To fabricate any solid device component, one must first select materials and adequate fabrication method.

For MEMS and microsystems components, the sizes are so small that no machine tools, e.g. lathe, milling machine, drilling press, etc. can do the job. There is simply no way one can even grip the work piece.

Consequently, radically different techniques, non-machine-tool techniques need to be used for such purpose.

Most physical-chemical processes developed for “shaping” and fabricating ICs are adopted for microsystems fabrications. This is the principal reason for using silicon and silicon compounds for most MEMS and microsystems – because these are the materials used to produce ICs.
Microfabrication
by physical-chemical processes

Traditional Manufacturing
by machine tools
Microfabrication Processes

- Photolithography
- Ion implantation
- Diffusion
- Oxidation
- Chemical vapor deposition
- Physical vapor deposition (Sputtering)
- Deposition by epitaxy
- Etching
Photolithography process involves the use of an optical image and a photosensitive film to produce desired patterns on a substrate.

The “optical image” is originally in macro scale, but is photographically reduced to the micro-scale to be printed on the silicon substrates.

The desired patterns are first printed on light-transparent mask, usually made of quartz.

The mask is then placed above the top-face of a silicon substrate coated with thin film of photoresistive materials.

The mask can be in contact with the photoresistive material, or placed with a gap, or inclined to the substrate surface:
Photolithography - Cont’d

Processes:
(a) Development
(b) Etching
(c) Photoresist removal

Positive resist:
(a)
(b)
(c)

Negative resist:
(a)
(b)
(c)

Substrate
Photoresist
Substrate
Mask

UV light or other sources
The two kinds of photoresists:

- Positive resists:

There are two kinds of positive resists:
(1) the **PMMA** (polymethylmethacrylate) resists,
(2) the **two-component DQN resist** involving diazoquinone ester (DQ) and phenolic novolak resin (N).

In the latter kind, the first component takes about 20-50% by weight in the compound.

**Positive resists are sensitive to UV lights** with the maximum sensitivity at a wavelength of 220 nm.

The PMMA resists are also used in photolithography involving electron beam, ion beam and x-ray. Most positive resists can be developed in alkaline solvents such as KOH (potassium peroxide), TMAH (tetramethy lammonium hydroxide), ketones or acetates.
Photolithography - Cont’d

- Negative resists:

  (1) Two-component bis (aryl) azide rubber resists, and
  (2) Kodak KTFR (azide-sensitized polyisotroprene rubber).

Negative resists are less sensitive to optical and x-ray exposures but more sensitive to electron beams.

Xylene is the most commonly used solvent for developing negative resists.

**Line definitions of photoresists:**

In general, positive resists provide more clear edge definitions than the negative resists. So, it is a better option for high resolution patterns for micro devices.

(a) by negative resists  
(b) by positive resists
The process begins with securing the substrate wafer onto the top of a vacuum chuck. A resist puddle is first applied to the center portion of the wafer from a dispenser. The wafer is then subjected to high speed spinning at a rotational speed from 1500 to 8000 rpm for 10 to 60 seconds. The speed is set depending on the type of the resist, the desired thickness and uniformity of the resist coating. The centrifugal forces applied to the resist puddle cause a uniform spread of the fluid over the entire surface of the wafer. Typically the thickness is between 0.5 – 2 µm with ±5 nm variation. For some microsystems applications, the thickness had been increased to 1 cm.

Reduce size by controlled spinning speed
Light sources

Photoresist materials used in micro fabrication are sensitive to light with wavelength ranging from **300 to 500 nm**.

Most popular light source for photolithography is the **mercury vapor lamps**. This light source provides a wavelength spectrum from **310 to 440 nm**.

**Deep UV (ultra violet) light** has a wavelength of **150-300 nm** and the **UV light source** has wavelengths between **350-500 nm**.

In special applications for extremely high resolutions, **x-ray** is used. The wavelength of x-ray is in the range from **4 to 50 Angstrom**. (an Angstrom, \(= 0.1 \text{ nm or } 10^{-4} \mu \text{m}\)).
**Photolithography ends**

### Photoresist development

- The same spinner may be used for development after exposure with dispensing development solvent.
- A rising distilled water follows the development. A rising distilled water follows the development.
- Developers agent for +ve resistor are KOH or TMAH. Xylene is the agent for –ve resistors.

### Photoresist removal and postbaking

- After development and the desired pattern is created in the substrate, a descumming process takes place.
- The process uses O₂ plasma to remove the bulk of photoresist.
- Postbaking to remove the residue of solvent at 120°C for 20 minutes.
- Etching will remove all residue photoresist.
- It is **physical process** used to dope silicon substrates.
- It involves “forcing” **free charge-carrying ionized atoms of B, P of As** into silicon crystals.
- These ions associated with sufficiently **high kinetic energy** will be penetrated into the silicon substrate.
- Physical process is illustrated as follows:

![Diagram of ion implantation process](See Figure 3.4)
### Required energy for ion implantation:

<table>
<thead>
<tr>
<th>Dopants</th>
<th>p- or n-type</th>
<th>Ionization Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphorus (P)</td>
<td>n</td>
<td>0.044</td>
</tr>
<tr>
<td>Arsenic (As)</td>
<td>n</td>
<td>0.049</td>
</tr>
<tr>
<td>Antimony (Sb)</td>
<td>n</td>
<td>0.039</td>
</tr>
<tr>
<td><strong>Boron (B)</strong></td>
<td>p</td>
<td><strong>0.045</strong></td>
</tr>
<tr>
<td>Aluminum (Al)</td>
<td>p</td>
<td>0.057</td>
</tr>
<tr>
<td>Gallium (Ga)</td>
<td>p</td>
<td>0.065</td>
</tr>
<tr>
<td>Indium (In)</td>
<td>p</td>
<td>0.160</td>
</tr>
</tbody>
</table>
Density distribution in depth

Ion implantation

\[ N(x) = \frac{Q}{\sqrt{2\pi} \Delta R_p} \exp \left[ -\frac{(x - R_p)^2}{2\Delta R_p^2} \right] \]  

(8.1)

where \( R_p \) = projected range in \( \mu m \),
\( \Delta R_p \) = scatter or “straggle” in \( \mu m \), and
\( Q \) = dose of ion beam (atoms/cm\(^2\))
## Ion Implantation – Cont’d

### Density distribution in depth – Cont’d

(a) At 30 KeV energy level:

<table>
<thead>
<tr>
<th>Ion</th>
<th>Range, $R_p$ (nm)</th>
<th>Straggle, $\Delta R_p$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boron (B)</td>
<td>106.5</td>
<td>39.0</td>
</tr>
<tr>
<td>Phosphorous (P)</td>
<td>42.0</td>
<td>19.5</td>
</tr>
<tr>
<td>Arsenic (As)</td>
<td>23.3</td>
<td>9.0</td>
</tr>
</tbody>
</table>

(b) At 100 KeV energy level:

<table>
<thead>
<tr>
<th>Ion</th>
<th>Range, $R_p$ (nm)</th>
<th>Straggle, $\Delta R_p$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boron (B)</td>
<td>307.0</td>
<td>69.0</td>
</tr>
<tr>
<td>Phosphorous (P)</td>
<td>135.0</td>
<td>53.5</td>
</tr>
<tr>
<td>Arsenic (As)</td>
<td>67.8</td>
<td>26.1</td>
</tr>
</tbody>
</table>
Example 8.1

A silicon substrate is doped with boron ions at 100 KeV. Assume the maximum concentration after the doping is $30 \times 10^{18}/\text{cm}^3$. Find:
(a) the dose, $Q$ in Eq. (8-1),
(b) the dopant concentration at the depth 0.15 $\mu$m,
(c) the depth at which the dopant concentration is at 0.1% of the maximum value.

Solution:

(1) To find the dose:

From Table 8.2, we find $R_p = 307$ nm $= 307 \times 10^{-7}$ cm and $\Delta R_p = 69 \times 10^{-7}$ cm at 100 KeV energy level.

Since we have the maximum concentration, $N_{\text{max}} = 30 \times 10^{18}/\text{cm}^3$ at $x = R_p$ in Eq. (8-1), so from the same equation, we will have:

$$N_{\text{max}} = \frac{Q}{\sqrt{2\pi\Delta R_p}}$$

from which, we have the dose:

$$Q = (2\pi)^{0.5}(\Delta R_p)N_{\text{max}} = (6.28)^{0.5}(69 \times 10^{-7} \text{ cm})(30 \times 10^{18} \text{ cm}^{-3}) = 5.2 \times 10^{14}/\text{cm}^2$$
Example 8.1 – Cont’d

(2) To find the concentration at \( x = 0.15 \) µm:

We may use the following relationship derived from Eq. (8-1):

\[
N(0.15\mu m) = N_{\text{max}} \exp \left[ - \frac{(0.150 - 0.307)^2}{2(0.069)^2} \right] = (30 \times 10^{18}) \exp \left( - \frac{0.0246}{0.009522} \right) = 2.27 \times 10^{18} / \text{cm}^3
\]

(3) To find \( x = x_0 \) at which the concentration \( N(x_0) = (0.1\%)N_{\text{max}} = 3 \times 10^{16}/\text{cm}^3 \):

We may solve \( x_0 \) from the following equation:

\[
N(x_0) = \frac{5.2 \times 10^{14}}{\sqrt{2} \times 3.14 \times 69 \times 10^{-7}} \exp \left[ - \frac{(x_0 - 307 \times 10^{-7})^2}{2(69 \times 10^{-7})^2} \right] = 3 \times 10^{16}
\]

from which, we solve for \( x_0 = 563.5 \times 10^{-7} \) cm or 0.5635 µm.
Diffusion is another common technique for doping silicon substrates.

Unlike ion implantation, diffusion takes place at high temperature.

Diffusion is a chemical process.

The profile of the spread of dopant in silicon by diffusion is different from that by ion implantation:

Dopant profile by Diffusion

Dopant profile by ion implantation
Design analysis of diffusion

Fick’s law governs diffusion (Chapter 3):

\[ F = -D \frac{\partial N(x)}{\partial x} \]  
(8.2)

where

- \( F \) = Dopant flux, which is the number of dopant atoms passing through a unit area of the substrate in a unit time (atoms/cm\(^2\)-sec)
- \( D \) = Diffusion coefficient or diffusivity of the substrate to the dopant (cm\(^2\)/sec)
- \( N \) = Dopant concentration in the substrate per unit volume. (atoms/cm\(^3\))

The distribution of dopant, \( N(x,t) \) in the “depth” direction of the substrate at time \( t \) is obtained from the “Diffusion equation”:

\[ \frac{\partial N(x,t)}{\partial t} = D \frac{\partial^2 N(x,t)}{\partial x^2} \]  
(8.3)
Solution of diffusion equation

\[ \frac{\partial N(x,t)}{\partial t} = D \frac{\partial^2 N(x,t)}{\partial x^2} \]  

(8.3)

**Initial condition** \((t = 0)\):

\[ N(x,0) = 0 \]

meaning there is no impurity in the substrate when the diffusion process begins.

**Boundary conditions** \((at x = 0 and \infty)\):

\[ N(0,t) = N_s \]

which is the concentration at the surface exposed to the gaseous dopant.

\[ N(\infty, t) = 0 \]

meaning the diffusion of foreign substance is highly localized, and that the concentration far away from the contacting surface is negligible.

The solution of the diffusion equation in (8.3) with these conditions is:

\[ N(x,t) = N_s \text{erfc} \left( \frac{x}{2\sqrt{Dt}} \right) \]  

(8.4)

where erfc(x) is the **complementary error function** that has the form:

\[ \text{erfc}(x) = 1 - \text{erf}(x) = 1 - \frac{2}{\sqrt{\pi}} \int_0^x e^{-y^2} dy \]  

(8.5)
The diffusivity, D:

The diffusivity of silicon with common dopants can be obtained by an empirical formula:

$$\ln(\sqrt{D}) = aT' + b$$  \hspace{1cm} (8.6)

in which the temperature, $T' = 1000/T$ with $T$ = diffusion temperature in K.

The constants $a$ and $b$ for common dopants can be obtained from:

<table>
<thead>
<tr>
<th>Dopants</th>
<th>Constant, $a$</th>
<th>Constant, $b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boron</td>
<td>-19.9820</td>
<td>13.1109</td>
</tr>
<tr>
<td>Arsenic</td>
<td>-26.8404</td>
<td>17.2250</td>
</tr>
<tr>
<td>Phosphorus ($N_s = 10^{21}/cm^3$)</td>
<td>-15.8456</td>
<td>11.1168</td>
</tr>
<tr>
<td>Phosphorus ($N_s = 10^{19}/cm^3$)</td>
<td>-20.4278</td>
<td>13.6430</td>
</tr>
</tbody>
</table>
Example 8.2

A silicon substrate is subjected to diffusion of boron dopant at 1000°C with a dose $10^{11}$/cm². Find:
(a) the expression for estimating the concentration of the dopant in the substrate,
(b) the concentration at 0.1 µm beneath the surface after one hour into the diffusion process. The substrate is initially free of impurity.

Solution:

First, to find the diffusivity, $D$ with temperature $T' = \frac{1000}{1000+273} = 0.7855$. From the Table, we have constants, $a = -19.982$ and $b = 13.1109$. Thus, $D$ is: $0.005676$ µm²/h = $1.5766 \times 10^{-6}$ µm²/s, which is in a "ball park" agreement with that from Figure 3.12 on P. 95

(a) Since initially $N(x,0) = 0$, and $N(0,t) = N_s = 10^{11}$ atoms/cm², and $N(\infty,t) = 0$, from Eq. (8.4), we have:

$$N(x,t) = N_s \text{erfc} \left( \frac{x}{2\sqrt{Dt}} \right) = 10^{11} \text{erfc} \left( \frac{x}{2\sqrt{1.5766 \times 10^{-6} t}} \right) = 10^{11} \text{erfc} \left( \frac{398.21x}{\sqrt{t}} \right)$$

$$N(x,t) = 10^{11} \left[ 1 - \text{erf} \left( \frac{398.21x}{\sqrt{t}} \right) \right]$$
Example 8.2 – cont’d

(b) For $x = 0.1 \mu m$ at $t = 1$ h, or 3600 seconds into the diffusion, the concentration is:

\[
N(0.1\mu m,1\text{hour}) = 10^{11} \left[ 1 - \text{erf} \left( \frac{398.21 \times 0.1}{\sqrt{3600}} \right) \right] = 10^{11} \left[ 1 - \text{erf}(0.6637) \right] \\
= 10^{11} (1 - 0.6518) = 3.482 \times 10^{10} / cm^3
\]

The numerical value of the error function, \( \text{erf}(0.6637) \) is obtained from Figure 3.14 on P. 96.
SiO₂ is an important element in MEMS and microsystems. Major application of SiO₂ layers or films are:

1. To be used as thermal insulation media
2. To be used as dielectric layers for electrical insulation

- SiO₂ can be produced over the surface of silicon substrates either by:
  1. Chemical vapor deposition (CVD), or
  2. Growing SiO₂ with dry O₂ in the air, or wet steam by the following two chemical reactions at high temperature:

\[
\text{Si (solid) + O}_2 \text{ (gas)} \rightarrow \text{SiO}_2 \text{ (solid)}
\]
\[
\text{Si (solid) + 2H}_2\text{O (steam)} \rightarrow \text{SiO}_2 \text{ (solid) + 2H}_2 \text{ (gas)}
\]
Oxidation – Cont’d

Principle of thermal oxidation:

It is a combined continuous physical diffusion and chemical reactions

Oxidizing species: O₂ or steam

Silicon substrate

(1) At the inception of oxidation

(2) Formation of oxide layer by chemical reaction

Oxidizing species: O₂ or steam

Growing SiO₂ layer

Instantaneous SiO₂/Si boundary

(3) Growth of oxide layer with diffusion and chemical reactions
Rate of thermal oxidations:

Because of the extreme complexity of thermal oxidation, analytical methods for predicting the rate of this process is impossible. The following quasi-empirical formulas are used for the thickness of SiO₂ layer (x):

For small time, t:

\[ x = \frac{B}{A} (t + \tau) \]  

(8.9)

For larger time, t:

\[ x = \sqrt{B(t + \tau)} \]  

(8.10)

in which

\[ \tau = \frac{d_o^2 + 2D d_o}{k_s} \left( \frac{N_1}{2D N_o} \right) \]  

(8.11)

D = diffusivity of oxide in silicon, e.g. D = 4.4x10⁻¹⁶ cm²/sec at 900°C.
d₀ = initial oxide layer (∼ 200 nm in dry oxidation, = 0 for wet oxidation)
k_s = surface reaction rate constant.
N_o = concentration of oxygen molecules in the carrier gas.
    = 5.2x10¹⁶ molecules/cm³ in dry O₂ at 1000°C and 1 atm.
    = 3000x10¹⁶ molecules/cm³ in water vapor at the same temperature and pressure.
N₁ = number of oxidizing species in the oxide.
    = 2.2x10²² SiO₂ molecules/cm³ with dry O₂,
    = 4.4x10²² SiO₂ molecules/cm³ in water vapor.
Determination of constant A and B in Eqs. (8.9) and (8.10):

For small time, \( t \) in Eq. (8.9):

\[
\log \left( \frac{B}{A} \right) = aT' + b
\]  

(8.12)

For larger time, \( t \) in Eq. (8.10):

\[
\ln(B) = aT' + b
\]  

(8.13)

where \( T' = \frac{1000}{T} \), with temperature \( T \) in Kelvin, K. Constant \( a \) and \( b \) are from the Table:

<table>
<thead>
<tr>
<th>Constants</th>
<th>Coefficient (a)</th>
<th>Coefficient (b)</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear rate constant</td>
<td>-10.4422</td>
<td>6.96426</td>
<td>Dry O(_2), ( E_a = 2 ) eV, (100) silicon</td>
</tr>
<tr>
<td>Eq. (8-12)</td>
<td>-10.1257</td>
<td>6.93576</td>
<td>Dry O(_2), ( E_a = 2 ) eV, (111) silicon</td>
</tr>
<tr>
<td></td>
<td>-9.905525</td>
<td>7.82039</td>
<td>H(_2)O vapor, ( E_a = 2.05 ) eV, (110) silicon</td>
</tr>
<tr>
<td></td>
<td>-9.92655</td>
<td>7.948585</td>
<td>H(_2)O vapor, ( E_a = 2.05 ) eV, (111) silicon</td>
</tr>
<tr>
<td>Parabolic rate constant</td>
<td>-14.40273</td>
<td>6.74356</td>
<td>Dry O(_2), ( E_a = 1.24 ) eV, 760 Torr vacuum</td>
</tr>
<tr>
<td>Eq. (8-13)</td>
<td>-10.615</td>
<td>7.1040</td>
<td>H(_2)O vapor, ( E_a = 0.71 ) eV, 760 Torr vacuum</td>
</tr>
</tbody>
</table>
Example 8.3

Estimate the thickness of the SiO₂ layer over the (111) plane of a “clean” silicon wafer, resulting from both “dry” and “wet” oxidation at 950°C for one and half hours.

Solution:

Since oxidation take place on a new “clean” silicon wafer, we can use the condition that \( \zeta = 0 \). Thus, we may use:

\[
x = \frac{B}{A} t \quad \text{for small time, and } x = \sqrt{Bt} \quad \text{for larger time.}
\]

The constants, \( A \) and \( B \) in the above expressions are selected from Table 8.4 as follows:

<table>
<thead>
<tr>
<th>Conditions</th>
<th>a</th>
<th>b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry O₂</td>
<td>-10.1257</td>
<td>6.9357</td>
</tr>
<tr>
<td>Wet steam</td>
<td>-9.9266</td>
<td>7.9486</td>
</tr>
<tr>
<td>Dry O₂</td>
<td>-14.4027</td>
<td>6.7436</td>
</tr>
<tr>
<td>Wet steam</td>
<td>-10.6150</td>
<td>7.1040</td>
</tr>
</tbody>
</table>
Since we have \( T' = \frac{1000}{950+273} = 0.8177 \), we obtained the constants \( B/A \) and \( B \) from Eqs. (8.12) and (8.13) as:

<table>
<thead>
<tr>
<th></th>
<th>Dry oxidation</th>
<th>Wet oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td>( B/A ) (( \mu m/hr ))</td>
<td>0.04532</td>
<td>0.6786</td>
</tr>
<tr>
<td>( B ) (( \mu m/hr ))</td>
<td>0.006516</td>
<td>0.2068</td>
</tr>
</tbody>
</table>

The rates of oxidation in two conditions after 1.5 hours are thus obtained from the two equations available as:

<table>
<thead>
<tr>
<th></th>
<th>Dry oxidation (( \mu m ))</th>
<th>Wet oxidation (( \mu m ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( x = \frac{B}{A} t ) for small time</td>
<td>0.068</td>
<td>1.018</td>
</tr>
<tr>
<td>( x = \sqrt{Bt} ) for larger time</td>
<td>0.0989</td>
<td>0.5572</td>
</tr>
</tbody>
</table>

We observe that wet oxidation results in much faster rates in oxidation than dry oxidation.
Both SiO\textsubscript{2} and Si\textsubscript{3}N\textsubscript{4} layers have distinct color from the silicon substrates in which these layers grow.

In the case of SiO\textsubscript{2} layers, they are essentially transparent but with distinct light refraction index from that of the silicon substrate.

Consequently, when the surface is shone by the rays of white light one can view the surface exhibiting different colors corresponding to the layer’s thickness.

The color of the surface of a SiO\textsubscript{2} layer is the result of the interference of the reflected light rays.

However, the same color may repeat with different layer thickness, as shown below:

<table>
<thead>
<tr>
<th>SiO\textsubscript{2} layer thickness (µm)</th>
<th>0.050</th>
<th>0.075</th>
<th>0.275/0.465</th>
<th>0.310/0.493</th>
<th>0.50</th>
<th>0.375</th>
<th>0.390</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color</td>
<td>Tan</td>
<td>Brown</td>
<td>Red violet</td>
<td>Blue</td>
<td>Green to Yellow green</td>
<td>Green yellow</td>
<td>Yellow</td>
</tr>
</tbody>
</table>
Chemical vapor deposition (CVD) is the most important process in microfabrication. It is used extensively for producing thin films by depositing many different kind of foreign materials over the surface of silicon substrates, or over other thin films that have already been deposited to the silicon substrate.

Materials for CVD may include:
(a) Metals: Al, Ag, Au, W, Cu, Pt and Sn.
(b) Organic materials: Al$_2$O$_3$, polysilicon, SiO$_2$, Si$_3$N$_4$, piezoelectric ZnO, SMA TiNi, etc.

There are three (3) available CVD processes in microfabrication:
(a) APCVD: (Atmospheric-pressure CVD);
(b) LPCVD (Low-pressure CVD), and
(c) PECVD (Plasma-enhanced CVD).

CVD usually takes place at elevated temperatures and in vacuum in high class clean rooms.
Working principle of CVD:

- CVD involves the flow of a gas containing diffused reactants (normally in vapor form) over the hot substrate surface.

- The gas that carries the reactants is called “carrier gas”.

- The “diffused” reactants are foreign material that needed to be deposited on the substrate surface.

- The carrier gas and the reactant flow over the hot substrate surface, the energy supplied by the surface temperature provokes chemical reactions of the reactants that form films during and after the reactions.

- The by-products of the chemical reactions are then let to the vent.

- Various types of CVD reactors are built to perform the CVD processes.
Chemical Vapor Deposition – Cont’d

Reactors for CVD:

**Horizontal Reactor**
- Reactant and gas in
- Substrate
- Resistance heater
- By-products and gas out

**Vertical Reactor**
- Reactant and gas in
- Substrates
- Resistance heater
- To exhaust
Chemical reactions in CVD:

- **CVD of SiO$_2$ on silicon substrates:**
  \[ \text{SiH}_4 + \text{O}_2 \rightarrow \text{SiO}_2 + 2\text{H}_2 \]  
  at 400 – 500$^\circ$C

  **Carrier gases** are: $\text{O}_2$ (such as in the above reaction), $\text{NO}$, $\text{NO}_2$, $\text{CO}_2$ and $\text{H}_2$.

  The diffused reactant in the reaction is **Silane (SiH$_4$)** -a common reactant in CVD.

- **CVD of Si$_3$N$_4$ on silicon substrates:**
  \[ 3\text{SiH}_4 + 4\text{NH}_3 \rightarrow \text{Si}_3\text{N}_4 + 12 \text{H}_2 \]  
  at 650 – 750$^\circ$C

  \[ 3\text{SiCl}_4 + 4\text{NH}_3 \rightarrow \text{Si}_3\text{N}_4 + 12 \text{HCl} \]

  \[ 3\text{SiH}_2\text{Cl}_2 + 4\text{NH}_3 \rightarrow \text{Si}_3\text{N}_4 + 6\text{HCl} + 6\text{H}_2 \]

- **CVD of polysilicon on silicon substrates:**
  It is essentially a pyrolysis process of Silane at 600 – 650$^\circ$C.

  \[ \text{SiH}_4 \rightarrow \text{Si} + 2\text{H}_2 \]
Chemical Vapor Deposition – Cont’d

Rate of CVD Build-up:

- CVD is the principal technique for building the desired 3-D geometry of many MEMS and microsystems by means of thin film deposition.
- The rate of the build-up of these thin films obviously is a concern to process design engineers.
- Quantification of the rate of CVD is extremely complicated. A quasi-quantitative assessment of such rate of build-up may begin with the understanding of the physical-chemical principles on which CVD operates.
- Two major factors affect the rate of CVD:
  (a) The velocity of carrier gas and the diffused reactant, as measured by the Reynold’s number (Re) and the associated boundary layer (δ) thickness at the substrate-gas interface.
  (b) The Diffusion flux of the reactant (N).

![Diagram of CVD process](image)
Chemical Vapor Deposition – Cont’d

Rate of CVD Build-up – Cont’d:

Velocity, V
Reactant and gas flow

The Reynolds number:

\[ Re = \frac{\rho L V(x)}{\mu} \]  

where \( L \) = length of the substrate

Dynamic Viscosity (\( \mu \)) of Carrier Gases Used in CVD Processes

<table>
<thead>
<tr>
<th>Gas</th>
<th>Viscosity (micro poises, ( \mu P ))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>@0°C</td>
</tr>
<tr>
<td>Hydrogen, ( H_2 )</td>
<td>83</td>
</tr>
<tr>
<td>Nitrogen, ( N_2 )</td>
<td>153</td>
</tr>
<tr>
<td>Oxygen, ( O_2 )</td>
<td>189</td>
</tr>
<tr>
<td>Argon, ( Ar )</td>
<td>210</td>
</tr>
</tbody>
</table>

1 Poise (P) = 1 dyne-s/cm² = 0.1 N-s/m² = 0.1 Kg/m-s
Chemical Vapor Deposition – Cont’d

Rate of CVD Build-up – Cont’d:

- A **boundary layer** is created at the **interface** between the flowing carrier gas and the hot substrate surface.
- The carrier gas (together with the reactant) **diffuses through the boundary layer** to reach the hot substrate surface for chemical reactions.
- The **thickness** of the boundary layer thus has **significant effect** on the rate of CVD.

The thickness of boundary layer:
\[
\delta(x) = \frac{x}{\sqrt{\text{Re}(x)}}
\] (8.17)

The diffusion flux of reactant \((\vec{N})\) across the boundary layer is:
\[
\vec{N} = \frac{D}{\delta} (N_G - N_s) \quad \text{atoms or molecules/m}^2\text{-s}
\] (8.19)

where
- \(D\) = diffusivity of reactant in the carrier gas (cm\(^2\)/s)
- \(N_G\) = Concentration of reactant at the top of boundary layer (molecules/m\(^3\))
- \(N_s\) = concentration of reactant at the substrate surface (molecules/m\(^3\))
Rate of CVD Build-up - Cont’d:

Determination of $N_G$ and $N_s$:

Step 1: Use [Avogadro’s theory](#):
   (a) The volume occupied by one mole of any gas is $22.4 \times 10^{-3} \text{ m}^3$ at standard conditions ($20^{\circ}\text{C}$ or $293 \text{ K}$ at $1 \text{ atm}$, or $101.33 \text{ KPa}$), for ALL gases.
   (b) A [molar density](#) of $44.643 \text{ moles/m}^3$, and
   (c) [Avogadro number](#) = $6.022 \times 10^{23}$ molecules in one mole of gas.

Step 2: Find [molar mass](#) of commonly used gases:

<table>
<thead>
<tr>
<th>Gases</th>
<th>Hydrogen, $\text{H}_2$</th>
<th>Nitrogen, $\text{N}_2$</th>
<th>Oxygen, $\text{O}_2$</th>
<th>Argon, $\text{Ar}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar mass (g)</td>
<td>2</td>
<td>28</td>
<td>32</td>
<td>40</td>
</tr>
</tbody>
</table>

Step 3: Use [ideal gas law](#) to determine the molar density of the gas at the operating temperature and pressure.

Step 4: The concentrations, $N_G$ and $N_s$ can be determined by multiplication of the [Avogadro’s number](#) in Step 1 and molar density in Step 3.
A CVD process involves the reactant being diluted at 2% in the carrier oxygen gas at 490°C. Find the number of molecules in a cubic meter volume of the carrier gas. Pressure variation in the process is negligible.

**Solution:**

We may follow the steps outlined above begun with Step 3 for finding the volume of the carrier gas at 490°C using the ideal gas law:

\[
\frac{P_1 V_1}{P_2 V_2} = \frac{T_1}{T_2}
\]

Let \( V_1 = 22.4 \times 10^{-3} \) m\(^3\)/mol = the volume of the gas at the standard pressure (1 atm) and temperature (20°C or 293 K).

Since \( P_1 \approx P_2 \) and \( T_2 = 490 + 273 = 763 \) K, we have \( V_2 = V_1 T_2 / T_1 = 58.33 \times 10^{-3} \) m\(^3\)/mol

The molar density is \( d_2 = 1 / V_2 = 1 / 58.33 \times 10^{-3} = 17.1433 \) mol/m\(^3\)

The concentration \( N_G \) defined as the molecules of gas per m\(^3\) is:

\[
N_G = (\text{Avogadro’s number}) \times d_2 = 6.022 \times 10^{23} \times 17.1433 = 103.24 \times 10^{23} \text{ molecules/m}^3
\]
Since CVD is a process with coupled diffusion and chemical reactions, the amount of carrier gas and reactant mixture that can diffuse through the boundary layer thus has significant effect on the rate of deposition.

Let \( \vec{N} \) be the flux of carrier gas and reactant mixture,

\[
\vec{N} = K_s N_s
\]  \hspace{1cm} (8.20)

in which \( N_s \) = concentration of carrier gas and reactant at the substrate surface.

\( K_s \) = surface reaction rate constant may be determined by:

\[
k_s = k' \exp\left(-\frac{E_a}{kT}\right)
\]  \hspace{1cm} (8.21)

where \( k' \) = constant relating to the reaction and reactant concentration,

\( E_a \) = activation energy,

\( k \) = Boltzmann constant,

\( T \) = absolute temperature of the chemical reaction.
The flux of the carrier gas and the reactant, in Eq. (8-19):
\[
\dot{N} = \frac{D}{\delta} (N_G - N_S)
\]
may be expressed in terms of the surface reaction rate, \( k_s \) with the substitution of Eq. (8-20) as:
\[
\dot{N} = \frac{D N_G k_s}{D + \delta k_s}
\] (8.22)
in which \( \delta \) is the mean thickness of the boundary layer as expressed in Eq. (8-17).

The rate of the growth of the thin film over the substrate surface, \( r \), in m/sec, can be estimated by the following expressions:

For \( \delta k_s \geq D \):
\[
r = \frac{D N_G}{\gamma \delta}
\] (8.23a)

For \( \delta k_s \ll D \)
\[
r = \frac{N_G k_s}{\gamma}
\] (8.23b)

where \( \gamma \) is the number of atoms or molecules per unit volume of the thin film. The value of \( \gamma \) may be estimated by a postulation that the thin film is “densely” packed by atoms or molecules in spherical shapes with the radius according to the selected materials as listed in the following Table:
**Rate of CVD Build-up-Cont’d:**

Estimation of the number of atoms or molecules per unit volume of the thin film:

\[ \gamma = \frac{1}{v} = \frac{1}{\frac{4}{3} \pi a^3} \]

in which \( v \) = volume of the thin film with radius \( a \) from the Table:

<table>
<thead>
<tr>
<th>Reactant materials</th>
<th>Atomic radius (nm)</th>
<th>Ionic radius (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>0.046</td>
<td>0.154</td>
</tr>
<tr>
<td>Helium</td>
<td>0.046</td>
<td>0.154</td>
</tr>
<tr>
<td>Boron</td>
<td>0.097</td>
<td>0.02</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.071</td>
<td>0.02</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.060</td>
<td>0.132</td>
</tr>
<tr>
<td>Aluminum</td>
<td>0.143</td>
<td>0.057</td>
</tr>
<tr>
<td>Silicon</td>
<td>0.117</td>
<td>0.198</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>0.109</td>
<td>0.039</td>
</tr>
<tr>
<td>Argon</td>
<td>0.192</td>
<td></td>
</tr>
<tr>
<td>Iron</td>
<td>0.124</td>
<td>0.067</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.125</td>
<td>0.078</td>
</tr>
<tr>
<td>Copper</td>
<td>0.128</td>
<td>0.072</td>
</tr>
<tr>
<td>Gallium</td>
<td>0.135</td>
<td>0.062</td>
</tr>
<tr>
<td>Germanium</td>
<td>0.122</td>
<td>0.044</td>
</tr>
<tr>
<td>Arsenic</td>
<td>0.125</td>
<td>0.04</td>
</tr>
</tbody>
</table>
A CVD process is used to deposit $\text{SiO}_2$ film over a silicon substrate. Oxygen is used as the carrier gas following the chemical reaction:

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

Other conditions are identical to that given in Example 8-4 (i.e. the reactant, $\text{SiH}_4$ is diluted to 2% in the $\text{O}_2$ gas with silicon substrate at 490°C).

The CVD process is carried out in a horizontal reactor as illustrated below:
The supply carrier gas has a flux of $N = 10^{24}$ molecules/m$^2$-s.

Determine the following:

1. The density of the carrier gas ($\rho$),
2. The Reynolds number of the gas flow ($Re$),
3. The thickness of the boundary layer over the substrate surface ($\delta$),
4. The diffusivity of the carrier gas and reactant to the silicon substrates ($D$),
5. The surface reaction rate ($K_s$),
6. The deposition rate ($r$).
Example 8.5 – Cont’d

**Solution:**

(1) The *density* of the carrier gas ($\rho$):

We obtained the molar density of the carrier gas in Example 8.4 to be:

$$d_2 = 17.1433 \text{ mol/m}^3$$

and the molecular mass of $O_2$ is 32 g, which leads to the density, $\rho$ to be:

$$\rho = (32 \text{ g/mole})(17.1433 \text{ mole/m}^3) = 548.586 \text{ g/m}^3$$

(2) The **Reynolds number**, (Re):

We realize the facts: the diameter of the reactor for the flow, $D = 200 \text{ mm} = 0.2 \text{ m}$; the velocity of flow, $V = 50 \text{ mm/s} = 0.05 \text{ m/s}$; and the dynamic viscosity $\mu = 400 \times 10^{-6} \text{ P} \text{ (Table 8.6)} = 0.04 \text{ g/m-s}$. These values lead to the Reynolds number to be:

$$Re = \frac{\rho DV}{\mu} = \frac{(548.586)(0.2)(0.05)}{0.04} = 137.147$$
Example 8.5 – Cont’d

(3) The thickness of the boundary layer over the substrate surface ($\delta$):

From Eq. (8.17) using the length of the sled, $L = 150 \text{ mm} = 0.15 \text{ m}$, we have:

$$
\delta = \frac{L}{\sqrt{Re}} = \frac{0.15}{\sqrt{137.147}} = 0.01281 \text{ m}
$$

(4) The diffusivity of the carrier gas and reactant to the silicon substrates ($D$):

This value can be obtained from Eq. (8.19) with a dilution factor, 

$\eta = \%$ of dilution ($= 2\%$ in the present case):

$$
D = \frac{\delta \vec{N}}{\eta (N_G - N_s)}
$$

In which  

$\vec{N}$ = given carrier gas flux = $10^{24}$ molecules/m$^2$-sec

$N_G$ = Equivalent density of gas molecules = $103.24 \times 10^{23}$ molecules/m$^3$

from Example 8-4.

$N_s = 0$ (an assumed value for complete diffusion within the film)

Thus, we may calculate the diffusivity, $D$ of the carrier gas-reactant mixture as:

$$
D = \frac{(0.01281)(10^{24})}{(0.02)(103.24 \times 10^{23})} = 0.062 \text{ m}^2/\text{s}
$$
(5) The surface reaction rate ($K_s$):

We may use Eq. (8.22) to calculate $K_s$.

$$k_s = \frac{D\bar{N}}{D N_G - \delta \bar{N}} = \frac{(0.062)(10^{24})}{(0.062)(103.24 \times 10^{23}) - (0.01281)(10^{24})} = 0.09884 \text{ m/sec}$$

(6) The deposition rate ($r$):

We may use either Eq. (8.23a) or (8.23b) to predict the rate of CVD, depending on the value of $\delta k_s$. In this case, we have: $\delta k_s = (0.01281)(0.09884) = 0.0013 \ll D = 0.062$. So, Eq. (8.23b) will be used for the rate prediction, with a dilution factor, $\eta$:

$$r = \eta \frac{N_G k_s}{\gamma}$$

The density of SiO$_2$ in the thin film, $\gamma$ is:

$$\gamma = \frac{1}{\frac{4}{3} \pi (a_{SiO_2})^3} = \frac{1}{\frac{4}{3} (3.14)(0.177 \times 10^{-9})^3} = 4.3074 \times 10^{28} \text{ molecules/m}^3$$

with the radius of O$_2$ atoms, $a_{O_2} = 0.06 \text{ nm} + \text{ radius of Si} = 0.117 \text{ nm}$ to be

The radius of SiO$_2$ molecules, $a_{SiO_2} = 0.177 \times 10^{-9} \text{ m}$ from Table 8.7.

Hence, we have the rate of CVD to be:

$$r = \frac{N_G k_s}{\gamma} = \frac{(0.02)(103.24 \times 10^{23})(0.09884)}{4.3074 \times 10^{28}} = 0.4738 \times 10^{-6} \text{ m/s or 0.47 \mu m/s}$$
Enhanced CVD

The working principles of CVD process leads to the observations that the rates of CVD is proportional to the following physical parameters:

- The temperature, $T^{3/2}$.
- The pressure of the carrier gas, $P^{-1}$.
- The velocity of gas flow, $V^{-1}$.
- The distance in the direction of gas flow, $x^{1/2}$, in which $x$ is shown in Fig. 8-10 (b):

![Diagram of Enhanced CVD process with labels for reactant and gas flow, boundary layer, and hot silicon surface.]
Low-Pressure CVD (LPCVD):
From the previous observation, we may formulate the parameters that affect the rate of CVD:

\[ r \propto \frac{(T^{1.5})(x^{0.5})(D)}{(P)(V)(\delta)} \]

A few possibilities exist to enhance the rate of CVD:

1. To raise the process temperature, \( T \) would normally increase diffusivity, \( D \). However, it will harm the substrate.
2. To decrease the velocity, \( V \) may enhance the rate \( r \), but also results in lower Reynolds number that will increase the boundary layer thickness, \( \delta \). These two effects may cancel out each other. So, it is not a positive option.
3. This leaves with the last option to decrease the pressure of the gas, \( P \) with expectation to enhance the rate, \( r \) of the CVD.

Thus, **LPCVD** operates in vacuum at about 1 torr (1 mm Hg) has become a popular CVD process in microfabrication. The CVD operates at atmospheric pressure is called **APCVD**.
Enhanced CVD – Cont’d

Plasma Enhanced CVD (PECVD)

- Both APCVD and LPCVD operate at **elevated temperatures**, which often damage the silicon substrates.

- High substrate surface temperature is required to provide **sufficient energy** for diffusion and chemical reactions.

- The operating temperatures may be avoided if **alternative form of energy supply** can be found.

- CVD using **plasmas** generated from high energy **RF (radio-frequency) sources** is one of such alternative methods.

- This popular deposition method is called **“Plasma Enhanced CVD” or PECVD**.

- A typical PECVD reactor is shown:
## Summary and Comparison of 3 CVD Processes

<table>
<thead>
<tr>
<th>CVD Process</th>
<th>Pressure/Temperature</th>
<th>Normal Deposition Rates, $(10^{-10}$ m/min)</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>APCVD</strong></td>
<td>100-10 KPa/350-400°C</td>
<td>700 for $\text{SiO}_2$</td>
<td>Simple, high rate, low temperature</td>
<td>Poor step coverage, particle contamination</td>
<td>Doped and undoped oxides</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50-180 for $\text{SiO}_2$</td>
<td>Excellent purity and uniformity, large wafer capacity</td>
<td>High temperature and low deposition rates</td>
<td>Doped and undoped oxides, silicon nitride, polysilicon, and tungsten.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30-80 for $\text{Si}_3\text{N}_4$</td>
<td></td>
<td></td>
<td>Low-temperature insulators over metals, and passivation.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100-200 for polysilicon</td>
<td></td>
<td></td>
<td>Low-temperature insulators over metals, and passivation.</td>
</tr>
<tr>
<td><strong>LPCVD</strong></td>
<td>1-8 Torr/550-900°C</td>
<td>50-180 for $\text{SiO}_2$</td>
<td></td>
<td></td>
<td>Doped and undoped oxides, silicon nitride, polysilicon, and tungsten.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30-80 for $\text{Si}_3\text{N}_4$</td>
<td></td>
<td></td>
<td>Low-temperature insulators over metals, and passivation.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100-200 for polysilicon</td>
<td></td>
<td></td>
<td>Low-temperature insulators over metals, and passivation.</td>
</tr>
<tr>
<td><strong>PECVD</strong></td>
<td>0.2-5 Torr/300-400°C</td>
<td>300-350 for $\text{Si}_3\text{N}_4$</td>
<td>Lower substrate temperature; fast, good adhesion.</td>
<td>Vulnerable to chemical contamination</td>
<td>Low-temperature insulators over metals, and passivation.</td>
</tr>
</tbody>
</table>
Sputtering is a form of Physical Vapor Deposition.

- It is used to deposit thin metal films in the order of 100 Å (1 Å = 10⁻¹⁰ m) onto the substrate surface.

- Metal films are used as electrical circuit terminals as illustrated below:

- Sputtering process is carried out with plasmas under very low pressure in high vacuum up to 5x10⁻⁷ torr and at room temperature.

- No chemical reaction is involved in the deposition process.
• **Metal vapor** is created by the plasma generated by the high energy RF sources, such as the one illustrated below.

![Sputtering Diagram](image)

- Inert **Argon gas** is used as the carrier gas for metal vapor.
- The metal vapor forms the metal films after condensation of the substrate surface.
Deposition by Epitaxy

- Both CVD and PVD processes are used to deposit dissimilar materials on the silicon substrate surfaces.

- Epitaxy deposition process is used to deposit polysilicon films on silicon substrate surfaces.

- Most polisilicons are doped pure silicon crystals randomly oriented. They are used to conduct electricity at desired locations on silicon substrates.

- This process is similar to CVD with carrier gas with reactants that release the same material as the substrates.

- One may deposit GaAs to GaAs substrates using this technique.

- There are four epitaxy deposition methods available.

- We will focus our attention on the popular “Vapor-phase epitaxy” (VPE) process.
### The reactant vapors

<table>
<thead>
<tr>
<th>Reactant vapors</th>
<th>Normal process temperature (°C)</th>
<th>Normal deposition rate (µm/min)</th>
<th>Required energy supply (eV)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silane (SiH₄)</td>
<td>1000</td>
<td>0.1 – 0.5</td>
<td>1.6 – 1.7</td>
<td>No pattern shift</td>
</tr>
<tr>
<td>Dichlorosilane (SiH₂Cl₂)</td>
<td>1100</td>
<td>0.1 – 0.8</td>
<td>0.3 – 0.6</td>
<td>Some pattern shift</td>
</tr>
<tr>
<td>Trichlorosilane (SiHCl₃)</td>
<td>1175</td>
<td>0.2 – 0.8</td>
<td>0.8 – 1.0</td>
<td>Large pattern shift</td>
</tr>
<tr>
<td>Silicon tetrachloride (SiCl₄)</td>
<td>1225</td>
<td>0.2 – 1.0</td>
<td>1.6 – 1.7</td>
<td>Very large pattern shift</td>
</tr>
</tbody>
</table>

Typical chemical reaction:

\[ \text{SiH}_4 \rightarrow \text{Si} \ (\text{solid}) + 2\text{H}_2 \ (\text{gas}) \]
Reactors for epitaxy deposition

- Very similar to those used in CVD, except that many of the carrier gas used is \( \text{H}_2 \).
- For safety reason, \( \text{N}_2 \) gas is used to drive out any \( \text{O}_2 \) gas in the system before the process begins.
- The two types of reactors are illustrated below:
MEMS and microsystems consist of components of 3-dimensional geometry.

There are two ways to create 3-dimensional geometry:

- by adding materials at the desired locations of the substrates using vapor deposition techniques, or
- by removing substrate material at desired locations using the etching methods.

There are two types of etching techniques:

- Wet etching involving the use of strong chemical solvents (etchants), or
- Dry etching using high energy plasmas.

In either etching processes, masks made of strong-resisting materials are used to protect the parts of substrate from etching.

Both etching methods will be presented in detail in the subsequent chapter on Micromanufacturing.