Current Microfabrication and Nanofabrication Technologies
Nanoimprinting Lithography (NIL)

NIL Process

1. Press in mold
2. Heat up mold and substrate
3. Mold separation after cooling
4. O₂ RIE

- Sub-10nm feature size
- Large area (4-8 in.)
- High throughput
- Low cost

Nanonex NX-2000 Nanoimprinter

Up to 4” wafer
Sub-100 nm resolution
Up to 300°C, 600 psi, UV
Sub-10 nm Resolution of NIL

Imprint mold with 10nm diameter pillars

10nm diameter holes imprinted in PMMA

10nm diameter metal dots fabricated by NIL
Metallic Nanodot Arrays

Nanodots localize magnetic or electrical fields at very small scales. Applications for nanodots could include high-density information storage devices.
Laser-Assisted-Direct-Printing (LADI) in Silicon

LADI Process

- Fast speed
- Direct patterning semiconductors
- Complex structures (e.g. lens) in Si
- With sub-10 nm resolution

The Big Picture

Technology CAD

Microlithography

Oxidation

Metallization

Etching

Deposition

Diffusion

Ion Implantation

Bulk/Epi Crystal Growth

Silicon Substrate
Chemical Vapor Deposition (CVD):
Apply thin layers of semiconductor materials.
Transport and Reaction Processes of CVD

CVD of Si in a Si-Cl-H system

1. $\text{SiCl}_4(g) + 2\text{H}_2(g) \leftrightarrow \text{Si}(s) + 4\text{HCl}(g)$;
2. $\text{SiCl}_3\text{H}(g) + \text{H}_2(g) \leftrightarrow \text{Si}(s) + 3\text{HCl}(g)$;
3. $\text{SiCl}_2\text{H}_2(g) \leftrightarrow \text{Si}(s) + 2\text{HCl}(g)$;
4. $\text{SiClH}_3(g) \leftrightarrow \text{Si}(s) + \text{HCl}(g) + \text{H}_2(g)$;
5. $\text{SiCl}_2(g) + \text{H}_2(g) \leftrightarrow \text{Si}(s) + 2\text{HCl}(g)$;
6. $\text{SiH}_4(g) \leftrightarrow \text{Si}(s) + 2\text{H}_2(g)$;
Atmospheric Pressure Chemical Vapor Deposition (APCVD)

- Dielectrics and metals
- Atmospheric pressure or partial pressure in N₂
- Low film purity
- Temperature of 600-1150°C

SierraTherm APCVD Furnaces
Low-Pressure Chemical Vapor Deposition (LPCVD)

- Dielectrics and metals
- Performed at reduced pressure or “rough vacuum”
- 10^{-3} to 10^{-5} Torr (1 atm = 760 Torr)
- High purity
- High temperature

Tystar LPCVD Tube Furnaces
Plasma Enhanced Chemical Vapor Deposition (PECVD)

- Dielectrics only
- 'High' vacuum (10^{-6} Torr)
- 300-400°C
### Chemical Vapor Deposition Techniques

#### APCVD:

**Advantages:**
- Relatively low operating cost since no vacuum needed

**Disadvantages:**
- Uniformity of deposited layer compromised at higher temperatures and pressures
- Gas flow dynamics hard to control at high pressures

#### LPCVD:

**Advantages:**
- Lower reaction temperatures than APCVD reactors
- Good step coverage and uniformity
- Less dependence on gas flow dynamics

**Disadvantages:**
- More expensive than APCVD reactors
- Downstream depletion can occur in horizontal designs

#### PECVD:

**Advantages:**
- Combination of vacuum pressures and lower temperature produces better uniformity in the deposited layer.
- Reactor can be used in other microelectronic production process steps.

**Disadvantages:**
- More process variables to be controlled compared to other CVD reactors.
- Cost of operation is increased with increased number of components.
Atomic Layer Deposition (ALD)

- Depositing one atomic layer at a time
- Highly uniform
- Process can be thermal or plasma-enhanced
ALD Mechanism

1. Pulse of precursor is exposed to the surface.
2. Purge of excess unreacted precursor using inert gas.
3. Pulse of a second precursor followed by a surface reaction.
Physical vapor deposition (PVD): Deposit thin films by the condensation of a vaporized material onto substrate surface.

- Assure low contamination
- Large mean free path at low pressures
Evaporator Deposition:
The deposited materials are evaporated or sublimated, either by an electron beam or a heated source.
- Mainly metals
- High vacuum ($10^{-6}$ Torr)

Edwards E306A thermal evaporator  
Denton DV-502A e-beam evaporator
Sputter Deposition:
Sputtering involves the collisions of ions (Ar⁺) with target material, leading to the ejection of target atoms that are collected on a substrate.
- Metals and dielectrics
- High vacuum (10⁻⁶ Torr)
A high electric field ionizes argon atoms and accelerates them into a metal target.

- Forms very uniform films
- Excellent step coverage (distributed angles of impact)
- Sputtering allows easy deposition of alloys (Al-Cu-Si)
- Wafer heating less than 300°C
- Sputtering of dielectrics uses both DC and RF fields
Spin-on Deposition:
Coat the substrate with material which is originally in the liquid form. Liquid is dispensed onto the substrate surface and the substrate is rapidly rotated (during spinning, liquid is uniformly distributed on the surface by centrifugal forces), material is then solidified.
• Glass dielectrics
• Performed at atmosphere
• 100-1000°C
Factors governing step coverage in evaporation:

Perpendicular step on perpendicular substrate. No coverage.

Rotating planetaries with substrate inclination. Improved coverage.

Same as (b) with substrate heating. Further improved coverage. (Heat raises the surface mobility of atoms and improves step coverage)

Reduced slope of step, plus rotation and heating. No thinning over step.
Shadowed Deposition

Material deposition is highly dependent on the orientation angle of the samples due to the large mean free path of the depositing atoms.

Large mean free path ($\lambda$) allows a direct path from source to substrate.

Great for lift-off process
Materials of interest:

- Conductors: Al, Cu, Au, Cr
- Dielectrics: SiO₂, Si₃N₄, Polyimide
- Semiconductors: Si, GaAs

Etches are characterized by the **verticality and anisotropy**.

If $V_h$ is the horizontal etch rate and $V_v$ is the vertical etch rate, the anisotropy can be given by:

$$A = 1 - \frac{V_h}{V_v}$$

- $A=1$ for fully anisotropic etches ($V_h = 0$)
- $A=0$ for fully isotropic etches ($V_v = 0$)

Etches can be performed using **chemical solutions (wet)** or **plasmas (dry)**.
Wet etching of amorphous (polycrystalline) materials is usually **isotropic**, meaning no direction is favored.

- **SiO$_2$**: buffered hydrofluoric acid (HF)
- **Si$_3$N$_4$**: hot phosphoric acid (65-70 °C)
- **Al**: nitric/phosphoric/acetic acid (can’t use if on GaAs!) or hydrochloric acid (HCl; OK on GaAs)
- **PolySi**: HF and nitric acid
- **Cr**: potassium permanganate
- **Au**: potassium iodide and iodine (KI/I$_2$)
Wet etching of crystalline (single-crystal) materials is usually anisotropic, meaning some crystallographic directions are favored than others.

- Silicon – anisotropic etch: basis of silicon micromechanics.
- GaAs – anisotropic etch: bromine and methanol (highly exothermic!!) or hydrogen peroxide/sulfuric acid.

Pyramid shaped pits in Si (100)
Overview of Plasma Etch Mechanisms

1. **Chemical etching:**
   Spontaneous, isotropic, very selective.

2. **Ion enhanced etching:**
   Neutrals and ions involved, ion energy needed to stimulate chemical reaction or to remove reaction products. Anisotropic and selective.

3. **Physical etching:**
   Anisotropic and non-selective.

4. **Trenching:**
   Caused by ion deflection from sidewalls.

5. **Sidewall passivation:**
   Deposition of non-violate materials: Etch byproducts, surface reactions with gas or mask materials.

6. **Mask erosion:**
   Caused by ion bombardment/sputtering.

**Electron-Impact Dissociation:**

\[ e^- + O_2 \rightarrow O + O + e^- \]

\[ e^- + SF_6 \rightarrow SF_5 + F + e^- \]
Reactive ion etching (RIE)

- **Isotropic**: barrel configuration (or high gas pressure)
- **Anisotropic**: parallel plate configuration

Nanotech reactive ion etcher
Dry Etching Techniques 2 & 3

Barrel etcher
- Uniform stripping of films (e.g. resist)

Parallel plate etcher
- High anisotropy
Deep Reactive Ion Etch (DRIE)

Anisotropy arises from material processes as redeposition / passivation. Anisotropy enhanced by:

- Sputtering – physical removal of atoms
- Chemical reaction and heating due to bombardment
- Protective sidewall residue enhances vertical etch rate

**Passivation Step:** At the beginning of each cycle a $C_2F_6$ based plasma is used to conformally deposit a few monolayers of PTFE-like fluorocarbon polymer across all surfaces exposed to the plasma.

**Etch Step 1:** The plasma gas is then switched to $SF_6$ to create a plasma chemistry that isotropically etches silicon. Through the application of a d.c. bias to the platen, ions from the plasma bombard the surface of the wafer, removing the polymer. Increased ion energy in the vertical direction results in a much higher rate of removal of fluorocarbon polymer from surfaces parallel to the wafersurface.

**Etch Step 2:** Following selective polymer removal, the silicon surface at the base of the trench is exposed to reactive fluorine-based species that isotropically etch the unprotected silicon. The remaining fluorocarbon polymer protects the vertical walls of the trench from etching.
## Common Plasma Etchants

### Table 6-4 Plasma etchants for common microelectronic materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Common etch gases†.‡</th>
<th>Dominant reactive species</th>
<th>Product vapor pressure (torr at 25°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>Chlorine-containing</td>
<td>Cl, Cl₂</td>
<td>AlCl₃, 7 × 10⁻⁵</td>
</tr>
<tr>
<td>Copper</td>
<td>(Forms only low-pressure compounds)</td>
<td></td>
<td>CuCl₂, 5 × 10⁻²</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>Fluorine-containing</td>
<td>F</td>
<td>MoF₆, 530</td>
</tr>
<tr>
<td>Polymers of carbon</td>
<td>Oxygen</td>
<td>O</td>
<td>H₂O, 26</td>
</tr>
<tr>
<td>Silicon</td>
<td>Fluorine- or chlorine-containing</td>
<td>F, Cl, Cl₂</td>
<td>SiF₄, &gt; 1 atm</td>
</tr>
<tr>
<td>SiO₂</td>
<td>CF₄, CHF₃, C₂F₆, C₃F₆</td>
<td>CF₄</td>
<td>SiCl₄, 240</td>
</tr>
<tr>
<td>Tantalum</td>
<td>Fluorine-containing</td>
<td>F</td>
<td>TaF₃, 3</td>
</tr>
<tr>
<td>Titanium</td>
<td>Fluorine- or chlorine-containing</td>
<td>F, Cl, Cl₂</td>
<td>TiF₄, sublimes at low pressure</td>
</tr>
<tr>
<td>Tungsten</td>
<td>Fluorine-containing</td>
<td>F</td>
<td>TiF₃, &lt; 10⁻³</td>
</tr>
</tbody>
</table>

† Common chlorine-containing gases are BCl₃, CCl₄, Cl₂, and SiCl₄.
‡ Common fluorine-containing gases are CF₄, SF₄, and SF₆.

Superhydrophobic/Self-Cleaning Coatings

Hydrophilic

Hydrophobic
What does “Superhydrophobicity” mean?

**Hydrophilic Surface:**
Water Contact Angle $< 90^\circ$

**Hydrophobic Surface:**
Water Contact Angle $> 90^\circ$

**Superhydrophobic Surface:**
Water Contact Angle $> 150^\circ$
Water Contact Angle Measurement
Measure Water Contact Angle

Angles: [140.40°, 140.50°]
Lotus Effect: Water Contact Angle > 150°

Factors affect lotus effect:
- Hydrophobic surface
- High surface roughness

Young's Law: (Hydrophobic/ Hydrophilic Flat Surface)
\[
\cos \theta_V = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}
\]

Cassie's Law: (Hydrophobic Rough Surface)
\[
\cos \theta_c = f \cdot \left( \cos \theta_V + 1 \right) - 1
\]

\( f \): Solid Projected Area Fraction
\[
f = \frac{9a^2}{b^2}
\]
Superhydrophobic Coating Technologies

**Top-Down Method**
- Focus Ion Beam Etching
- Lithographic Patterning
- Reactive Ion Etching


**Bottom-Up Method**
- Multilayer Deposition Method
- Spin-coating Tech.
- Langmuir-Blodgett Method

Yang, H. et al, Submitted (2014)
Cassie's Law

$$\cos \theta_c = f \cdot (\cos \theta_y + 1) - 1$$

Fabrication Procedure

1. RIE (P=40mT, O₂=40, RF=100)
2. Wash by HF Sol. (2%)
3. Surface Modification
4. Fluorosilane

Silica
ETPTA
Silicon Wafer

What does “Self-Cleaning” mean?

Sliding Angle

\[ \text{Sliding Angle} = \text{Advancing Angle} - \text{Receding Angle} \]
Self-Cleaning Surface

Sliding Angle = Advancing Angle - Receding Angle

Advancing Angle 154° Receding Angle 149°
Self-Cleaning Property

**Flat ETPTA**

**Surface-Modified Flat ETPTA**

**Surface-Modified Macroporous ETPTA (0 Sec RIE)**

**Surface-Modified Macroporous ETPTA (30 Sec RIE)**

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**Spray Escherichia coli-ampicillin Solution**

**Offer an Inclining Angle of 5°**

**Submerge in LB Broth Medium Respectively**

**Culture at 37°C for 24 Hours Respectively**

**Account the CFU of E. coli in the LB Broth Agar Medium Respectively**

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![Graph showing Bacterium Culture (CFU)](image)

- **0 Sec RIE**
- **30 Sec RIE**

- **Flat ETPTA**
- **Surface-Modified Flat ETPTA**
- **Surface-Modified Macroporous ETPTA (0 Sec RIE)**
- **Surface-Modified Macroporous ETPTA (30 Sec RIE)**
Applications of Self-Cleaning Surface