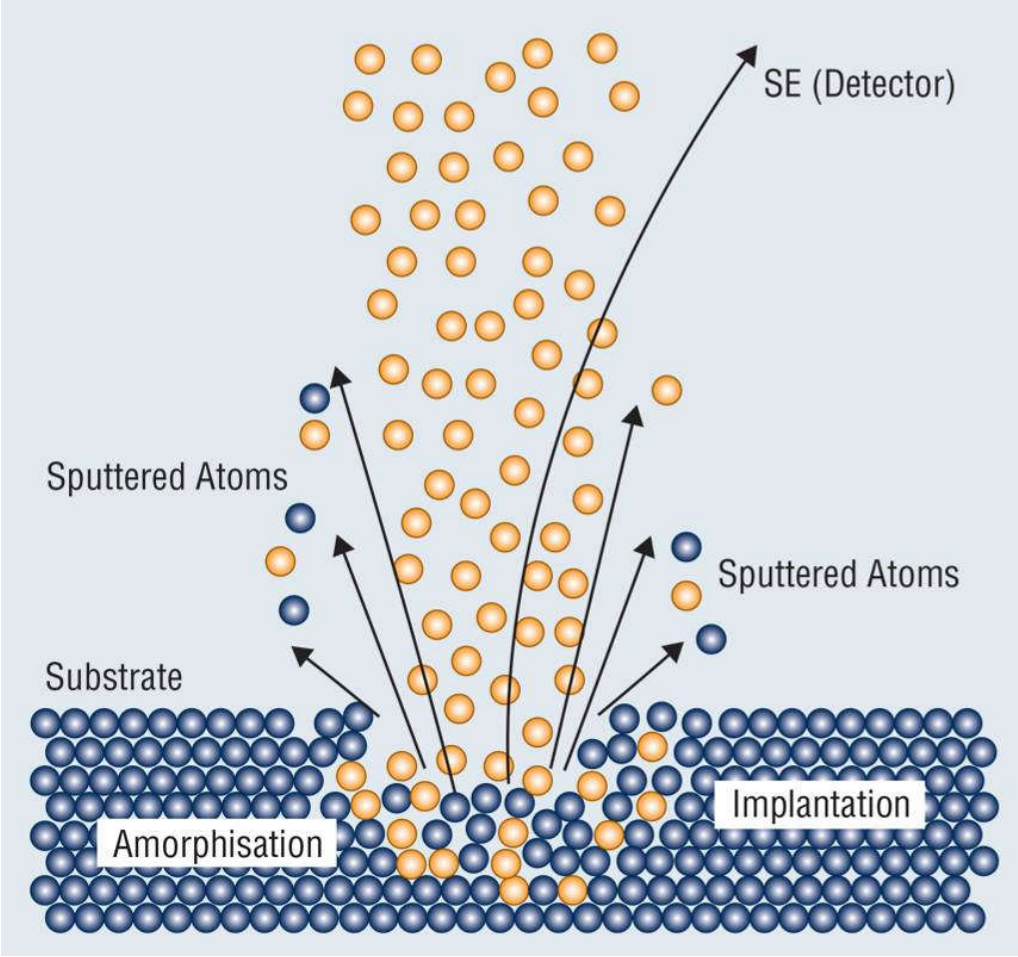






Ion Milling

- Heavy ions (e.g. Ar)
- Highly anisotropic
- Poor selectivity
  - for Au, Pt, ...



Ion Milling

- Heavy ions (e.g. Ar)
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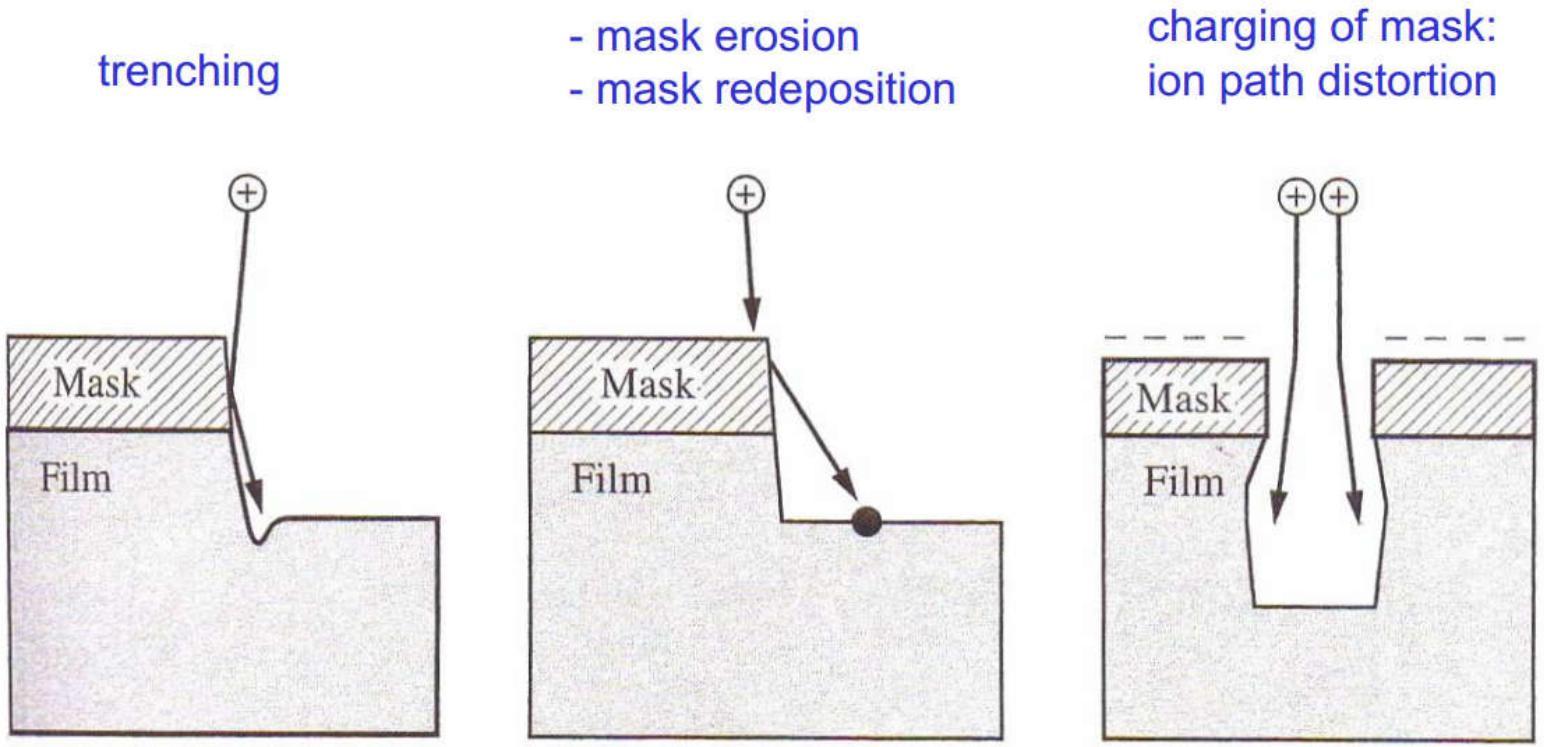
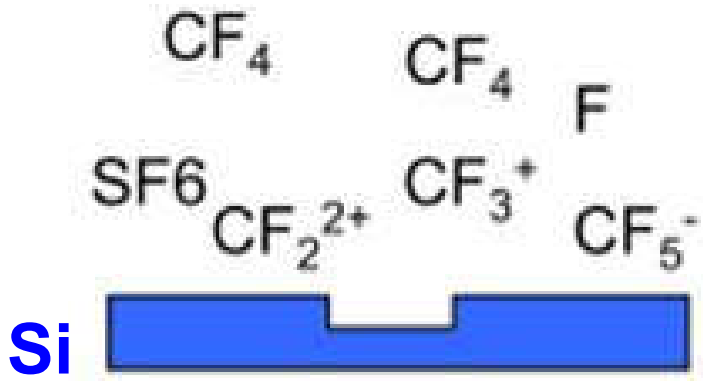


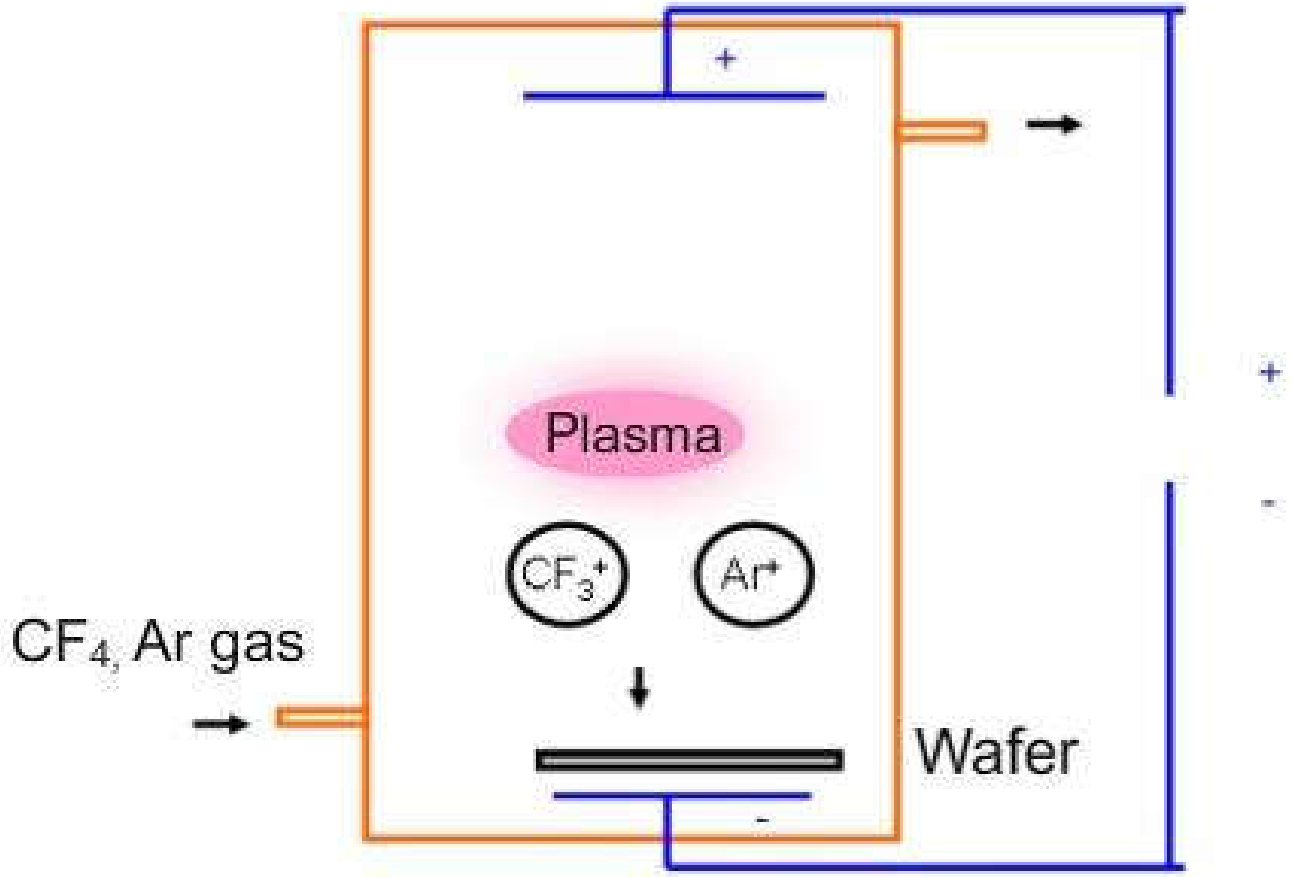
Plasma Etch

- **Chemically reactive ions**
  - improved selectivity
  - lower power
- **Example: Si etch**
  - CF_4 gas does not react with Si
  - energized F^- plasma can react with Si
  - SiF_4 is volatile (boiling point 4 ^oC)
- **Very isotropic**
  - no direction



Reactive Ion Etching (RIE)

- **Improved directionality by applied fields**
  - **more anisotropic**



RIE - Si and SiO_2

- Si
  - SF_6 plasma
- SiO_2
  - CF_4 / CHF_3 plasma
- Photoresists can be used as masks
  - F ions etch PR very slowly

RIE - Si and SiO_2

- Si
  - SF_6 plasma
- SiO_2
  - CF_4 / CHF_3 plasma

SF_6 is heavier than air

- Photoresists can be used as masks
  - F ions etch PR very slowly

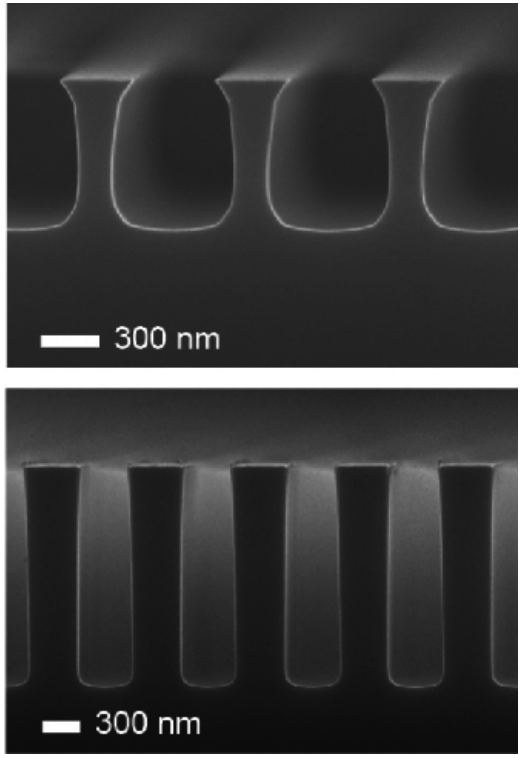
RIE - Organics

- O_2 plasma
  - $C\text{-}H\text{-}O + O^- = CO_2 + H_2O$
- O_2 plasma does not etch Si, SiO_2, or metals
  - SiO_2 / metal oxides are non-volatile

RIE - III-Vs

- Cl_2 / BCl_3 / $SiCl_4$ plasma
  - GaAs/AlGaAs, InP, GaN/InGaN, ...

Q: why?



GaAs trenches

product	boiling point (°C)
GaF_3	1000
AlF_3	> 1000
InF_3	> 1000
$GaCl_3$	200
$AlCl_3$	180
$AsCl_3$	130

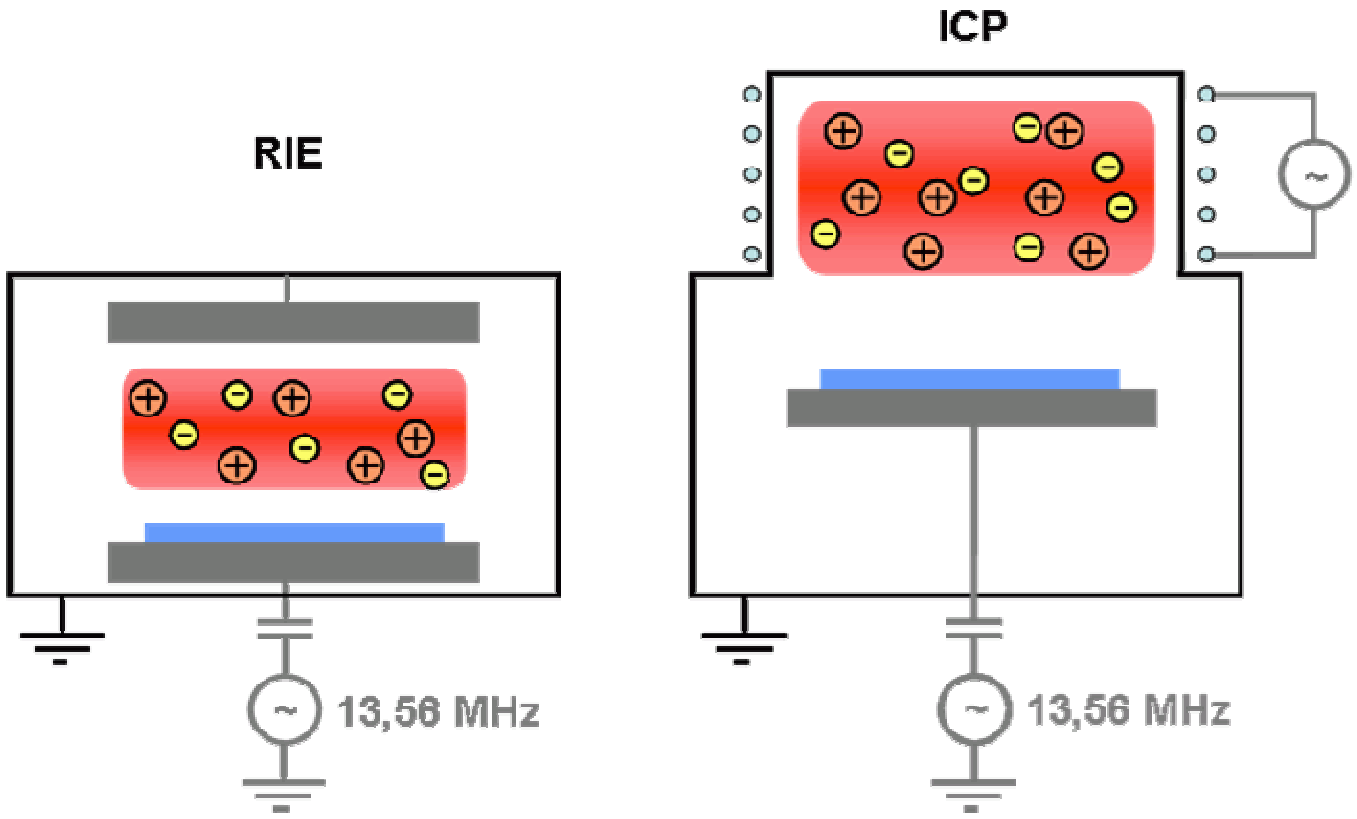
RIE - Recipes

Table 6.2 Materials and corresponding RIE gases

Materials to be etched	Chemical gases (multi choices)
Single-crystal silicon	CF_3Br, HBr/NF_3, SF_6/O_2
Polysilicon	$SiCl_4/Cl_2$, BCl_3/Cl_2, $HBr/Cl_2/O_2$, HBr/O_2, Br_2/SF_6
Al	$SiCl_4/Cl_2$, BCl_3/Cl_2, HBr/Cl_2
Al-Si-Cu, Al-Cu	$BCl_3/Cl_2 + N_2$
W	SF_6, NF_3/Cl_2
TiW	SF_6
WSi_2, $TiSi_2$, $CoSi_2$	CCl_2F_2/NF_3, CF_4/Cl_2
SiO_2	CCl_2F_2, CHF_3/CF_4, CHF_3/O_2, CH_3CHF_2
Si_3N_4	CF_4/O_2, CF_4/H_2, CHF_3, CH_3CHF_2
GaAs	$SiCl_4/SF_6$, $SiCl_4/NF_3$, $SiCl_4/CF_4$
InP	CH_4/H_2
Photoresists	O_2

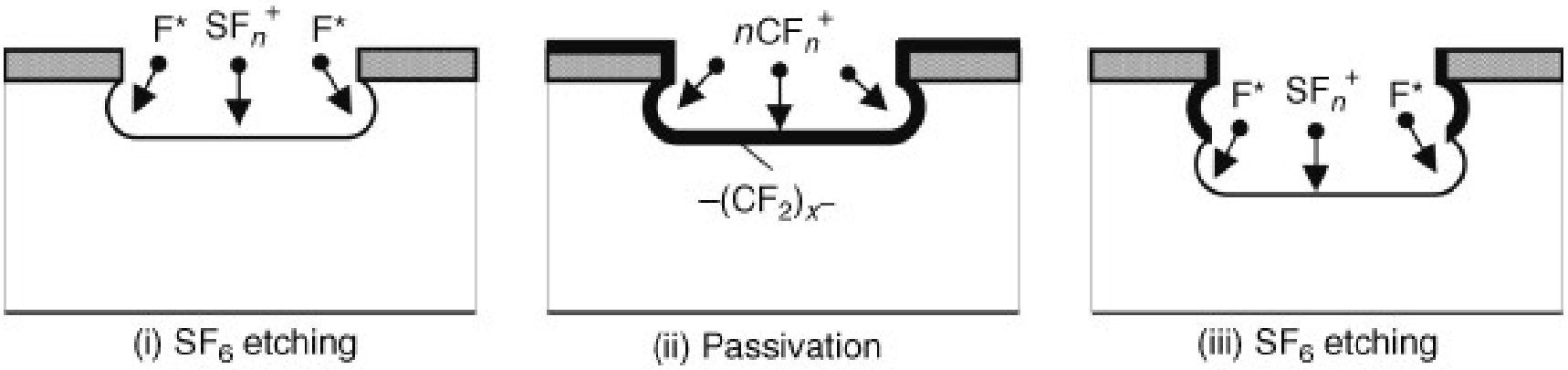
ICP-RIE

- **Inductively Coupled Plasma (ICP)**
  - higher power
  - mostly for III-Vs

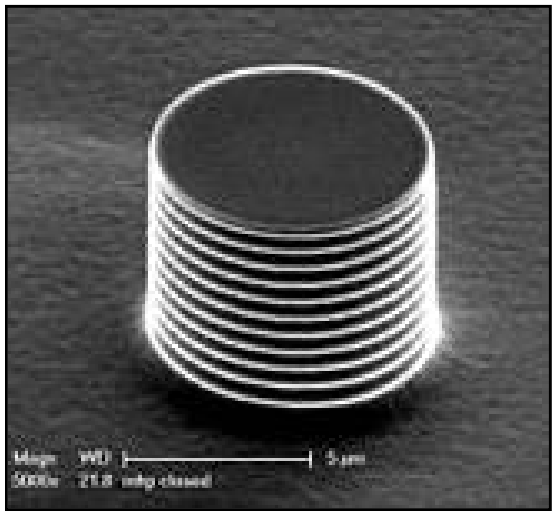


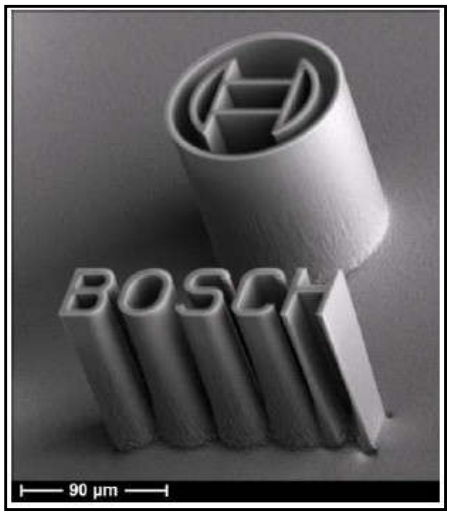
Deep RIE for Si

- **alternative etch / passivation** **'Bosch process'**

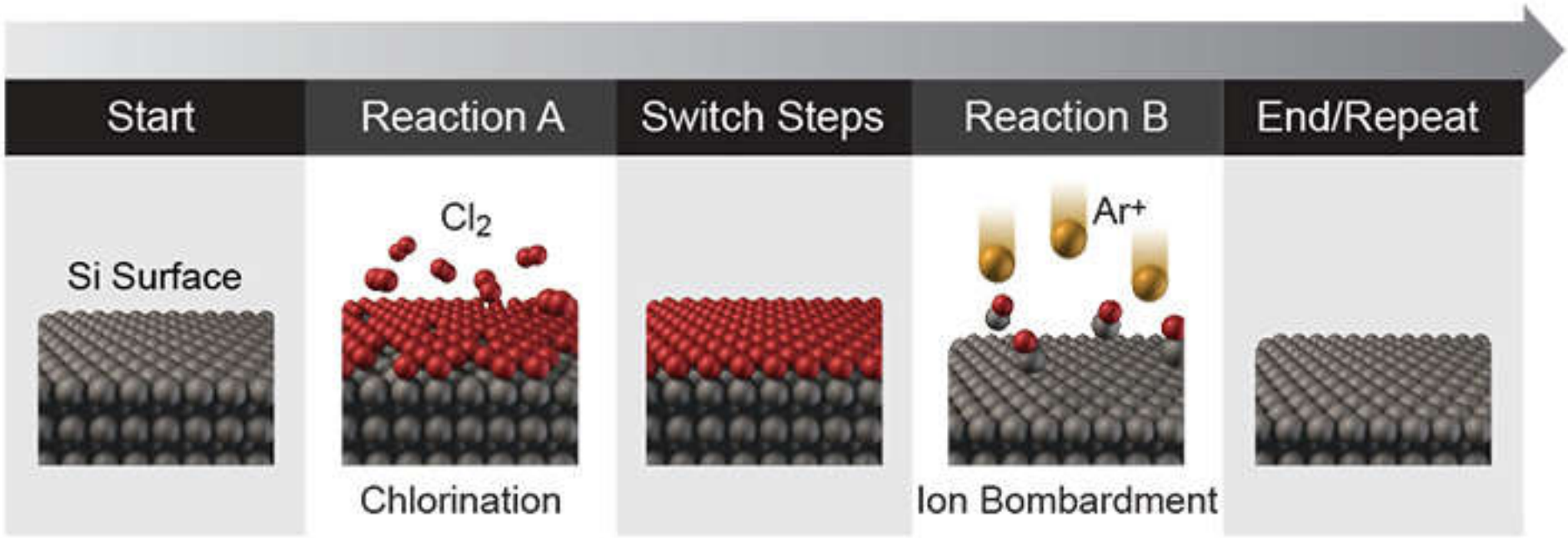


(i) SF_6 etching (ii) Passivation (iii) SF_6 etching





Atomic Layer Etching (ALE)



1. $Si + 2Cl_2 = SiCl_4$
2. $SiCl_4$ removed by plasma
3. Repeat 1 and 2

K. J. Kanarik, *et al.*, *J. Vac. Sci. Tech. A* **33,** 020802 (2015)

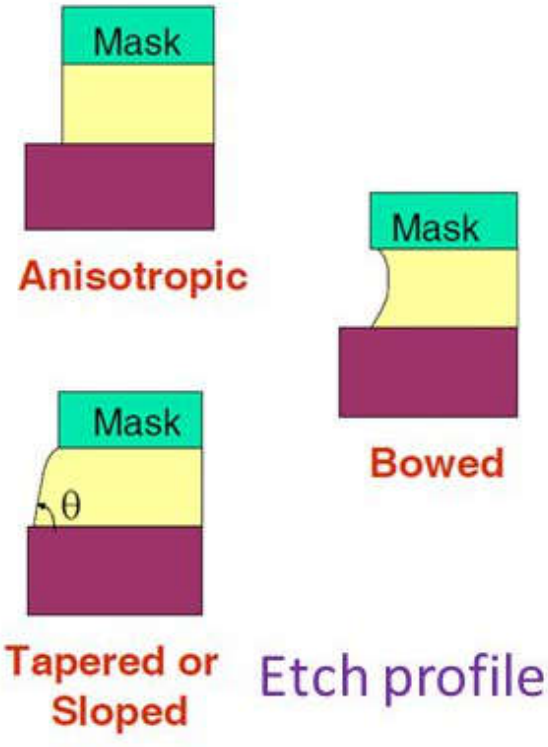
Issues in Dry Etch

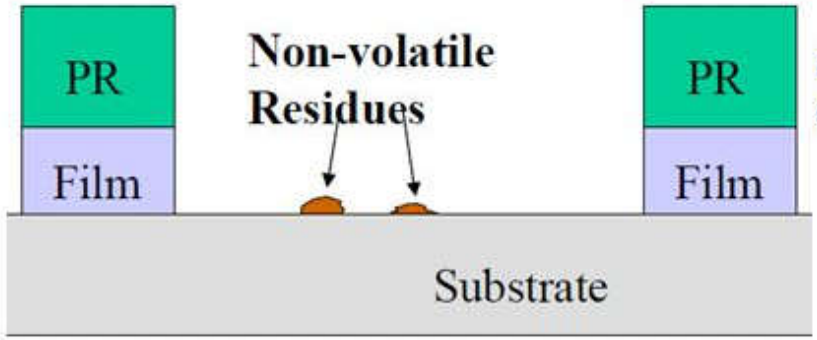
Profile → •Isotropic •Anisotropic •Mixed profile ← **Undercut, Aspect ratio, Pattern density**

Selectivity → •Flim/PR or Film/Mask •Film/Underlayer ← **CD Loss, Hard mask, Chemistry**

Uniformity → •Across a wafer (Local) •Variations with feature size •Wafer to wafer (Global) ← **Macro-loading, Micro-loading, ARDE effect**

Surface quality → •Contamination •Damage •Texture ← **Polymer Residue, Corrosion, Micro-trench & notch**





PR: photoresist
CD: critical dimension

2

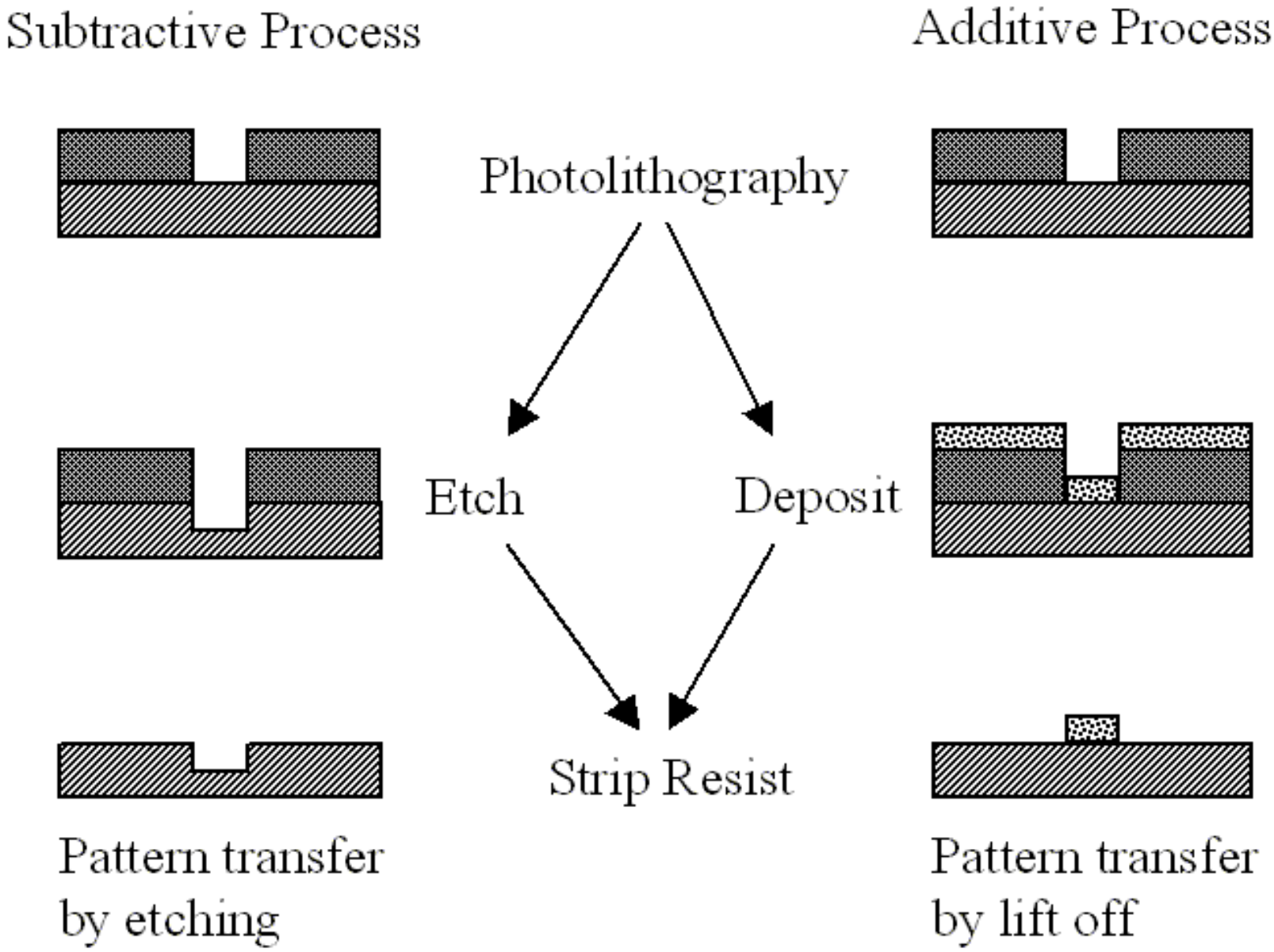
Summary of Dry Etch

Type of Etching	Excitation Energy	Pressure
Gas/Vapor Etching	none	high (760-1 torr)
- isotropic, chemical, very selective (e.g. XeF_2 gas etch Si even without plasma)		
Plasma Etching	10's to 100's of Watts	Medium (>100 torr)
- isotropic, chemical, selective		
Reactive Ion Etching	100's of Watts	Low (10-100 mtorr)
- directional, physical & chemical, fairly selective		
Sputter Etching	100's to 1000's of Watts	Low (~10 mtorr)
- directional, physical, low selectivity (e.g. ion beam etching/milling using Ar^+)		

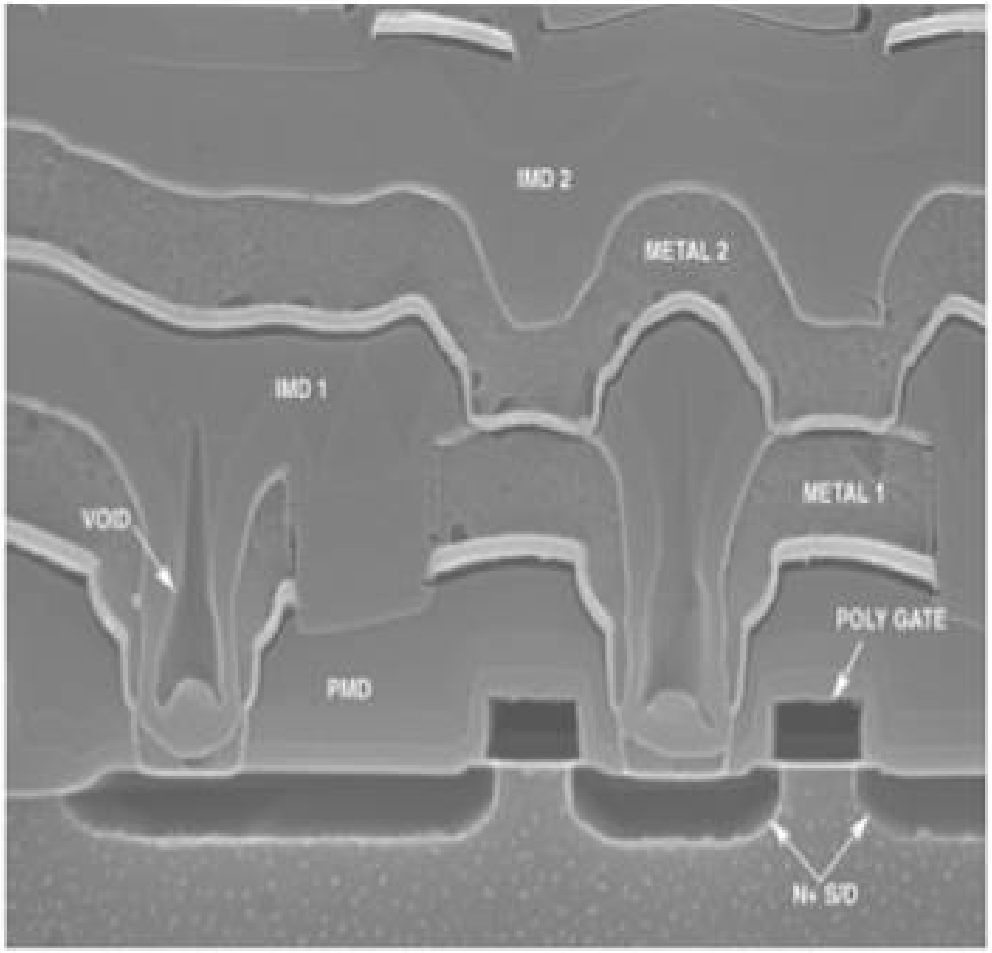
Etching Methods

- Wet Etching 湿法刻蚀
- Dry Etching 干法刻蚀
- CMP and other methods

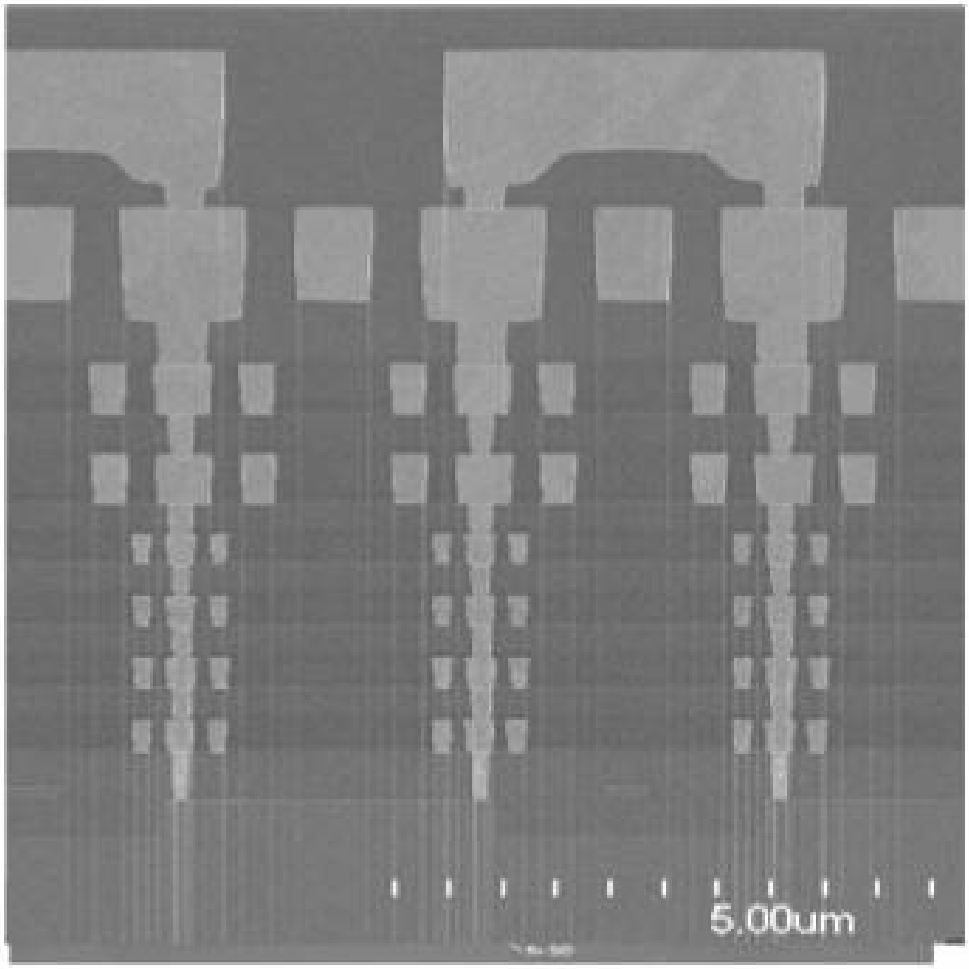
Pattern Formation



Planar Layers are Desirable

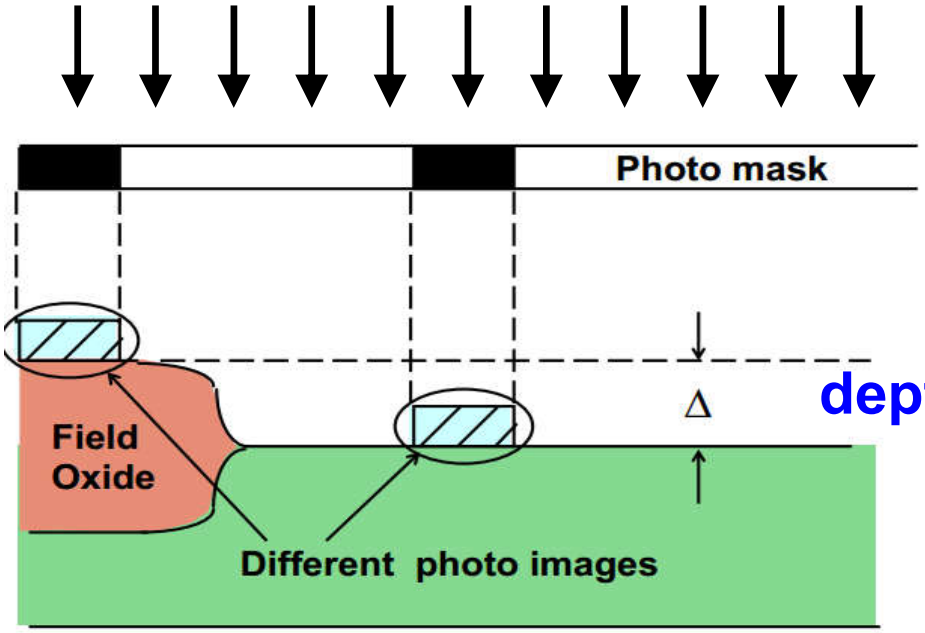


non-planarized IC



planarized IC

Issues with Depth of Focus (DOF)



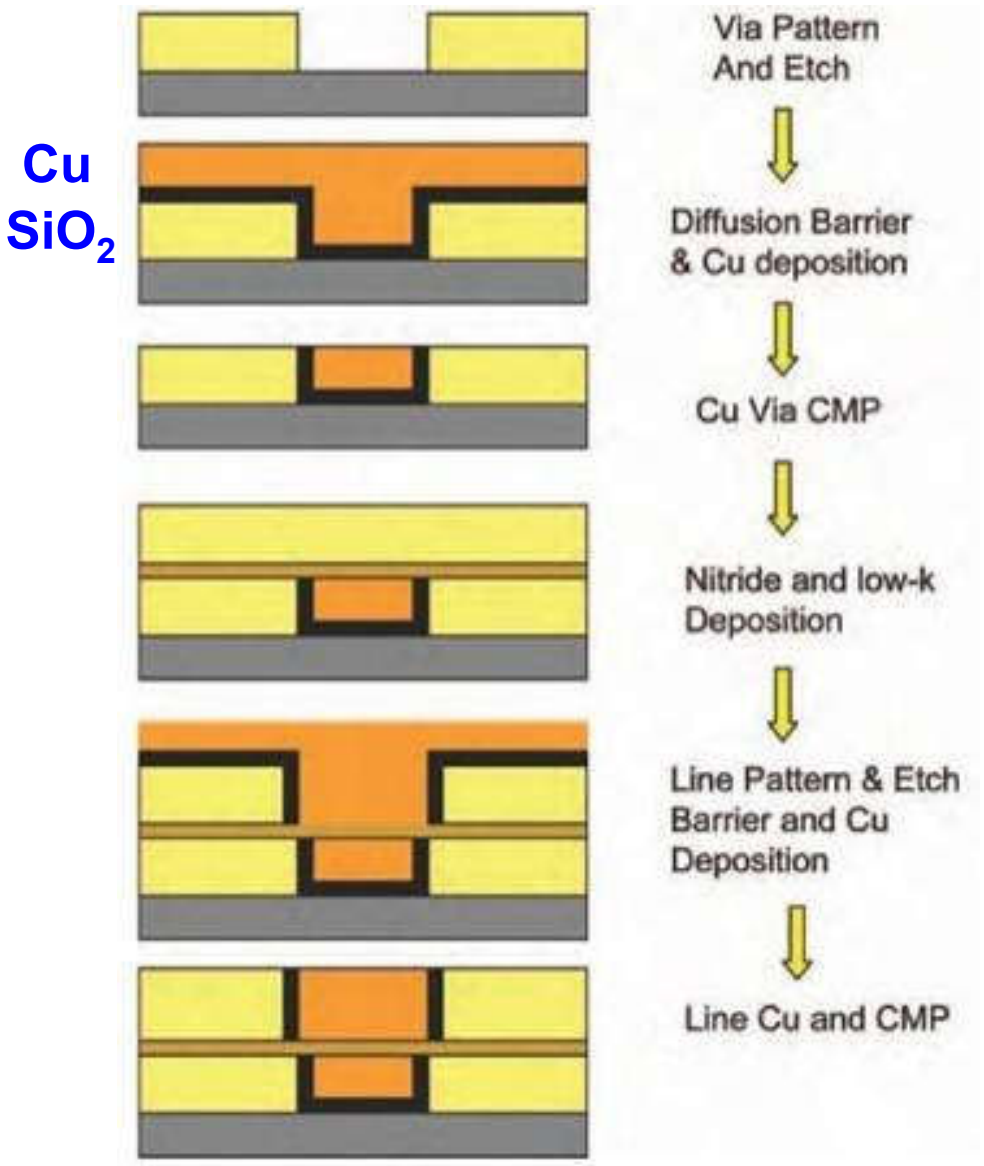
depth of focus
(DOF)

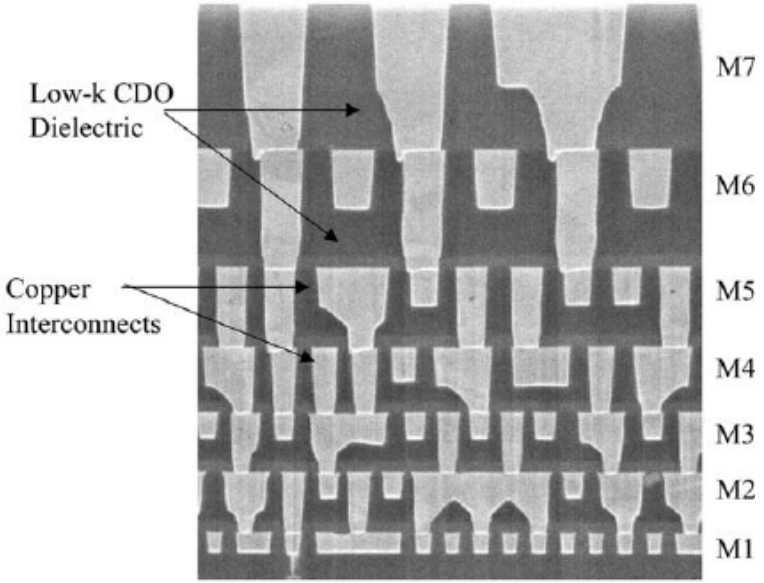
$$(1)\ l_m \cong 0.6\frac{\lambda}{NA} \quad want\ small\ l_m$$

$$(2) DOF = \pm\frac{\lambda}{2(NA)^2} \quad want\ large\ DOF$$

smaller λ, larger NA ----> smaller DOF

Damascene Process



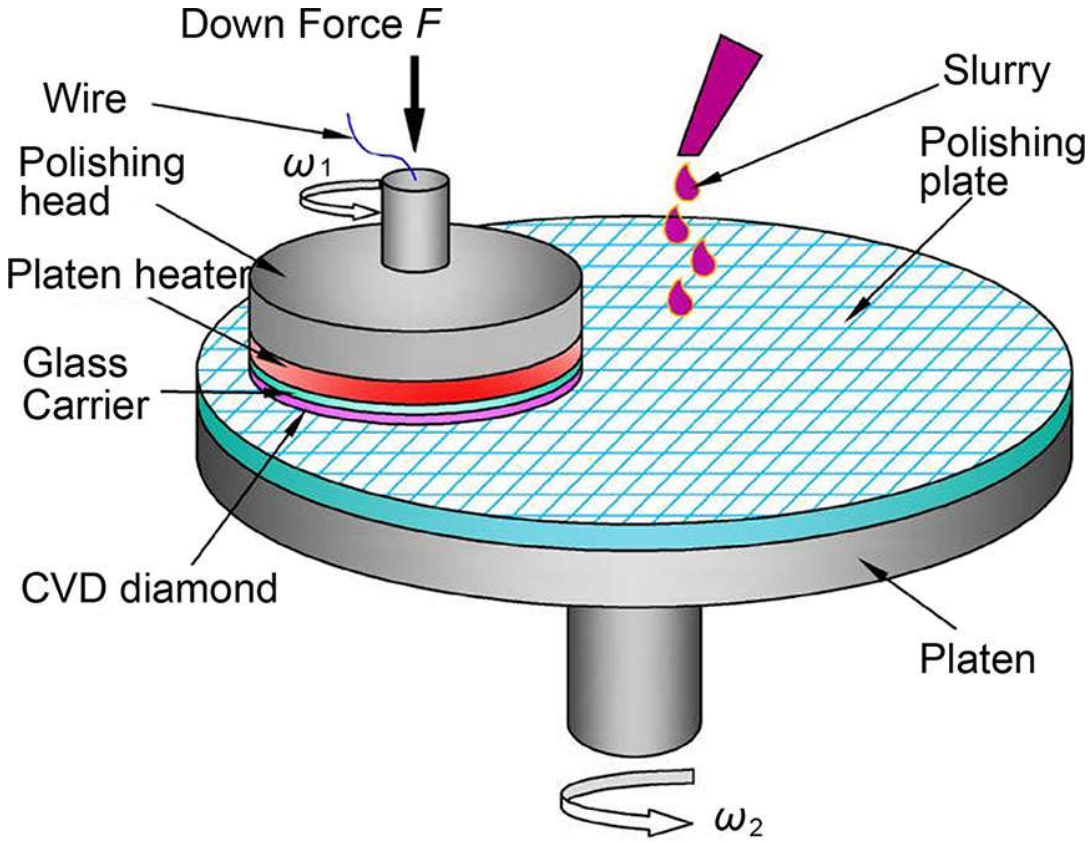


ancient art work

P. C. Andricacos, *et al.*, *IBM J. Res. Develop.* **42,** 567 (1998)

CMP: Chemical Mechanical Polishing

- **Chemical selectivity + Mechanical Planarization**
- **applied for Cu, W, SiO_2, ...**

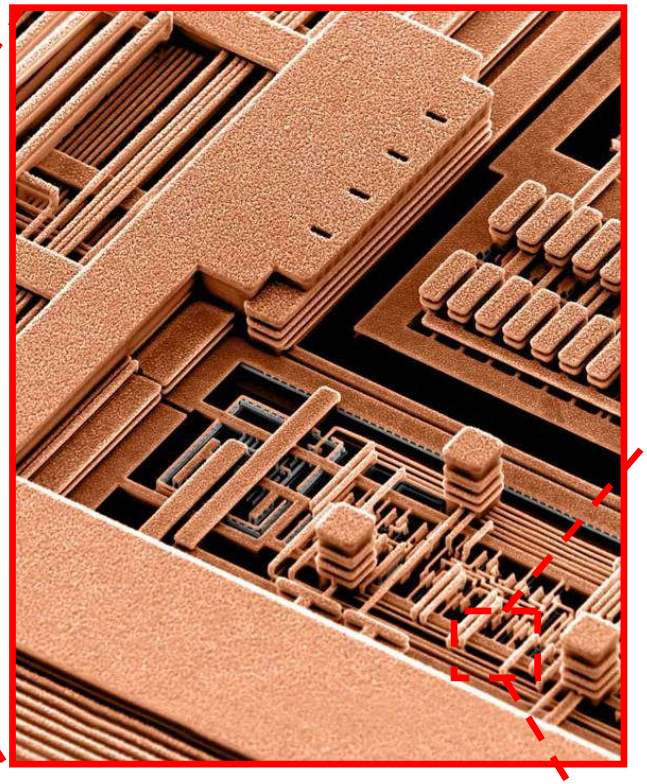


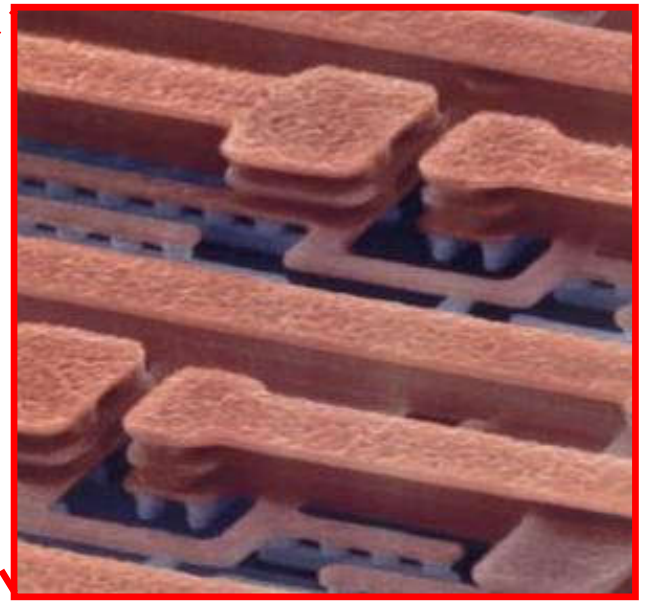
Video

3D IC

Electroplating + CMP

dirtiest process for the most advanced IC



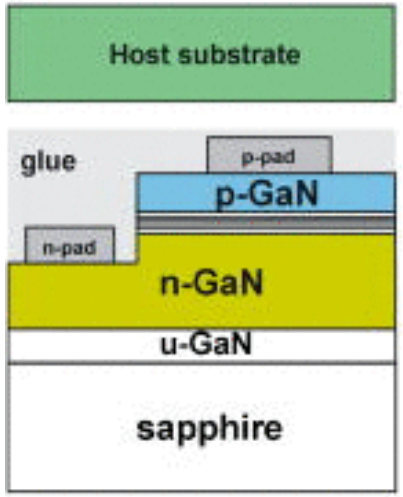


Other Methods for Etching

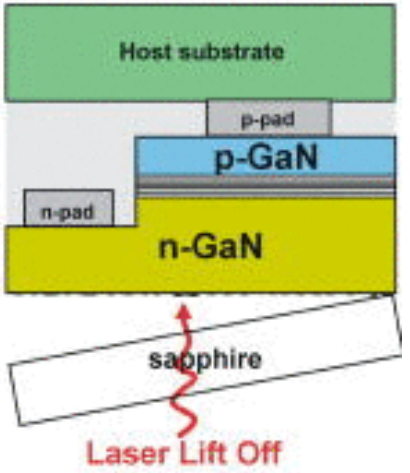
- Laser Lift-Off
- FIB: Focused Ion Beam
- Laser Milling
- ...

GaN Laser Liftoff

- GaN devices grown on sapphire
  - low cost
  - low thermal conductivity
  - electrically insulating
  - sapphire is very difficult to etch

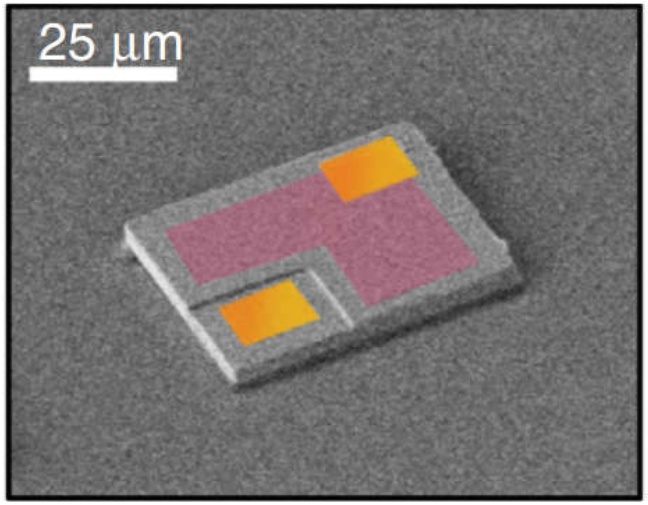


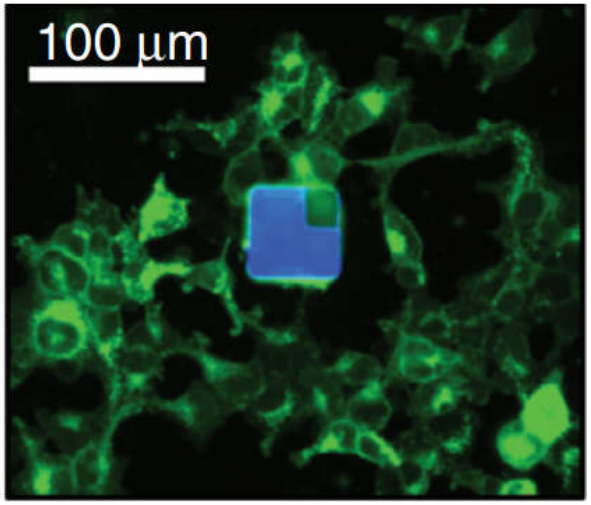
- Release by laser liftoff
  - KrF excimer UV laser (248 nm)
  - GaN = Ga + N_2 (gas)
  - bonding onto new substrates

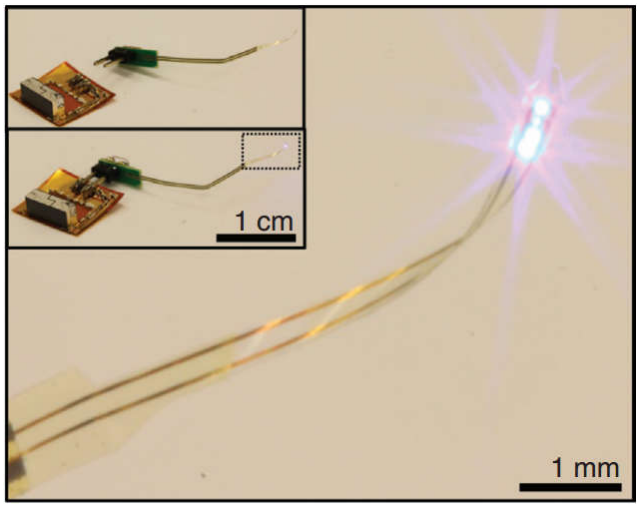


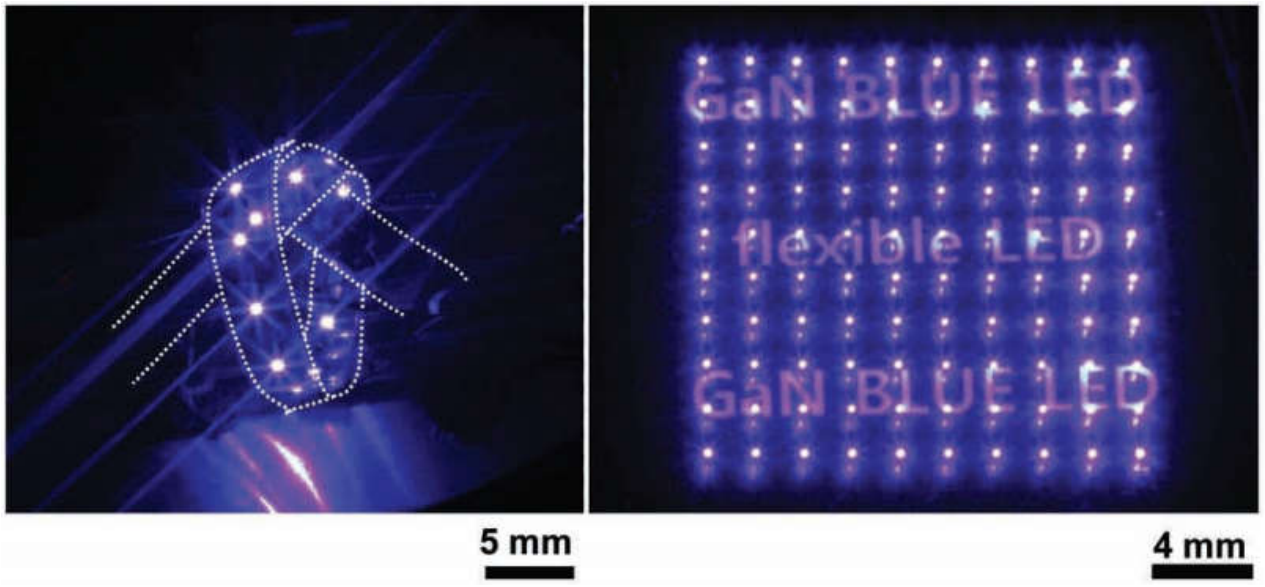
W. S. Wong, *et al.*, *Appl. Phys. Lett.* **72,** 599 (1998)

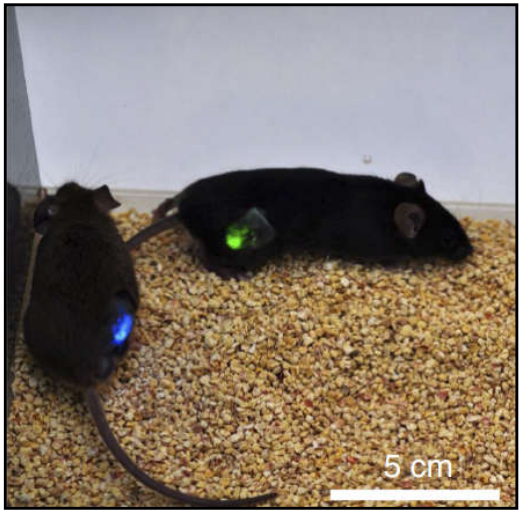
Flexible GaN blue LEDs





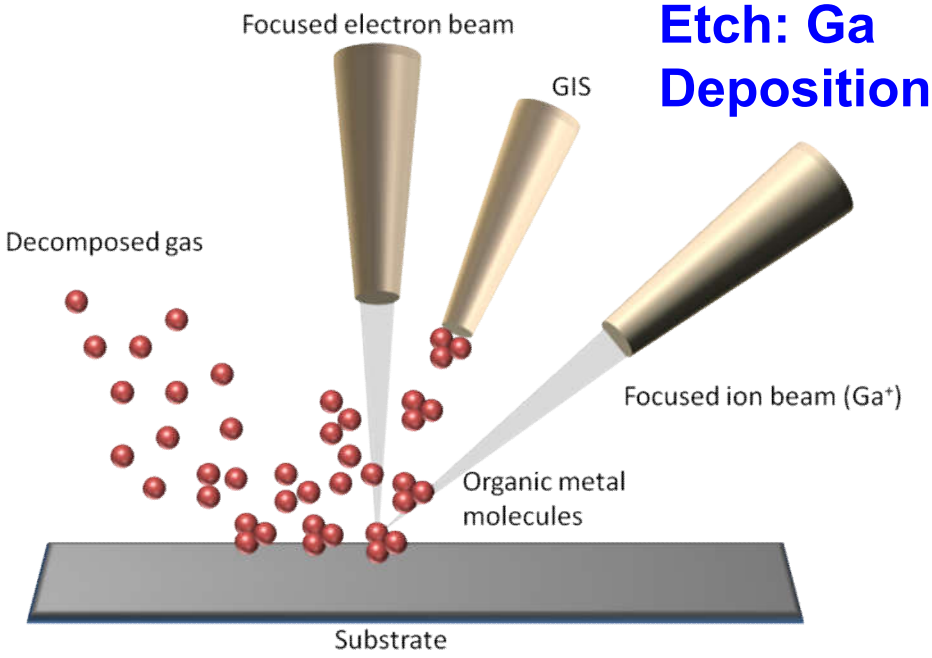




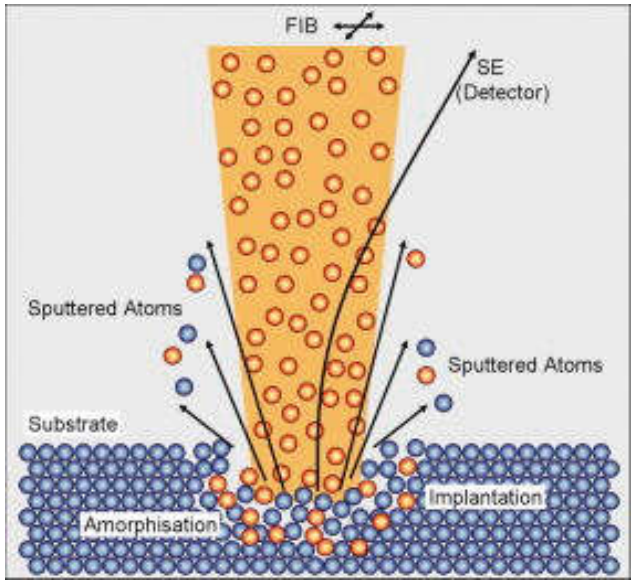


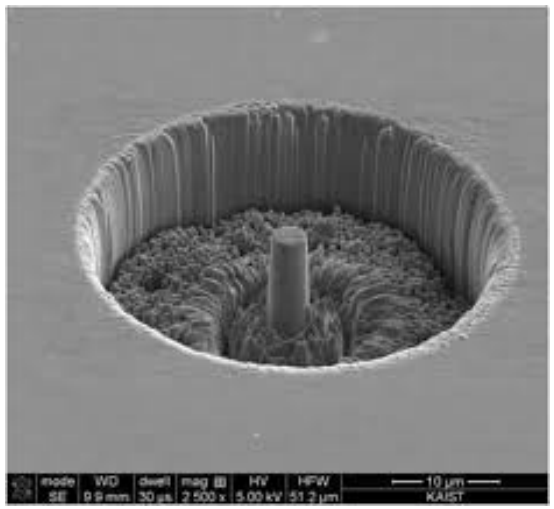
T. Kim, *et al.*, *Science* **340,** 211 (2003)

FIB: Focused Ion Beam



Etch: Ga
Deposition: Pt

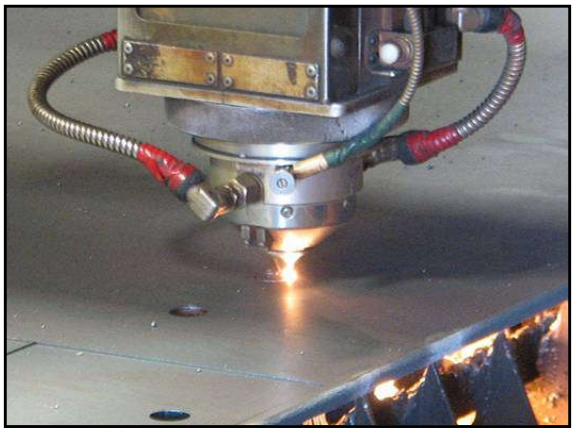




- **nanostructures**
- **SEM/TEM sample preparation**
- **doping**

Laser Milling

- **Types**
  - CO_2 laser 10 μm
  - Near-IR laser 1064 nm
  - UV laser 365 nm
  - Excimer laser 248 nm, 193 nm
  - ps/fs laser ...
- **Applications**
  - die cut, PCB cut, ...



shorter wavelength
shorter pulse

↓

better resolution