Metal-assisted Chemical Etching (MacEtch)

Wet etch, Dry etch, and now MacEtch

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Outline

• What is MacEtch?
• Background and Mechanism
• Characteristics
• Device applications
• Inverse MacEtch (I-MacEtch)
• Magnetic-field MacEtch (h-MacEtch)
• Summary
**Wet Etch**

- **isotropic** -
  - most wet etches are isotropic
  - i.e., they etch equally in all directions
  - isotropic etches result in **undercutting**

For an isotropic etch, radius = depth

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rate determining steps -
- diffusion of reactants to the surface
- reaction rate at the surface
- desorption of reaction products

reaction equation

$$mA + nB \rightarrow \text{reaction products}$$

reaction rate

$$r = k[A]^m[B]^n e^{-\frac{E_A}{RT}}$$
Dry Etch

- **Goal:**
  - enhance anisotropy
  - without losing selectivity
  - without causing damage
  - maintain controllable etch rate

- **Mechanism:**
  - Chemical:
    - plasma etch - small degree of anisotropy
  - Physical:
    - sputtering, directional but no selectivity

- **Techniques:**

  ![Dry Etch Techniques Diagram](https://www.crystec.com/trietche.htm)
Dry Etching Issues

- Charging
- Undercutting
- Sidewall residue
- Trenching
- Mask erosion
- Surface damage

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Metal-Assisted Chemical Etching (MacEtch)

Scalable, high throughput, low cost

- Process Flow
  - Pattern metal
  - Immerse in HF/H$_2$O$_2$
  - Etching takes place underneath the metal

- Contrast with
  - wet vs dry etch
  - bottom-up growth

MacEtch: wet etch but directional
Metal-Assisted Chemical Etching (MacEtch)

- Patents: 4 issued and 3 pending

Metal
- not stationary
- not a mask
- not consumed

Not limited to Au
MacEtch mechanism

**Local electrochemical reactions:**

- **Cathode reaction (at metal):**
  \[ \text{H}_2\text{O}_2 + 2\text{H}^+ \rightarrow 2\text{H}_2\text{O} + 2\text{H}^+ \]
  \[ 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \uparrow \]

- **Anode reaction (at Si):**
  \[ \text{Si} + 4\text{H}^+ + 4\text{HF} \rightarrow \text{SiF}_4 + 4\text{H}^+ \]
  \[ \text{SiF}_4 + 2\text{HF} \rightarrow \text{H}_2\text{SiF}_6 \]

- **Overall reaction:**
  \[ \text{Si} + \text{H}_2\text{O}_2 + 6\text{HF} \rightarrow 2\text{H}_2\text{O} + \text{H}_2\text{SiF}_6 + \text{H}_2 \uparrow \]

- **Mechanism:** metal is a catalyst
- **Rate determining step:** charge or mass transport
- **Simplicity:** no bias, no high energy ions, no light

"Metal-assisted chemical etching in HF/H\textsubscript{2}O\textsubscript{2} produces porous silicon", X. Li and P.W. Bohn, Appl. Phys. Lett.77, 2572 (2000).
MacEtch

CHARACTERISTICS


Extremely High Aspect Ratio

Si nanowire array: 550 nm diameter, 51 μm height
produced by Au-MacEtch in 20 mins

Scalability
MacEtch of poly and amorphous
MacEtch has been realized using metal catalyst formed by the following techniques:

- Electroless plating (e.g. from AgNO₃ solution)
- Colloidal nanoparticles
- Optical lithography
- Electron beam lithography
- Nanoimprint/soft lithography
- Superionic solid state stamping
- Nanosphere lithography
- High aspect ratio shadow mask
- Tip-based lithography (AFM, STM)
Applicability to different semiconductors

- Si
- Ge
- GaAs
- InGaAs
- AlGaAs
- InP
- GaN

- Heterojunctions and p-n junctions
Sidewall morphology

• No high energy ion induced sidewall damage
• **Sidewall smoothness is determined entirely by the edge roughness of the metal pattern**
• No porosity in the pillars if the MacEtch condition is tuned as a function of semiconductor doping level
3D patterns formed by MacEtch

by periodic variation of etchant concentration

Magnetic-Field Guidance (h-MacEtch)

- Use Au/Fe/Au Tri-Layer catalyst
- Guidance
- Programmability

- a – c: Increasing External magnetic field guidance

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Inverse MacEtch: InP

- Metal edge roughness no longer limits sidewall smoothness
- Limited aspect ratio (height/width) because of the inverse nature

Examples of semiconductor nanostructures produced by MacEtch

- **a)** 100/1 aspect ratio Si NWs
- **b)** n-GaAs pillars
- **c)** GaAs p-i-n pillars
- **d)** Sub-15 nm InP Fins
- **e)** Curvy-linear Si
- **f)** Holey Si from SOI
## MacEtch vs wet and dry etch

<table>
<thead>
<tr>
<th></th>
<th>Wet Etch</th>
<th>Dry Etch</th>
<th>MacEtch</th>
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</thead>
<tbody>
<tr>
<td><strong>Directionality</strong></td>
<td>Isotropic</td>
<td>Anisotropic</td>
<td>Anisotropic</td>
</tr>
<tr>
<td><strong>Aspect Ratio</strong></td>
<td>Low</td>
<td>Medium</td>
<td>High</td>
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<tr>
<td><strong>Ion Induced Damage</strong></td>
<td>None</td>
<td>Mild to Severe</td>
<td>None</td>
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<tr>
<td><strong>Crystal-Orientation Dependence</strong></td>
<td>Some</td>
<td>Weak</td>
<td>Weak</td>
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<tr>
<td><strong>Etch Rate</strong></td>
<td>Fast</td>
<td>Slow</td>
<td>Fast</td>
</tr>
<tr>
<td><strong>Sidewall Smoothness</strong></td>
<td>Smooth</td>
<td>Not Smooth</td>
<td>Smooth or Rough</td>
</tr>
<tr>
<td><strong>Chemical Selectivity</strong></td>
<td>Good</td>
<td>Poor</td>
<td>Depends</td>
</tr>
<tr>
<td><strong>Cost</strong></td>
<td>Low</td>
<td>High</td>
<td>Low</td>
</tr>
</tbody>
</table>

MacEtch

APPLICATIONS

- Solar cells
- LEDs
- Photonic Crystals
- Thermoelectrics
- Transistors
GaAs p-i-n Pillar Based LED by MacEtch

"III-As pillar array-based light emitting diodes fabricated by metal-assisted chemical etching,"
P. K. Mohseni, S. H. Kim, X. Zhao, K. Balasundaram, J. D. Kim, L. Pan, J. A. Rogers, J. J. Coleman, and X. Li,
GaAs p-i-n Pillar Based LED by MacEtch


- Pillar showed stronger emission at all injection levels
- Enhancement is stronger at higher $I$

![Graph 1](image1.png)

![Graph 2](image2.png)
MacEtched Si NW PV cell

Efficiency limited by surface area

It is all about the surfaces!

MacEtched Ph.C. Reflectors

[Image of etched reflector pattern]

[Graph showing reflection percentage vs wavelength with 'MR by MacEtch' and 'Simulation' curves]

APPLIED PHYSICS LETTERS 103, 214103 (2013)
I-MacEtch of InP

- Aspect ratio > 40:1
- MOSFETs – excellent offstate performance

Song et al. unpublished.
Publications on MacEtch from Illinois

http://mocvd.ece.illinois.edu

- "Silicon nanowires with controlled sidewall profile and roughness fabricated by thin-film dewetting and metal-assisted chemical etching," Bruno Azeredo, Jyothi Sadhu, Jun Ma, Kyle Jacobs, Junhwan Kim, KunHyuck Lee and James Eraker, Xiuling Li, Sanjiv Sinha, Nicholas Fang, Placid Ferreira and Keng Hsu, Nanotechnology, 24, 225305 (2013).
- “Sub-100 nm Si nanowire and nano-sheet array formation by MacEtch using a non-lithographic InAs Nanowire Mask,” Jae Cheol Shin, Chen Zhang and Xiuling Li, Nanotechnology, 23, 305305 (2012).
MacEtch Patent Portfolio

- TF00067 metal-assisted chemical etching to produce porous silicon  US 6790785
- TF00154 metal assisted chemical etch to produce group III-V porous material and porous silicon  US 6762134
- TF08145 method of forming nanoscale three-dimensional patterns in a porous material  US 8486843
- TF09098 method of forming an array of high aspect ratio semiconductor nanostructures  US2013/0052762
- TF11074 metal assisted chemical etching to produce III-V semiconductor nanostructures  US2013/0280908
Defying text definition of wet etch, **MacEtch** is an anisotropic wet etching method that could potentially replace, improve dry etch for various electronics, photonics, and energy applications.
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