Lecture 6

Week 3, 2nd lecture

Lithography

Optical, E-beam and x-ray
Concept of mask transfer for IC fabrication

- Quartz plate
- Chromium pattern to block light

The wafer is coated with photosensitive resist, exposed and then developed and rinsed
Process sequence of a typical lithographic process.

Note that for a Pentium chip, about 80 iterations of this sequence must be undertaken.
Definition of positive and negative resist: Positive resist dissolves when exposed with radiation, whereas negative resist stays.

Description of some of the terminology for alignment of masks. The critical dimension is the desired dimension on the sample.
Three commonly used methods for exposing resists: contact printing often wears out the masks, and both contact and proximity printing need mask features equal to the sample features.

Projection printing allows a 5:1 or 10:1 reduction of the feature sizes from mask to sample.

The light source can also be an excimer (fluoride) laser (ArF or KrF).

This lens may contain many (100) elements.

Throughput = 20 wafers/hour.

U-V photolithography relies mainly on 5:1 or 10:1 steppers like this one.

For research applications with odd shaped samples, contact aligners are sometimes used.
Diffraction effects will be different for proximity and projection exposure methods. Phase shift masks are used so the projection printing intensity profile becomes more square.
Resist coverage over nonplanar substrates:

The interference pattern which is built up at the reflecting wafer surface will result in high and low field regions in the resist. This results in the resist being non-uniformly exposed in the vertical direction. The photoresist develops in "steps".
Typically, the resist is chosen for resolution and contrast.
Adhesion promoter: This is a material which helps the surface bonding between photoresist and substrate. Typically, a good adhesion promoter minimizes delamination during further processing like wet etching etc.

Immersion Lithography for ever-smaller features
Vector-scanned electron beam lithography is the highest resolution lithography method presently available. Resolution below 10 nm is obtainable with this technique, since the wavelength of electrons is much shorter than the wavelength of light.

Similar to a CRT tube, except with much smaller spot size.
Claudius Ptolemy 2nd Century BC describes light refraction

Salvino D’Armate 12th Century

1590 - Two Dutch spectacle makers, Zacharias Jansen and his father Hans started experimenting by mounting two lenses in a tube, the first compound microscope.

1609 - Galileo Galilei develops a compound microscope with a convex and a concave lens.

1665 - Robert Hooke's book called Micrographia officially documented a wide range of observations through the microscope.

1674 - Anton van Leeuwenhoek used his knowledge of grinding lenses to achieve greater magnification which he utilized to make a microscope, enabling detailed observations to be made of bacteria.

A brief History of the Microscope

1826 - Joseph Jackson Lister created an achromatic lens to eradicate the chromatic effect caused by different wavelengths of light.

1860s - Ernst Abbe discovers the Abbe sine condition (a condition that must be fulfilled by a lens or other optical system in order for it to produce sharp images), a breakthrough in microscope design, which was until then largely based on trial and error.

1931 - Ernst Ruska starts to build the first electron microscope.
Evolution of Microscopes

Electron Microscopes

Ruska, Borries
Electron Lenses:
Electromagnetic Lens

Electrostatic lens
Vector-scanned electron beam lithography

A focused electron beam is scanned over the sample to define small lithographic patterns.

Problems with low throughput

Electron beam lithography
Polymethylmethacrylate or plexi-glass is a common high contrast positive e-beam resist

Difference between positive and negative electron beam resists: The dose, given in Coulombs/cm² determines the ultimate speed at which the pattern can be written
Nanostructures

Comparison of the resolution and sensitivity of some electron beam resists. Notice that the linewidth has shrunk to 0.01 microns by now.
Concept of “proximity effect”. Secondary electrons and backscattered electrons from a beam-written feature can expose features close to the beam. This leads to problems in dense patterns.

No secondary electrons expose the ends and the exposure dose is low

Too many secondary electrons expose inside corners of patterns

Here is a result of the problems caused by “proximity effects”.
Schematic of the SCALPEL process (Lucent)

A high voltage electron beam is transmitted through a silicon nitride membrane with high mass/thickness contrast features to form a shaped electron beam.

TEM Projection Lithography
SCALPEL projector design

Electromagnetic lenses project the features from the mask onto the sample.

Lens distortion limits the maximum field of exposure.

High voltages are needed to avoid chromatic aberration.

X-ray lithography
Simple high-energy x-ray lithography system. In many ways, this resembles an optical contact mask aligner.

The Be window is used to allow x-rays to pass through from the Pd target in the vacuum.

He is added between sample and window for minimum scattering.

Geometric considerations for proximity x-ray exposure system.
X-ray resists are very similar to electron beam resists. PMMA is a common x-ray resist, too.

Table 1 Properties of a few x-ray resists†

<table>
<thead>
<tr>
<th>Resist</th>
<th>Tone</th>
<th>Major Abs elements</th>
<th>λ</th>
<th>Sensitivity (mJ/cm^2)</th>
<th>Resolution (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>COP</td>
<td>(−)</td>
<td>0</td>
<td>4.37 Å Pd_Lα</td>
<td>175</td>
<td>1.0</td>
</tr>
<tr>
<td>PBS</td>
<td>(+)</td>
<td>S</td>
<td>4.37 Å Pd_Lα</td>
<td>94</td>
<td>0.5</td>
</tr>
<tr>
<td>PMMA</td>
<td>(+)</td>
<td>0</td>
<td>8.34 Å Al_Kα</td>
<td>600–1000</td>
<td>&lt;0.1</td>
</tr>
</tbody>
</table>

†After Taylor, Ref. 27.

It is desirable for the x-rays to be absorbed strongly in Au and PMMA, but not in the Be window and the atmosphere.

Fig. 19 Absorption coefficients of PMMA, Be, Si, and Au in the x-ray wavelength range used in x-ray lithography. (After Spiller and Feder, Ref. 28.)
Addition of organometallic materials to the resist make the x-ray resists more sensitive, since more x-rays get absorbed in these materials.

In this schematic, the process sequence of a surface enhanced resist is shown. In such a resist, the surface is selectively made more resistant to a later oxygen etch. Another common method to do this is by “surface silation” or diffusion of silicon into the unexposed regions of the resist.

The down side of proximity x-ray lithography: a very thin x-ray transparent mask has to be constructed with features which efficiently absorb x-rays. The feature height (0.6 microns) here severely limits the minimum lateral feature size which can be exposed.

**Fig. 21** An x-ray mask. (After Maydan, Ref. 25.)
Concept of multilevel resist which can be used for planarization. This becomes extremely important as the depth of focus is reduced in modern Deep-UV optical lithography.

Fig. 23 Schematic of a multilevel resist system. (After Lin et al., Ref. 35.)

Concept of an inorganic resist. GeSe used to be a popular self-developing resist.

Fig. 24 (After Yoshikawa et al., Ref. 36.)
Application ranges of different lithography systems: Note that resolution and throughput will make you choose an exposure method.

EUV lithography

A soft x-ray beam is projected through several reflective x-ray mirrors onto the sample. (4:1 reduction)

A very high brightness x-ray beam is needed to compensate for absorption losses.
Mask inspection and repair are still unresolved problems.
Beam path of EUV systems

Recent progress in high power lasers \(\Rightarrow\) LPP-based sources,

At the SEMATECH workshop, 12 suppliers and R&D groups described the readiness and development plans of three types of high power laser systems designed to bombard tin to produce EUV light.

Pulsed CO2 lasers generate the most power (7 kilowatts), but are still being developed and have not been subjected to continuous operation.

Nd:YAG laser modules with 1500 W power capable of continuous operation are already available as commercial products, with 3000 W modules in development. (Nd:YAG systems utilize a neodymium yttrium aluminum garnet crystal as the lasing medium.)

Fiber-based lasers require less electricity, cost less and can be easily scaled but are also less developed than CO2 and Nd:YAG lasers.

Although each of these LPP-based approaches falls short of the 10-20 kilowatts of laser power that will be needed for commercial EUV scanners, the necessary wattage can be obtained by “multiplexing” less powerful systems.
### EUV lithography development

<table>
<thead>
<tr>
<th>Available Year</th>
<th>EUV Tool</th>
<th>Resolution</th>
<th>Throughput</th>
<th>Dose, Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>2006</td>
<td>ADT</td>
<td>32 nm</td>
<td>4 WPH</td>
<td>5 mJ/cm², ~8W</td>
</tr>
<tr>
<td>2010</td>
<td>NXE:3100</td>
<td>27 nm</td>
<td>60 WPH</td>
<td>10 mJ/cm², &gt;100W</td>
</tr>
<tr>
<td>2012</td>
<td>NXE:3300B</td>
<td>22 nm</td>
<td>125 WPH</td>
<td>15 mJ/cm², &gt;250W</td>
</tr>
<tr>
<td>2013</td>
<td>NXE:3300C</td>
<td>Depends on resist diffusion length</td>
<td>150 WPH</td>
<td>15 mJ/cm², &gt;350W</td>
</tr>
</tbody>
</table>

### EUV system
ASML
EUV on track
for commercial use

CYMER
Extreme Ultraviolet (EUV)
Lithography Light Sources
Working Principle of ELIPS

**Focussing Condition:**

\[ 1 - \frac{\pi}{Bd} \sqrt{\frac{2mV}{\epsilon}} = \sqrt{\frac{V}{c \cos \alpha}} \]

**Figure 1. The ELIPS principle**

Specimen Holder Geometry

**Figure 4. Sample and mask holder assembly of ELIPS**
Electron Image Projection without Magnetic Field

Electron Image Projection Lithography

Projected pattern

Mask pattern

Projected image of Caltech logo
Figure 5. Prototype ELIPS vacuum system

The sample is transferred into the high magnetic field of a warm bore NMR magnet and the pattern is projected from below using a Hg light source.

Electron Image Projection System (ELIPS) operation

- Magnetically coupled feedthrough
- Load-lock
- Turbo-pump
- High-field Magnet
Test Gratings of Au on Silicon Substrates.

We have demonstrated 90 nm resolution.

Ion Etched Test Structures on ELIPS patterned Si

Optical Gratings

Magnetic Media
Nanoimprint Lithography

A mold is pressed into a resist to form the pattern

Unresolved questions:
Uniformity over large areas?
Wear of die?

Epitaxial Deposition
I. CVD deposition processes: Si epitaxy

CVD: Chemical Vapor Deposition

Epitaxy: from Greek *epi* (upon) *taxis* (ordered)

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Boundary layer formation in a horizontal Si CVD reactor

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Two approaches to epitaxial growth: CVD and MBE.

In CVD a gas is flowed over a crystalline “seed” substrate, whereas in MBE an evaporation is used.

Discrete BJTs were made in bulk wafers, but the resulting excessive collector resistance limited high-frequency response.

Solved by epitaxial growth of high-R layer on low-R substrate.

Two fundamental advantages of epitaxial over bulk wafers:
1. One or more epi layers allows control over doping profile.
2. Physical properties of epi layer are different from bulk (generally O<sub>2</sub> and C-free.)
Isotherms in a CVD reactor

Influence of Reynolds number on the deposition uniformity

\[ R_e = \frac{D_r \cdot v}{\mu} \]

Diameter gas velocity viscosity
Gas density

CVD reaction to deposit Si from silicon tetrachloride/hydrogen

\[ \text{SiCl}_4 \text{(gas)} + 2\text{H}_2 \text{(gas)} \Rightarrow \text{Si(solid)} + 4\text{HCl(gas)} \]

However, the overall reaction is more complicated

\[
\begin{align*}
\text{SiCl}_4 + \text{H}_2 & \quad \leftrightarrow \quad \text{SiHCl}_3 + \text{HCl} \\
\text{SiHCl}_3 + \text{H}_2 & \quad \leftrightarrow \quad \text{SiH}_2\text{Cl}_2 + \text{HCl} \\
\text{SiH}_2\text{Cl}_2 & \quad \leftrightarrow \quad \text{SiCl}_2 + \text{H}_2 \\
\text{SiHCl}_3 & \quad \leftrightarrow \quad \text{SiCl}_2 + \text{HCl} \\
\text{SiCl}_2 + \text{H}_2 & \quad \leftrightarrow \quad \text{Si} + 2\text{HCl}
\end{align*}
\]
Temperature variation of the equilibrium gas phase composition at 1 atm and Cl/H = 0.01

At different temperatures, different species are stable and the composition of the gas changes.

Species detected by IR spectroscopy in a real reactor containing silicon tetrachloride and hydrogen.
Note that the growth rate depends on temperature and the gas source used.

CVD layer growth rate of Si versus temperature. Note that it is negative at low and high temperatures.

Schematic image of the CVD process showing the influence of the addition of arsine for doping Si.
Gas reaction for arsine gas used to dope Si layers

\[ 2\text{AsH}_3\text{(solid)} \rightarrow 2\text{As(gas)} + \text{H}_2\text{(gas)} \]
\[ \rightarrow 2\text{As(solid)} \rightarrow 2\text{As}^+\text{(solid)} + 2e \]

The influence of the growth rate on the Arsenic concentration in the layer
The layer can also be unintentionally doped by dopants which are in the substrate. These can volatilize and redeposit in the new layer which is grown.

Radiant-heated barrel reactor

Three common susceptor shapes
Susceptor geometries which are commonly used in CVD reactors.

It does not pay to be too impatient…

Maximum growth rate for which monocrystalline silicon can be obtained as a function of temperature.

<table>
<thead>
<tr>
<th>Chemical deposition</th>
<th>Nominal growth rate (μm/min)</th>
<th>Temperature range (°C)</th>
<th>Allowed oxidizer level (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiCl₄</td>
<td>0.4–1.5</td>
<td>1150–1250</td>
<td>5–10</td>
</tr>
<tr>
<td>SiH₄Cl₂</td>
<td>0.4–2.0</td>
<td>1100–1200</td>
<td>5–10</td>
</tr>
<tr>
<td>SiH₂Cl₂</td>
<td>0.4–3.0</td>
<td>1050–1150</td>
<td>&lt;5</td>
</tr>
<tr>
<td>SiH₆</td>
<td>0.2–0.3</td>
<td>950–1050</td>
<td>&lt;2</td>
</tr>
</tbody>
</table>
MOLECULAR BEAM EPITAXY

\[ L = 5 \times 10^{-3} / p \]

Pressure in Torr

Mean free path in cm

MBE allows integration of analytical techniques into the system for in-situ monitoring.
Flux of various dopant species versus oven temperature

The defect density of the MBE grown layers depends on the background pressure used.

This means that the system has to be pumped down very well.
The defect density also depends on the growth temperature used.

A interesting fact about silicon is that the refractive index changes significantly when the material is heavily doped… free carrier absorption?
II. Dielectric deposition techniques:

For poly-silicon films we can use this simple reaction (pyrolyzing silane) at 600-650 degrees C in a low-pressure reactor

$$\text{SiH}_4 \rightarrow \text{Si} + 2\text{H}_2$$

<table>
<thead>
<tr>
<th>Product</th>
<th>Reactants</th>
<th>Deposition temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon dioxide</td>
<td>$\text{SiH}_4 + \text{CO}_2 + \text{H}_2$</td>
<td>850–950</td>
</tr>
<tr>
<td></td>
<td>$\text{SiCl}_2\text{H}_2 + \text{N}_2\text{O}$</td>
<td>850–900</td>
</tr>
<tr>
<td></td>
<td>$\text{SiH}_4 + \text{N}_2\text{O}$</td>
<td>750–850</td>
</tr>
<tr>
<td></td>
<td>$\text{SiH}_4 + \text{NO}$</td>
<td>650–750</td>
</tr>
<tr>
<td></td>
<td>$\text{SiOC}_2\text{H}_5\text{H}_4$</td>
<td>650–750</td>
</tr>
<tr>
<td></td>
<td>$\text{SiH}_4 + \text{O}_2$</td>
<td>400–450</td>
</tr>
<tr>
<td>Silicon nitride</td>
<td>$\text{SiH}_4 + \text{NH}_3$</td>
<td>700–900</td>
</tr>
<tr>
<td></td>
<td>$\text{SiCl}_2\text{H}_2 + \text{NH}_3$</td>
<td>650–750</td>
</tr>
<tr>
<td>Plasma silicon nitride</td>
<td>$\text{SiH}_4 + \text{NH}_3$</td>
<td>200–350</td>
</tr>
<tr>
<td></td>
<td>$\text{SiH}_4 + \text{N}_2$</td>
<td>200–350</td>
</tr>
<tr>
<td>Plasma silicon dioxide</td>
<td>$\text{SiH}_4 + \text{N}_2\text{O}$</td>
<td>200–350</td>
</tr>
<tr>
<td>Polysilicon</td>
<td>$\text{SiH}_4$</td>
<td>600–650</td>
</tr>
</tbody>
</table>
These are some geometries which are suitable for CVD deposition.

Sometimes it is desirable to deposit in a plasma, and this is then called PE-CVD. This method generates very high quality films.
The downside to CVD deposition of materials:

Table 2 Properties of common gases used in CVD

<table>
<thead>
<tr>
<th>Gas</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silane</td>
<td>Toxic, flammable, pyrophoric</td>
</tr>
<tr>
<td>Dichlorosilane</td>
<td>Toxic, flammable, corrosive</td>
</tr>
<tr>
<td>Phosphine</td>
<td>Very toxic, flammable</td>
</tr>
<tr>
<td>Diborane</td>
<td>Very toxic, flammable</td>
</tr>
<tr>
<td>Arsine</td>
<td>Very toxic, flammable</td>
</tr>
<tr>
<td>Hydrogen chloride</td>
<td>Toxic, corrosive</td>
</tr>
<tr>
<td>Ammonia</td>
<td>Toxic, corrosive</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>Nontoxic, flammable</td>
</tr>
<tr>
<td>Oxygen</td>
<td>Nontoxic, supports combustion</td>
</tr>
<tr>
<td>Nitrous oxide</td>
<td>Nontoxic, nonflammable</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>Usually inert</td>
</tr>
<tr>
<td>Argon</td>
<td>Inert</td>
</tr>
</tbody>
</table>

Arrhenius plot for polysilicon deposition shows the partial pressure dependence of the growth rate.

\[ \text{SiH}_4 \rightarrow \text{Si} + 2\text{H}_2 \]
Deposition of Silicon dioxide by CVD

Note: This reaction can be done at a low enough temperature so that SiO₂ can be deposited after aluminum metallization.

\[
\text{SiH}_4 + \text{O}_2 \rightarrow \text{SiO}_2 + 2\text{H}_2
\]

\[
4\text{PH}_3 + 5\text{O}_2 \rightarrow 2\text{P}_2\text{O}_5 + 6\text{H}_2
\]

Often, phospho-silicate glasses (PSG) are deposited to planarize devices and to protect circuits from degradation. This is because such glasses have a low melting temperature.

\[
\text{Si(OC}_2\text{H}_5)_4 \rightarrow \text{SiO}_2 + \text{by-products}
\]

Tetraethoxysilane (TEOS) deposition is normally done at 650-750 C (provides excellent uniformity and conformal step coverage).

\[
\text{SiCl}_2\text{H}_2 + 2\text{N}_2\text{O} \rightarrow \text{SiO}_2 + 2\text{N}_2 + 2\text{HCl}
\]

Dichlorosilane deposition is done at 900 C.

PSG (phosphosilicate glass) is a very popular material for semiconductor processing. It is a mixture of SiO₂ and P₂O₅:

Any amount of P₂O₅ can be incorporated into SiO₂.

Si becomes more hygroscopic as P₂O₅ content is increased.

The P₂O₅ content is usually 2-8 wt%.

For undoped SiO₂, the built-in stress is 3x10⁸ N/m² (tensile).

For 2 wt% P₂O₅, the stress is close to 0.

The thermal expansion coefficient of PSG can also be altered with the composition of phosphorus. PSG can be designed to thermally match the underlying Si substrate.

PSG is sometimes used as a phosphorus doping source for semiconductor doping.
Oxygen can be used to surface-catalyze the deposition reaction.

The deposition temperature strongly influences the deposition rate, since it determines how efficiently the source material is decomposed.
Good step coverage of the deposited oxide is very desirable to avoid short circuits and high electric field regions in the circuit. Mostly, step coverage of the sidewalls is used to characterize the deposition quality.

Fig. 13 Step coverage of deposited films. (a) Conformal coverage resulting from rapid surface migration. (b) Nonconformal step coverage for long mean-free path and no surface migration. (c) Nonconformal step coverage for short mean-free path and no surface migration.

Scanning electron micrographs of 4.6 wt% P-glass annealed in steam at 1100 C for:
- 0 minutes
- 20 minutes
- 40 minutes
- 60 minutes

3200X magnification
The quality of the silicon dioxide depends on the deposition reaction, and the temperature. Notice that the dielectric strength and the etch resistivity are highest for high-temperature deposited oxides.

Table 3 Properties of deposited silicon dioxide

<table>
<thead>
<tr>
<th>Deposition</th>
<th>Plasma</th>
<th>SiH₄ + O₂</th>
<th>TEOS</th>
<th>SiCl₂H₃ + N₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>200</td>
<td>450</td>
<td>700</td>
<td>900</td>
</tr>
<tr>
<td>Composition</td>
<td>SiO₂_H(H)</td>
<td>SiO₂(H)</td>
<td>SiO₂</td>
<td>SiO₂(Cl)</td>
</tr>
<tr>
<td>Step coverage</td>
<td>Nonconformal</td>
<td>Nonconformal</td>
<td>Conformal</td>
<td>Conformal</td>
</tr>
<tr>
<td>Thermal stability</td>
<td>Looses H</td>
<td>Densifies</td>
<td>Stable</td>
<td>Looses Cl</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>2.3</td>
<td>2.1</td>
<td>2.2</td>
<td>2.2</td>
</tr>
<tr>
<td>Refractive index</td>
<td>1.47</td>
<td>1.44</td>
<td>1.46</td>
<td>1.46</td>
</tr>
<tr>
<td>Stress (10⁴ dyn/cm²)</td>
<td>3C-3T</td>
<td>3T</td>
<td>1C</td>
<td>3C</td>
</tr>
<tr>
<td>Dielectric strength</td>
<td>3–6</td>
<td>8</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Etch rate (Å/min)</td>
<td>400</td>
<td>60</td>
<td>30</td>
<td>30</td>
</tr>
</tbody>
</table>

Silicon nitride deposition by CVD

Silane/ammonia reactions are commonly used between 700 °C and 900 °C. Silane can also be replaced by dichlorosilane.

\[
3\text{SiH}_4 + 4\text{NH}_3 \rightarrow \text{Si}_3\text{N}_4 + 12\text{H}_2
\]

\[
3\text{SiCl}_2\text{H}_2 + 4\text{NH}_3 \rightarrow \text{Si}_3\text{N}_4 + 6\text{HCl} + 6\text{H}_2
\]
Resistivity of the plasma silicon nitride versus composition. Note that the higher silicon content layers are more conductive.
Some plasma-assisted CVD reactions:

SiO$_2$ is formed from silane and nitrous oxide in an argon plasma

Si$_3$N$_4$ is formed by reacting silane and ammonia in an argon plasma or by reacting silane in a nitrogen discharge

\[
\begin{align*}
\text{SiH}_4 + 4\text{N}_2\text{O} & \rightarrow \text{SiO}_2 + 4\text{N}_2 + 2\text{H}_2\text{O} \\
\text{SiH}_4 + \text{NH}_3 & \rightarrow \text{SiNH} + 3\text{H}_2 \\
2\text{SiH}_4 + \text{N}_2 & \rightarrow 2\text{SiNH} + 3\text{H}_2
\end{align*}
\]

Summary of CVD deposition techniques and their advantages and problems

<table>
<thead>
<tr>
<th>Deposition properties</th>
<th>Atmospheric-pressure CVD</th>
<th>Low-temperature LPCVD</th>
<th>Medium-temperature LPCVD</th>
<th>Plasma-assisted CVD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature ($^\circ$C)</td>
<td>300—500</td>
<td>300—500</td>
<td>500—900</td>
<td>100—350</td>
</tr>
<tr>
<td>Materials</td>
<td>SiO$_2$, P-glass</td>
<td>SiO$_2$, P-glass</td>
<td>Poly-Si, SiO$_2$, P-glass</td>
<td>SiN, SiO$_2$</td>
</tr>
<tr>
<td>Uses</td>
<td>Passivation, insulation</td>
<td>Passivation, insulation</td>
<td>Gate metal, insulation, passivation</td>
<td>Passivation, insulation</td>
</tr>
<tr>
<td>Throughput</td>
<td>High</td>
<td>High</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Step coverage</td>
<td>Poor</td>
<td>Poor</td>
<td>Conformal</td>
<td>Poor</td>
</tr>
<tr>
<td>Particles</td>
<td>Many</td>
<td>Few</td>
<td>Few</td>
<td>Many</td>
</tr>
<tr>
<td>Film properties</td>
<td>Good</td>
<td>Good</td>
<td>Excellent</td>
<td>Poor</td>
</tr>
<tr>
<td>Low temperature</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
</tr>
</tbody>
</table>
Summary:

APCVD is a simple process, has relatively poor step coverage, and suffers from contamination problems. It is usually used to deposit low-T oxides.

LPCVD provides excellent purity and uniformity oxides, can be used on large wafers, has a low deposition rate and requires high temperatures.

PECVD provides low-temperature, fast deposition and good step coverage. It sometimes suffers from chemical contamination, and often is used for low-temperature insulator deposition.

Thermal oxidation of Silicon: This is one of the most thoroughly studied materials systems in the world.

Silicon can be oxidized either using molecular oxygen or water vapor:

\[ \text{Si(solid)} + \text{O}_2 \rightarrow \text{SiO}_2\text{(solid)} \]
\[ \text{Si(solid)} + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2\text{(solid)} + 2\text{H}_2 \]

Silicon dioxide: \( E_g = 8 \text{eV} \)
Density: 2.27 g/cm\(^3\)
Resistivity: \(10^{14} - 10^{15} \text{ ohm.cm} \)
Etch rate in Buffered HF: 100 nm/min
Refractive index: 1.46
Melting point: 1700 C

\[ \Delta H_f = 210 \text{ kcal/mole} \]
\[ = 1 \text{eV/molecule} \]
As the oxide layer grows, it consumes some of the silicon from the surface of the wafer. In fact, for an oxide of thickness $d$, a layer of silicon $0.44d$ thick is consumed.

Si oxidation fluxes $F_1$, $F_2$, $F_3$. These should be equal at equilibrium, and the rate of oxidation is limited by the slowest of the three.
The gas phase flux can be linearly approximated by assuming that the flux of oxidant from the gas phase at the gas/oxide interface is proportional to the difference between the oxidant concentration in the bulk of the gas $C_G$ and the oxidant concentration adjacent to the oxide surface $C_s$.

\[ F_1 = h_G (C_G - C_s) \]

Gas-phase mass transfer coefficient

Henry’s law constant = H

Equilibrium concentration in the oxide at the outer surface

The equilibrium bulk concentration of the oxide

C* = oxidant which would be in equilibrium with partial pressure of gas. The driving force for the reaction is $C^* - C_0$

**Derivation of F1:**

\[ C_0 = H_p \]

Equilibrium oxidizing species concentration in the oxide to that in the gas phase is

Partial pressure of oxygen adjacent to the oxide surface

Partial pressure of oxygen in the bulk of the gas

F1: Reaction at the surface of the SiO$_2$/gas interface

We use Henry’s law along with the ideal gas law to rewrite $C_G$ and $C_s$

\[ C_G = \frac{p_G}{kT} \]
\[ C_s = \frac{p_s}{kT} \]

Therefore, combining all of the equations

\[ F_1 = h (C^* - C_0) \]

Gas-phase mass transfer coefficient in terms of the concentration in the solid

Where $h = h_G/H_kT$
F2: Diffusion of oxygen through the oxide layer

\[ F_2 = -D \frac{dC}{dd} \]

This is just the diffusion flux resulting from the concentration gradient in the oxide

F3: Reaction at the SiO2/Si interface to form new oxide

We can assume that the reaction speed for oxidation of Si is proportional to \( C_i \)

\[ F_3 = k_s C_i \]

Chemical rate constant for reaction
When we set $F_1=F_2=F_3$, we can solve simultaneous equations and obtain expressions for $C_i$ and $C_0$:

$$C_i = \frac{C^*}{1 + \frac{k_s}{h} + \frac{k_s d_0}{D}}$$

$$C_0 = \frac{C^*}{1 + \frac{k_s d_0}{D}}$$

Several possibilities could occur:

a. When the diffusivity is very small, $C_i \approx 0$ and $C_0 \approx C^*$. This is the diffusion-controlled case. $F = DC_0k_s/(D+k_s d)$

b. When $D$ is large, $C_i = C_0 = C^*/(1+k_s/h)$ and this is the reaction-controlled case.

Now let us assume that $N_1$ is the number of oxidant molecules incorporated into a unit volume of the oxide layer. Since the oxide has $2.2 \times 10^{22}$ SiO$_2$ molecules/cm$^3$ and one O$_2$ is incorporated into each SiO$_2$ molecule, whereas 2 H$_2$O molecules are incorporated into each SiO$_2$ molecule, $N_1$ equals $2.2 \times 10^{22}$ cm$^{-3}$ for dry oxygen and twice this number for water-vapor oxidation.

The flux of oxidants reaching the oxide-silicon interface:

$$N_1 \frac{dd_0}{dt} = F_3 = \frac{k_s C^*}{1 + \frac{k_s}{h} + \frac{k_s d_0}{D}}$$

Solution to this differential equation

$$A = 2D \left[ \frac{1}{k_s} + \frac{1}{h} \right]$$

$$B = \frac{2DC^*_s}{N_1}$$

The shift in the time coordinate to account for the presence of the initial oxide layer $d$:

$$\tau = \frac{d^2 + Ad_0}{B}$$
The thickness of oxide as a function of time:

For $t \gg \tau$:
(parabolic rate)

$$d_0^2 = Bt$$

For short oxidation times when $(t+\tau) \ll A^2/4B$: (rate is linear)

$$d_0 = \frac{B}{A}(t + \tau)$$

$$\frac{B}{A} = \left( \frac{k_2 h}{k_1 + h} \right) \left[ \frac{C}{N_1} \right]$$

The effect of temperature on the linear rate constant $B/A$ in microns/hr.

### Table 3 $C^*$ values in SiO$_2$ at 1000°C

<table>
<thead>
<tr>
<th>Species</th>
<th>$C^*$ (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_2$</td>
<td>$5.2 \times 10^{16}$</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>$3.0 \times 10^{19}$</td>
</tr>
</tbody>
</table>
Oxide thickness versus oxidation time for several temperatures in dry oxygen
Note that this is a log/log plot.

Oxide thickness versus oxidation time for silicon in water vapor at 640 Torr (close to an atmosphere)

Typical values for A, B, for different temperatures and Si surface orientations are given here:

<table>
<thead>
<tr>
<th>Oxidation temperature (°C)</th>
<th>Orientation</th>
<th>A (µm)</th>
<th>B (µm²/h)</th>
<th>Linear rate constant B/A (µm/h)</th>
<th>B/A ratio (111)/(100)</th>
</tr>
</thead>
<tbody>
<tr>
<td>900</td>
<td>(100)</td>
<td>0.95</td>
<td>0.143</td>
<td>0.150</td>
<td>1.68</td>
</tr>
<tr>
<td></td>
<td>(111)</td>
<td>0.60</td>
<td>0.151</td>
<td>0.252</td>
<td></td>
</tr>
<tr>
<td>950</td>
<td>(100)</td>
<td>0.74</td>
<td>0.231</td>
<td>0.311</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(111)</td>
<td>0.44</td>
<td>0.231</td>
<td>0.524</td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>(100)</td>
<td>0.48</td>
<td>0.314</td>
<td>0.664</td>
<td>1.68</td>
</tr>
<tr>
<td></td>
<td>(111)</td>
<td>0.27</td>
<td>0.314</td>
<td>1.163</td>
<td></td>
</tr>
<tr>
<td>1050</td>
<td>(100)</td>
<td>0.295</td>
<td>0.413</td>
<td>1.400</td>
<td>1.75</td>
</tr>
<tr>
<td></td>
<td>(111)</td>
<td>0.18</td>
<td>0.415</td>
<td>2.307</td>
<td>1.65</td>
</tr>
<tr>
<td>1100</td>
<td>(100)</td>
<td>0.175</td>
<td>0.521</td>
<td>2.977</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(111)</td>
<td>0.105</td>
<td>0.517</td>
<td>4.926</td>
<td></td>
</tr>
</tbody>
</table>

Average 1.68
Effect of dopants on the oxidation rate: Typically, the reaction rates are increased when silicon is heavily doped.

**Case for Boron doped Si:**

![Graph showing oxidation rate for different dopant concentrations and temperatures.](attachment:image1.png)

*Fig. 6 Oxidation of boron-doped silicon in wet oxygen (95°C H₂O) as a function of temperature and concentration. (After Deal and Sklar, Ref. 28.)*

**Effect of Phosphorous dopants on the oxidation rate**

![Graph showing oxidation rate for different dopant concentrations and temperatures.](attachment:image2.png)

*Fig. 7 Oxidation of phosphorus-doped silicon in wet oxygen (95°C H₂O) as a function of temperature and concentration. (After Deal and Sklar, Ref. 28.)*
Boron and phosphorus increase the oxidation rate. Chlorine and HCl additions can change the oxidation rate:

\[ 2\text{HCl} + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{Cl}_2 \]

High pressure also increases the oxidation rate: Note that this oxidation is done at 20 atmospheres steam.

**Fig. 10** Oxidation thickness versus oxidation time for pyrogenic steam at 900°C for (100) and (111) silicon and pressures up to 20 atm. (After Raseok, Lie, and Deel, Ref. 40.)
Dependence of the oxidation rate constants on the temperature and pressure of steam

What happens when we oxidize a doped silicon surface? Dopants from the Si can redistribute themselves and either prefer the oxide or avoid it.

Table 7 Diffusion constants in SiO₂

<table>
<thead>
<tr>
<th>Dopants</th>
<th>Diffusion constants at 1100°C (cm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>3.4 × 10⁻¹⁷ to 2.0 × 10⁻¹⁴</td>
</tr>
<tr>
<td>Ga</td>
<td>5.3 × 10⁻¹¹</td>
</tr>
<tr>
<td>P</td>
<td>2.9 × 10⁻¹⁶ to 2.0 × 10⁻¹³</td>
</tr>
<tr>
<td>As</td>
<td>1.2 × 10⁻¹⁶ to 3.5 × 10⁻¹⁵</td>
</tr>
<tr>
<td>Sb</td>
<td>9.9 × 10⁻¹⁷</td>
</tr>
</tbody>
</table>

Note that the oxide is an excellent diffusion mask for B, but not for Gallium.
Typical charges in a thermally oxidized silicon. Note that Na and K are positive charges which can be incorporated into the oxide if care is not taken to clean the wafers before oxidation.

Note: HCl addition to oxides can passivate the oxide (i.e. traps and neutralizes positively charged ions)

Redistribution of impurities during oxidation:

We can define a segregation coefficient $m$, such that:

$$m = \frac{\text{equilibrium concentration of impurity in Si}}{\text{equilibrium concentration of impurity in oxide}}$$

When $m>1$, the oxide rejects the impurity

When $m<1$, the oxide concentrates the impurity

Even when $m=1$, redistribution can occur since the oxide/semiconductor interface is advancing into the Si substrate.

B has a $m < 1$  P has a $m > 1$
Impurity segregation at the Si/SiO$_2$ interface resulting from thermal oxidation.

(a) Diffusion in oxide is slow (Boron),

(b) Diffusion in oxide is fast (Boron)

(c) Diffusion in oxide is slow (Phosphorus)

(d) Diffusion in oxide is fast (Gallium)

Notice that boron likes to go into the oxide, whereas P dopants want to avoid it.

Fig. 15 Boron segregation coefficient as a function of temperature for dry, near dry, and wet oxidation (After Fair and Tsai, Ref. 56.)
The segregation coefficient \( m \) shows the equilibrium concentration of the impurity in silicon to that in the oxide at the interface. Most of the work on these coefficients has been done for Boron:

1. Pure dry \( O_2 \), orientation independent
   \[
   m_{\text{eff}} = 13.4 \exp \left( \frac{-0.33 \text{ eV}}{kT} \right)
   \]  
   (20)

2. Near dry or wet \( O_2 \)
   \[
   m_{110(001)} = 65.2 \exp \left( \frac{-0.66 \text{ eV}}{kT} \right)
   \]  
   \[
   m_{100(001)} = 104.0 \exp \left( \frac{-0.66 \text{ eV}}{kT} \right)
   \]  
   (21)  
   (22)

For phosphorous, arsenic, and antimony, where the dopant segregates into the silicon (pile-up), segregation coefficient values of approximately 10 are usually quoted, although higher values (up to 800 at 1050°C) have been determined for arsenic. With gallium, which diffuses rapidly in the oxide, a value of approximately 20 is given. 

Metallization
For low doping in a semiconductor, the contact resistance can be represented by:

$$R_c = \left[ \frac{\partial J}{\partial V} \right]_{V=0}^{-1}$$

At higher doping concentrations, the barrier width decreases, and tunneling becomes important:

$$R_c \approx \exp \left[ \frac{4\pi \sqrt{\varepsilon_{\text{Si}} m^*}}{\hbar} \left( \frac{\phi_B}{\sqrt{N_D}} \right) \right]$$

A*: Richardson constant

Measured and modeled contact resistance as a function of the donor concentration and barrier height
Barrier heights for several metal systems for both n- and p-type Silicon

<table>
<thead>
<tr>
<th>Contact material</th>
<th>$\phi_B$ (V) for n-type Si</th>
<th>$\phi_B$ (V) for p-type Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0.72</td>
<td>0.58</td>
</tr>
<tr>
<td>Cr</td>
<td>0.81</td>
<td>0.50</td>
</tr>
<tr>
<td>Mo</td>
<td>0.68</td>
<td>0.42</td>
</tr>
<tr>
<td>Ni</td>
<td>0.61</td>
<td>0.51</td>
</tr>
<tr>
<td>Pt</td>
<td>0.90</td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>0.50</td>
<td>0.61</td>
</tr>
<tr>
<td>W</td>
<td>0.67</td>
<td>0.45</td>
</tr>
<tr>
<td>CoSi</td>
<td>0.68</td>
<td></td>
</tr>
<tr>
<td>CoSi$_2$</td>
<td>0.64</td>
<td></td>
</tr>
<tr>
<td>IrSi</td>
<td>0.93</td>
<td></td>
</tr>
<tr>
<td>Ni$_2$Si</td>
<td>0.7—0.75</td>
<td></td>
</tr>
<tr>
<td>NiSi</td>
<td>0.66—0.75</td>
<td></td>
</tr>
<tr>
<td>NiSi$_2$</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>PdSi</td>
<td>0.84</td>
<td></td>
</tr>
<tr>
<td>Pd$_3$Si</td>
<td>0.72—0.75</td>
<td></td>
</tr>
<tr>
<td>TaSi$_2$</td>
<td>0.59</td>
<td></td>
</tr>
<tr>
<td>TiSi$_2$</td>
<td>0.60</td>
<td></td>
</tr>
<tr>
<td>WSi$_2$</td>
<td>0.65</td>
<td></td>
</tr>
</tbody>
</table>

Schematic view of an evaporator: The high vacuum pump may be a diffusion pump, an ion pump, a cryopump, or a turbopump

Note that substrates may be arranged on a hemispherical holder and rotated for even evaporation
Pump-down rate of a vacuum system:

If we assume that a vacuum station has a volume $V$ (in liters), and no leaks, and is equipped with a pump with speed $S$ (in liter/sec). $P$, the pressure at time $t$, is related to the pumping time by:

$$ P = P_0 \exp \left( \frac{-St}{V} \right) + \frac{Q}{S} \tag{4} $$

Here, $P_0$ is the initial pressure, and $Q$ is the outgassing rate of the vacuum system.

Note that after the initial pumping time, the second term dominates the vacuum pressure.

Thickness measurement and monitoring. If a microbalance is used to weigh the substrate before and after deposition, the increase in mass $m$ can be related to the thickness $t$ by:

$$ \text{Volume} = \frac{\Delta m}{\rho_D} = At $$

Most modern vacuum deposition systems have quartz microbalances right in the evaporation path to measure thickness during evaporation.

$$ t = \frac{\Delta m}{\rho_D A} $$

Density of the sample

Area of deposited sample
The Kinetic Theory of Gases:
This theory yields two concepts that are useful in vapor deposition:
The rate of bombardment of an exposed surface in a chamber is:

\[ N = (2\pi mkT)^{-\frac{1}{2}}p \]

Where \( N \) is the bombardment rate in molecules cm\(^{-2}\) s\(^{-1}\) for a gas of molecular mass \( m \) at temperature \( T \) in kelvins and pressure \( p \); Another way of writing this relationship is:

\[ N = 6.4 \times 10^{19} (MT)^{-\frac{1}{2}}p \]

The mean-free path can also be expressed:

\[ \lambda = \frac{kT}{p\pi m^{\frac{1}{2}}} \]

The fraction of total molecules not not suffering a collision while traveling distance \( d \) is:

\[ \frac{n}{n_0} = \exp(-d/\lambda) \]

The rate of evaporation of metal from a melt is estimated by the Hertz-Knudsen equation:

\[ N_e = (2\pi mkT)^{-\frac{1}{2}}p_e \]  \hspace{1cm} (11)

where \( N_e \) is the number of molecules per unit area per time, \( m \) is the molecular (atomic) mass, \( k \) is Boltzmann’s constant, \( T \) is the surface temperature in kelvins, and \( p_e \) is the equilibrium vapor pressure of the evaporant. This vapor pressure may be written as a rate of mass loss per unit area from the source:

\[ R = 4.43 \times 10^{-4} \left( \frac{M}{T} \right)^{\frac{1}{2}} p_e \hspace{1cm} \text{g/cm}^2\cdot\text{s} \]  \hspace{1cm} (12)

where \( M \) is the gram-molecular mass and \( p_e \) is in Pa. For example, \( p_e \) (Al) \( \approx 1.5 \) Pa at 1500 K.

The total loss \( R_T \) per unit time from the source may be found by integrating over the source area:

\[ R_T = \int R \, dA \]
The deposition rate can be determined from the geometry of the system and the source/sample distance.

\[
\frac{D}{D_0} = \left[ 1 + \left( \frac{L}{H} \right)^2 \right]^{-2}
\]

\[\cos \theta = \cos \phi = \frac{r}{2r_0}\]

\[D = \frac{R_f}{4\pi r_0^2}\]

Metallization sources:

1) Thermal evaporation from a W coil acting as support and heat source
2) E-beam evaporation source (note the magnetic field causes the electrons to curve
3) Inductively heated source
Problem with step coverage from a vapor deposition system with low surface mobility

Is is obviously very difficult to metallize onto structures which are undercut and still have good step coverage
Another method for metallization commonly used is sputter deposition: Here, we show a planar magnetron system, where the magnets are permanent or electromagnets. Note the selective erosion of the target.

Sputter deposition often provides more conformal sidewall coverage.

Views of lift-off cross-sections for (a) evaporated metal and (b) sputtered metal. Note that the high-shadowing features in evaporation and the undercut masks which must be used in sputtering.
Chemical Vapor Deposition for Metallization: Usually, we start with a gas source containing the metal (metalorganic), which breaks apart at the hot sample surface.

- Example: WF$_6$ can be broken down using three mechanisms:
  
  \[ \text{WF}_6 + \text{thermal energy} \rightarrow \text{W} + 3\text{F}_2 \]

  \[ \text{WF}_6 + 3\text{H}_2 \rightarrow \text{W} + 6\text{HF} \]

  \[ \text{WF}_6 + \text{plasma or optical energy} \rightarrow \text{W} + 3\text{F}_2 \]

  Note that low-pressure CVD provides excellent step coverage.

CVD reactions for typical refractory metals used in the semiconductor industry. Note the high temperatures needed for deposition:

\[ 2\text{MoCl}_5 + 5\text{H}_2 \xrightarrow{800^\circ C} 2\text{Mo} + 10\text{HCl} \]

\[ 2\text{TaCl}_5 + 5\text{H}_2 \xrightarrow{600^\circ C} 2\text{Ta} + 10\text{HCl} \]

\[ 2\text{TiCl}_5 + 5\text{H}_2 \xrightarrow{600^\circ C} 2\text{Ti} + 10\text{HCl} \]
Aluminum can be CVD deposited by using tri-isobutyl-aluminum:

\[
\text{[(CH}_3\text{)}_2\text{CH–CH}_2\text{]}_3\text{Al} \rightarrow \text{[(CH}_3\text{)}_2\text{CH–CH}_2\text{]}_2\text{AlH} \\
+ \text{(CH}_3\text{)}_2\text{C=CH}_2
\]

Followed by:

\[
\text{[(CH}_3\text{)}_2\text{CH–CH}_2\text{]}_2\text{AlH} \rightarrow \text{Al} + \frac{3}{2}\text{H}_2 \\
+ 2\text{(CH}_3\text{)}_2\text{C=CH}_2
\]

Simplified view of a low-pressure CVD reactor system. To obtain enhanced reactions, the furnace could be augmented with a plasma source or an intense light source.
The reason for Al spikes stem from the local dissolution of Si, which can occur generally in IC processing. The problem is very important in VLSI processing, where the spikes can alloy through shallow junctions of the order of 0.3 microns deep. One method to avoid spiking is to incorporate Si into the aluminum evaporant to match the equilibrium concentration at a follow-on process temperature.
Another way to avoid spiking is the use of noble silicide contacts which act as diffusion barriers.

Failure modes of metal layers: The layer morphology, and in particular the grain size, is very important in determining the conductor lifetime. Here the median lifetime $t(50\%)$ is plotted.
Electromigration failure of e-beam evaporated Al on polysilicon. (a) metal is on polysilicon (b) metal is etched to reveal the polysilicon.

Electromigration failure (a) S-gun magnetron-deposited Al-0.5wt%Cu and (b) in-source-evaporated Al-0.5% Cu.
 Median conductor lifetime versus linewidth for Al alloys deposited in three different ways

Silicides and intermetallics for gates and interconnections

S-gun deposition rate vs. power for Ta and Si

Sputter sources (magnetrons) and planetary system for co-sputter deposition
Properties of some common silicides which are used for contact materials

### Table 2 Silicide resistivities (300 K)

<table>
<thead>
<tr>
<th>Material</th>
<th>Starting form</th>
<th>Resistivity ($\mu\Omega$-cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiSi$_2$</td>
<td>Metal/polysilicon</td>
<td>13—16</td>
</tr>
<tr>
<td></td>
<td>Co-sputtered</td>
<td>25</td>
</tr>
<tr>
<td>ZrSi$_2$</td>
<td>Metal/polysilicon</td>
<td>35—40</td>
</tr>
<tr>
<td>HfSi$_2$</td>
<td>Metal/polysilicon</td>
<td>45—50</td>
</tr>
<tr>
<td>TaSi$_2$</td>
<td>Metal/polysilicon</td>
<td>35—45</td>
</tr>
<tr>
<td></td>
<td>Co-sputtered</td>
<td>50—55</td>
</tr>
<tr>
<td>MoSi$_2$</td>
<td>Co-sputtered</td>
<td>100</td>
</tr>
<tr>
<td>WSi$_2$</td>
<td>Co-sputtered</td>
<td>70</td>
</tr>
<tr>
<td>CoSi$_2$</td>
<td>Metal/polysilicon</td>
<td>17—20</td>
</tr>
<tr>
<td></td>
<td>Co-sputtered</td>
<td>25</td>
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<tr>
<td>NiSi$_2$</td>
<td>Metal/polysilicon</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>Co-sputtered</td>
<td>50—60</td>
</tr>
<tr>
<td>PtSi</td>
<td>Metal/polysilicon</td>
<td>28—35</td>
</tr>
<tr>
<td>Pd$_2$Si</td>
<td>Metal/polysilicon</td>
<td>30—35</td>
</tr>
</tbody>
</table>

Typical heat-treatment sequence used for decreasing the resistance of a TaSi$_2$ contact. Notice the change in the tensile stress with treatment.
And when everything is done correctly, we have

R-C time constant per unit length for three conductive materials as a function of feature size. Also shown is the delay per stage of ring oscillators as a function of feature size.
Concept of multilayer metallization levels

Subtractive and additive processing sequences for creating a patterned structure on a substrate

**Etch**

**Lift-off**
Wet etching of SiO$_2$:

\[
\text{SiO}_2 + 6 \text{ HF} \rightarrow \text{H}_2\text{SiF}_6 + 2\text{H}_2\text{O} \text{ (rate } \sim 100\text{ nm/min)}
\]

In practice, HF is diluted and buffered with NH$_4$F. This replenishes the F and provides a more even etch.

Phosphosilicate glass (PSG) is etched faster than SiO$_2$, at about 250-300 nm/min.

Wet etching of Si$_3$N$_4$:

Si$_3$N$_4$ is etched in H$_3$PO$_4$ (rate ~ 12 nm/min)

Pure Si$_3$N$_4$ is more or less inert to HF (rate < 1-2 nm/min), but if it is deposited in presence of oxygen, this rate dramatically increases.

Example of why directional pattern transfer is desirable. Here, the mask width would have to be compensated for the undercut during an etch.

It is much more desirable to avoid the undercut and use an anisotropic etch as shown on the left:
Often, the mask itself is not anisotropic and may have beveled edges. In that case, even an anisotropic etch can be compromised.

Glow-discharge tube (Ne-bulb)

The dc glow illustrates three common characteristics of gaseous discharges:

1. Because electrons are much more mobile than ions, positive space charge tends to form adjacent to the negative electrode. In fact, the disparity in mobilities also causes these "ion sheaths" to form at any surface immersed in the plasma.
2. The ion sheath is a poor conductor compared to regions of higher electron density; consequently, the largest voltage drops occur across the ion sheaths.
3. The mean electron energy is increased as pressure is reduced or more precisely as the parameter $E/p$ is increased, where $E$ is the electric field and $p$ is the pressure. Since the electron mean free path is inversely proportional to $p$, $E/p$ is a measure of the energy imparted to an electron by the field between collisions.
Schematic view of an r-f discharge. The potential is shown as a function of position in the discharge for the case where the area of the powered electrode is much less than the area of all grounded surfaces in contact with the discharge.

Note that in an r-f discharge, if symmetric, the field would not result in ions being attracted to either contact.

To break this symmetry, either a capacitor is introduced on the RF side, or the relative areas of anode vs. cathode are changed.

This establishes a “bias potential” which then attracts ions to the cathode, which is sputtered away.

Sputter deposition is a popular metallization technique in the semiconductor industry.

Argon is ionized in a plasma and accelerated to the cathode, which in this case is a plate of aluminum.
Simple plasma etch reactor: Gases are introduced and ionized. The wafers are on the cathode and are bombarded by the positive ions.

**Simple ionization**

\[
\text{Ar} + e \rightarrow \text{Ar}^+ + 2e \\
\text{O}_2 + e \rightarrow \text{O}_2^+ + 2e
\]

**Dissociative ionization**

\[
\text{CF}_4 + e \rightarrow \text{CF}_3^+ + \text{F} + 2e
\]

**Dissociative ionization with attachment**

\[
\text{CF}_4 + e \rightarrow \text{CF}_3^+ + \text{F}^- + e
\]

Vacuum of 1mTorr to 1 Torr (760 Torr=1 atm)

- Freons are ideal for Si and SiO₂ etching since SiF₄ is a gas
- Sometimes the wafer is heated to increase the etch rate
- Could be mechanically pumped or diffusion pumped depending on the vacuum required

Reactive ion etching or Plasma etching process
More complex reactive ion etch reactor design. In this geometry, the reactive gas is forced to flow over the surface of the wafers in a radial flow. Notice that the pressure, the distance from anode to cathode, and the r-f power will determine the bias voltage.

Note that positive and negative ions, atoms, radicals, and electrons are generated in typical plasmas. Examples are given here:

\[
\begin{align*}
O_2 + e &\rightarrow 2O + e \\
&\rightarrow O + O^- \\
CF_3Cl + e &\rightarrow CF_3 + Cl^- + e \\
C_2F_6 + e &\rightarrow 2CF_3 + e
\end{align*}
\]

There are also loss mechanisms for ions due to recombination:

For example, dissociative recombination occurs:

\[ e + O_2^+ \rightarrow 2O \]

And dissociative attachment occurs:

\[ e + CF_4 \rightarrow CF_3 + F^- \]
Schematic of an ion milling system. In this case, a confined plasma is used to generate ions, which are then accelerated through a grid towards the sample.

Chlorine or XeF₂

In such a system, it is also possible to spray reactive gas onto the surface of the sample and to accelerate the etching process 30-fold.

One of the first observations of chemically assisted ion beam etching (CAIBE)
Commonly used gases to enhance the etch rate of semiconductors:
Note that the gases are usually selected to provide volatile reaction products (i.e. fluorine forms SiF₄ which can be pumped away, and chlorine forms AlCl₃ which can also easily be volatilized)

### Table 1 Some gases used in dry etching for VLSI

<table>
<thead>
<tr>
<th>Material</th>
<th>Gases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>CF₂, CF₄+O₂, SF₆, SF₆+O₂, NF₃</td>
</tr>
<tr>
<td></td>
<td>Cl₂, CCl₄, CCl₃F₅, CCl₂F₂, CClF₃</td>
</tr>
<tr>
<td>SiO₂, Si₃N₄</td>
<td>CF₄, CF₄+H₂, C₂F₆, C₃F₈, CHF₃</td>
</tr>
<tr>
<td>Al, Al−Si</td>
<td>CCl₄, CCl₃+Cl₂, SiCl₄, BCl₃,</td>
</tr>
<tr>
<td>Al−Cu</td>
<td>BCl₃+Cl₂</td>
</tr>
</tbody>
</table>

Note that silicon will only etch fast in mixtures of O₂ and CF₄, since without oxygen, there is a carbon buildup on the sample which will prevent further etching.
Example of etch chemistry of CF$_4$ in a plasma etcher:

\[
\text{CF}_4 + e \rightarrow \text{CF}_x + \text{F} + e \\
\frac{1}{2} \text{H}_2 + \text{F} \rightarrow \text{HF}
\]

Silicon dioxide can be etched by CF$_4$

\[
\text{CF}_x + \text{SiO}_2 \rightarrow \text{SiF}_4 + (\text{CO}, \text{CO}_2, \text{COF}_2)
\]

\[
\text{CF}_x + \text{Si} \rightarrow \text{C adsorbed on Si}
\]

Silicon is not etched by pure CF$_4$. To etch it, one needs to add oxygen, or hydrogen to volatilize the carbon

Relative etch rates of silicon and some resists in a CF$_4$/H$_2$ mixture. Note that oxygen would etch away the organic resists much more rapidly
Typical mask erosion occurs by beveling the resist first, since the maximum milling rate is typically at 60 degrees.

Trenching is commonly observed during ion milling and is a result from ions deflecting from the edges of the etched structure. Such trenches can be avoided by adding reactive gas to the etch and avoiding overcut.
Typical gas chemistries and etch rates for materials found in VLSI electronics

<table>
<thead>
<tr>
<th>Etched Material (M)</th>
<th>Gas</th>
<th>Etch rate (Å/min)</th>
<th>Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al, Al–Si, Al–Cu</td>
<td>BCl$_3$ + Cl$_2$</td>
<td>500</td>
<td>5–8, 3–5</td>
</tr>
<tr>
<td>Polysilicon</td>
<td>Cl$_2$</td>
<td>500–800</td>
<td>5</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>CF$_4$ + H$_2$</td>
<td>500</td>
<td>5</td>
</tr>
<tr>
<td>PSG</td>
<td>CF$_4$ + H$_2$</td>
<td>800</td>
<td>8</td>
</tr>
</tbody>
</table>