Technology Excellence for Specialty Markets (and Etching Basics)

Corporate Introduction
Semiconductor Equipment Manufacturing

- USA manufacturing
- Focus on high growth specialty markets
- Lab-to-Fab solutions
- Multiple production facilities
- ISO-9000/9001

Plasma-Therm, Florida, USA
Advanced Vacuum Lomma, Sweden
Rev-Tech, Florida, USA
**Etch and Deposition Solutions Leveraged Across Markets and Materials**

<table>
<thead>
<tr>
<th>Market</th>
<th>Solutions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wireless</td>
<td>Etch Solutions: ICP, RIE, PE, PHF-RIE, DRIE</td>
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<tr>
<td>Solid State Lighting</td>
<td>Deposition Solutions: PECVD, ICP CVD</td>
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<tr>
<td>Photonics</td>
<td>Plasma Dicing Solutions</td>
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<tr>
<td>MEMS NEMS</td>
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<td>Power</td>
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<td>Failure Analysis</td>
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<td>R&amp;D</td>
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**Etch Solutions:**
- ICP
- RIE
- PE
- PHF-RIE
- DRIE

**Deposition Solutions:**
- PECVD
- ICP CVD

**Plasma Dicing Solutions:**
Configuration Flexibility
From Lab to Fab

Open → Loadlock → Cluster → Fab Integration

Single wafer → Cassette-to-cassette

Plasma-Therm
Product Innovation

VERSALINE®

Singulator™

Etch and Deposition

LAPECVD™

Mask Etcher®
Advanced Vacuum product lineup
Open load and single wafer loadlock

Vision 300  Vision 400  Apex SLR
Supporting Over 640 Customers Worldwide

- **Americas** (St. Petersburg, FL)
  - Sales and Service distributed throughout the US.
  - 1 Spares warehouse location

- **EMEA**
  - France, Germany, Ireland, United Kingdom, Sweden, Israel, South Africa
  - 1 Spares Warehouse

- **Asia-Pacific**
  - Japan, China, Taiwan, Australia, Indonesia, Korea, Singapore, India, Malaysia
  - 4 Spares warehouses
Customer Recognized Service and Support

- Global service organization operating 24/7
- Customer recognition of leadership
- VLSIresearch 10 BEST/THE BEST Awards for 17 years
- 2015 RANKED 1st in Etch & Clean Equipment Suppliers
Etching Basics: Plasma Reactors Mechanisms

Etching: creating faithful reproduction of a pattern
Plasma Etching: Fundamentals, Mechanisms, Applications

- Wet vs. Dry
- What is plasma?
- Hardware/reactors overview
- Basic Low-Pressure Processes
  - Physical
  - Chemical etching
  - Ion driven etching, Ion enhanced etching
  - Ion enhanced + Inhibitor (sidewall passivation)
- Trends and Tradeoffs
  - Power
  - Temperature
  - Pressure
Why all the Focus on Dry Etching? What’s Wrong with Wet Etching?

**Benefits**
- Purely chemical
- No physical damage
- Can be highly selective
- Wide choice of chemicals
- Can etch many materials
- Low capital cost

**Disadvantages**
- Limited CD geometry and control
- Isotropic and/or crystallographic
- Requires rinse and dry steps
- Hazardous or toxic chemicals
- Resist/wafer interface failure (undercutting)
- Potential contamination sources
Plasma Basics: Why Pursue Dry Etching?

- Many materials can be wet etched
- And plasma……
  - requires a lot of technology to make it work
  - involves many environmental health and safety aspects
  - is expensive

- **But plasma can do things wet can’t**
  - Less reactants required
  - Higher purity reactants
  - Lower contamination risk
  - Compatible with other dry processes

- Anisotropic Etching (Isotropic possible)
  - Pattern smaller geometries
  - Improved CD control

*Directionality: Pattern fidelity*
Plasma Basics: What is a Plasma – Tornado in a Trashcan?

- Chemical “soup”, 4th state of matter
  - Neutrals     Ions     Electrons
  - Overall charge quasi-neutral
  - Most molecules/atoms not ionized
  - Non-equilibrium, constant creation/loss of species
  - Plasma electrons - small mass → move fast
    - ~9 x 10^{-28}g
  - Plasma ions - big mass → move slow
  - Plasma neutrals - big mass → move slow

Dynamic!
Plasma Basics: How to make a plasma?

- Add enough energy to a gas to cause ionization
  - Electrical
  - Thermal
  - Other – e.g. electro-magnetic energy (radiation)

- Low Pressure
  - Neon sign

- Very low pressure
  - Inter-stellar space

- High Pressure
  - Lightning
  - Electric welding arc
Plasma Basics: What is an Ion?

Ne

Ne+ + e-

10 protons 9 electrons (2 + 7)

Extra positive charge

Simplified view

Atom

10 protons 10 electrons (2 + 8)

Charge balanced

Electron

Impact

Ion

10 protons + Ejected Electron

9 electrons (2 + 7)

Extra positive charge
Plasma Basics: Formation of Radicals by Electron Impact (e.g. Cl₂)

Cl₂ → e⁻ → Cl + Cl

Cl₂ Molecule
Charge balanced
Happy to share an electron
Full outer shell

Cl Radicals
Neutral but “unhappy”
Hungry to have just one more electron
to complete the outer shell

Simplified view
Plasma Basics: What makes up plasma? Focus on RF Generated Plasma

- $n_e$: electrons concentration
- $n_o$: neutral concentration
- $n_i^+$: positive ion concentration
- $f(E)$: distribution of energy
- $\tau$: residence time

Factors:
- Excitation frequency
- Excitation power
- Gas flow rate
- Nature of gas
- Pumping speed
- Chamber design
Plasma Basics: **Simple** Plasma Processes

- **Ion production**
  - \( X + e^- \rightarrow X^+ + e^- + e^- \)

- **Dissociation**
  - \( AB + e^- \rightarrow A + B + e^- \) (formation of neutrals and radicals)

- **Ion loss mechanisms**
  - \( X^+ + e^- \rightarrow X \) (unlikely)
  - \( X + e^- \rightarrow X^- \) (electron attachment, e.g. SF\(_6\))
  - \( X^+ + \text{wall (}e^-\text{)} \rightarrow X \) (a major ion loss mechanism)

- **Light emission**
  - \( X + e^- \rightarrow X^* + e^- \) (excitation)
  - \( X^* \rightarrow X + h\nu \) (photon emission)
    - Emission at specific energy (wavelength)

Many more processes than those shown

Used for endpoint
Basic Vacuum Processing System

Throttle Valve
(controls pressure)

Basic Vacuum Processing System

We’ll talk about plasma a bit later…

MFC = mass flow controller
Basic Vacuum Processing System

We’ll talk about plasma in just a minute…

Throttle Valve
(controls pressure)

MFC = mass flow controller
Plasma Basics: Equipment Configuration

- **Need**
  - Low pressure
  - Gas
  - Electrical energy
    - Generator - Power source

- **Matching Network** (to be discussed later)
  - Minimizes reflected power
    - Increases power dissipation in the discharge
  - Protects the generator
  - Acts as blocking capacitor
Plasma Reactors: Low Density Plasma Sources

RIE is a confusing name – uses plasma (reactive species, ions)
RIE technology includes other configurations
RIE is a specific configuration (|| plate)
RIE = CCP
ICP = RIE ICP

PE = Plasma Etching
CCP = RIE = Reactive Ion Etching
Summary Etching is a Balance
(ACP is a Good Compromise)

**Chemical** controlled with ICP power

**Physical** controlled with substrate bias power

**Neutrals - Chemical**

**Ions - Physical**

Inhibitors complicate the balance
Plasma Reactors: High Density Plasma Sources

Magnetically Enhanced

**Two RF supplies**
More control of ions and radicals

Advanced Vacuum
A Plasma-Therm Company
Plasma Etching Processes

- Many simultaneous processes
- Modeling gas dynamics, electromagnetics, reaction kinetics, surface interactions, etc.

- Excellent references to the study of plasma etching
  - Plasma Etching: Fundamentals and Applications, M. Sugawara
  - Plasma Etching: An Introduction, D. Manos and D. Flamm
  - [http://www.chm.bris.ac.uk/~paulmay/misc/msc/msc1.htm](http://www.chm.bris.ac.uk/~paulmay/misc/msc/msc1.htm)

Source: Oehrlein and Rembetski
Sputter Etching (“physical” etching)

- High energy ions impact substrate surface and eject material - billiard ball effect
- Yield/Etch Rate typically decreases with increasing process pressure
- Etch Rate typically highest at low pressure (mTorr)
Sputter Etching

- Characterized by non-volatile byproducts
  - Fluorine based chemistry (e.g. LiF, CaF: tungsten, titanium, silicon)
  - Chlorine based chemistry (CuCl2)
  - No easily made byproducts (e.g. gold, platinum)
- High bond energies (e.g. GaN, Al2O3), characterized by low selectivity

- Gaseous
- Etchable at RT
- Sputter etch
- May be able to etch
- Unknown

<table>
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<tr>
<th>Period</th>
<th>Group</th>
<th>Elements</th>
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<td>Li, Be, Na, Mg, K, Ca, Rb, Sr, Cs, Ba</td>
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</table>

Plasma-Therm
Sputtering Process

- Ions create a cascade of collisions on the surface.
- Multiple collisions eject (or 'sputter') atoms from the surface.
- Sputter yield depends on:
  - Target material (how tightly bound and density)
  - Incoming ion mass (typically Ar, He too light, Xe too expensive, hard on turbos)
  - Energy of the incoming ion

Note: Si has very low sputter yield, so does graphite

<table>
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<tr>
<th>Material</th>
<th>Sputter Yield*</th>
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<tr>
<td>Silver</td>
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<tr>
<td>Gold</td>
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<tr>
<td>Copper</td>
<td>2.3</td>
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<tr>
<td>Platinum</td>
<td>1.6</td>
</tr>
<tr>
<td>Nickel</td>
<td>1.5</td>
</tr>
<tr>
<td>Iron</td>
<td>1.3</td>
</tr>
<tr>
<td>Al</td>
<td>1.2</td>
</tr>
<tr>
<td>Si</td>
<td>0.5</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.05</td>
</tr>
</tbody>
</table>

*600 eV Ar ions

Source: Angstrom Sciences
www.angstromsciences.com/ref.sputtering-yields
Sputter Etching – Purely physical
Common Reactor Configuration

- “RIE” mode (common configuration)
- Sputtering mode with inert gas (usually Ar)
- Low etch rates but can remove non-volatile materials
- Profile may be directional (but rarely vertical)
- Ion energy, flux and radical conc. not independent
- Low selectivity- most materials sputter equally
  - Mask choice is important but not always a problem. May produce desired result
- “Dirty”– Process products not volatile and accumulate on chamber and feature surfaces

Inert Gas (e.g. Ar)
Capacitive Plasma
Matching Network
Typically 13.56 MHz
Substrate

Plasma-Therm

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A Plasma-Therm Company
Angular Dependence of Sputter Yield

- Results in enhanced etch rate at angle of max. value ($\theta_{\text{max}}$)
- Etch profile will develop at this angle
  - “faceting” of mask

![Graph showing sputter rate vs. angle (degrees) with max. sputter yield angle $\theta_{\text{max}}$]
Sputter Etching and Development of Sloped Etch Profile

- As mask material is sputtered away it preferentially is lost at the corner (some part of the corner equals $\theta_{\text{max}}$)

Example: resist after etching

Angle approaches angle of max. sputter rate

Substrate
Sputter Etching: Mask Profile Can Affect Feature Profile

- Lateral erosion of resist mask can cause feature size shrinkage or roughness

Another description is that forward sputtering will always round a corner
Angled Profile
Sometimes it’s not a problem, it’s a solution!

Starting resist profile

Beginning of mask faceting

Mask slope transferring to feature

Desired result (patterned sapphire for LED manufacturing)
Sloped Masks Make Vertical Etching Difficult

- Selectivity = \( \frac{ER_{\text{mask}}}{ER_{\text{film}}} = \tan(\theta_{\text{film}})/\tan(\theta_{\text{mask}}) \)
- Use to predict slope.

<table>
<thead>
<tr>
<th>Selectivity</th>
<th>Mask ( \theta_{\text{mask}} )</th>
<th>Best Profile</th>
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<tr>
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<td>75</td>
<td>75.0</td>
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<tr>
<td>1</td>
<td>80</td>
<td>80.0</td>
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<td>85</td>
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<td>85</td>
<td>87.5</td>
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<td>75</td>
<td>84.9</td>
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<td>3</td>
<td>80</td>
<td>86.7</td>
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<td>3</td>
<td>85</td>
<td>88.3</td>
</tr>
<tr>
<td>10</td>
<td>75</td>
<td>88.5</td>
</tr>
</tbody>
</table>
Sputter Etching:
Can create “grass” or sidewall redisposition

- Micro-masking
- Often redeposited mask material
- Depends on mask material, bias, ion mass
- Tends to be less farther from masking material

- Not the only source of micromasking (e.g. excessive passivation, to be discussed later)
Sidewall redeposition
Gold Etching – Process Example

After “etch”

“Dog ears”

After mask removal
Sputter Etching: Can be a source of “trenching”

- Deflected ions
- Increased etch rate at mask edge
- Depends on mostly on bias and ion mass

Bias Power

200 W 250 W 300 W
Chemical Etching

- Dominated by neutral **reactive** species (atoms, radicals, molecules)
- Radicals react with film surface
  - Reaction is spontaneous – ion assistance not required
- Purely isotropic (nondirectional) and low damage
- Reaction by-products are volatile
Etch Product Volatility Guidance

<table>
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<tr>
<th>Elements</th>
<th>Fluorides</th>
<th>Boiling temperature (°C)</th>
<th>Chlorides</th>
<th>Boiling temperature (°C)</th>
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<td>WBr₅</td>
<td>333</td>
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Chemical Etching: Common Reactor Configurations

**CCP = RIE**
*Reactive Ion Etching*
Lower electrode powered
Run at low power to avoid unwanted sputtering

**PE = Plasma Etching**
*Upper* electrode powered

**ICP = Inductively Coupled Plasma Etching**
Substrate bias and high density plasma

**Low density plasmas**

**High density plasmas**
Chemical Etching
Reactor Configuration

- **PE configuration**
  - Little ion bombardment – almost “purely” chemical etch
  - Least flexible configuration

- **RIE = CCP configuration**
  - High pressure operation to minimize ion reactions
  - Low plasma/radical density (low etch rates)
  - RF power/ion bombardment not independent

- **ICP configuration**
  - High plasma/radical density (high etch rates)
  - Can operate with no bias – almost purely chemical etch
  - Plasma density/ion bombardment are independent

Low density plasmas

High density plasmas

Plasma-Therm
Chemical Etching: Examples

- Spontaneous etch reactions (examples)
  - Si with SF$_6$ (F radical)
  - SiN$_x$ with SF$_6$ (F radical)
  - GaAs with Cl$_2$ (Cl radical) (Interestingly NOT etching Si with Cl$_2$)
  - Al with Cl$_2$ (Cl radical)
  - HC polymers (e.g. PR) with O$_2$ (O radical)

- Choice of chemistry can provide high selectivity
  - SiN$_x$/SiO$_2$ using SF$_6$
  - GaAs over InGaAs or AlGaAs using Cl$_2$
Chemical Etching: Examples

- Silicon trench, $\text{SF}_6$
- GaAs, HCl (crystallographic)
- Silicon pillar, $\text{SF}_6$
- InP, HBr
- GaAs, Cl$_2$
Chemical Etching: Characteristics

- High etch rates possible
  - High radical concentrations possible in plasma (particularly ICP)
    - Higher density at higher pressure
  - Rate limited by mass flow balance (what goes out, must come in)

- Load dependent etch rate
  - Etch rate lower as etched area increases
    - Consequence of mass flow balance

- Frequently classic “bulls-eye” uniformity profile
  - Edge of substrate etches faster than center
    - Same # radicals at substrate edge but less area
Chemical Etching: Edge Effect

Edge has less area for available reactant flux.

Gas Phase Reactants

Etch rate

Edge Center Edge

substrate

film

substrate
Chemical Etching: Reduction of edge effect

Gas Phase Reactants

Physical barrier limits species access to edge

![Graph showing etch rate with corrected and uncorrected data points]

Other solutions:
- High pump speeds, dilution
Modest changes in gas phase chemistry can have strong impact on etching.

- In this case, adding ~15% O₂ increases etch rate ~4x
- \( \text{Si} + \text{F} \rightarrow \text{SiF}_x \)

Formation of F:
- \( \text{CF}_4 + e^- \rightarrow \text{CF}_3 + \text{F} + e^- \) (electron impact)
- \( \text{CF}_3 + e^- \rightarrow \text{CF}_2 + \text{F} + e^- \)

Radical recombination:
- \( \text{CF}_3 + \text{F} \rightarrow \text{CF}_4 \) (loss of F)
- \( \text{CF}_2 + \text{F} \rightarrow \text{CF}_3 \)

Addition of O₂:
- \( \text{CF}_2 + \text{O} \rightarrow \text{COF} + \text{F} \) (generation of F)
- \( \text{COF} + \text{O} \rightarrow \text{CO}_2 + \text{F} \)

Chemistry Choice - Volatility of By-product(s)


<table>
<thead>
<tr>
<th>Fluorides</th>
<th>Chlorides</th>
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<tbody>
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<td>AlF₃</td>
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<tr>
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<td>Cu₃Cl₃</td>
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<td>WCl₆</td>
</tr>
<tr>
<td>18</td>
<td>347</td>
</tr>
</tbody>
</table>

Use vapor pressures when available or boiling points as a guide when they are not.
Chemistry Choice - Volatility of By-product(s)

<table>
<thead>
<tr>
<th>Chemistry</th>
<th>Primary Films Etched</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl – based (e.g. Cl₂, BCl₃, SiCl₄)</td>
<td>Al (+ alloys), Ti, TiN, W, Cr, Hf, W, Mo</td>
</tr>
<tr>
<td>F – based (e.g. SF₆, CF₄, CHF₃)</td>
<td>Ti, W, TiW, WN, Mo, Ta, silicides</td>
</tr>
</tbody>
</table>

Other factors play a role:
- masking materials
- additive gases,
- film quality,
- desired results,
- etc.
Ion Enhanced Etching

Physical and chemical components: individually slow but together increase the etch rate and anisotropy

- Combination of radicals and ions etch wafer
- Ions striking the surface enhance reactions and product desorption
Ion Enhanced Etching: Common Reactor Configurations

- **CCP = RIE configuration**
  - Low pressure operation to maximize ion formation
  - Low plasma/radical density (low etch rates)
  - Ion density/ion energy not independent

- **ICP configuration**
  - High ion density
  - Plasma density/ion bombardment are independent
    - ICP power → ion and radical densities
    - Bias power → Ion energy
Ion Enhanced Etching
Experiment shows role of ions/radicals

- Illustrates the dramatic affect of combining radicals and ions

<table>
<thead>
<tr>
<th>Radicals</th>
<th>Radicals + Ions</th>
<th>Only Ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>XeF₂ gas only</td>
<td>Ar⁺ ion beam + XeF₂ gas</td>
<td>Ar⁺ ion beam only</td>
</tr>
</tbody>
</table>

- **Models**
  - Reactive spot (energy addition)
    - Tachi (1985)
  - Damage & enhancement
    - Coburn & Winters (1978)

![Graph showing etch rate over time](image)

**Source:** J.W. Coburn, H.F. Winters, J. Appl. Phys. 50, 3189 (1979)
Other early studies of ion effects

Si etching with Ar+ CF₄
CF₄ is not adsorbed on Si surface


Si etching with Ar+ Cl₂
SiCl₄ volatile


Al with Ar+ + F₂
Low volatility of AlF₃, Al alone sputters faster

Ion Enhanced Etching
Ions contribute to anisotropy

- Example: XeF$_2$ etching of Si

- Anisotropy = $1 - \frac{ER_{\text{horizontal}}}{ER_{\text{vertical}}}$

- Higher anisotropy with higher energy ions

- Penalty for anisotropy by increasing ion flux or energy – but typically lower selectivity, trenching, damage

Source: P. Martin, Vacuum Technology & Coating, 28, (Nov. 2009)
(Not the original reference)
Ion Enhanced Etching Examples

SiC with SF$_6$: ions assist formation of SiF$_x$ and CF$_x$ etch products

SiO$_2$ with CF$_4$: ions assist formation of Si and C etch products

Al$_2$O$_3$ with BCl$_3$: ions assist formation of AlCl$_x$ etch products

GaN with Cl$_2$: ions assist desorption of GaCl$_x$ etch products
Ion Enhanced Etching

- Ion bombardment is necessary to break strong bonds
  - Si – O 8.2 eV
  - Al – O 9.3 eV
- By products must still be volatile (e.g. SiF₄, AlCl₃)
- Vertical ion bombardment → vertical etch
  - Mask erosion may result in sloped profile (similar to sputter etch)
- Choice of radicals can provide selectivity
  - e.g. etching SiO₂ with CF₄ (CF₂ and CF₃ radicals)
  - Selectivity less than Chemical etch and greater than Sputter etch
- Loading effects < chemical etch
  - Rate rarely mass flow limited
Ion Enhanced Etching + Inhibitor (Sidewall passivation)

- Inhibitor (often polymer forming) can passivate surfaces
  - Minimal ion bombardment on sidewalls to remove inhibitor
  - Surface protected from etching
- Passivation removed from horizontal surfaces by ion bombardment
  - Surface open for etching (chemical or ion assisted)
Ion Enhanced Etching + Inhibitor

- Most highly anisotropic processes fall in this category

- Inhibitor introduced intentionally
  - Si etch using SF$_6$ plus C$_4$F$_8$
  - Al etch using BCl$_3$/Cl$_2$ plus CH$_4$
  - InP etch using HBr or Cl$_2$ plus N$_2$

- Inhibitor introduced “unintentionally”
  - Etching using photo resist mask
    - Resist etch by-product is polymer precursor
    - Etch result depends on resist loading
  - Anisotropic etch with resist mask, isotropic with “hard” mask
  - e.g. GaAs via etch with resist mask

Source: after M. Mieth and A. Barker, Semiconductor International, 5, 222 (May, 1984)
Materials which act as inhibitors

- Photoresist etch by-product (particularly from Cl etch)
- Hydrocarbons e.g. CH₄
- Chlorinated hydrocarbons e.g. CHCl₃ (most banned)
- Freons
  - CHF₃ ≈ C₄F₈ > C₂F₆ > CF₄
  - F:C ratio and oxidation capability of surface determines effectiveness as polymer precursor (e.g. O from SiO₂ can provide oxidation source)
- N₂ for some processes, e.g. Al, InP
- O₂ can oxidize sidewall e.g. silicon (e.g. cryo black silicon process)
Ion Enhanced Etching + Inhibitor

Example: Multilayer InP/InGaAs/InP

HBr/CH$_4$/BCl$_3$
Preferentially etches InGaAs layer

HBr/N$_2$
Inhibition of InGaAs etching

Requires understanding of how inhibitors participate (e.g. CH$_4$ sometimes an inhibitor, sometimes an etchant)
Ion Enhanced Etching + Inhibitor

Anisotropic GaAs etch (via etch) using Ar/Cl₂
Resist by-products provide sidewall passivation

Polymer provides sidewall protection
GaAs Profile Control  
- Isotropic to Anisotropic

- Selectivity increases with Cl$_2$ partial pressure: etch rate and isotropy increases

- Resist implicated in controlling profile
Tungsten Etch Example

- SF$_6$ / CF$_4$ / Ar
- F for reaction, CF$_4$ for passivation
- Vertical profile
- Sidewall roughness transferred from mask roughness

Process temperature 20°C
Selectivity to PR ~5:1
~2000 A/min
Tungsten Etching with Fluorine Chemistry

**CF<sub>4</sub> / O<sub>2</sub> vs. SF<sub>6</sub> / O<sub>2</sub>:** Etch rate and Relative F Atom Density
- F is primary etchant (similar activation energies) for SF<sub>6</sub> and CF<sub>4</sub>
- O<sub>2</sub> increase rate for CF<sub>4</sub> / O<sub>2</sub> with more available F. O and F compete for W sites
- O<sub>2</sub> decrease rate for SF<sub>6</sub> / O<sub>2</sub>, interaction with SF<sub>x</sub> and W? (adding O<sub>2</sub> doesn’t help)

Mark Salimian, Plasma Etching, Technologies and Processes, 1993
Mask material is often important

RIE with $\text{SF}_6$

Data suggests O from $\text{SiO}_2$ attacks sulfur (S) protection layer on $\text{W}$

More efficient removal of inhibitor than N from $\text{SiNx}$

Source: Mark Salimian, Plasma Etching, Technologies and Processes, 1990
Ion Enhanced Etching + Inhibitor Characteristics

- Often involved in achieving anisotropic profiles
- **Balance** of etchant and inhibitor
  - Profile, uniformity sensitive to ratio
  - Too little inhibitor, profile → isotropic
  - Too much inhibitor, etch rate decreases, polymer formation, micro-masking

  ![Excess inhibitor deposition causing grass](image)

- Balance can change with
  - Aspect ratio (mass transfer issues)
  - Temperature sensitive
  - Polymer deposition (affects profile) changes with temperature
- Potential for deposition on chamber surfaces
  - Reduced at elevated temperatures
Al Etch – General Considerations

- Typical Al process steps:
  - Breakthrough (remove native oxide) → Main etch → Post etch treatment

- Material composition issues
  - Al-Si: Si residues may require post F-plasma treatment (e.g. CF₄) to remove unetched Si (this may impact underlayer)
  - Al-Cu: Cu difficult to etch, susceptible to “grassing” from precipitates
    - Requires higher temperature and more ion bombardment
      - Cu₃Cl₃ a temperature of about 200°C
  - Al deposition quality: no O₂ present
    - Reduce Al₂O₃ formation during deposition: no leaks, loadlock, high purity Ar
  - Al₂O₃ formation from poor vacuum conditions (e.g. leaks, outgassing)

- Mask profile (sloped, rough, or poor adhesion)
- Corrosion (post etch)
Al Etching
Another example of sidewall passivation

- Photoresist erosion assists sidewall passivation
  - Resist condition (e.g. slope, bake temperature)
- Surface AlCl₃ reacts with moisture exposure to make HCl which corrodes Al
- Cl residues in resist & sidewall deposits also react to form HCl
- Treatments
  - In-situ PR strip (O₂ ash) (best)
  - F replacement of Cl using CF₄ (O₂) (possibly SF₆)
  - CHF₃ will deposit polymer protecting the wafer from moisture attack.
  - Immediate rinsing of wafer and removal of resist after Al etch
  - High temperature bake (usually not available due to PR)
Al Etching – Breakthrough Removal of Native oxide

- Surface reacts to ambient atmosphere to make 20-50Å Al₂O₃
- Cl₂ alone won’t work. Al₂O₃ + Cl₂ → AlCl₃ + O₂ (makes more Al₂O₃)
- BCl₃ to needed to reduce Al₂O₃
  - Al₂O₃ + BCl₃ → AlCl₃ + B₂O₃ (BOCl)
  - BCl₃ acts as an O₂ scavenger
  - CClₓ could be used but carcinogenic (Al₂O₃ + CClₓ (x ≤ 4) → AlCl₃ + CO)

- Even with reducing chemistry and energetic ion bombardment, the etch rate of Al₂O₃ is >300x less than Al
Al Etching – Main Etch

- Al (unlike Al₂O₃) can be etched in Cl₂ (or with Br)
  - Cl₂ reacts spontaneously at RT (without plasma or ion bombardment)
  - AlCl₃ sufficiently volatile at 20°C to desorb
    - Desire high pumping speed (low residence τ) reduces AlCl₃ partial pressure
    - Heated chamber walls (reduce re-deposition)
    - Load lock (safety and low oxygen presence)
  - Highly load dependent (chemical component) may require diffusion barriers to improve uniformity
  - Al not etched in F-containing gases. AlF₃ only volatile at elevated temperatures (i.e. chamber should be free of F)
Plasma Etch
Feature Profile Defects

- Physical effects (ions)
  - Mask faceting
  - Ion scattering
  - Off-angle ions

Neutral beam solutions?

- Chemical effects
  - Over passivation
  - Under passivation

Damage Effects
Process and device dependent

- Multiple types of damage can result from processes
  - Ion damage to lattice (e.g. ion penetration, vacancies, interstitials)
  - Carrier passivation (carrier concentrations)
  - Surface contamination (surface states) (e.g. fluorocarbon layers)
  - Recombination centers
  - Surface morphology
  - Insulator breakdown/leakage
- Depth can be surprisingly deep
  - Surface to many 100s Å

Many sources
Damage examples

Buried Quantum Well Photoluminescence for Monitoring Etch Damage Depth

- H ion penetrates ~5x deeper
- UV/VUV penetrates deeper with O₂ plasma but fewer defects near surface


Damage Example
InP Etching: RIE vs. ICP

- CH$_4$/H$_2$ chemistry

RIE has lower etch rate
RIE 2x P surface loss enhanced
RIE P depleted layer ~2x ICP
RIE 2-3x thicker amorphous layer

**Summary - Etching Mechanisms**

- **Sputtering**
- **Ion Enhanced**
- **Chemical**
- **Ion Enhanced + Inhibitor**
Summary
Basic Low Pressure Etching Mechanisms

- **Sputter Etching**
  - Ions strike surface and eject or sputter material
  - Nonvolatile reaction products

- **Chemical Etching**
  - Neutral dominated (atoms, radicals, molecules)
  - Isotropic, non-directional, can be reagent limited

- **Ion Driven Etching**
  - Ions strike surface and enhance reactions
  - Both physical and chemical components
  - Allows “fast” anisotropic etching

- **Ion Enhanced + Inhibitor Formation**
  - Polymer forming components passivate sidewalls where ion bombardment is minimal
  - Prevention of lateral etching
Pressure Effects

Strong effects

High pressure
- Requires additional control mechanism (e.g. passivation)
- More neutral influence

Low pressure
- Stronger ion influence
- More directional (CD control)
- Potential for more damage

Ratio of sheath thickness and mean free path of ion

Ion Energy

Pressure (mTorr)

Neutral flux

Ion flux

Physical (sputtering)

Ion Assisted (chemical and physical)

Neutral flux

Chemical (radicals)
Pressure Effects
Strong effects

- Affects ion energy, density, bias, electron temperature
  - Reduction in pressure increases electron temperature and this results in an increase in DC bias (more electrons “leave” the plasma)

- Chemical based processes – etch rate usually increases with pressure (longer residence time for reactants)

- Ion enhanced processes – Etch rate might actually decrease with increasing pressure (lower ion energies)

- Profile affected: mass transport (lag), sidewall passivation
Power Effects

- Increased ICP power $\rightarrow$ increased concentration of radicals
- Increased electrode bias power $\rightarrow$ increased DC bias
  - Increases the effect of ions (more energetic and more of them)
- Mask erosion increases $\rightarrow$ selectivity decreases
  - Possible to actually have better selectivity if material of interest etch rate goes up faster than mask erosion
- Wafer cooling becomes more important as either ICP or bias power increases

Wafer gets hot with all the energy being delivered (and exothermic reactions)

Need to manage thermal budget!
Temperature Effects

- Wafer temperature affects etch rate, selectivity, surface roughness and anisotropy
- Chemical processes affected the most
  - Temperature ↑, isotropy ↑ (and often roughness)
  - Temperature ↑, Etch rate ↑
  - Temperature ↑, Selectivity ↓ (usually but not always)
- Consider Si etching masked by SiO₂ (example)
  - \[ \text{Rate}_F(\text{SiO}_2) = 6.14 \times 10^{-13} n_F T^{1/2} e^{-0.163/kT} \text{ Å/min} \]
  - \[ \text{Rate}_F(\text{Si}) = 2.91 \times 10^{-12} n_F T^{1/2} e^{-0.108/kT} \text{ Å/min} \]
  - \[ \text{Selectivity} = \frac{R_F(\text{Si})}{R_F(\text{SiO}_2)} = 4.7 e^{+0.055/kT} \text{ (higher T, lower selectivity)} \]
- Changes in T can have large effect on selectivity (e.g. InP etching)
- Photoresist etch rate increases with temperature

Source: Flamm et al., VLSI Electronics, Vol. 8, Chap (1984)
General Process Trends

<table>
<thead>
<tr>
<th>Process Parameter</th>
<th>Etch Rate</th>
<th>Selectivity (to mask)</th>
<th>Mechanism Trend</th>
<th>Uniformity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bias Power</td>
<td>Increases</td>
<td>Decreases</td>
<td>More physical</td>
<td>Weak effect</td>
</tr>
<tr>
<td>Electrode Size (power density)</td>
<td>Decreases</td>
<td>Increases</td>
<td>Less physical</td>
<td>Weak effect</td>
</tr>
<tr>
<td>Source Power</td>
<td>Increases</td>
<td>Increases</td>
<td>More chemical</td>
<td>Weak effect</td>
</tr>
<tr>
<td>Pressure</td>
<td>Usually increases</td>
<td>Weak effect</td>
<td>More chemical</td>
<td>Usually worse</td>
</tr>
<tr>
<td>Substrate Temperature</td>
<td>Increases</td>
<td>Depends</td>
<td>More chemical</td>
<td>Weak effect</td>
</tr>
</tbody>
</table>

**Important Caveat:** material dependent
Advanced Plasma Developments
Interest in removing ions & controlling neutral energies

Multiple frequencies
Pulsing ICP source
Pulsing bias

Pulsed gases
Neutral control – grids, ion filters

Source: adapted from Ankur Agarwal et. al., J. of Applied Physics, 106, 103305, (2009)
Temporal Etching
Atomic Layer Etching (ALE)
**Time-Multiplexed Etching**  
**Atomic Layer Etching (ALE)**

**Potential Benefits**
- Monolayer control of etch
- Elimination of profile defects
- Elimination of ARDE

**Limitations**
- Extremely low etch rates
- Narrow process window to achieve monolayer control

**Status**
- Demonstrated in Si Cl-based chemistries
- 4 step cycle demonstrated
  - 280 ALE cycles
  - 150sec cycle times

Spatially Multiplexed Etching

DRIE

Spatial DRIE Approach

Spatial ALD Reactor

Source: Roozeboom, F. et al., ECS Trans. 50 (32), 73-82 (2013).
Summary

Usually there are Tradeoffs

- Uniformity
- Profile
- Etching Rate

- Damage
- Selectivity
- Surface Morphology
Thank you