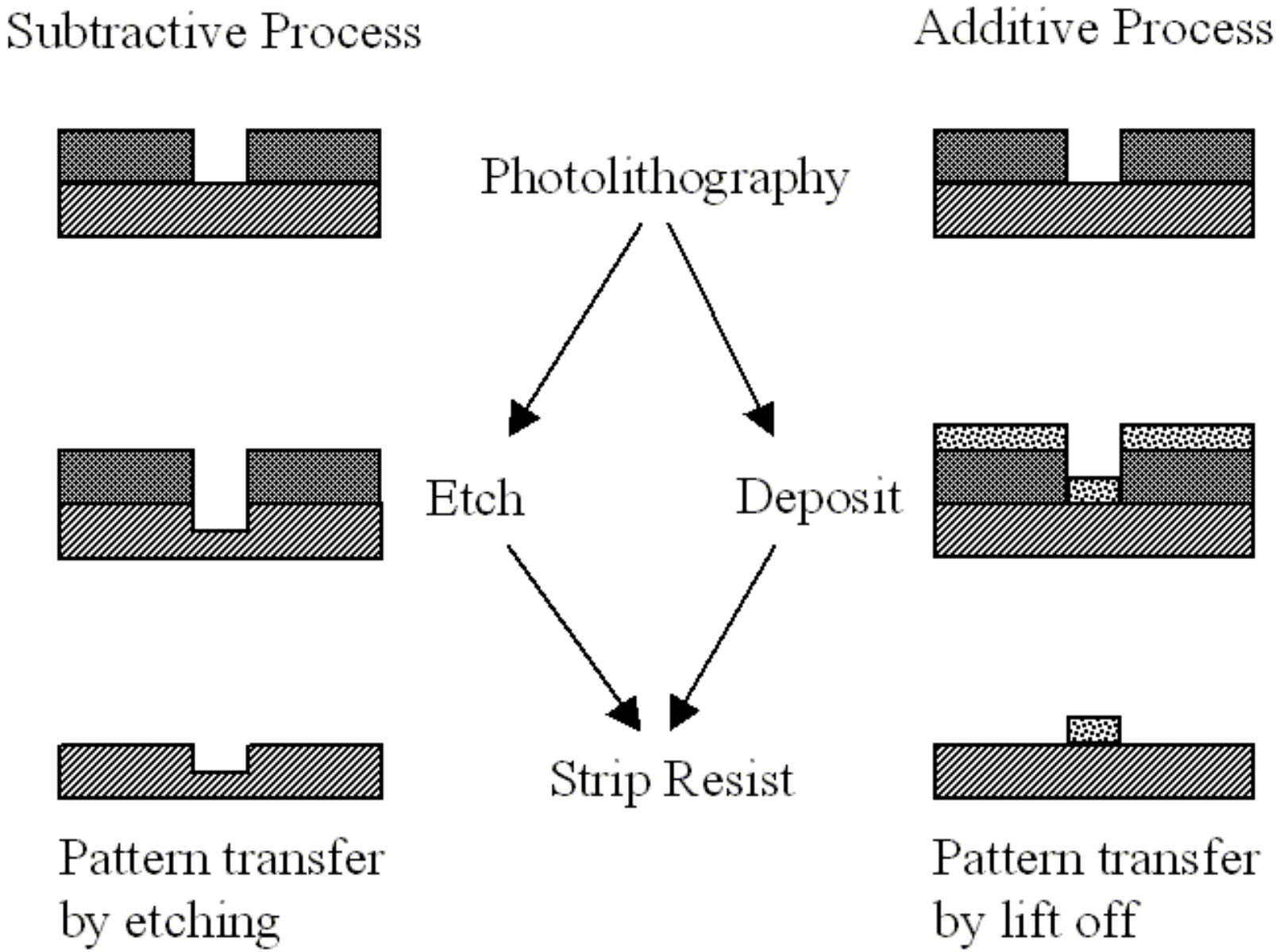
微纳光电子材料与器件工艺原理

Etching
Part I: Wet Etching 湿法刻蚀

Xing Sheng 盛 兴

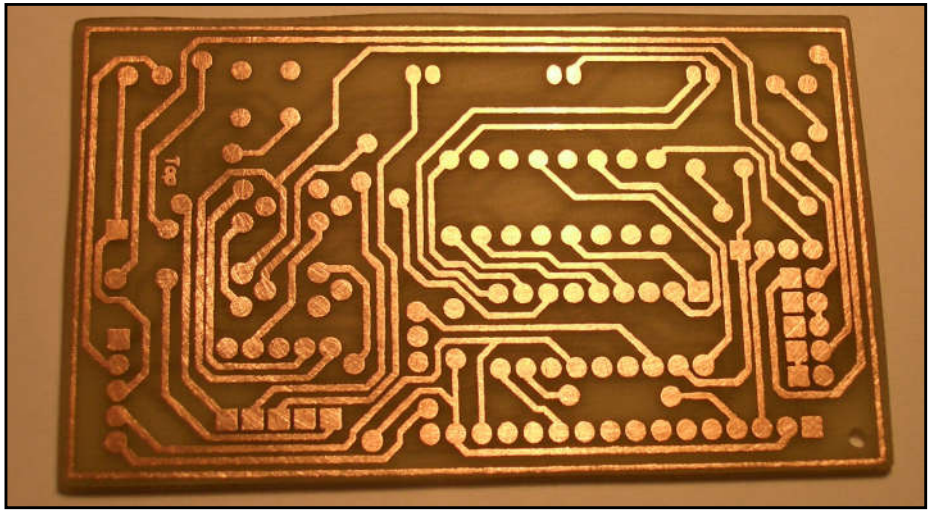
Department of Electronic Engineering
Tsinghua University
xingsheng@tsinghua.edu.cn

Pattern Formation



Etching vs. Corrosion

Etching (刻蚀)



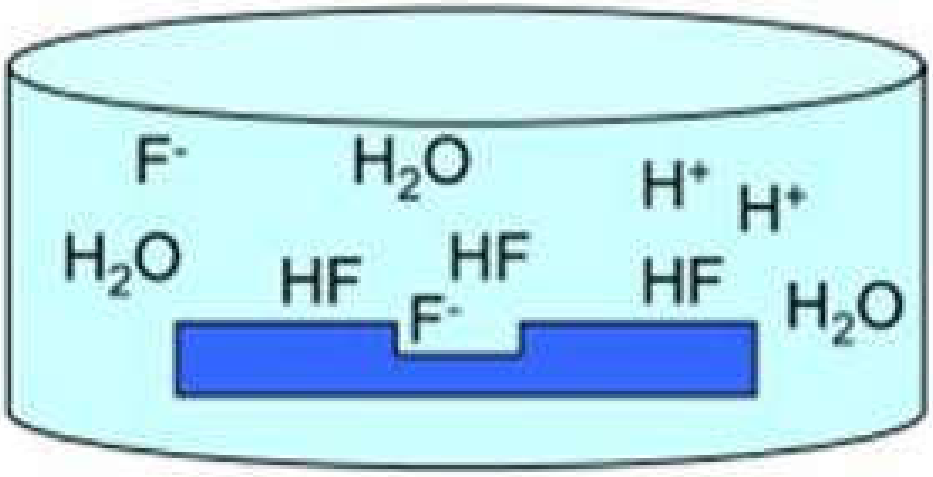
wanted

Corrosion (腐蚀)

unwanted

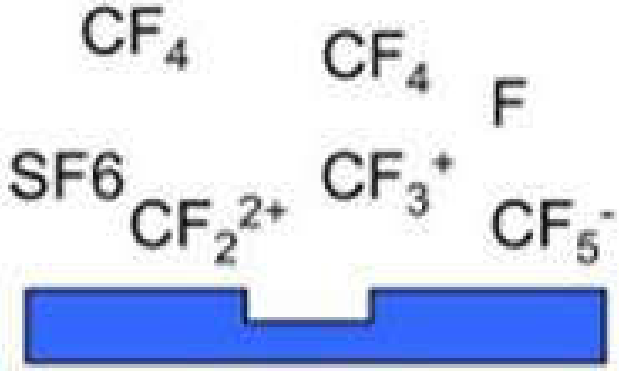
Wet vs. Dry

liquid source



Wet Etch

gas source



Dry Etch

- **Control parameters**
  - **Etch rate**
  - **Selectivity**
  - **Anisotropy / Isotropy**

Trends of Etching

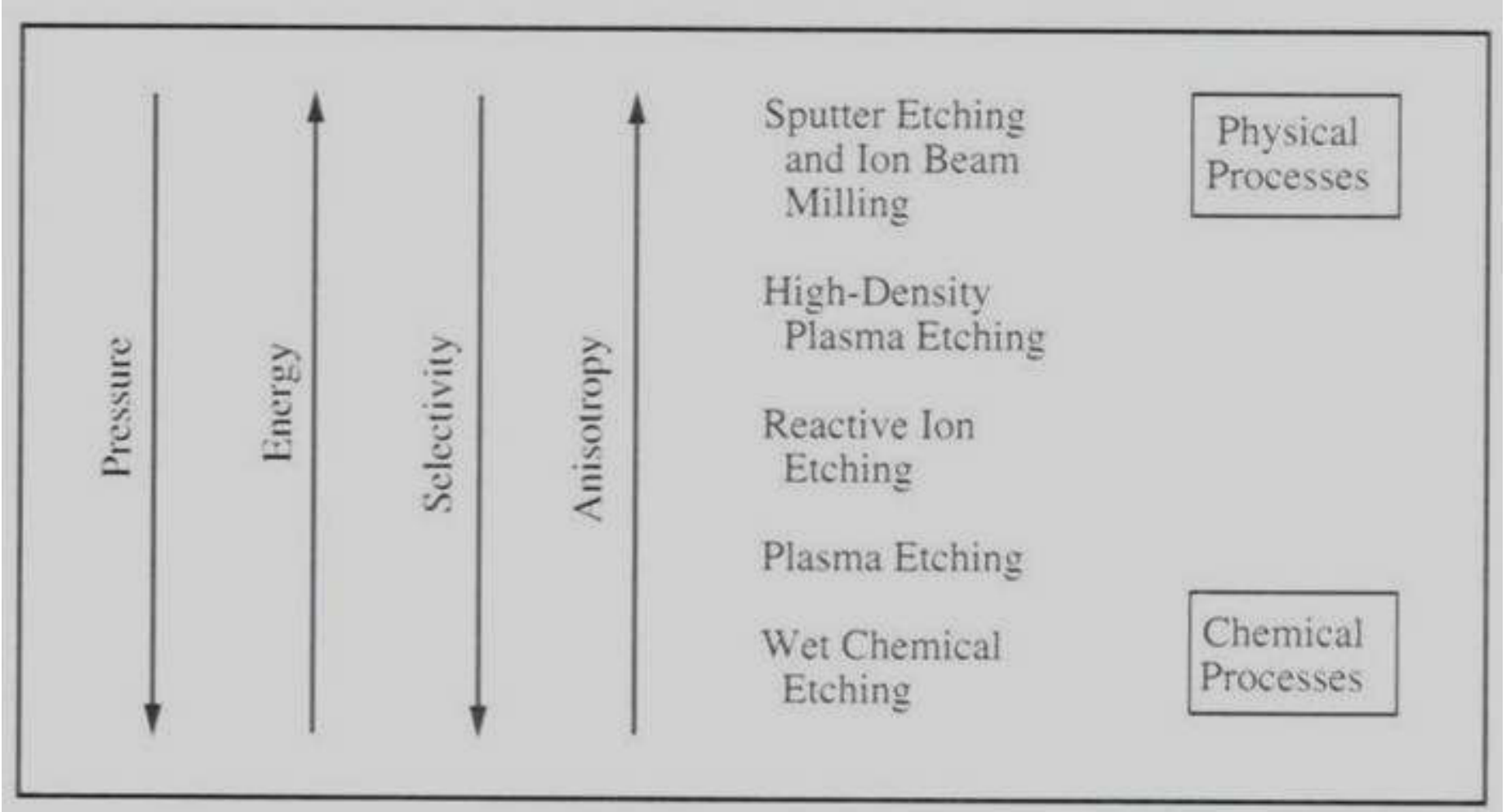


Figure 10–19 Summary of trends of different etch systems.

Isotropic vs. Anisotropic

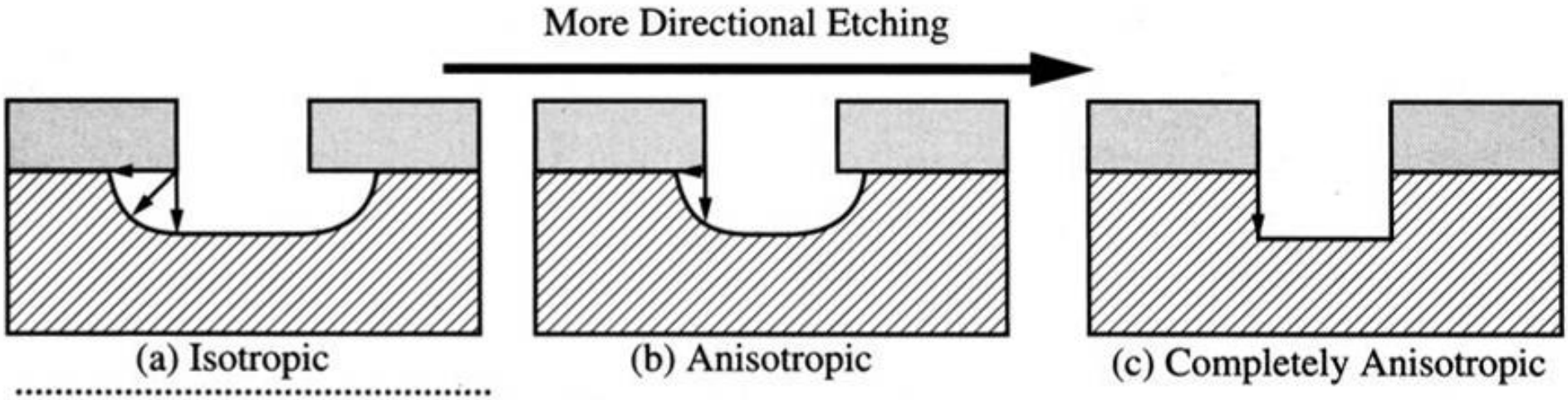
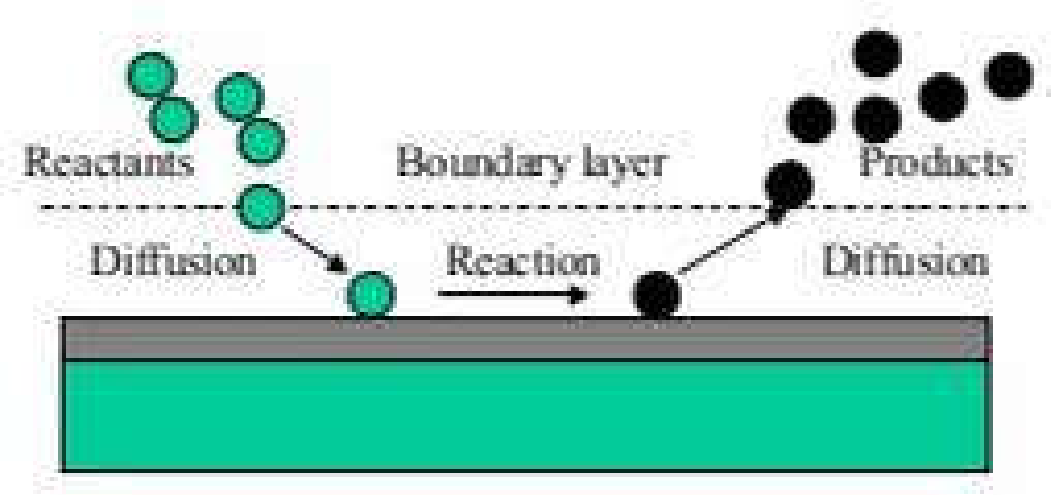


Figure 10–3 Etch profiles for different degrees of anisotropic, or directional, etching: (a) purely isotropic etching; (b) anisotropic etching; (c) completely anisotropic etching.

chemical → **physical**

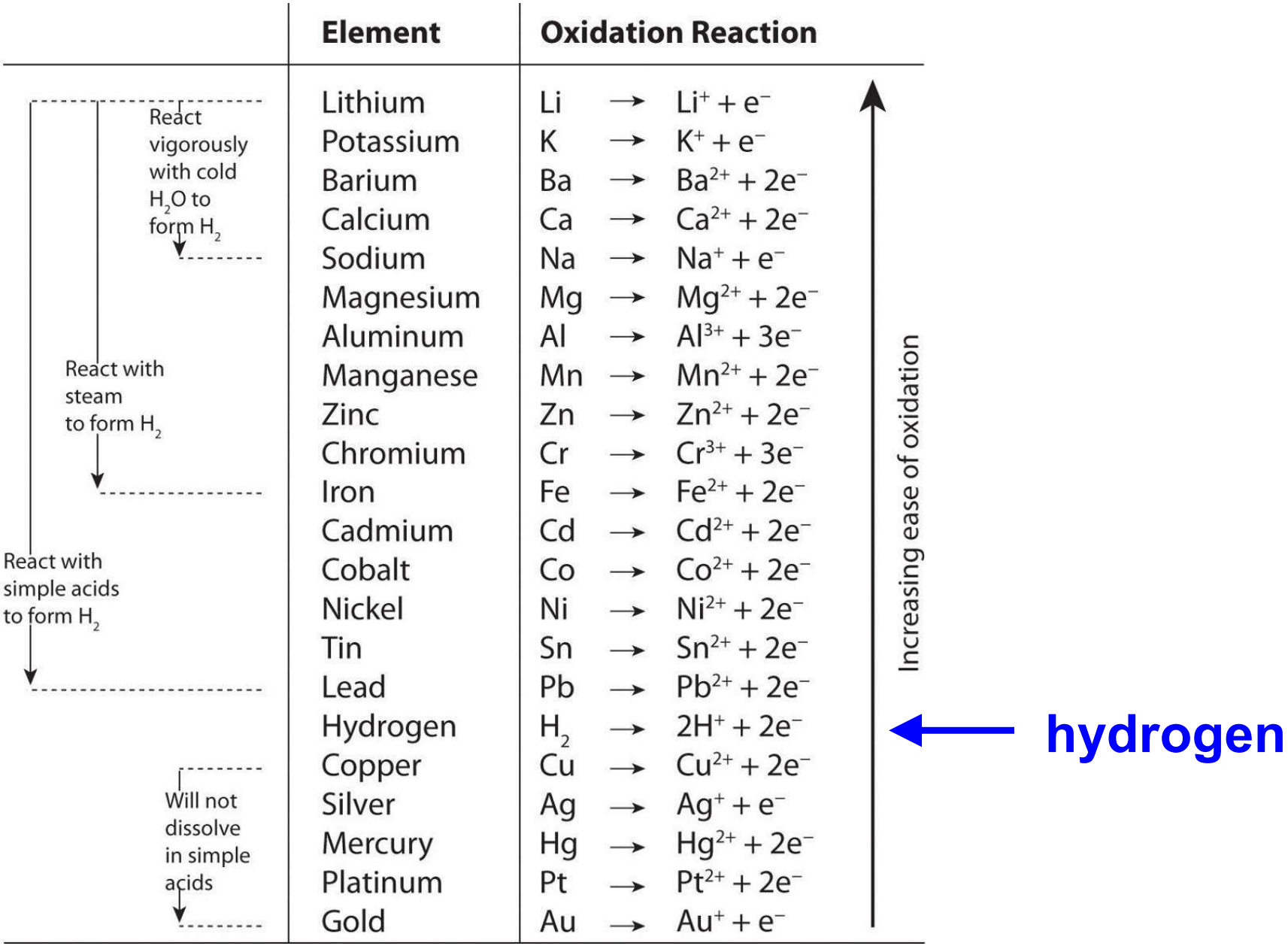
Wet Etching

diffusion - reaction - diffusion



1. chemical reactions occur
2. products should be dissolvable

Metal Dissolution in Acids



Element	Oxidation Reaction
Lithium	$Li \rightarrow Li^+ + e^-$
Potassium	$K \rightarrow K^+ + e^-$
Barium	$Ba \rightarrow Ba^{2+} + 2e^-$
Calcium	$Ca \rightarrow Ca^{2+} + 2e^-$
Sodium	$Na \rightarrow Na^+ + e^-$
Magnesium	$Mg \rightarrow Mg^{2+} + 2e^-$
Aluminum	$Al \rightarrow Al^{3+} + 3e^-$
Manganese	$Mn \rightarrow Mn^{2+} + 2e^-$
Zinc	$Zn \rightarrow Zn^{2+} + 2e^-$
Chromium	$Cr \rightarrow Cr^{3+} + 3e^-$
Iron	$Fe \rightarrow Fe^{2+} + 2e^-$
Cadmium	$Cd \rightarrow Cd^{2+} + 2e^-$
Cobalt	$Co \rightarrow Co^{2+} + 2e^-$
Nickel	$Ni \rightarrow Ni^{2+} + 2e^-$
Tin	$Sn \rightarrow Sn^{2+} + 2e^-$
Lead	$Pb \rightarrow Pb^{2+} + 2e^-$
Hydrogen	$H_2 \rightarrow 2H^+ + 2e^-$
Copper	$Cu \rightarrow Cu^{2+} + 2e^-$
Silver	$Ag \rightarrow Ag^+ + e^-$
Mercury	$Hg \rightarrow Hg^{2+} + 2e^-$
Platinum	$Pt \rightarrow Pt^{2+} + 2e^-$
Gold	$Au \rightarrow Au^+ + e^-$

Metal Dissolution in Acids

Strong Acids + Strong Oxidants

Piranha $H_2SO_4 : H_2O_2 = 3:1$

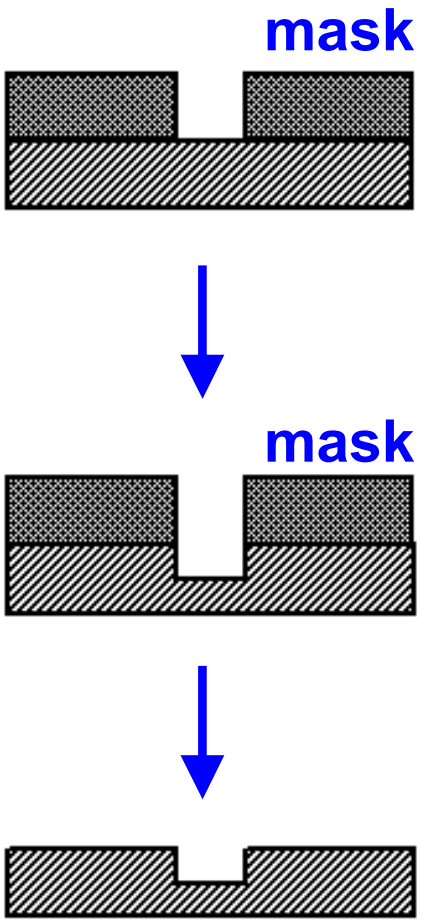
dissolves most metals and organics

Aqua Regia (王水) HCl : HNO3 = 3:1

even dissolves Au, Pt

However, difficult to obtain ideal selectivity ...

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

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

References

- Etch Rates for Micromachining Processing
- Etch Rates for Micromachining Processing-Part II

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

- Guide to references on III-V semiconductor chemical etching

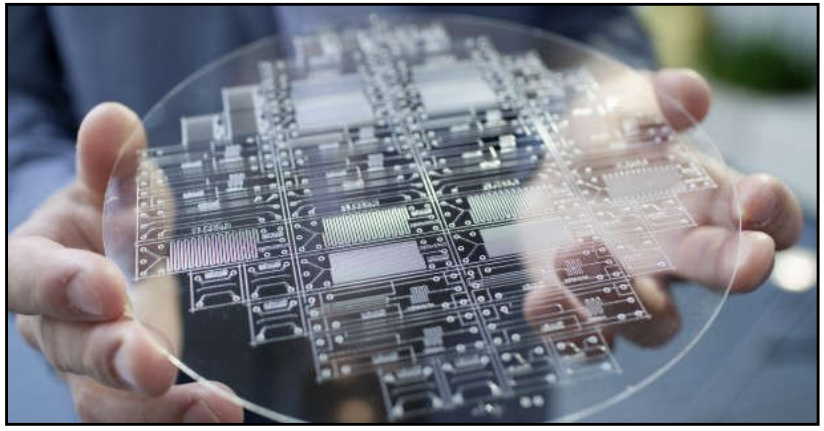
http://www.sciencedirect.com/science/article/pii/S0927796X00000279

SiO_2 etching

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

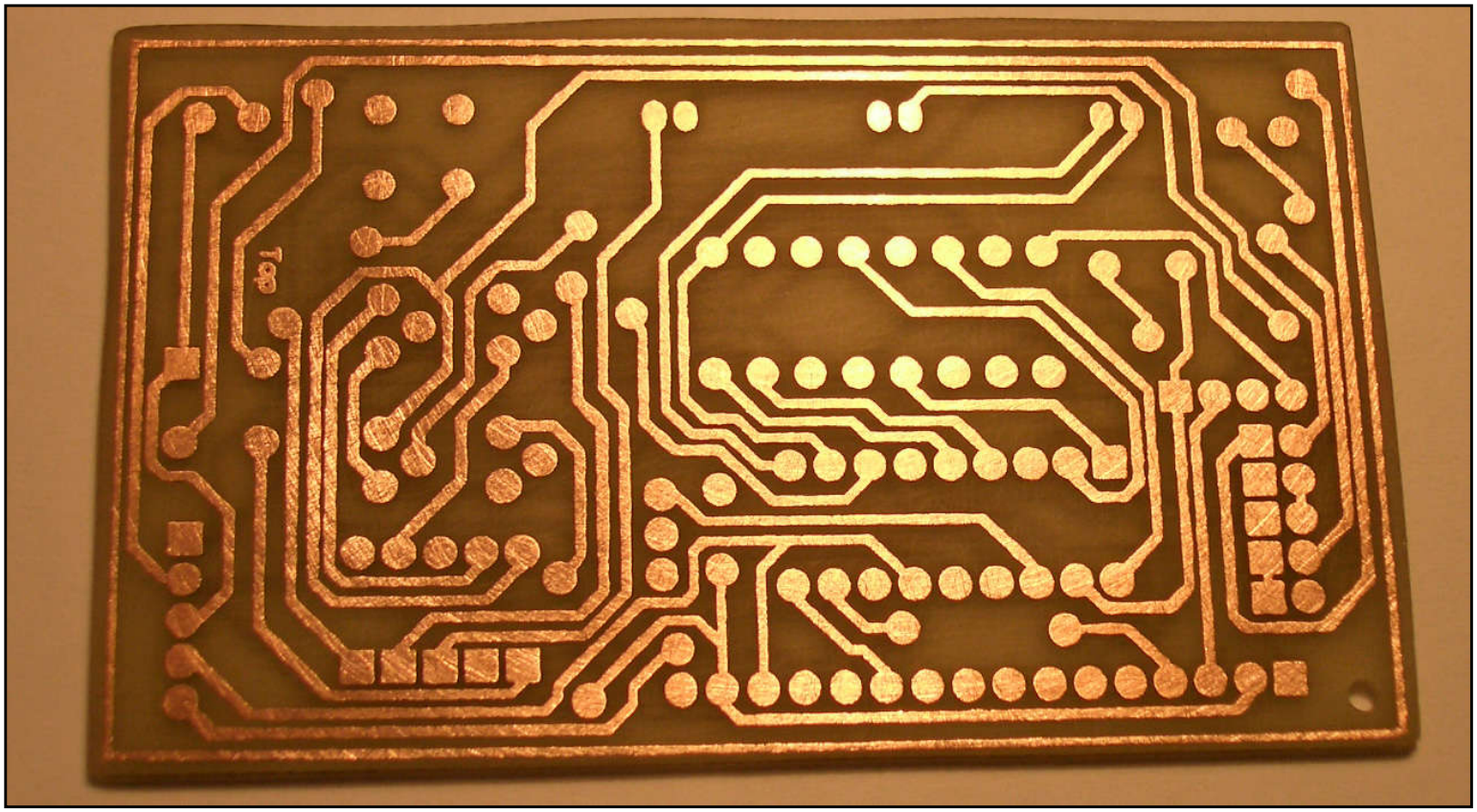
glass art by HF etch

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



Cu etching

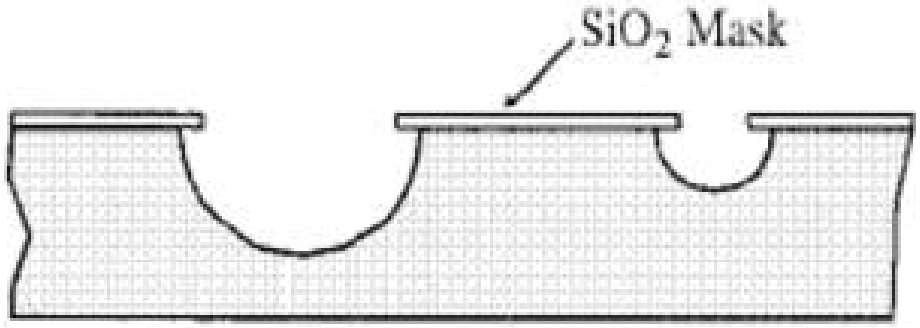
- $Cu + 2FeCl_3 = CuCl_2 + 2FeCl_2$



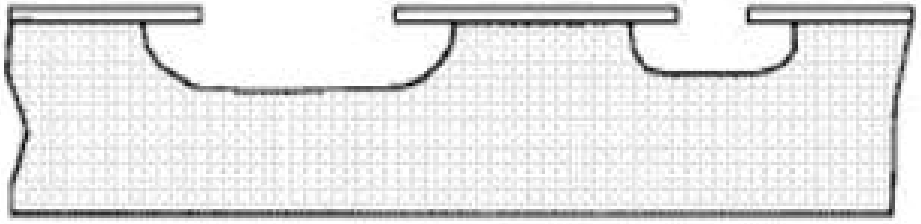
Si etching

- HNO_3 + HF
  - isotropic etch

Isotropic wet etching: Agitation



Isotropic wet etching: No Agitation

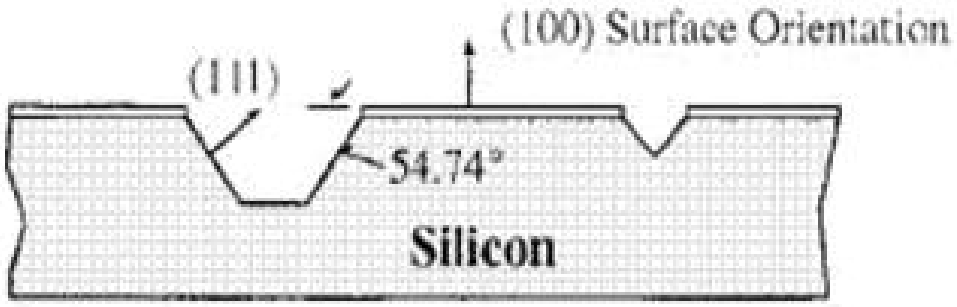


Si etching

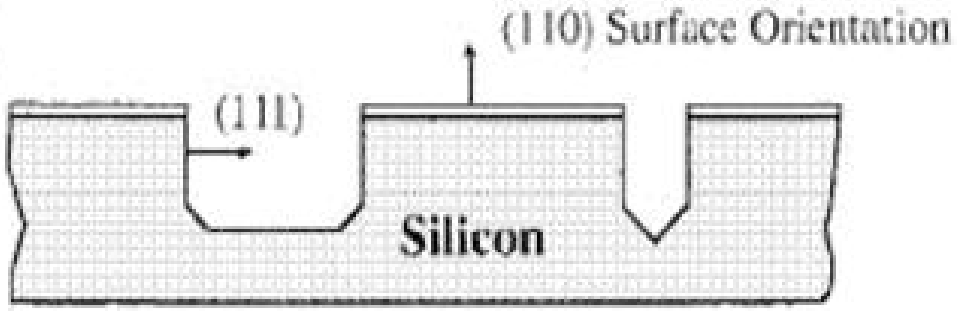
- **KOH**
  - **anisotropic etch**
  - **etch rate (111):(110):(100) ~ 1:600:400**
  - **mask: SiO_2, Si_3N_4, Cr/Au, ...**

Q: why?

Anisotropic wet etching: (100)



Anisotropic wet etching: (110)

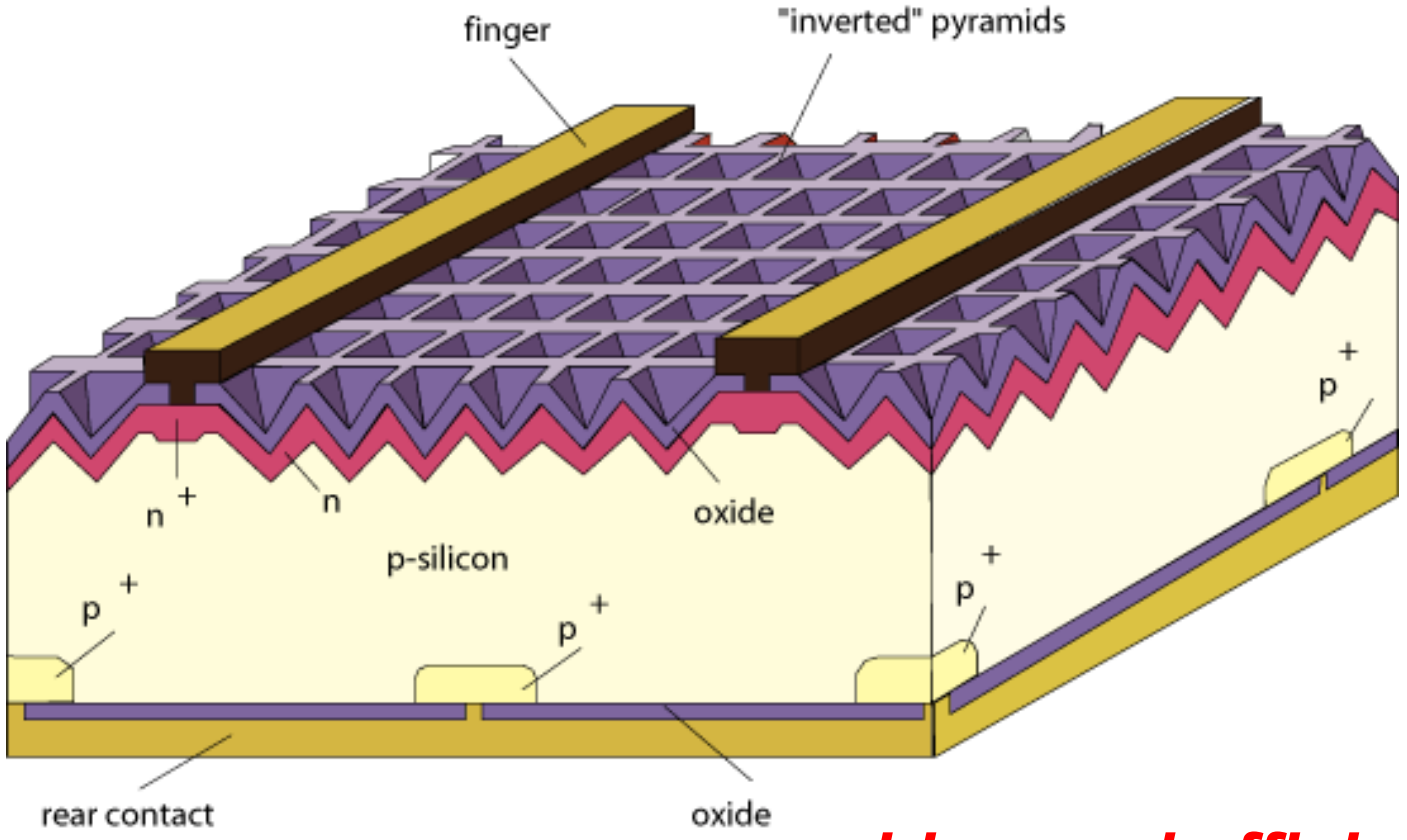


- **Other chemistries**
  - **TMAH: Tetramethyl ammonium hydroxide**
  - **EDP: Ethylene diamine pyrochatecol**

Si etching

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

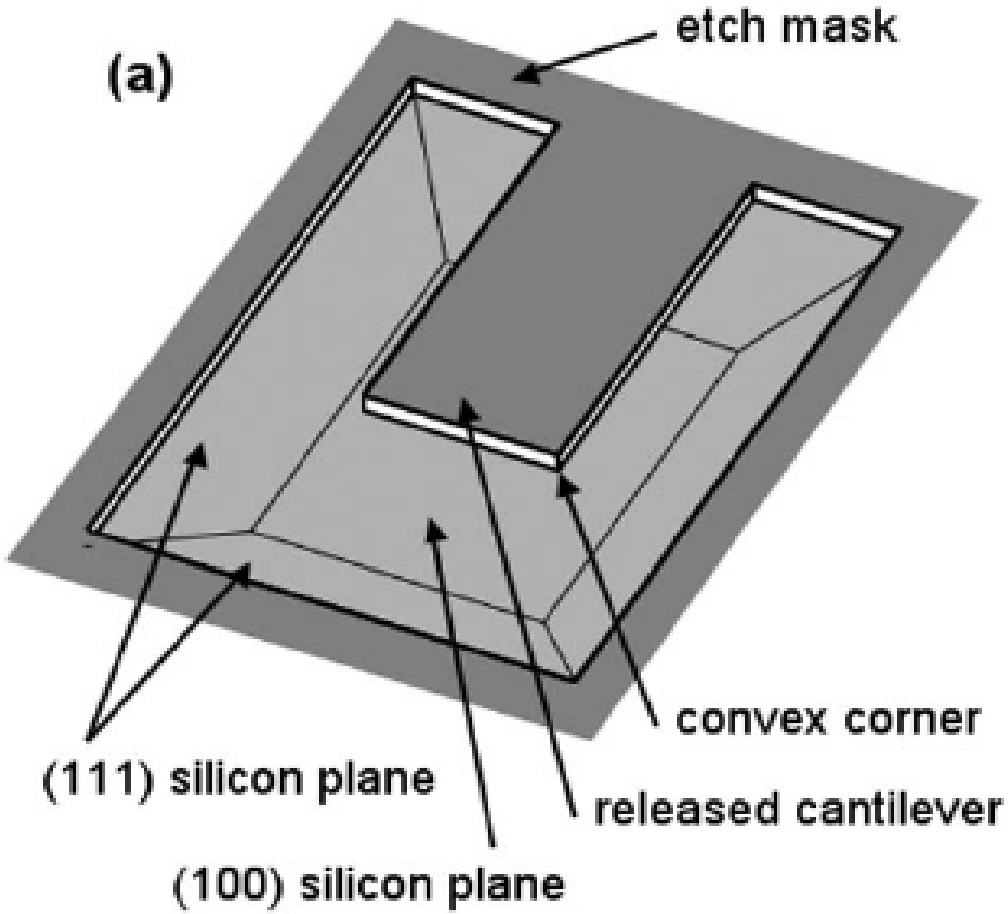
optical trapping and antireflection

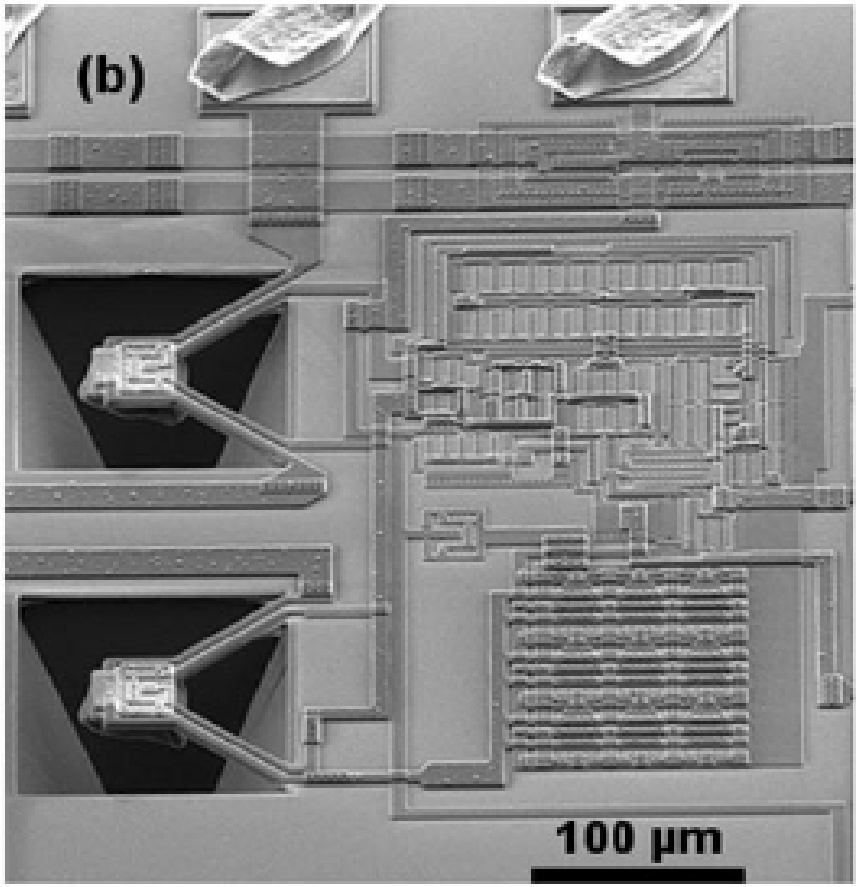


world record efficiency: 26%

Si etching

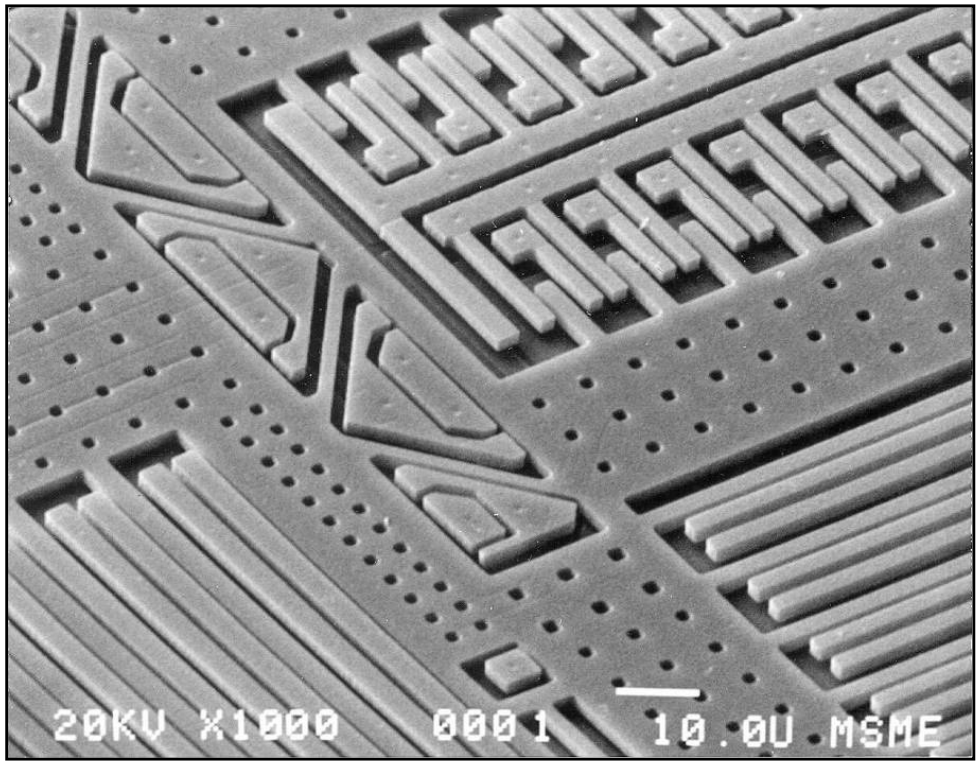
- **Si cantilever beam**
  - **KOH anisotropic etch**





Si etching

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

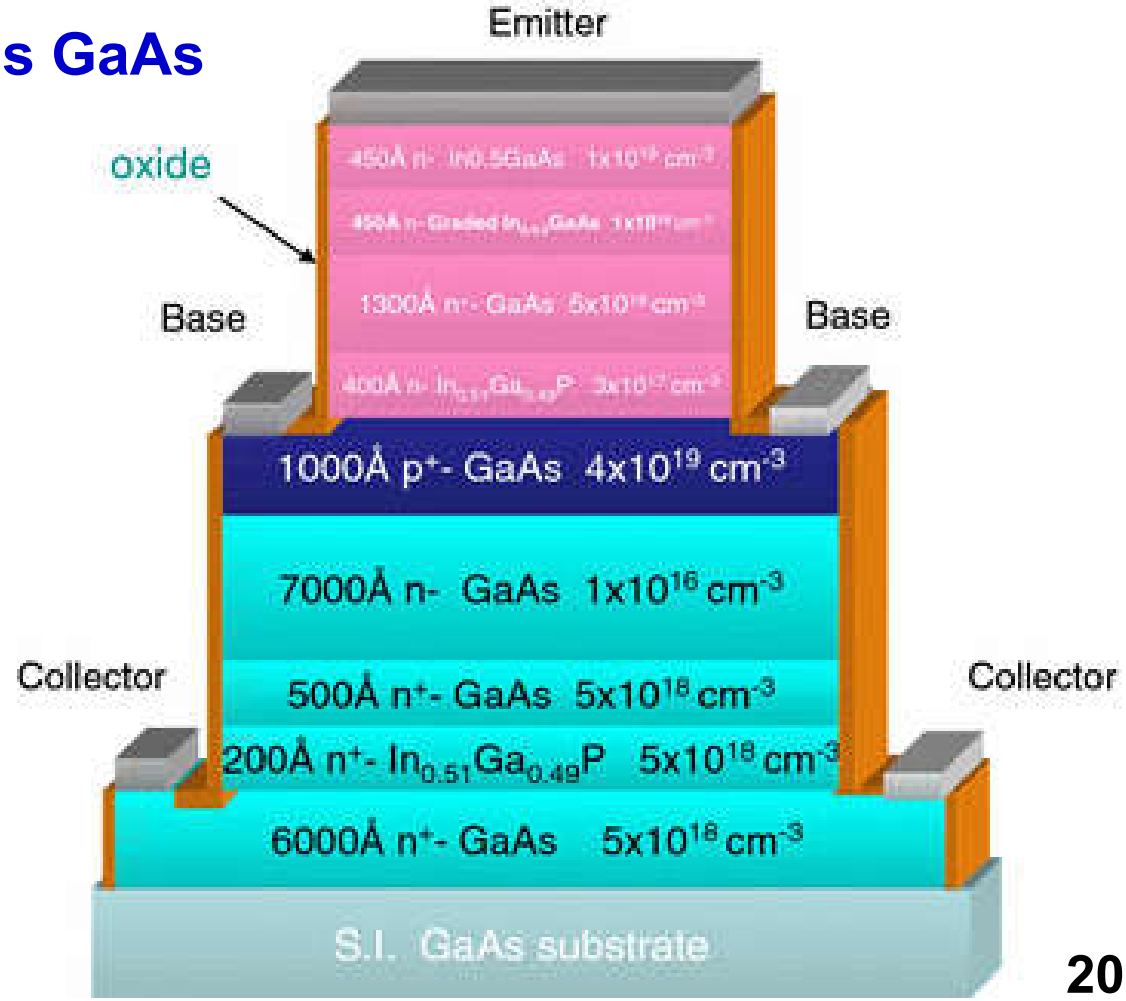


III-V etching

- 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 ...

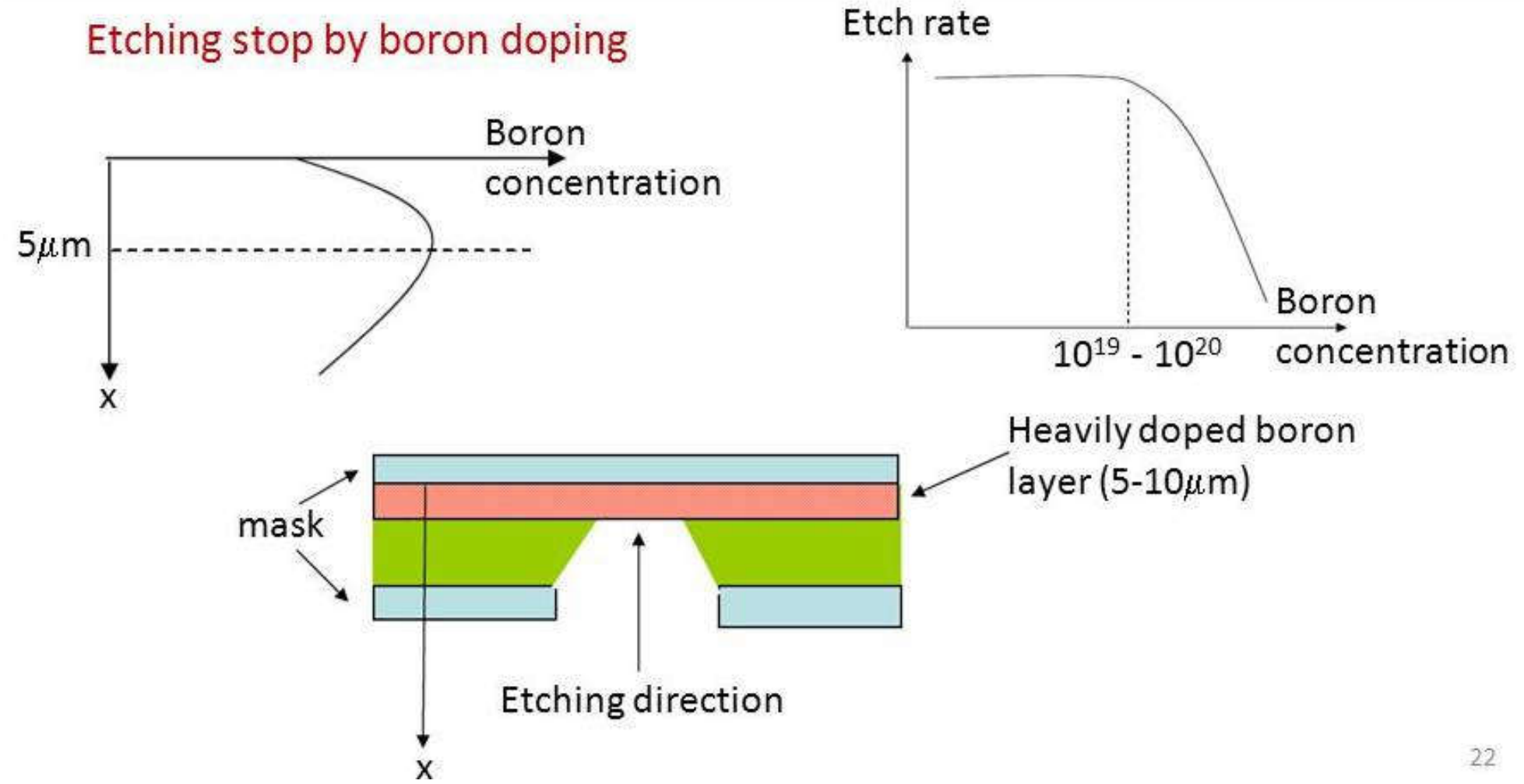
Etch Stops

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



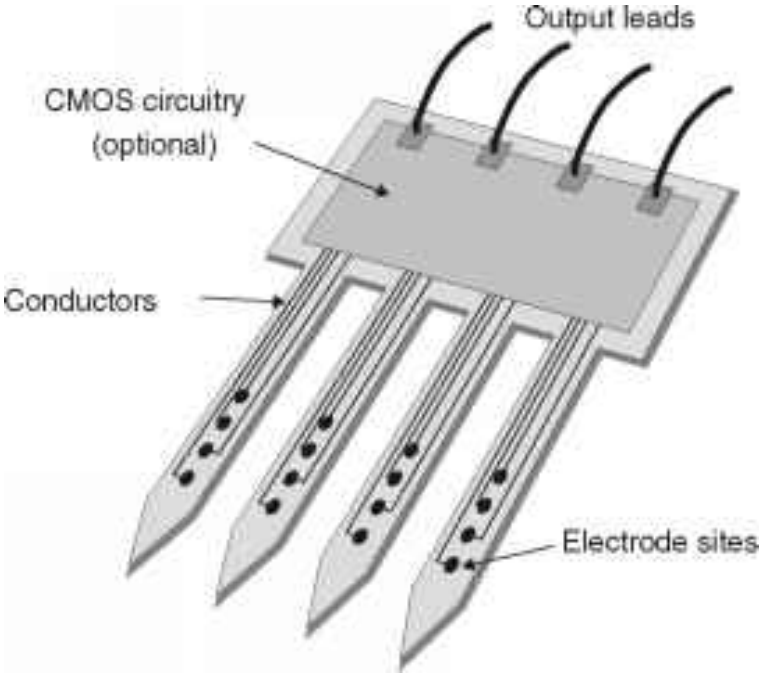
Etch Stops

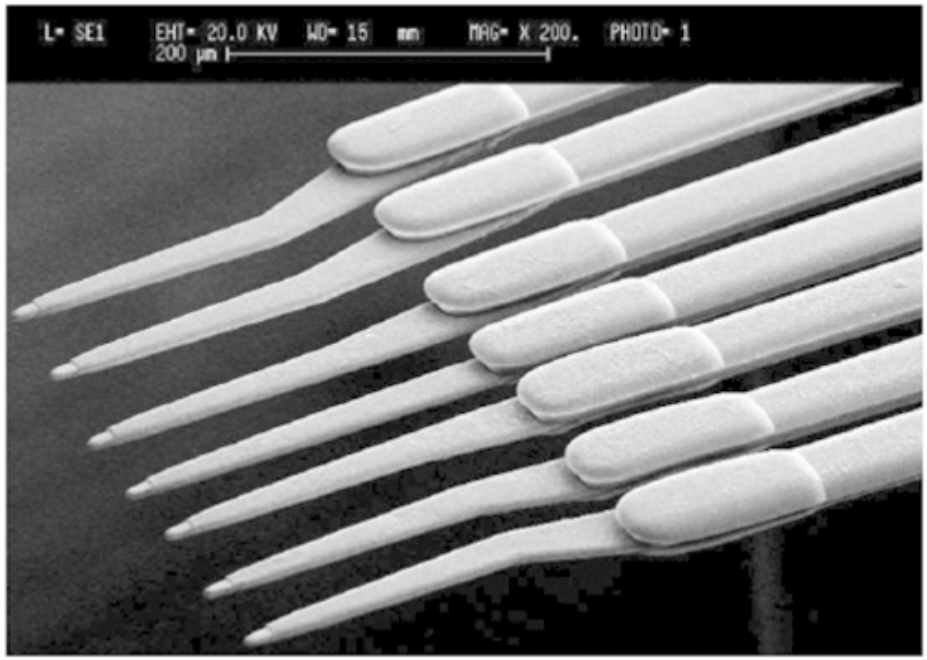
- highly p-dope Si is resistant to KOH



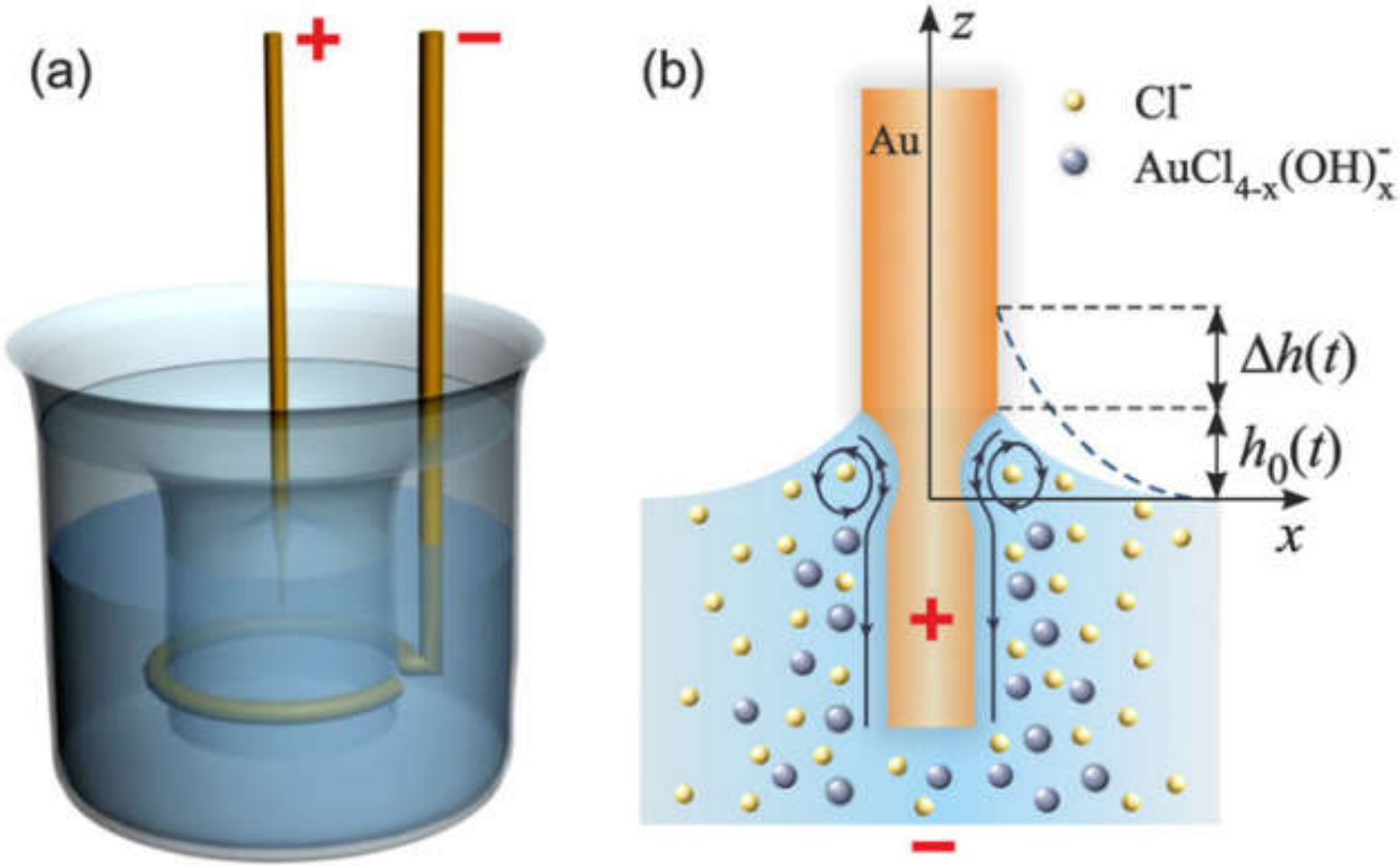
Etch Stops

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

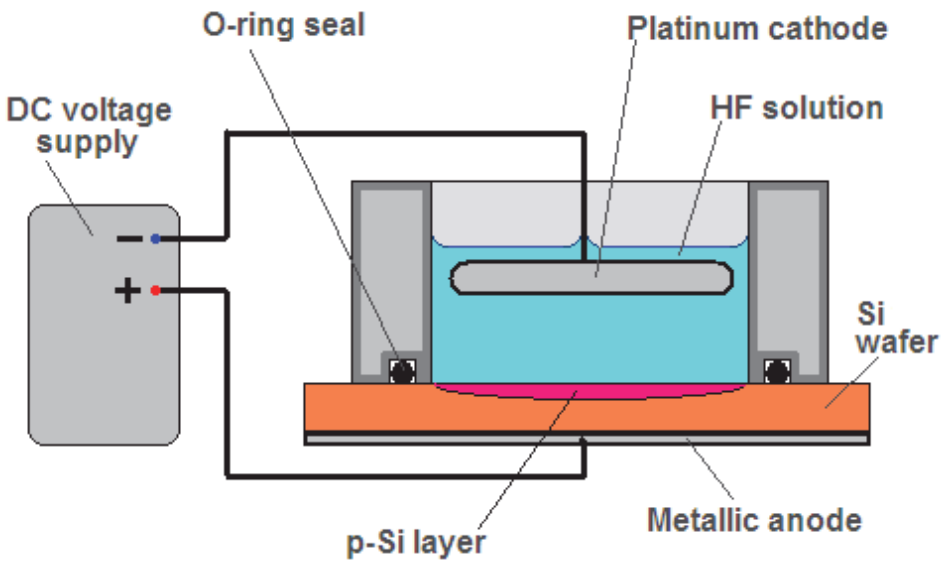


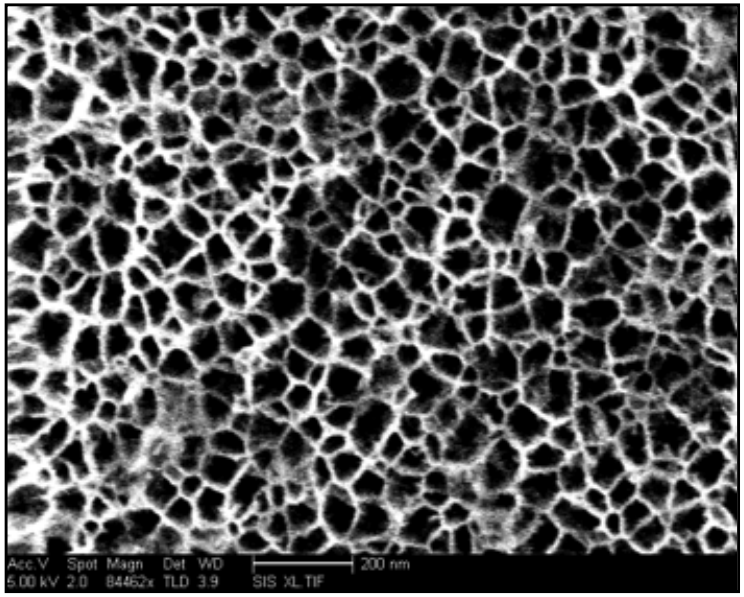


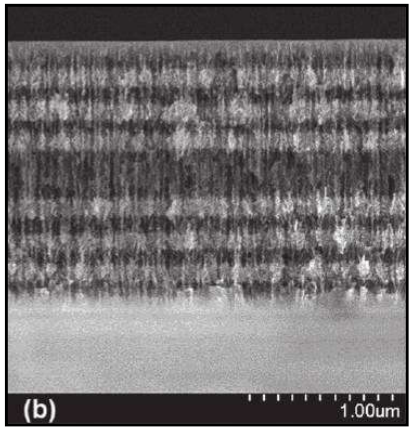
Electrochemical Etch

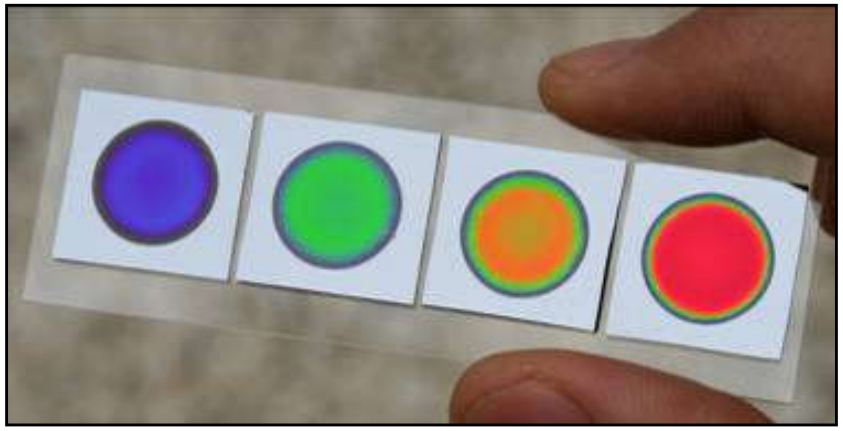


Anodization (阳极氧化) - Porous Si

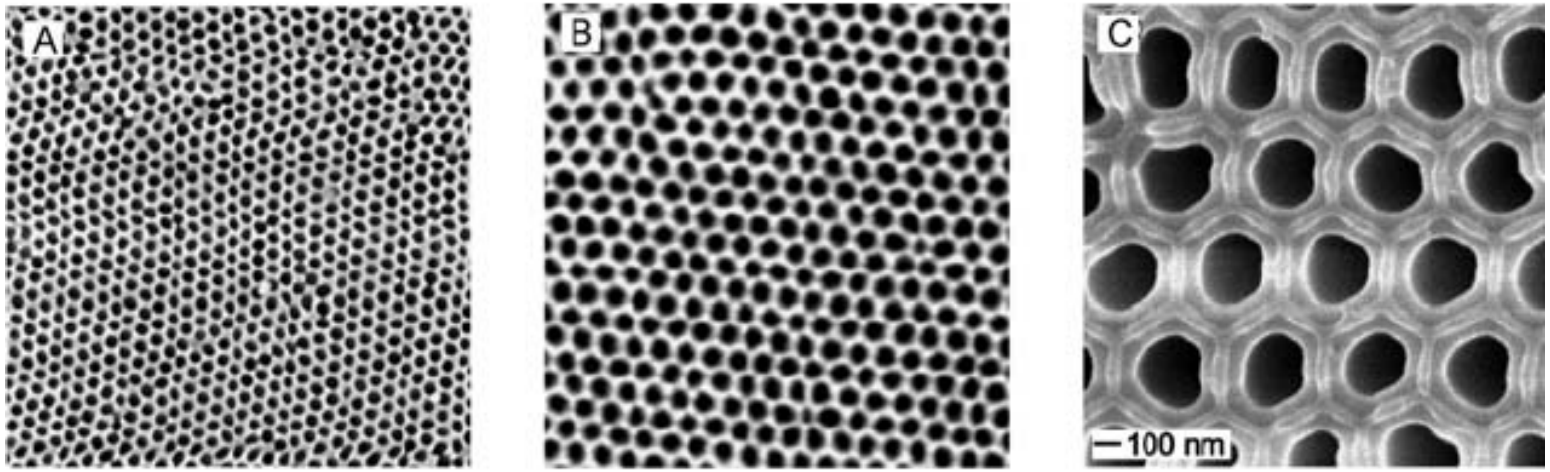


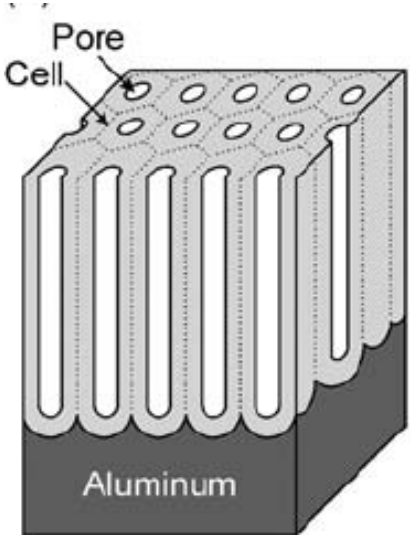


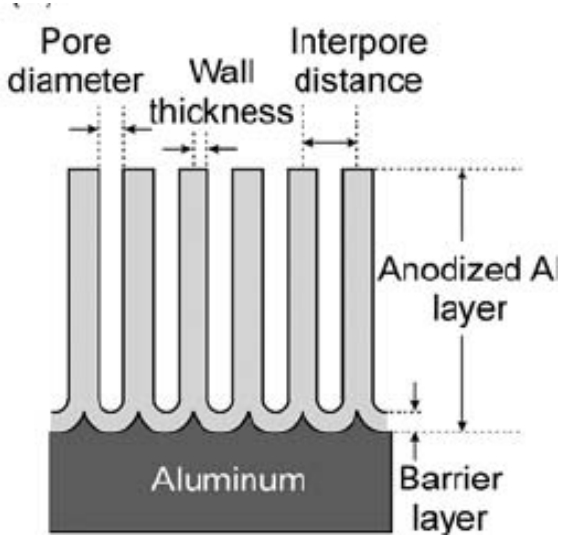


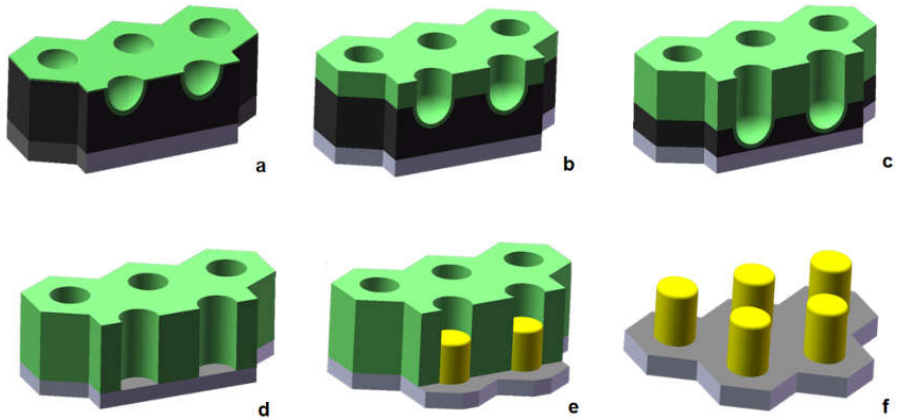


Anodization - Porous Al_2O_3



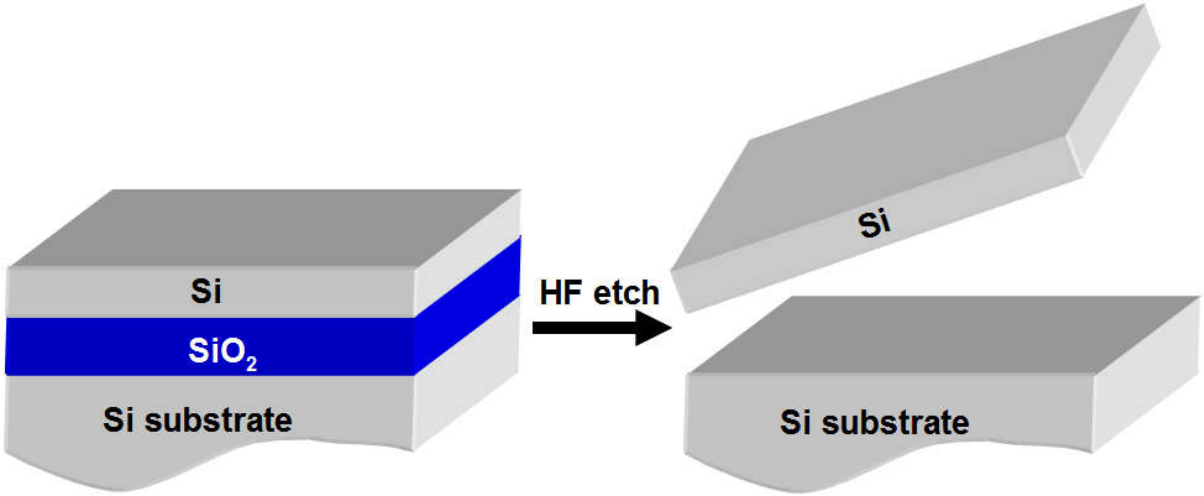


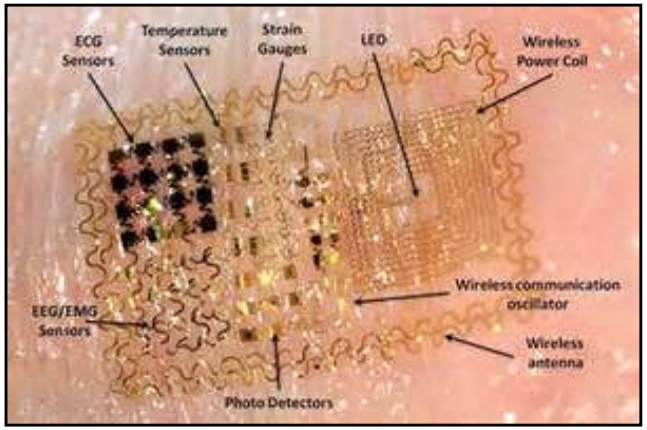




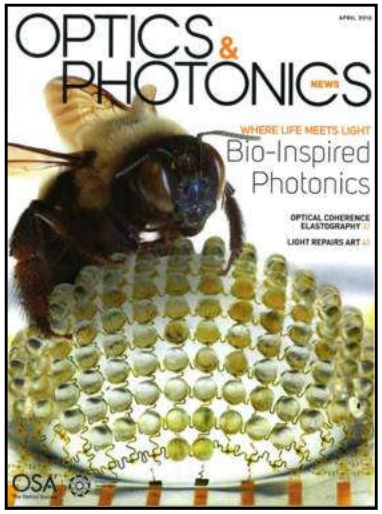
H. Masuda and K. Fukuda, *Science* **268,** 1466 (1995)

Thin-Film Si from SOI wafers





human eyes



compound eyes

'epidermal' electronics

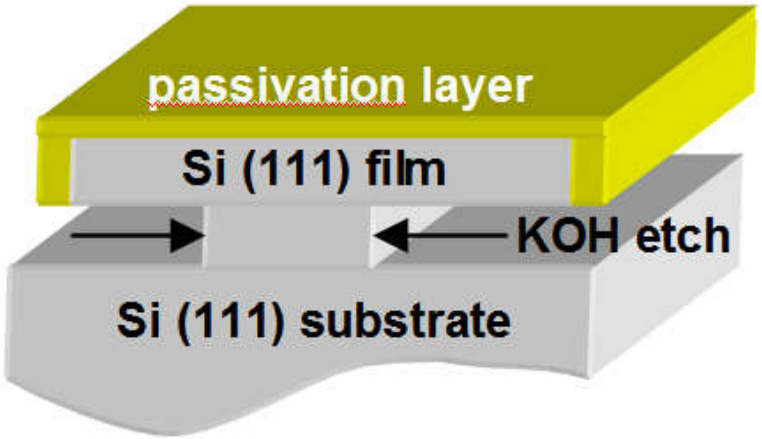
H. C. Ho, *et al.*, *Nature* **454,** 748 (2008)

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

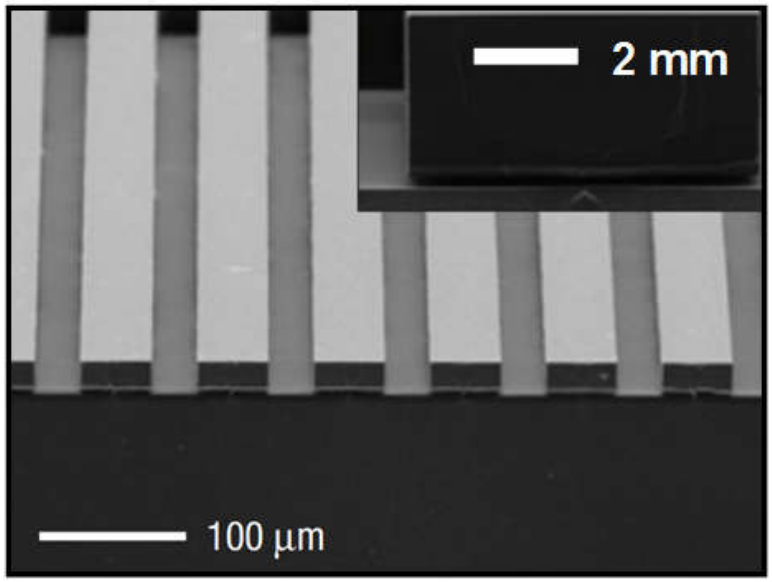
D. Kim, *et al.*, *Science* **333,** 838 (2011)

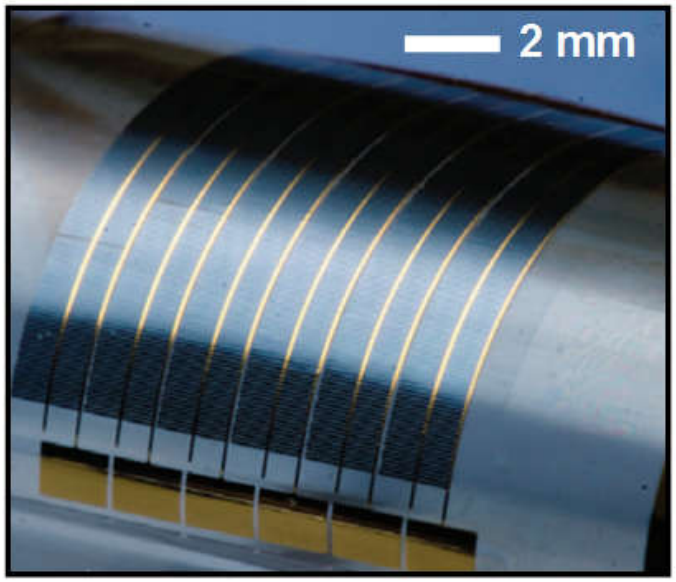
Thin-Film Si from Si (111)

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



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

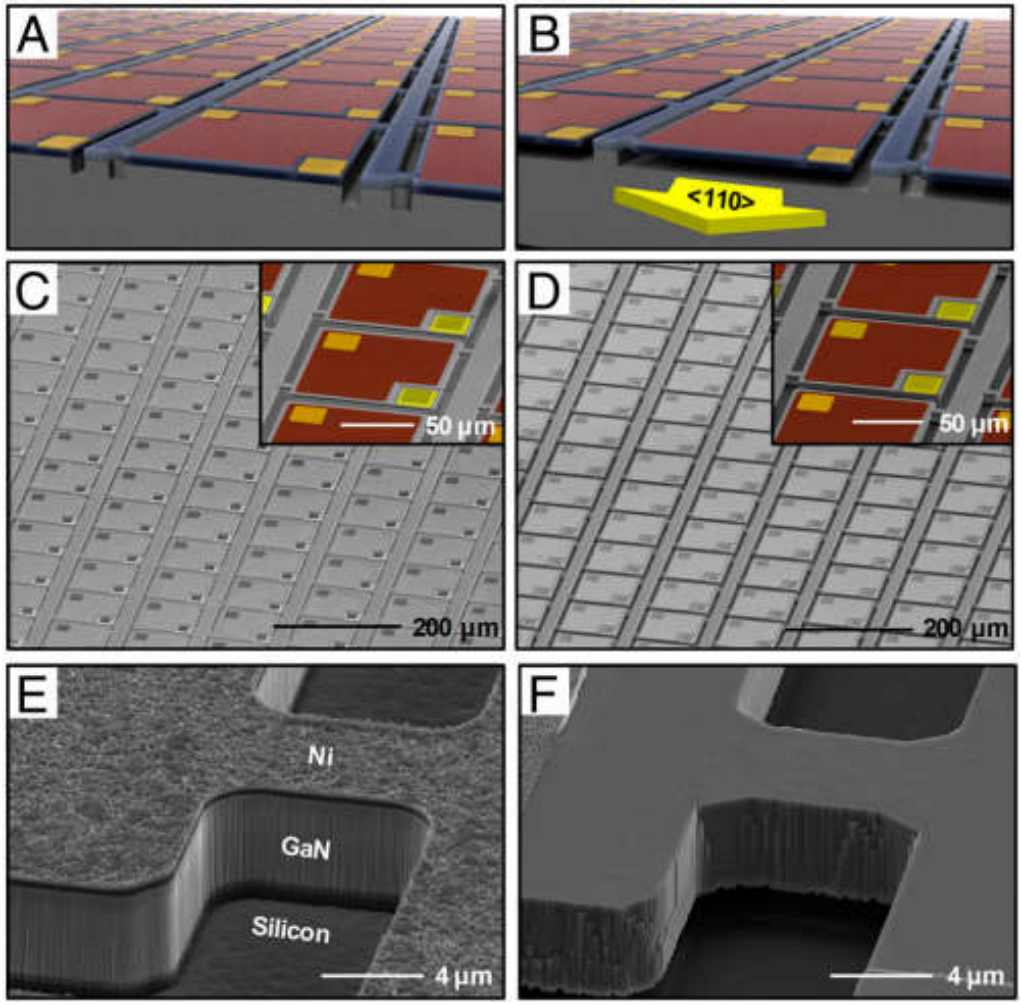


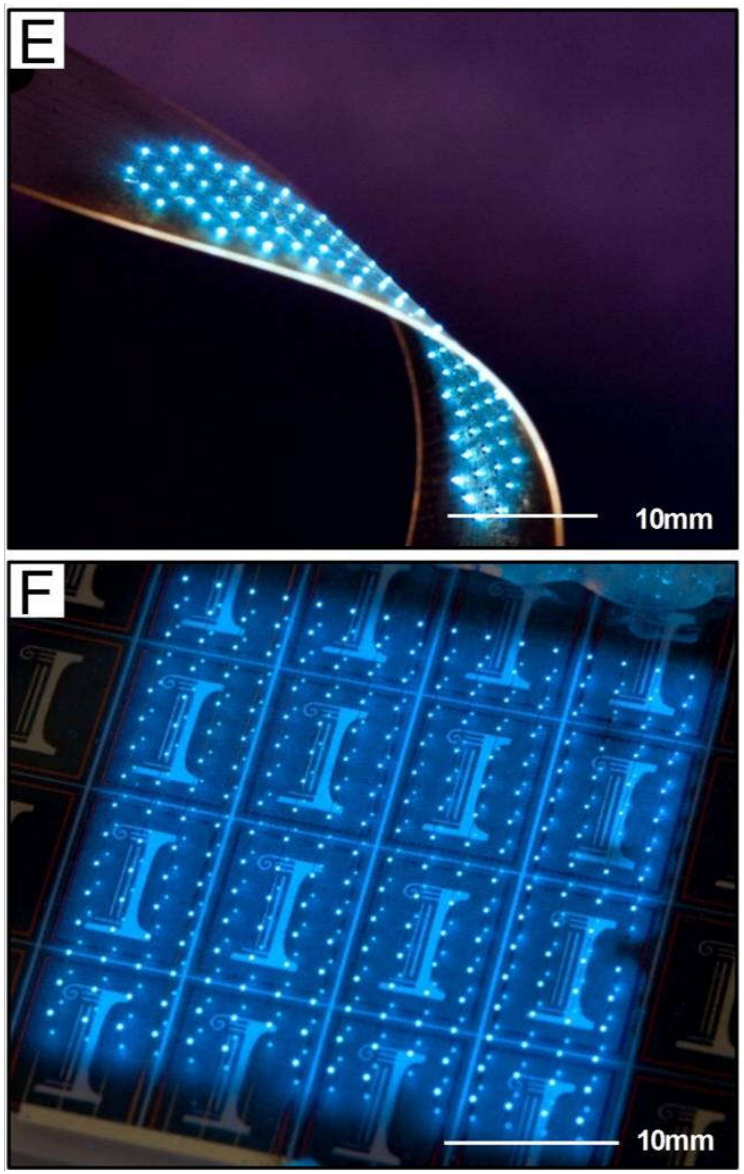


J. Yoon, *et al.*, *Nature Mater.* **7,** 907 (2008)

GaN on Si (111)

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

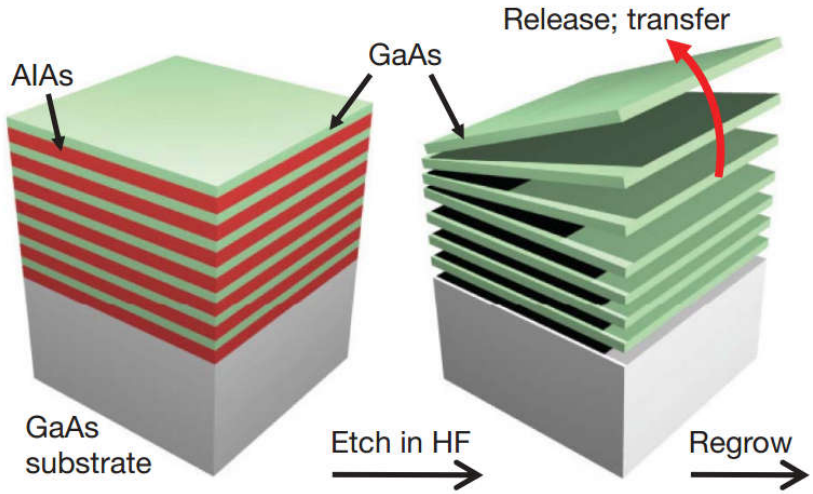


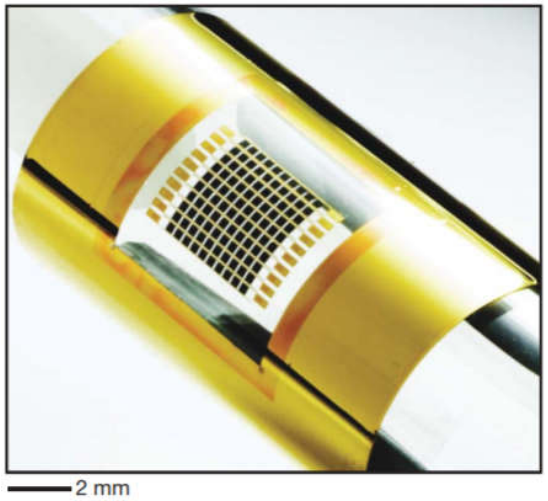


H. Kim, *et al.*, *Proc. Natl. Acad. Sci.* **108,** 10023 (2011)

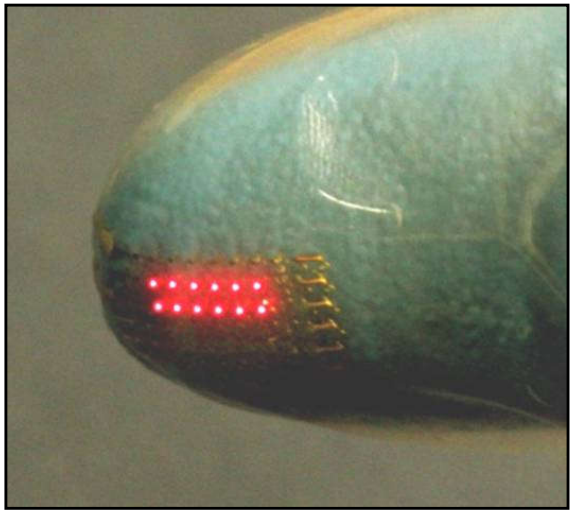
GaAs Device Liftoff

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

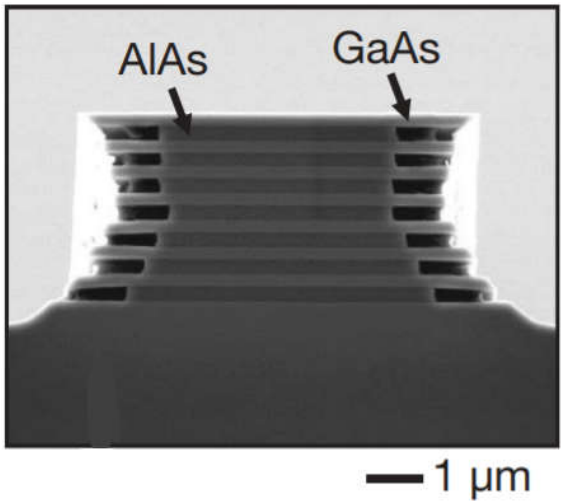




solar cells



LED



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

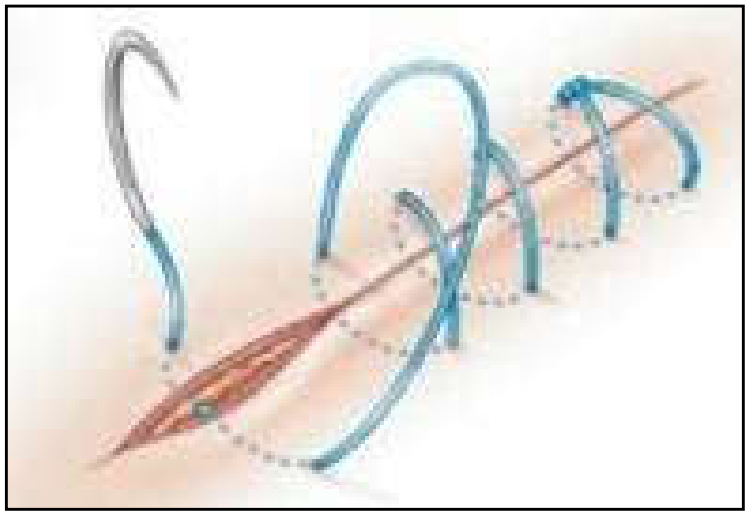
Epitaxy Liftoff

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

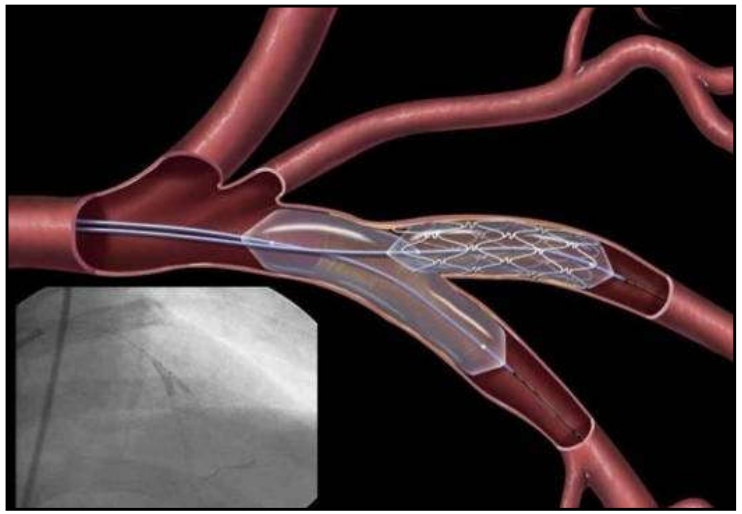
X. Sheng, *et al.*, *Unpublished*

Bio-degradable Materials

Materials that can be dissolved in the body.



Biodegradable Suture



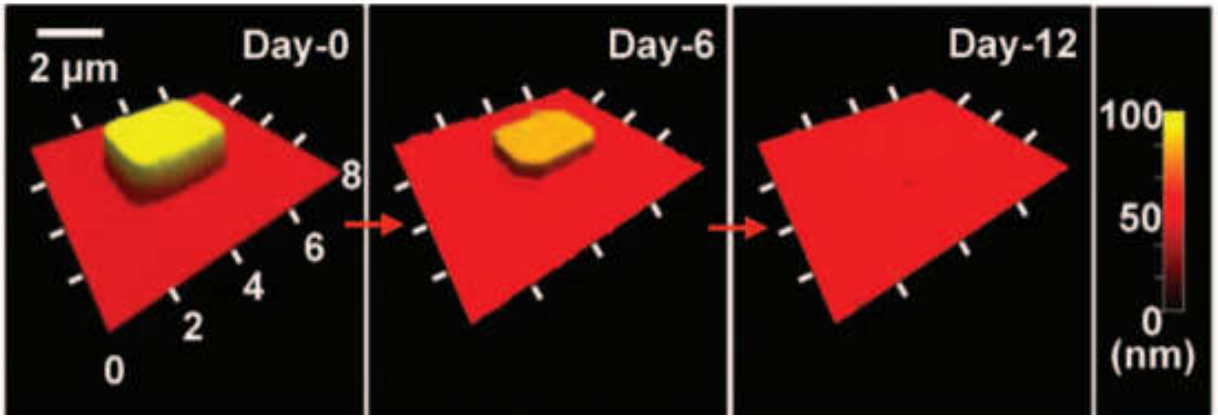
Cardiovascular Stent

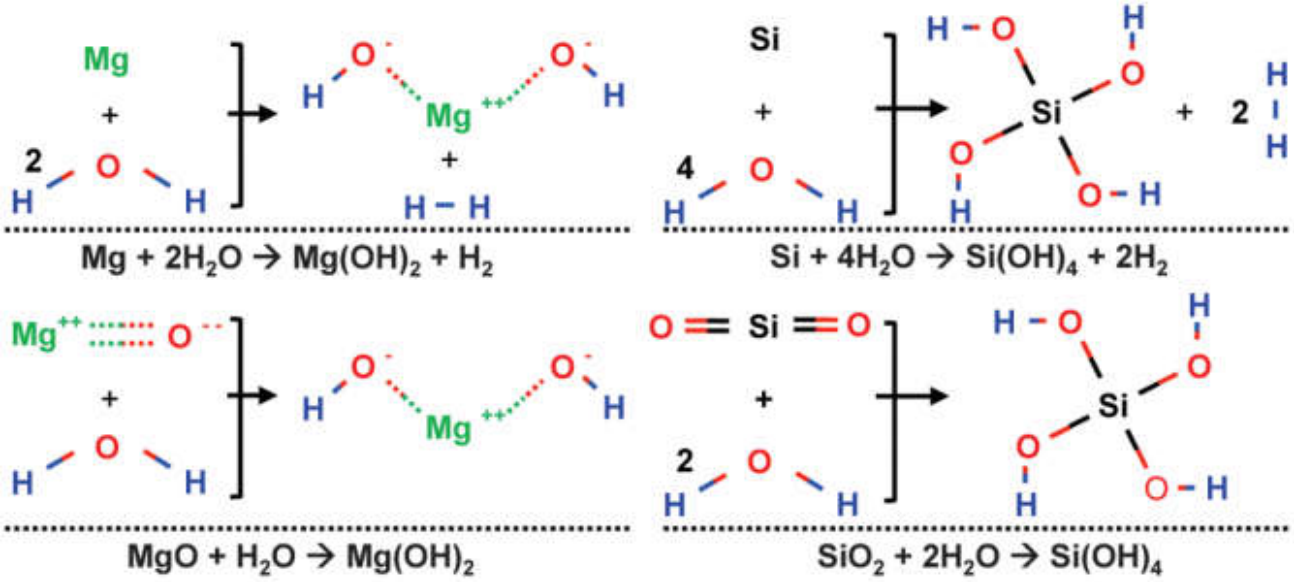
Bone Scaffold

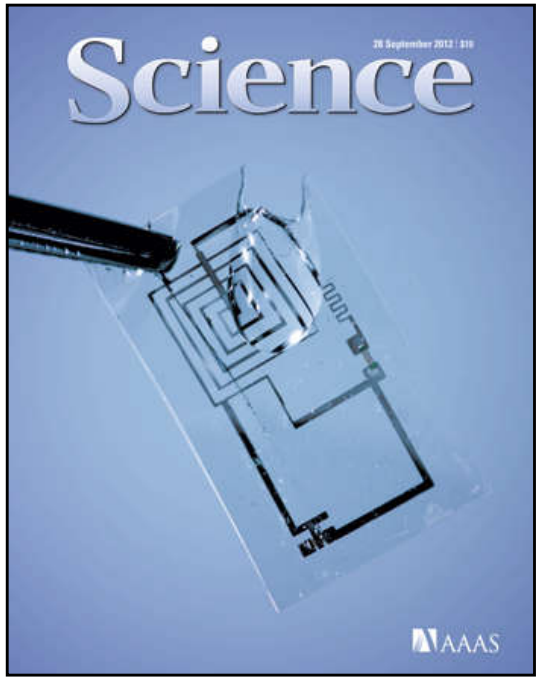
- **Biocompatible and Degradable Materials**
  - **Organic:** PLGA, PLA, silk, ...
  - **Metals:** Mg, Ca, Zn, Fe, ...
  - ***Semiconductors:*** *Si, Ge, ...*

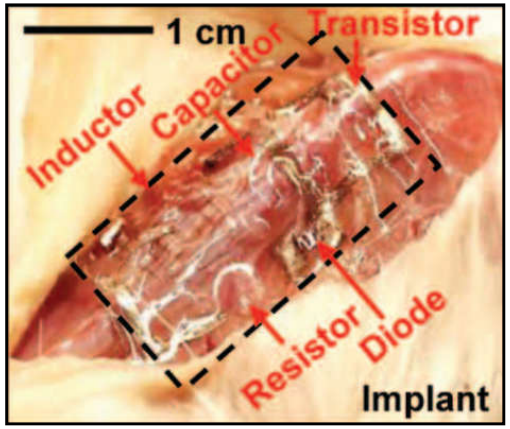
Bio-degradable Electronics

Si devices that can be dissolved by body fluids.









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

Video

Thank you for your attention