

Principles of Micro- and Nanofabrication for Electronic and Photonic Devices

Etching 刻蚀 Part II: Wet 湿法

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Etching Methods

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

Wet Etching - 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

	Element	Oxidation Reaction	
<div style="text-align: center;"> <p>React vigorously with cold H₂O to form H₂</p> <p>↓</p> <p>React with steam to form H₂</p> <p>↓</p> <p>React with simple acids to form H₂</p> <p>↓</p> <p>Will not dissolve in simple acids</p> </div>	Lithium	Li → Li ⁺ + e ⁻	<div style="display: flex; flex-direction: column; align-items: center;"> <div style="margin-bottom: 20px;">↑</div> <div style="writing-mode: vertical-rl; transform: rotate(180deg);">Increasing ease of oxidation</div> <div style="margin-top: 20px;">←</div> </div>
	Potassium	K → K ⁺ + e ⁻	
	Barium	Ba → Ba ²⁺ + 2e ⁻	
	Calcium	Ca → Ca ²⁺ + 2e ⁻	
	Sodium	Na → Na ⁺ + e ⁻	
	Magnesium	Mg → Mg ²⁺ + 2e ⁻	
	Aluminum	Al → Al ³⁺ + 3e ⁻	
	Manganese	Mn → Mn ²⁺ + 2e ⁻	
	Zinc	Zn → Zn ²⁺ + 2e ⁻	
	Chromium	Cr → Cr ³⁺ + 3e ⁻	
	Iron	Fe → Fe ²⁺ + 2e ⁻	
	Cadmium	Cd → Cd ²⁺ + 2e ⁻	
	Cobalt	Co → Co ²⁺ + 2e ⁻	
	Nickel	Ni → Ni ²⁺ + 2e ⁻	
	Tin	Sn → Sn ²⁺ + 2e ⁻	
	Lead	Pb → Pb ²⁺ + 2e ⁻	
	Hydrogen	H ₂ → 2H ⁺ + 2e ⁻	
	Copper	Cu → Cu ²⁺ + 2e ⁻	
	Silver	Ag → Ag ⁺ + e ⁻	
Mercury	Hg → Hg ²⁺ + 2e ⁻		
Platinum	Pt → Pt ²⁺ + 2e ⁻		
Gold	Au → Au ⁺ + e ⁻		

easy

hydrogen

hard

Metal Dissolution in Acids

Strong Acids + Strong Oxidants

Piranha $\text{H}_2\text{SO}_4 : \text{H}_2\text{O}_2 = 3:1$
dissolves most metals and organics

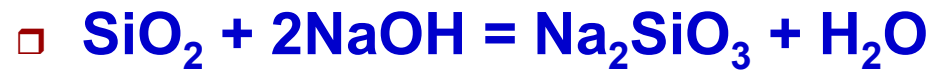
Aqua Regia (王水) $\text{HCl} : \text{HNO}_3 = 3:1$
even dissolves Au, Pt



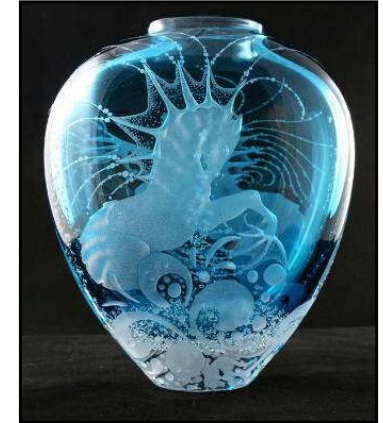
However, difficult to obtain ideal selectivity ...

SiO₂ etching

- Alkali (NaOH, etc) slowly etches SiO₂



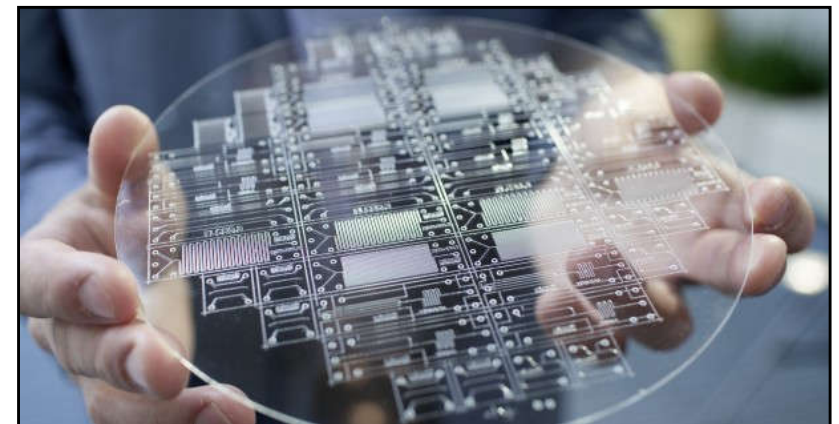
- HF strongly etches SiO₂



glass art by HF etch

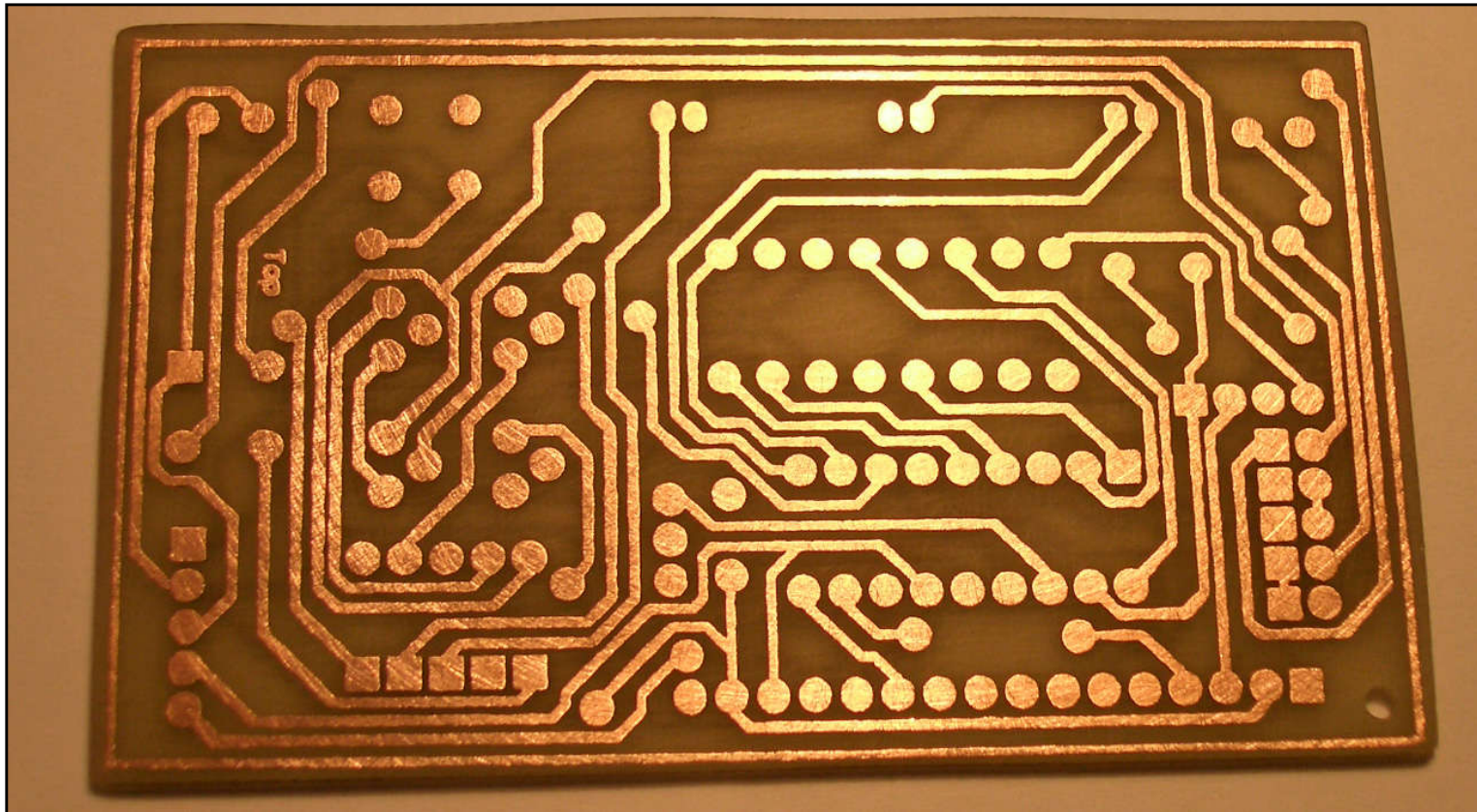
- Buffered HF (BHF/BOE)

- HF + NH₄F
 - lower etch rate
 - safer for use

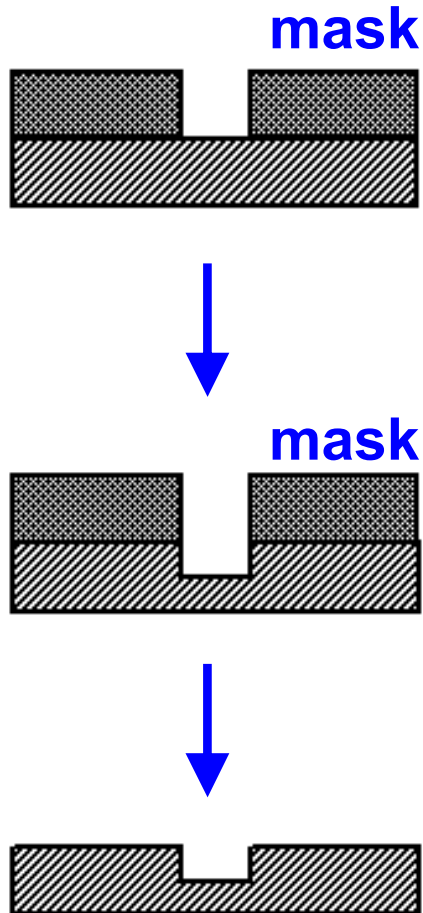


Cu etching

- $\text{Cu} + 2\text{FeCl}_3 = \text{CuCl}_2 + 2\text{FeCl}_2$



Selectivity for Wet Etch

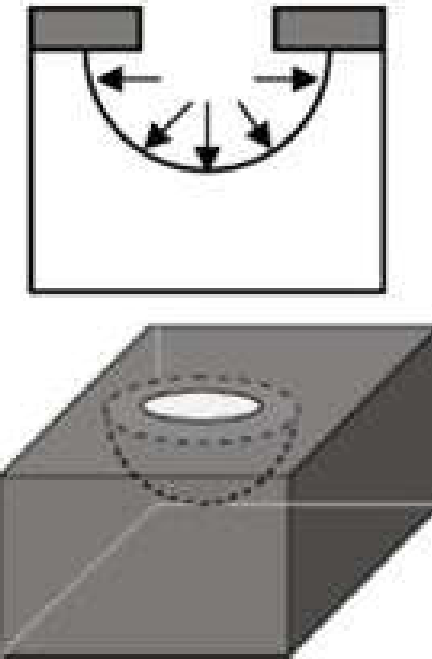


Films	Etchant	Mask
SiO ₂	HF	PR
Si	KOH	Si ₃ N ₄
GaAs	H ₃ PO ₄ + H ₂ O ₂	PR
GaP	KOH + K ₃ [Fe(CN) ₆]	SiO ₂
Cu	FeCl ₃	PR
Au	KI + I ₂	PR

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

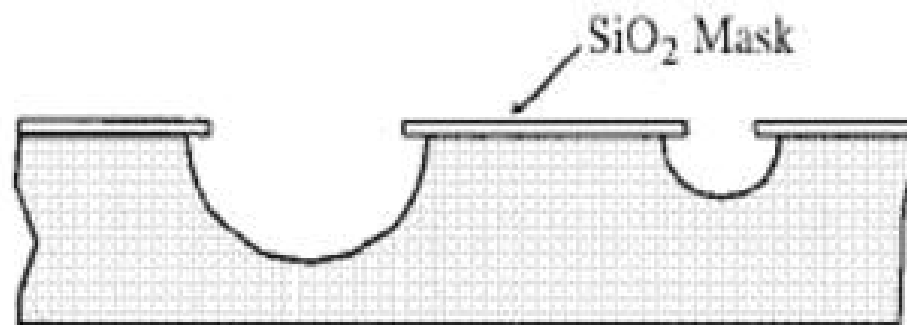


isotropic
 $A = 0$

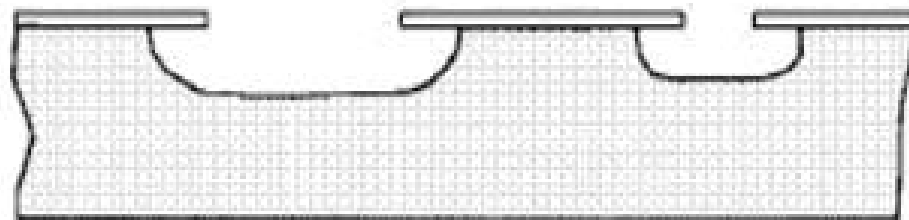
Si etching

- $\text{HNO}_3 + \text{HF}$
 - isotropic etch

Isotropic wet etching: Agitation



Isotropic wet etching: No Agitation



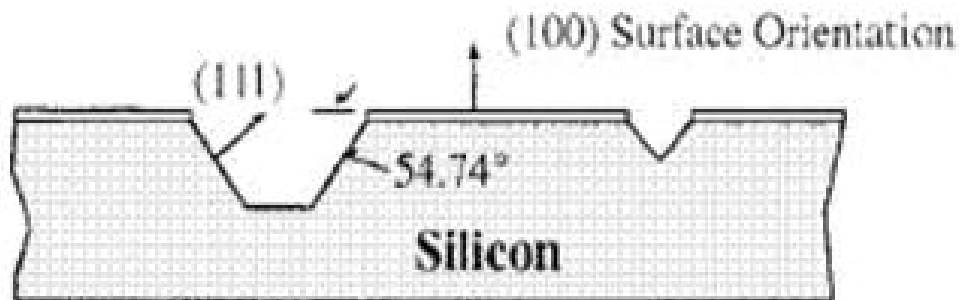
Si etching

■ KOH

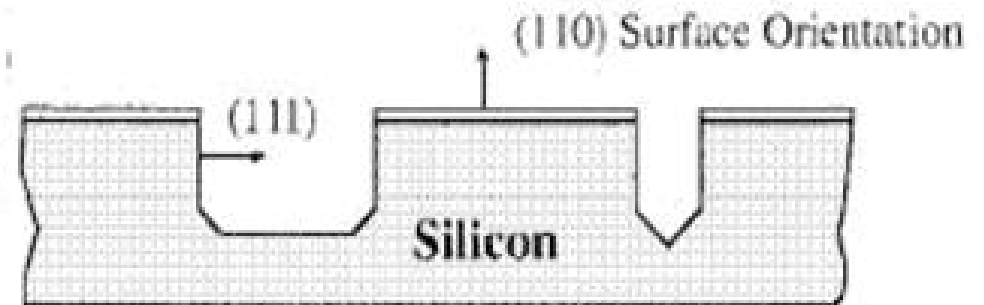
- **anisotropic etch**
- **etch rate (111):(110):(100) ~ 1:600:400**
- **mask: SiO₂, Si₃N₄, Cr/Au, ...**

Q: why?

Anisotropic wet etching: (100)



Anisotropic wet etching: (110)



■ Other chemistries

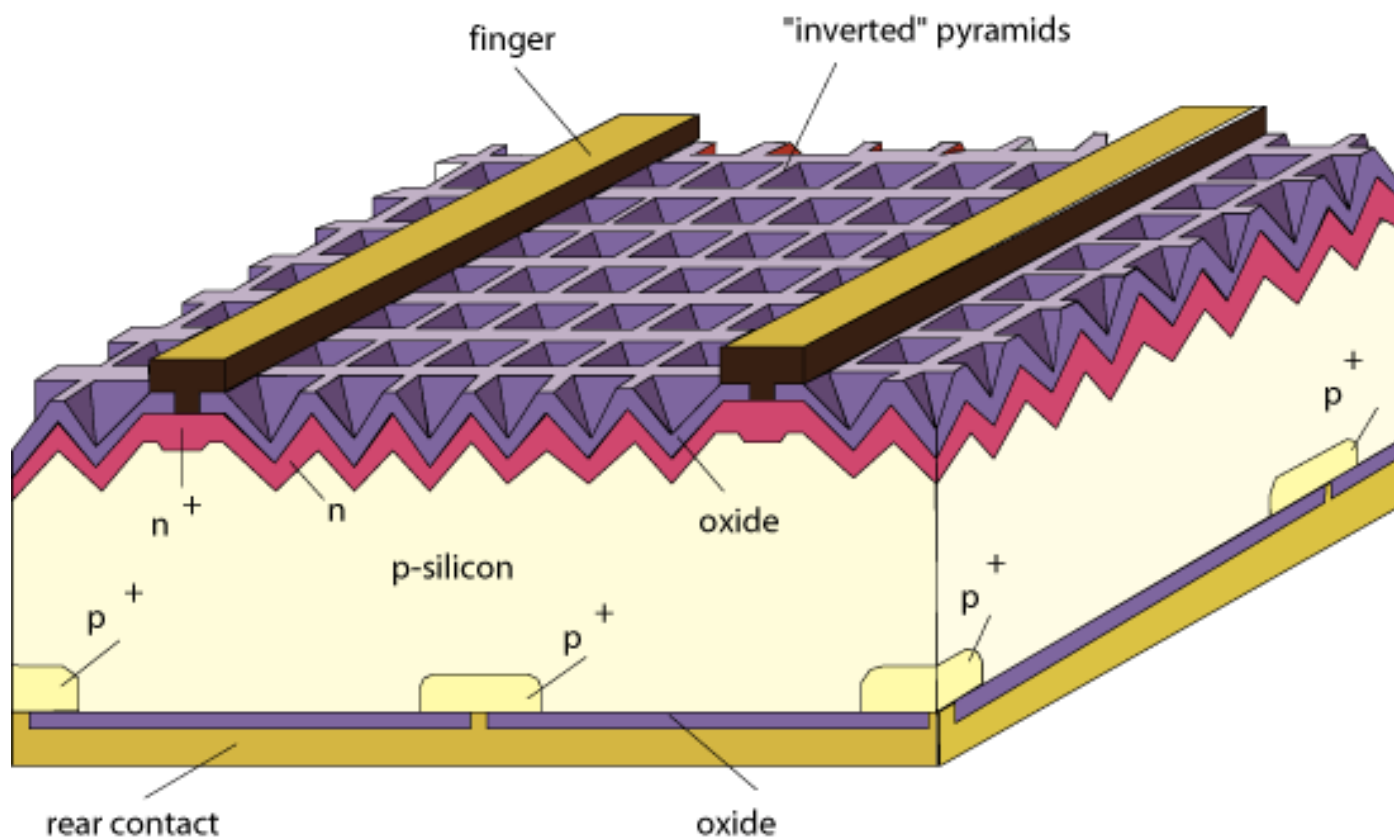
- **TMAH: Tetramethyl ammonium hydroxide**
- **EDP: Ethylene diamine pyrochatecol**

Si etching

■ Single Crystalline Si Solar Cells

- KOH anisotropic etch

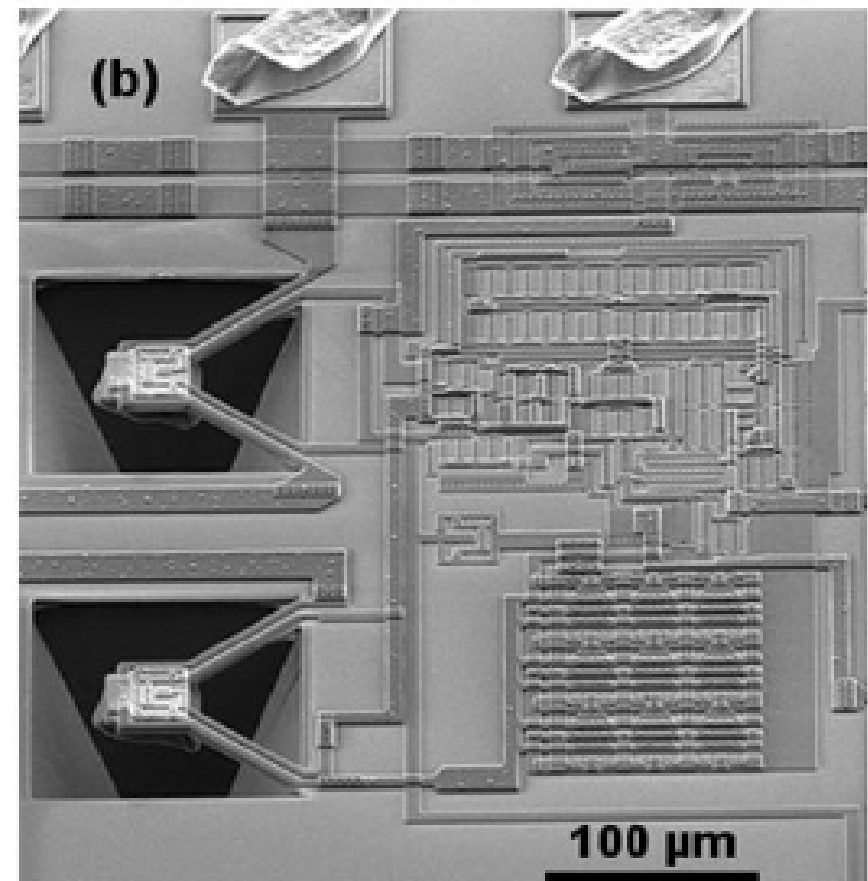
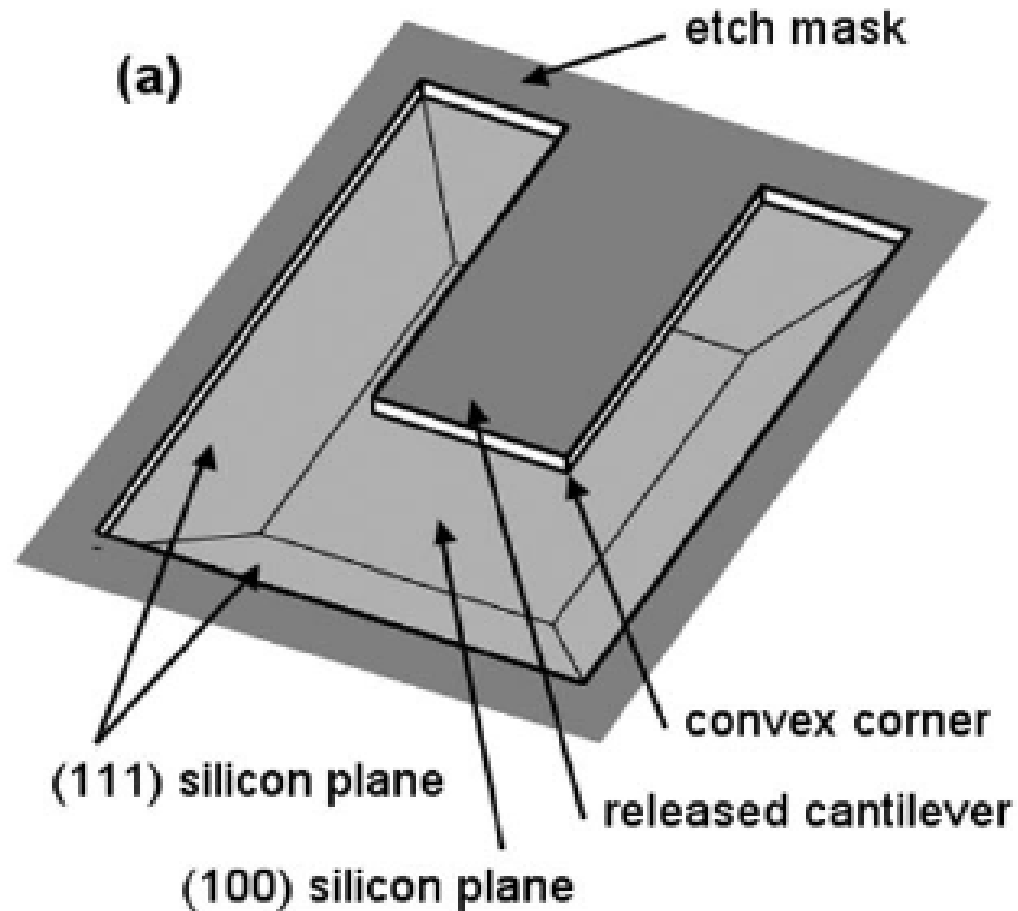
optical trapping and antireflection



world record efficiency: 26%

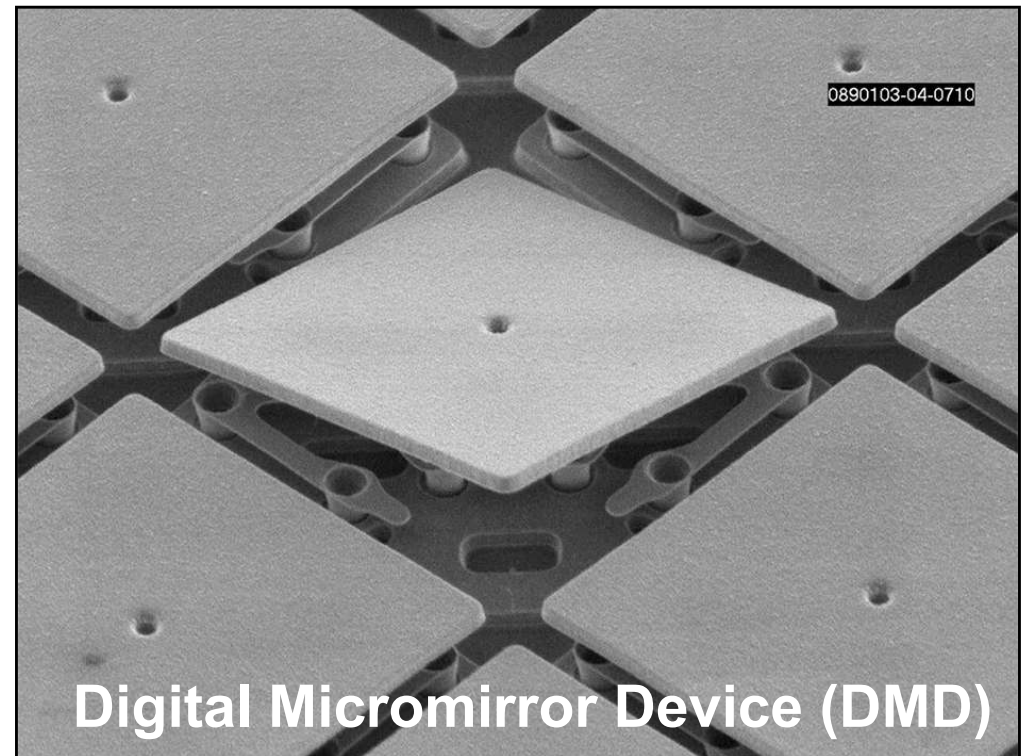
Si etching

- Si cantilever beam
 - KOH anisotropic etch



Si etching

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



Digital Micromirror Device (DMD)

[Video](#)

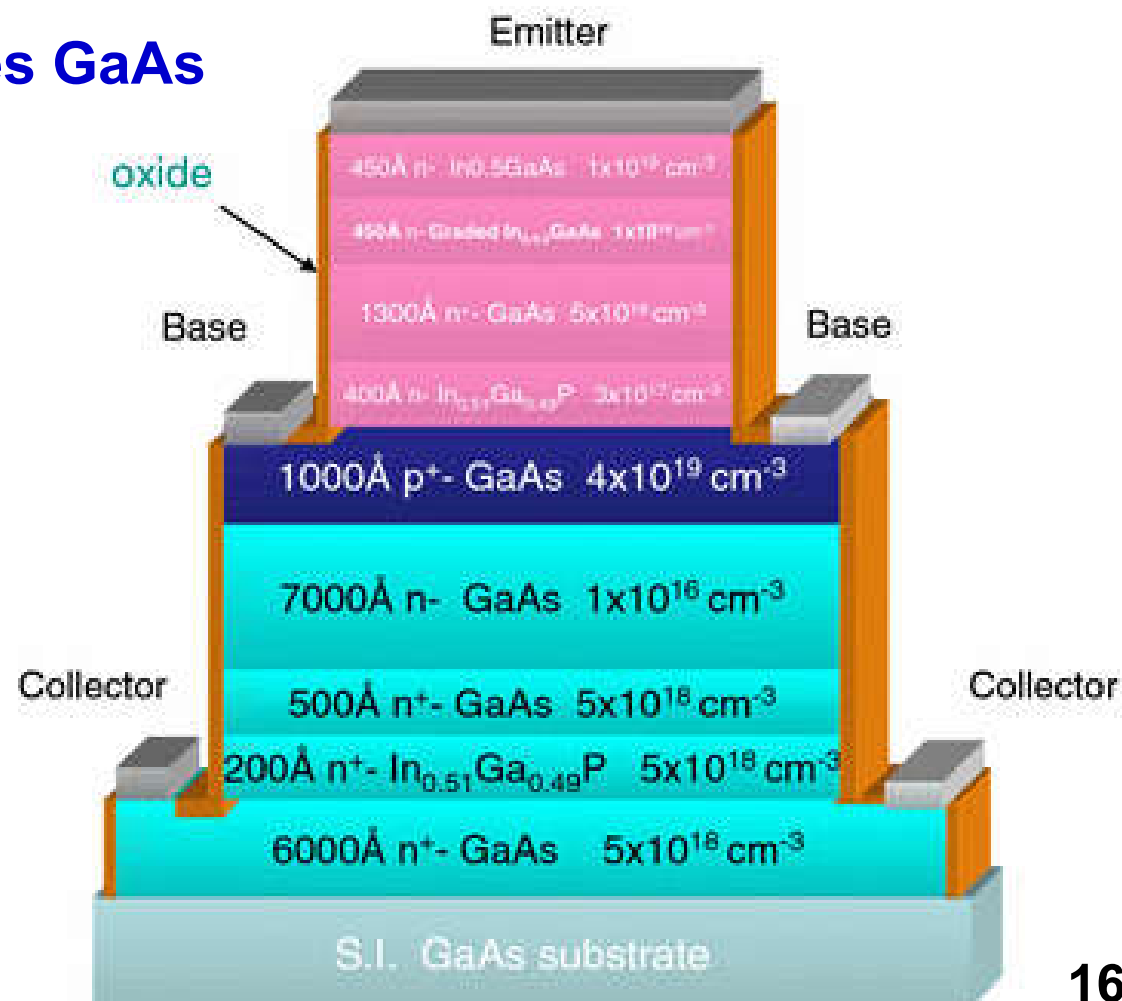
III-V etching

- **GaAs, AlGaAs, InGaAs**
 - $\text{H}_3\text{PO}_4 + \text{H}_2\text{O}_2$
 - $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$
- **AlGaAs**
 - when Al > 70%, HF and HCl etch
- **InP, InGaP, InAlP**
 - HCl
- **GaN, InGaN**
 - no reliable wet etchants ...

Etch Stops

■ InGaP / GaAs

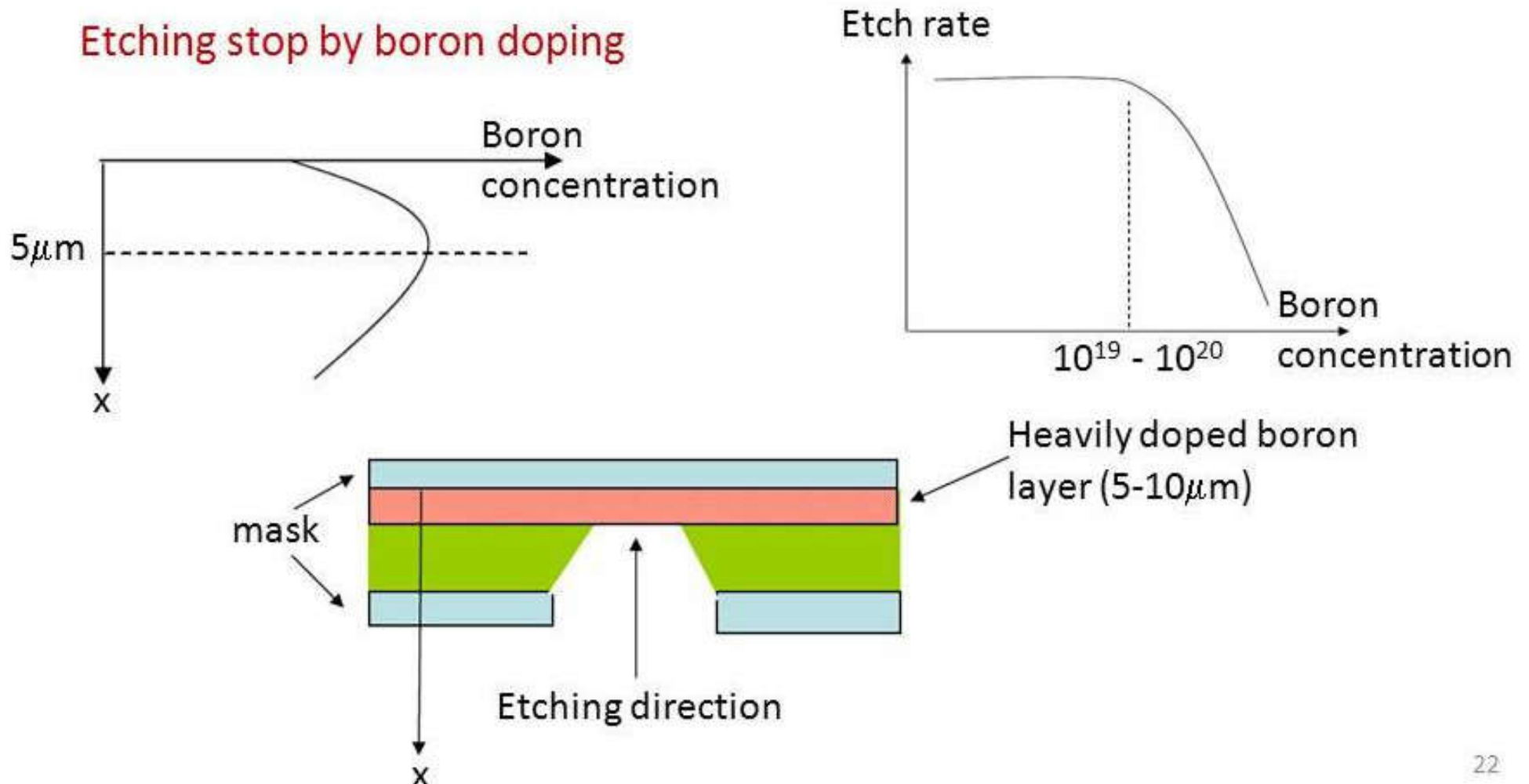
- lattice matched epitaxy
- $\text{H}_3\text{PO}_4 + \text{H}_2\text{O}_2$ only etches GaAs
- HCl only etches InGaP



Etch Stops

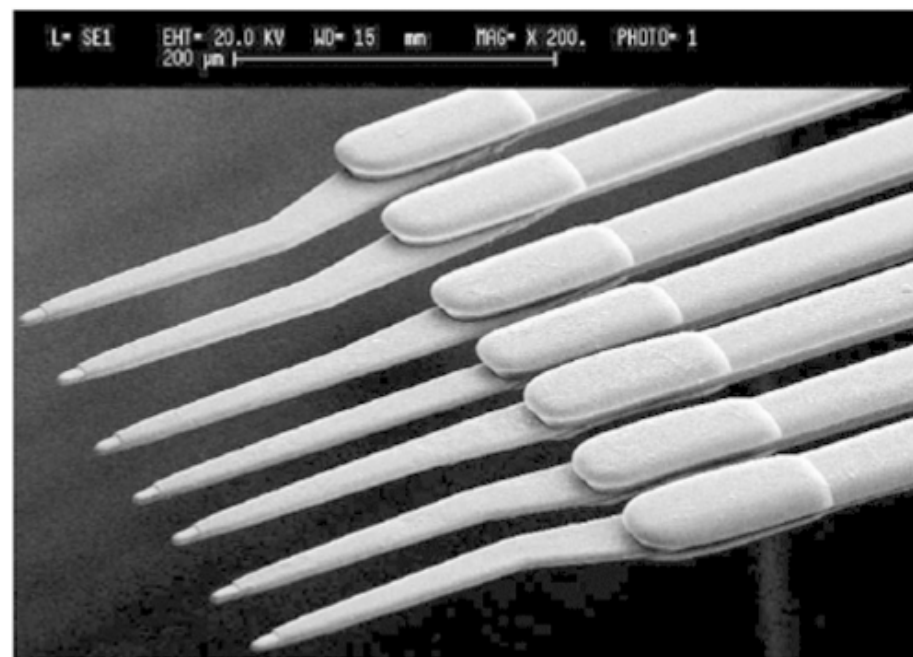
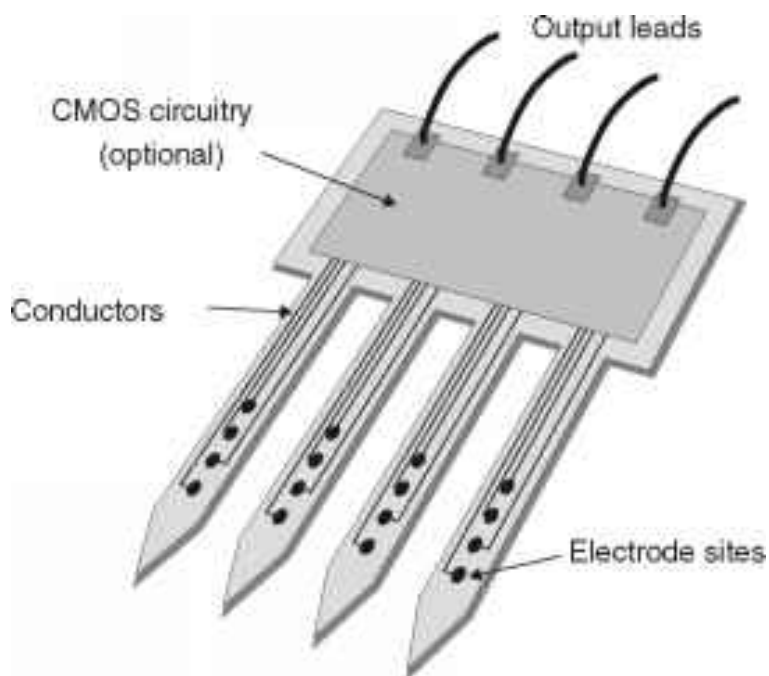
- highly p-dope Si is resistant to KOH

Etching stop by boron doping

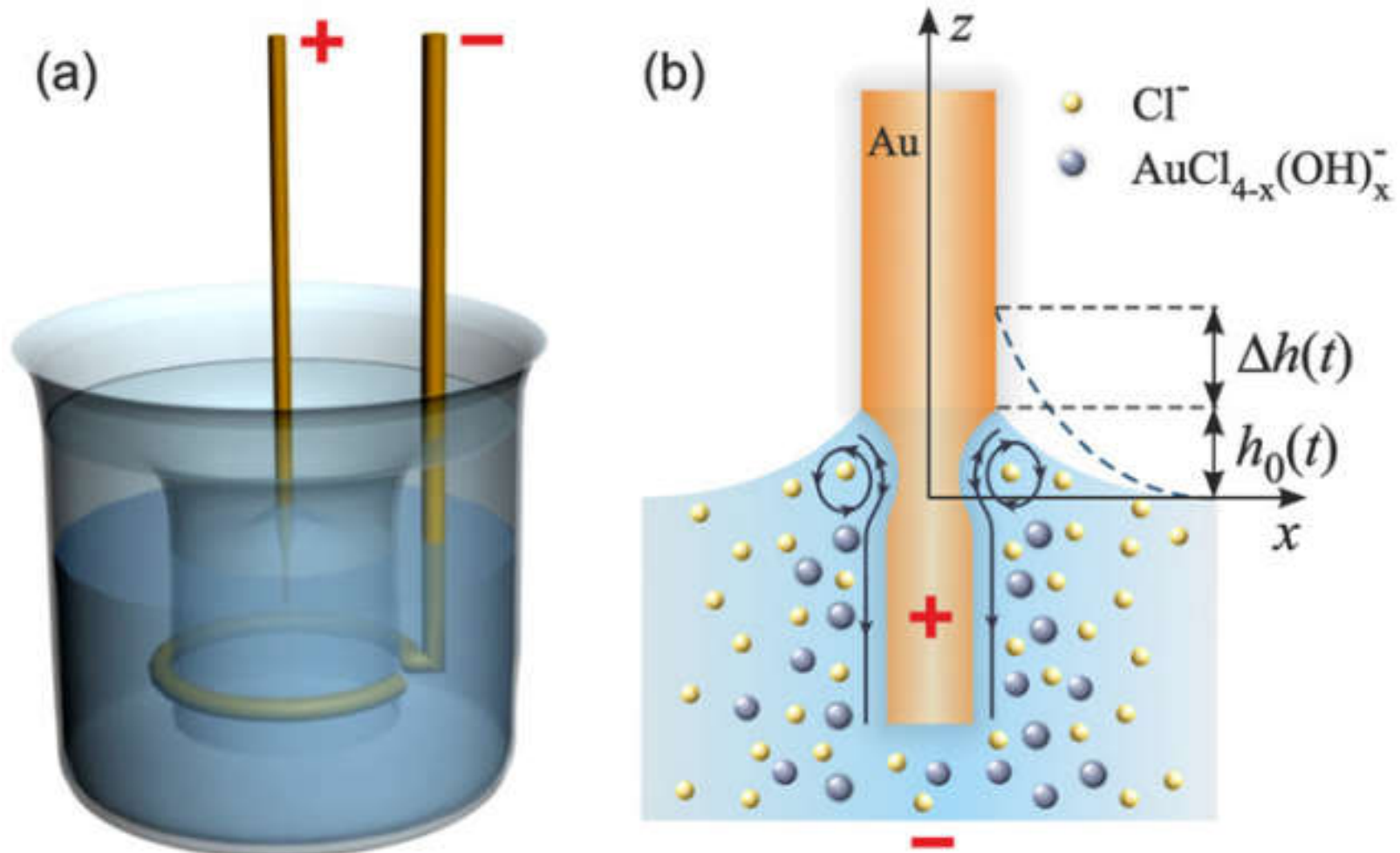


Etch Stops

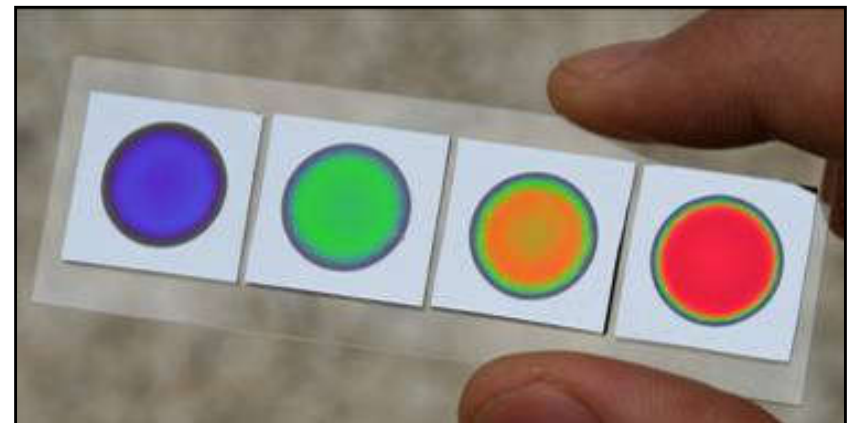
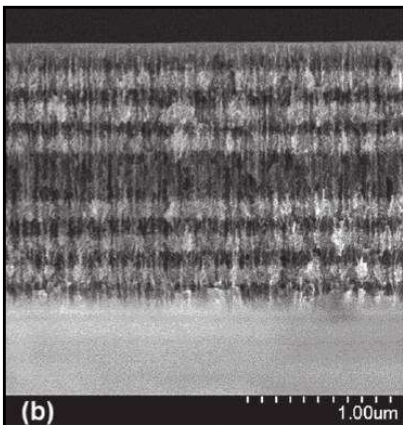
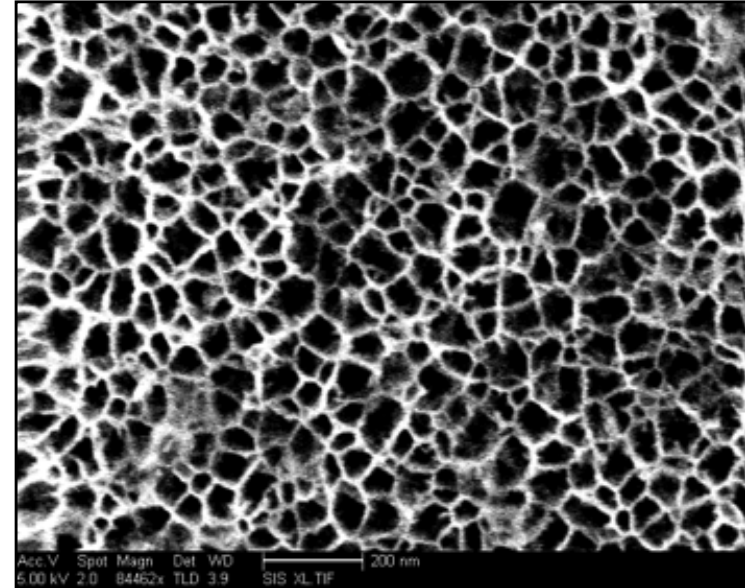
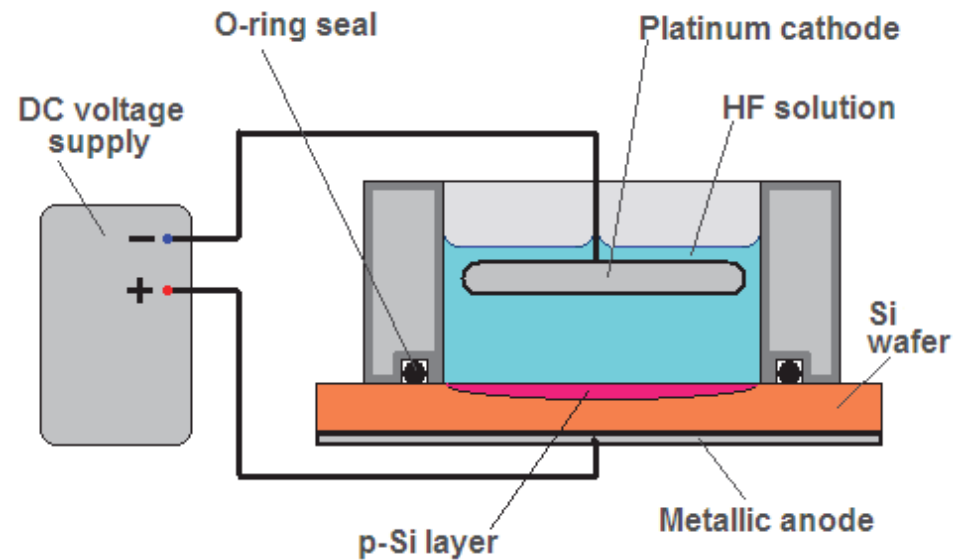
- Silicon based 'Michigan Probe' for neuroscience



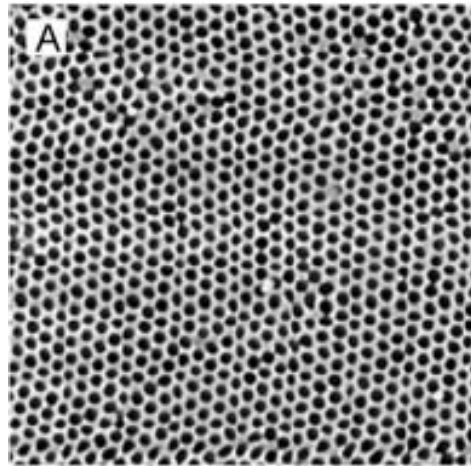
Electrochemical Etch



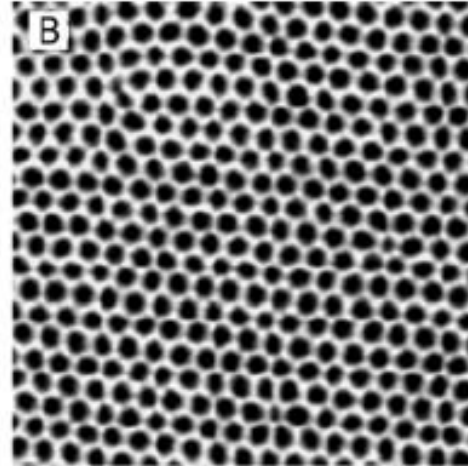
Anodization (阳极氧化) - Porous Si



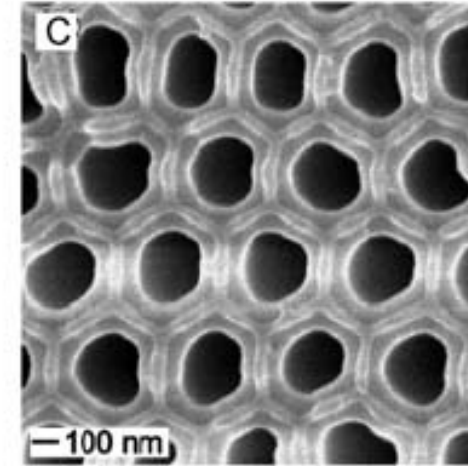
Anodization - Porous Al_2O_3



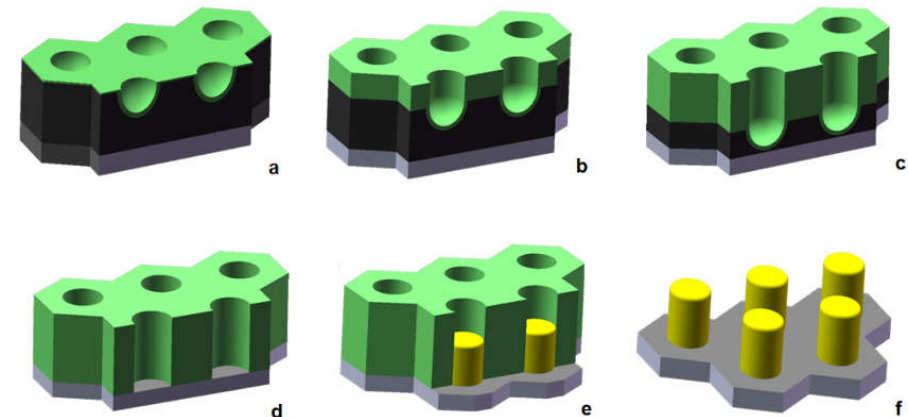
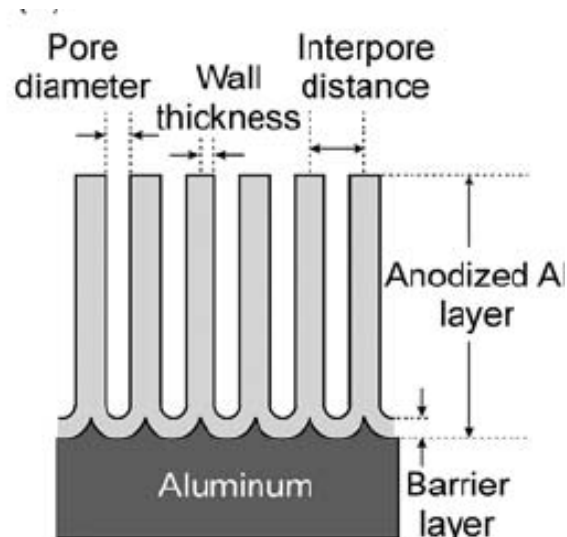
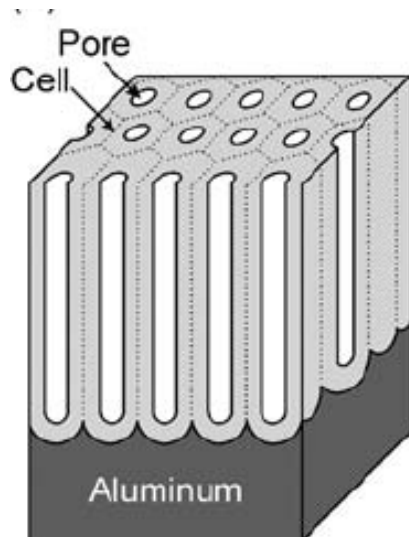
0.3 M H_2SO_4 , 25 V
 $D_p = 60$ nm



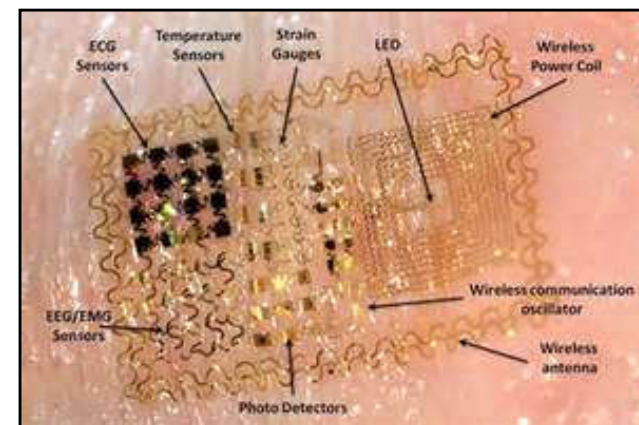
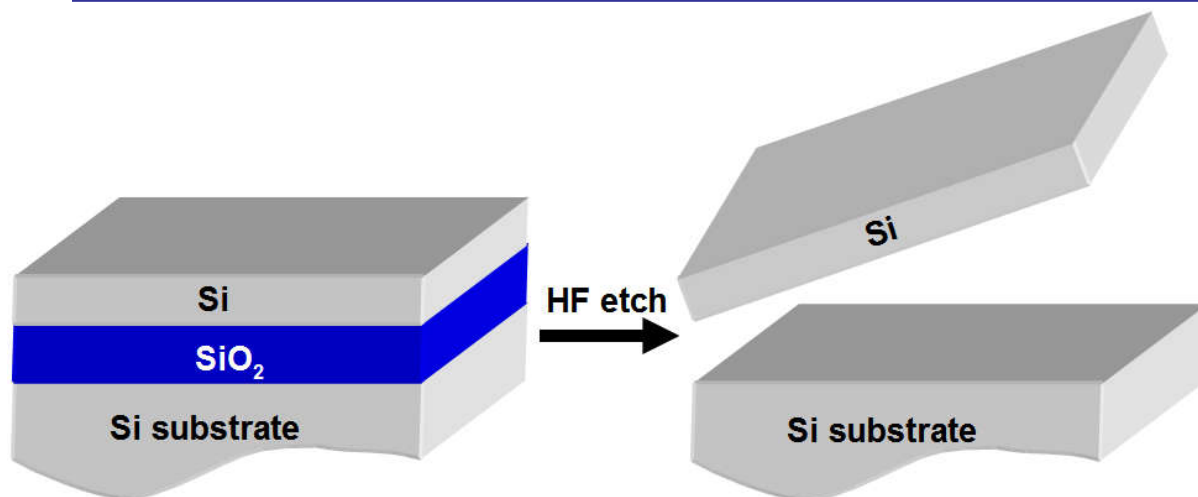
0.5 $\text{C}_2\text{H}_2\text{O}_4$, 40 V
 $D_p = 100$ nm



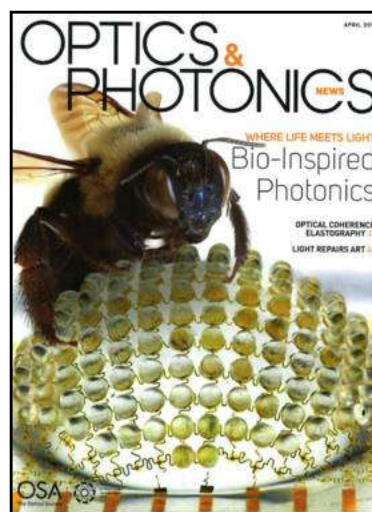
1.1 M H_3PO_4 , 160 V
 $D_p = 420$ nm



Thin-Film Si from SOI wafers



human eyes



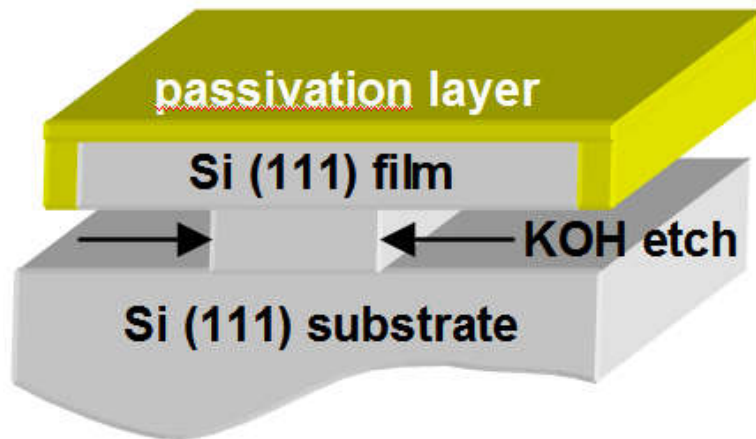
compound eyes



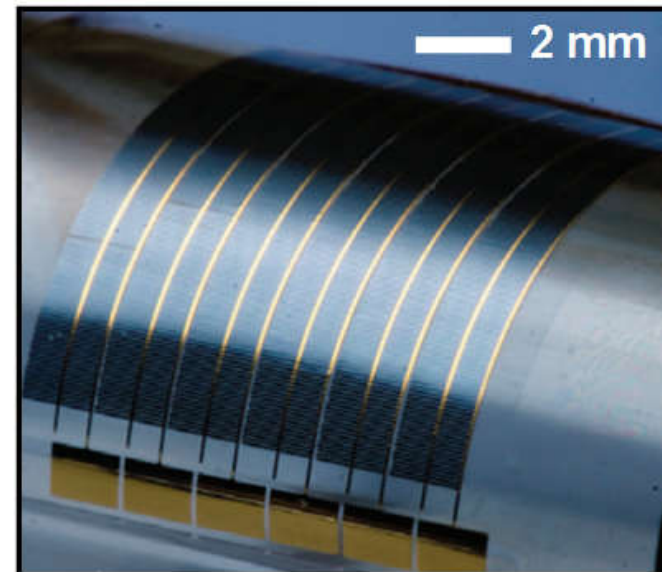
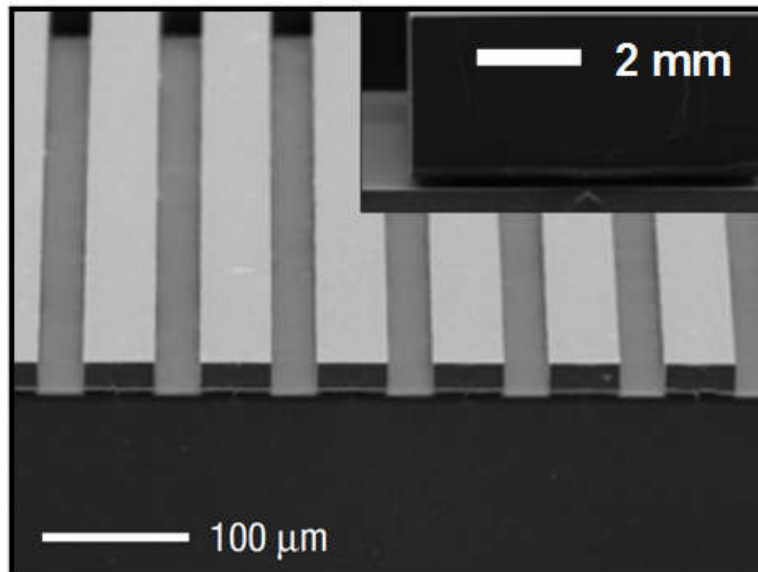
'epidermal' electronics

Thin-Film Si from Si (111)

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

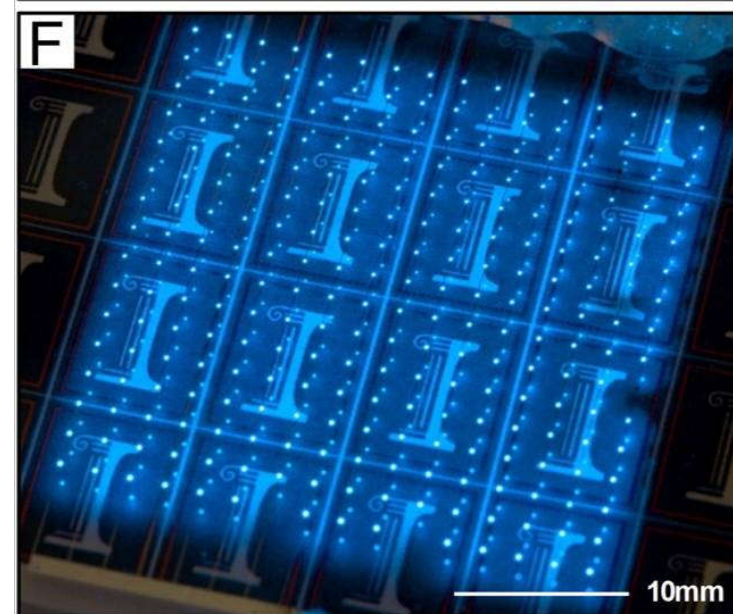
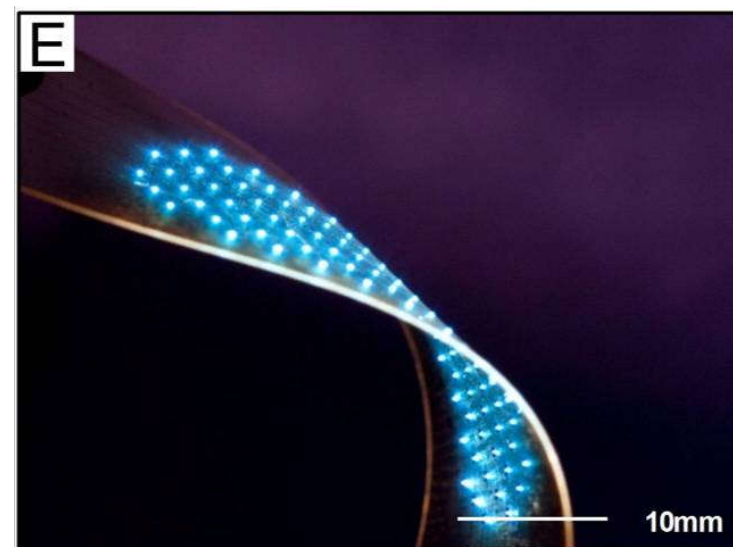
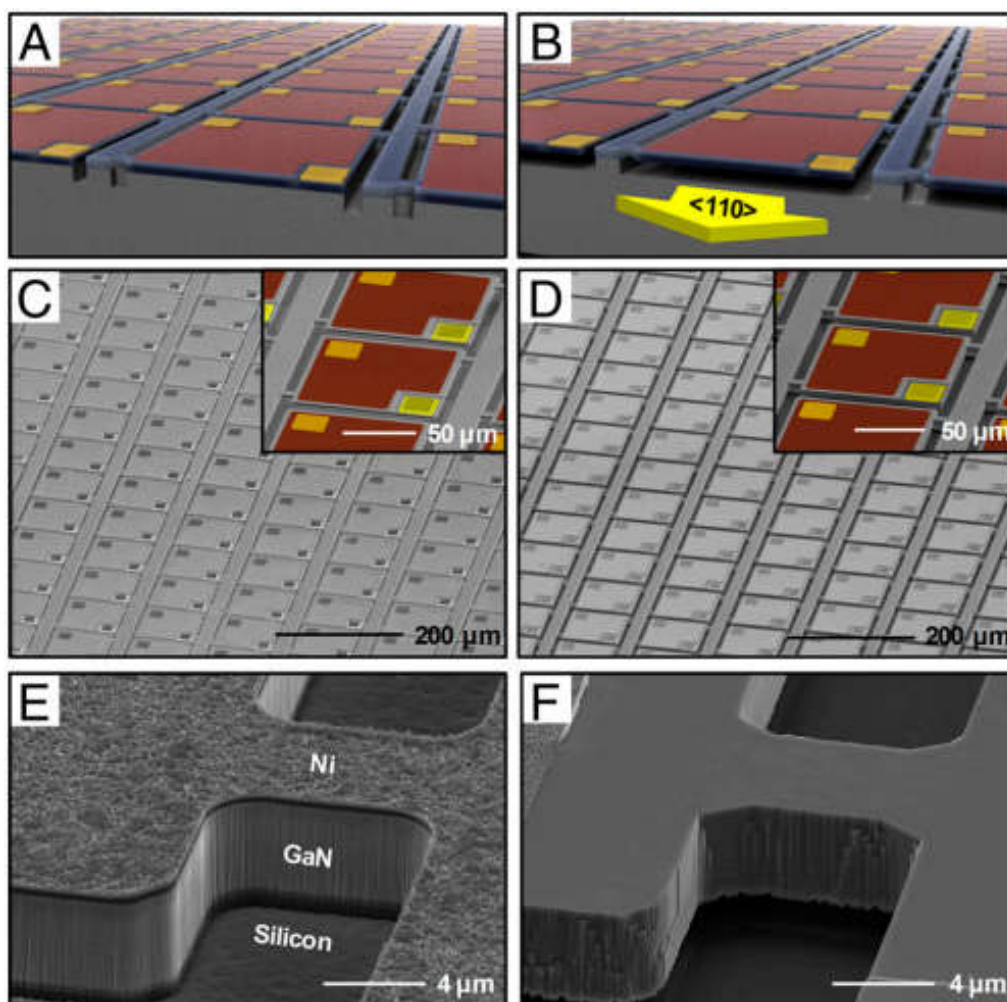


- **Thin-film Si solar cells**
 - **High efficiency (Single Crystal)**
 - **Flexible**
 - **Low cost (wafer reuse)**



GaN on Si (111)

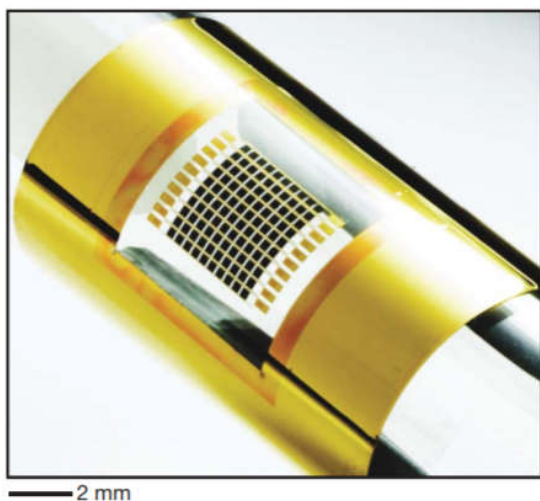
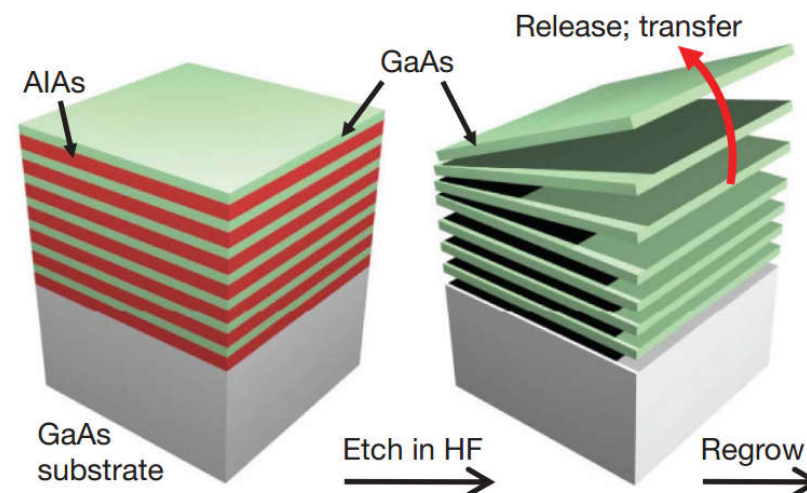
KOH etches faster for Si (100) than (111)



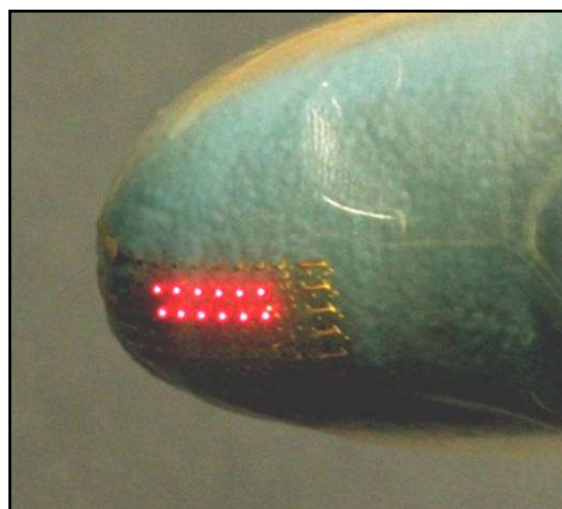
GaAs Device Liftoff

- **GaAs and AIAs**
 - lattice matched growth
 - AIAs is selectively etched by HF

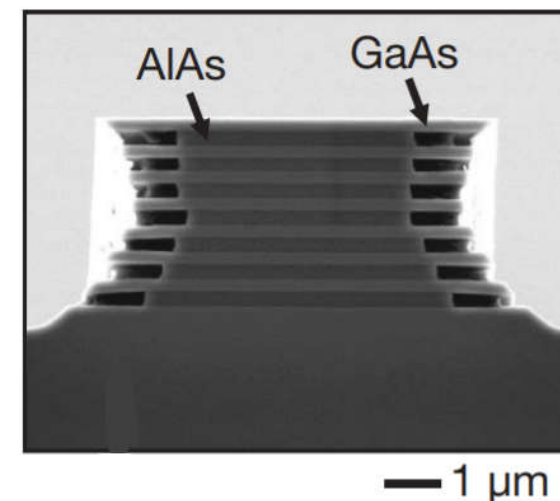
- **flexible III-V devices**



solar cells



LED

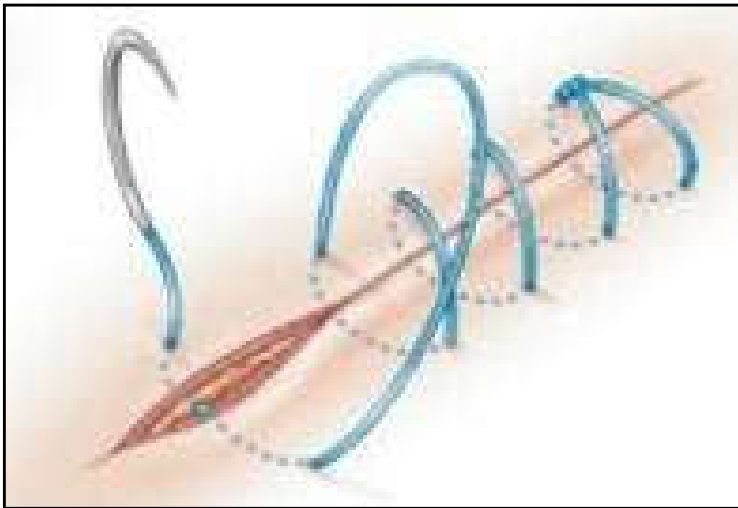


Epitaxy Liftoff

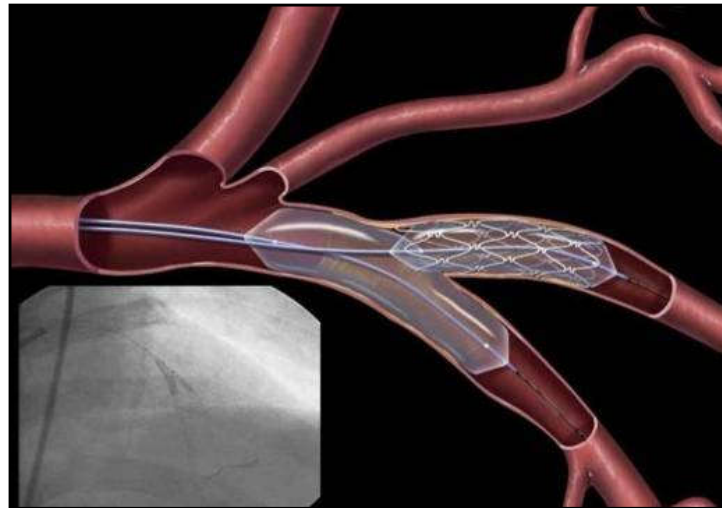
Materials	Sacrificial layers	Substrates	Release methods
Si	SiO ₂	Si	HF wet etch
Si (111)	-	Si (111)	KOH wet etch
Ge	SiO ₂	Si	HF wet etch
SiC	SiO ₂	Si	HF wet etch
GaAs / InGaP	AlAs	GaAs	HF / HCl wet etch
GaAs / InGaP	InAlP	GaAs	HCl wet etch
InGaAs / InP	InGaAs	InP	FeCl ₃ wet etch
GaN	ZnO	sapphire	HCl wet etch
GaN	-	Si (111)	KOH wet etch
InAs	InGaSb	GaSb	NH ₄ OH wet etch

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.

