NANYANG TECHNOLOGICAL UNIVERSITY

Course: EE3013/ Semiconductor Devices and Processing

School: School of Electrical and Electronic Engineering

Week 7 – Thermal Oxidation

Wafer Processing

Learning Objectives

At the end of this lesson, you will be able to:

- Explain the mechanisms, pros and cons, and applications of dry and wet oxidation in semiconductor processing.
- Explain Fick's first law of diffusion and how it is used to derive the formulae for calculating the oxide thickness.
- Explain the characteristics of short time and long time oxidation, and the associated linear rate coefficient and parabolic rate coefficient.
- Determine the oxide thickness using formulae and graphical methods.
- Explain the different factors affecting the oxidation rate.
- Explain how oxide is used for masking purpose and how to determine the required thickness needed.
- Explain what are some examples of thermal oxidation process used in semiconductor processes.
- Describe the various types of thermal oxidation tools.
- Describe the different techniques for oxide thickness measurements.

Examples of Oxidation

- In semiconductor, we make use of intentional oxidation process to our advantage.

Rusting of Nails

Banana

Apple

Canyon

Statue of Liberty

Thermal Oxidation

- A process by which a layer of oxide is formed/ grown on a silicon substrate at high temperature.
- Oxide in Si-Technology means **Silicon Dioxide (SiO_2)**. (GaAs, Ge, and other semiconductors don't form native oxides).
- SiO_2 can be formed on Si surface in air at room temperature but can be formed at high rate at high temperature.
- There are two oxidation methods:
  - Dry oxidation, and
  - Wet oxidation.

Dry and Wet Oxidation

- **Dry oxidation:**

  Oxidation is carried out by passing oxygen (gas) into a quartz tube where the silicon slices are maintained at a temperature between 900 to 1200°C.

$$Si + \boldsymbol{O_2} \rightarrow SiO_2$$

- **Wet Oxidation:**

  Instead of oxygen, steam (H_2O) diffuses into a quartz tube and reacts with silicon to form oxide:

$$Si + \boldsymbol{2\,H_2O} \rightarrow SiO_2 + 2H_2$$

How Does Oxidation Take Place?

- Oxidation of silicon occurs when either O_2 or H_2O reacts with Si.
- The **chemical reaction occurs at SiO_2 and Si interface** as oxygen can easily diffuse to Si surface but Si can hardly diffuse through oxide.

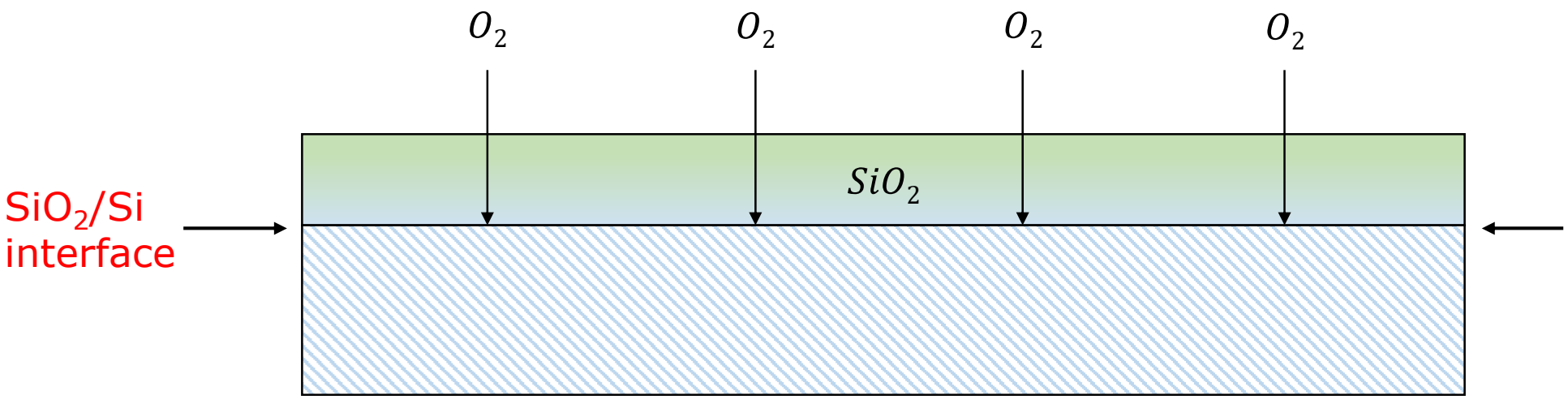


Figure 4.2

Consumption of Silicon During Oxidation

- For a layer of SiO_2 with a thickness t_{ox}, the layer of Si consumed is **44%** of the total oxide thickness.

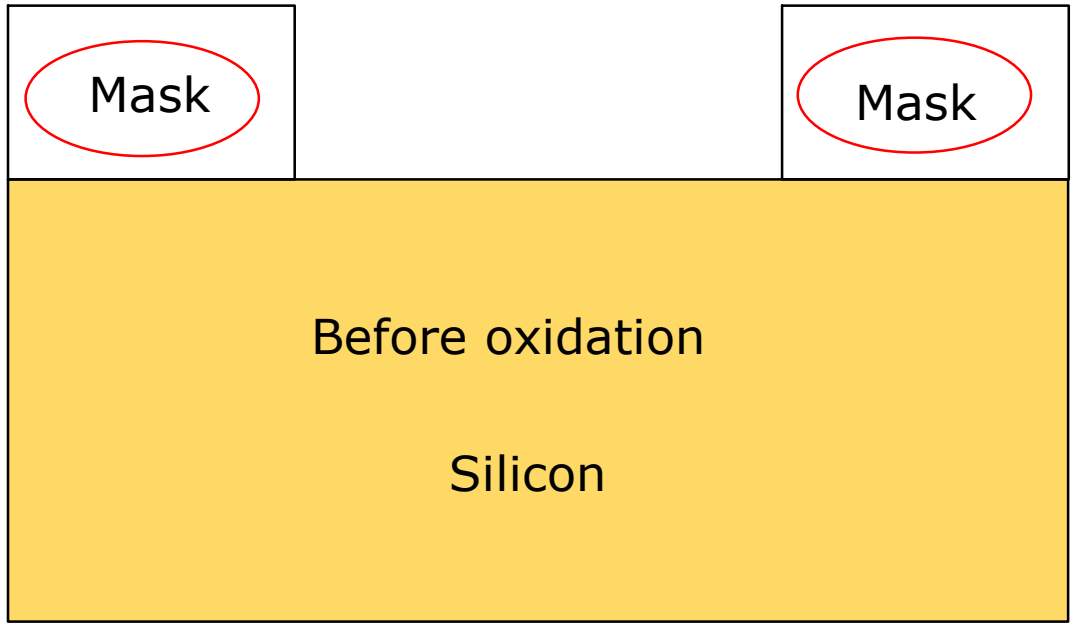


Figure 4.3a

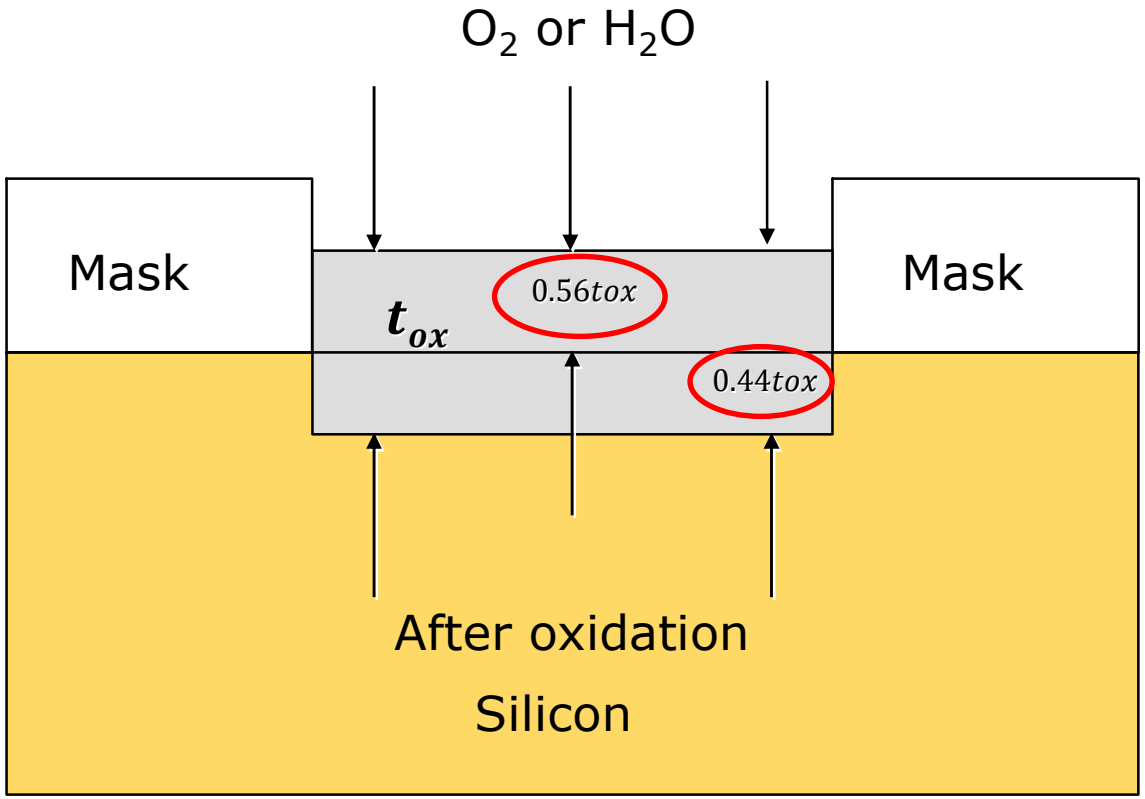


Figure 4.3b

Properties of SiO_2

- SiO_2 is amorphous
- High resistivity, $\rho > 1 \times 10^{20}\ ohm - cm$
- Large band gap (insulator), $E_g = 9\ eV$
- Stable and low interface trap density (between Si and SiO_2)
  - **Gate dielectric for MOSFET**
- Low diffusivity for common dopants like $B, P, As, Sb\ (DSiO_2 \ll D_{si})$
- Easy to etch
  - **Used for masking in fabrication process**

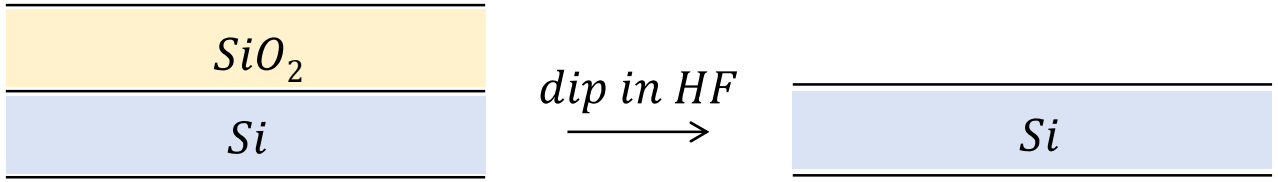


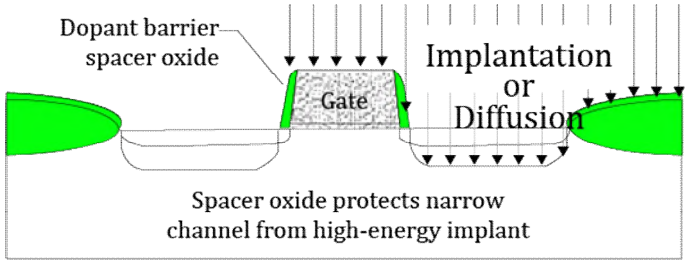
Figure 4.4

Comparison of Oxide Quality

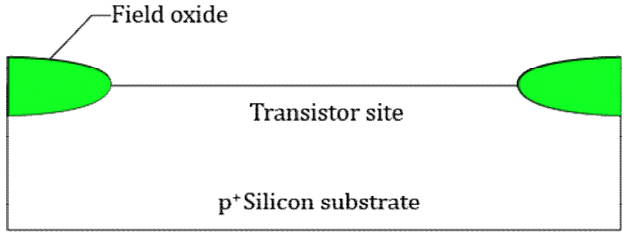
- **Dry oxidation**
  - Results in a **higher quality oxide** that is denser and has a higher breakdown voltage $(5 - 10\ MV/cm)$ and low leakage current
  - But **Low oxidation rate**
  - **Thin gate oxides** in MOS devices are usually formed using dry oxidation
- **Wet oxidation**
  - Produces **poorer** quality oxide
  - But **high** rate due to higher diffusivity of H_2O compared with O_2
  - Usually used for **masking** purpose

Applications of Oxide

(1) Mask for implantation and diffusion

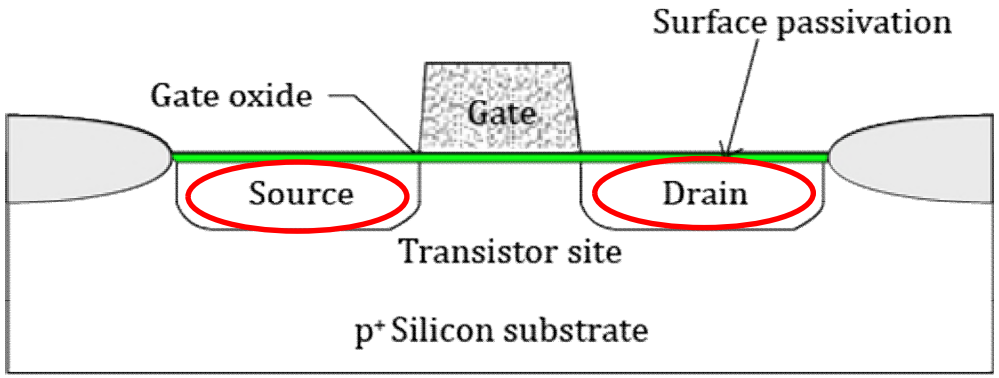


(2) Isolation



(3) Gate oxide of MOS structures for insulation

(4) Surface passivation



Oxidation Modeling

Fick's first law of diffusion:

- Particle flux *J* is proportional to the negative gradient of the particle concentration.

$$J = -\mathrm{D}\frac{\partial N(z,t)}{\partial z} \qquad \textit{(Equation 4.1)}$$

$$Particle\ flux\ =\ particle\ flow\ per\ unit\ area$$

- The negative sign indicates that particles tend to move from a region of high concentration to a region of low concentration.

Oxidation Modeling (Cont'd.)

- Assume that oxygen flux passing through the oxide is constant (no oxygen accumulation)

$$J = -D\frac{N_i - N_0}{t_{ox}} \quad \textit{(Equation 4.2)}$$

where,

t_{ox}: Oxide thickness at a given time

N_i: Concentration of oxygen at interface

N_0: Concentration at oxide surface

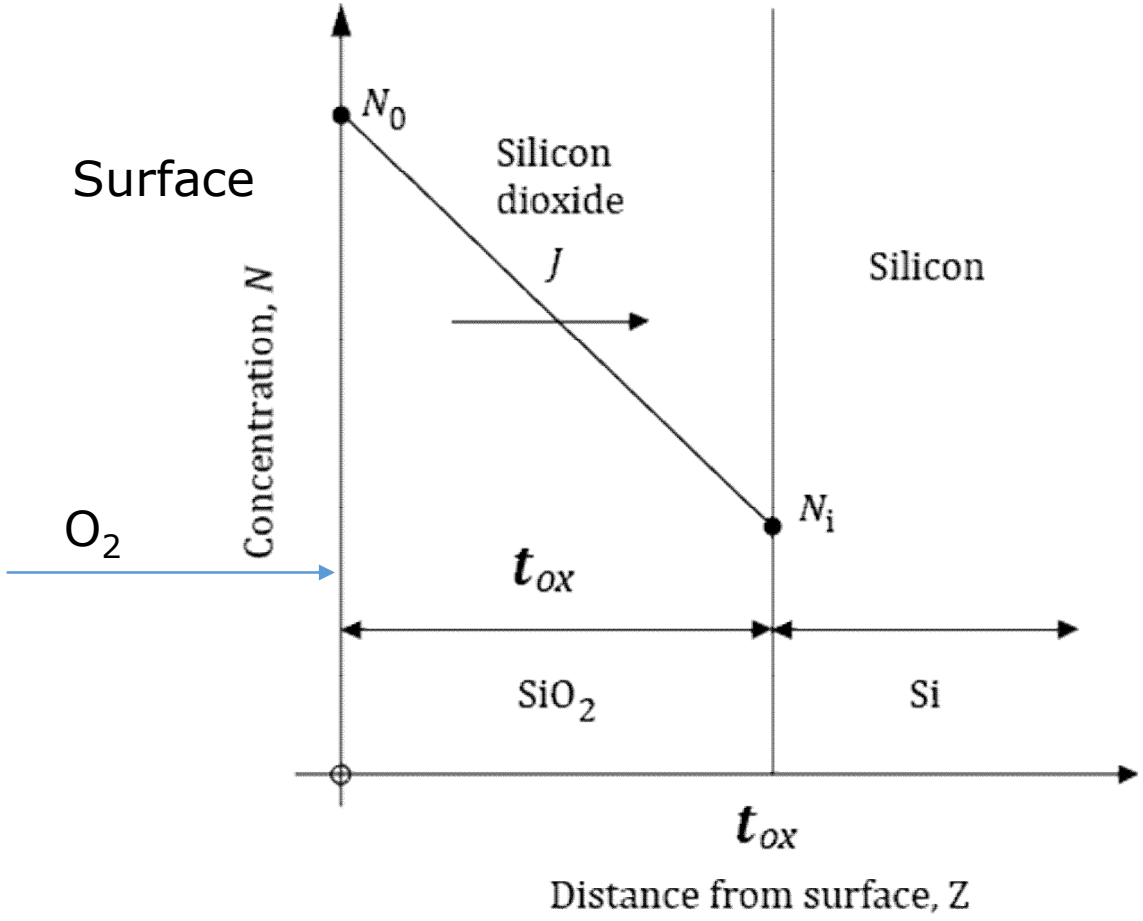


Figure 4.6

Oxidation Modeling (Cont'd.)

- Assume that oxidation rate is proportional to concentration of oxygen. So, the flux at interface is

$$J = k_s N_i \quad \textit{(Equation 4.3)}$$

where k_s is rate constant for reaction at $Si - SiO_2$ interface.

- Eliminating N_i using the last two equations, we have:

$$J = -D \frac{N_0}{t_{ox} + \frac{D}{K_s}} \quad \textit{(Equation 4.4)}$$

- The oxidation rate is given by the oxidising flux divided by the number of oxygen molecules M in a unit volume of oxide.

$$\frac{dt_{ox}}{dt} = \frac{J}{M} = \frac{DN_o}{M(t_{ox} + \frac{D}{K_s})} \quad \textit{(Equation 4.5)}$$

Oxidation Modeling (Cont'd.)

- Solving the differential equation by using the boundary condition $t_{ox} = t_{oxi}$ at $t = 0$, we have

$$t = \frac{t^2{}_{ox}}{B} + \frac{t_{ox}}{B/A} - \tau \quad \text{or} \quad t^2{}_{ox} + At_{ox} = B(t + \tau) \qquad \textit{(Equation 4.6)}$$

$$t_{ox} = \frac{-A + \sqrt{A^2 + 4B(t + \tau)}}{2} \qquad \textit{(Equation 4.7)}$$

where $A = \frac{2D}{k_s}$, $B = \frac{2DN_0}{M}$ and $\tau = \frac{t_{oxi}^2}{B} + \frac{t_{oxi}}{B/A} = \frac{t_{oxi}^2 + At_{oxi}}{B}$

- ***t* is time, t_{oxi} is the initial oxide thickness on the wafer before oxidation** and τ is the time required to grow the initial oxide.

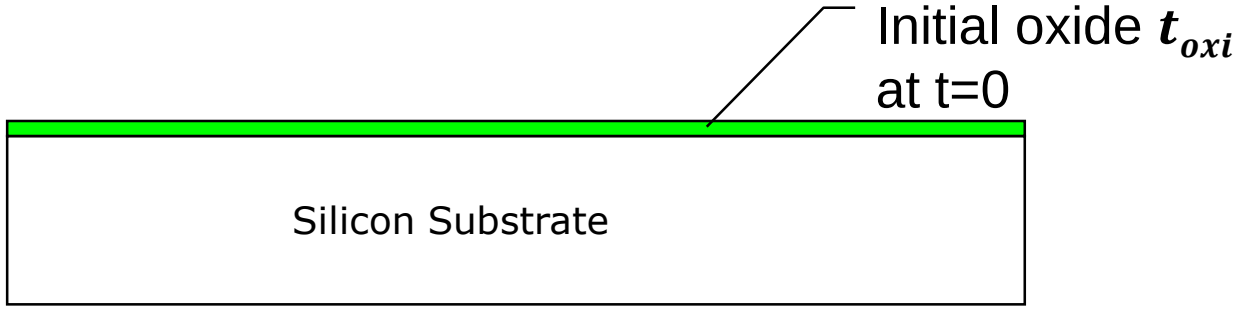


Figure 4.7

Thickness of Oxide

$$t_{ox} = \frac{-A + \sqrt{A^2 + 4B(t+\tau)}}{2} \qquad \textit{(Equation 4.8)}$$

- For **short time** with $t + \tau << A^2/4B$:

$$t_{ox} = \frac{B}{A}(t+\tau) \qquad \textit{(Equation 4.9)}$$

(Please refer to the next slide for derivation)

- For **long time** with $t + \tau >> A^2/4B, \quad t > \tau$:

$$t_{ox} = \sqrt{Bt} \qquad \textit{(Equation 4.10)}$$

Note:

- B/A is called **linear rate** coefficient. (Growth rate is limited by the reaction at the silicon interface; it depends on Si-Si bond strength and not by diffusivity.)
- B is called **parabolic rate** coefficient. (Oxidation rate is diffusion limited.)

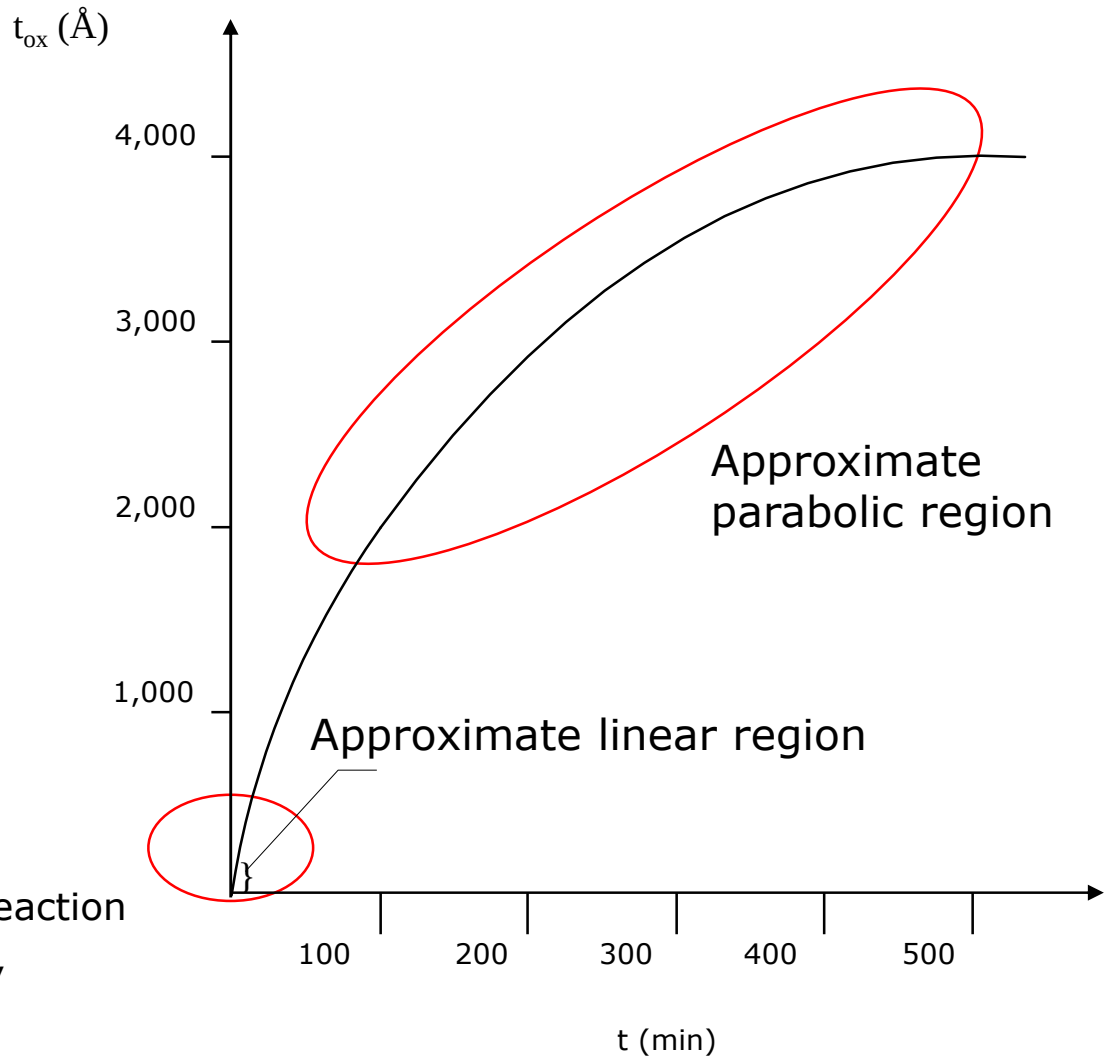


Figure 4.8

Derivation

- For **short time** with $t+\tau \ << A^2/4B$:

$$t_{ox} = \frac{-A+\sqrt{A^2+4B(t+\tau)}}{2} = \frac{-A+A\sqrt{1+4B(t+\tau)/A^2}}{2}$$

$$= \frac{-A+A\left[1+\frac{4B(t+\tau)}{2A^2}\right]}{2} = \frac{-A+A+\frac{4B(t+\tau)}{2A}}{2} = \frac{\frac{4B(t+\tau)}{2A}}{2} = \frac{4B(t+\tau)}{4A} = \frac{B}{A}(t+\tau)$$

For $t+\tau \ << A^2/4B$

$$\sqrt{1+4B(t+\tau)/A^2} = (1+4B(t+\tau)/A^2) = 1+\frac{4B(t+\tau)}{2A^2}$$

- Hence $t_{ox} = \frac{B}{A}(t+\tau)$

Oxidation Coefficient Table

Table 4.1 Values for Coefficient D_0 and Activation Energy E_A for Wet and Dry Oxygen*				
	Wet $O_2(Xi = 0nm)$		Dry $O_2(Xi = 25nm)$	
	D_0	E_A	D_0	E_A
<100> Silicon				
Linear (B/A)	$9.70 \times 10^7\ \mu m/hr$	$2.05\ eV$	$3.71 \times 10^6\ \mu m/hr$	$200\ eV$
Parabolic (B)	$386\ \mu m^2/hr$	$0.78\ eV$	$772\ \mu m^2/hr$	$1.23\ eV$
<111> Silicon				
Linear (B/A)	$1.63 \times 10^8\ \mu m/hr$	$2.05\ eV$	$6.23 \times 10^6\ \mu m/hr$	$200\ eV$
Parabolic (B)	$386\ \mu m^2/hr$	$0.78\ eV$	$772\ \mu m^2/hr$	$1.23\ eV$

Table 4.2 Oxidation Coefficients for Silicon				
Temp (^oC)	**Dry**		**Wet (640 torr)**	
	$A\ (\mu m)$	$B\ (\mu m^2/hr)$	$A\ (\mu m)$	$B\ (\mu m^2/hr)$
800	0.370	0.0011	-	-
920	0.235	0.0049	0.50	0.203
1000	0.165	0.0117	0.226	0.287
1100	0.090	0.027	0.11	0.510
1200	0.040	0.045	0.05	0.720

Factors Affecting Oxidation Rate

1. Growth techniques: Wet versus Dry
2. Growth temperature
3. Pressure
4. Crystal orientation: (100) versus (111)
5. Impurity doping

Factors Affecting Oxidation Rate (Cont'd.)

1. Growth techniques: Wet versus Dry

- Oxidation rate: Wet is faster than Dry irrespective of the crystal orientation.

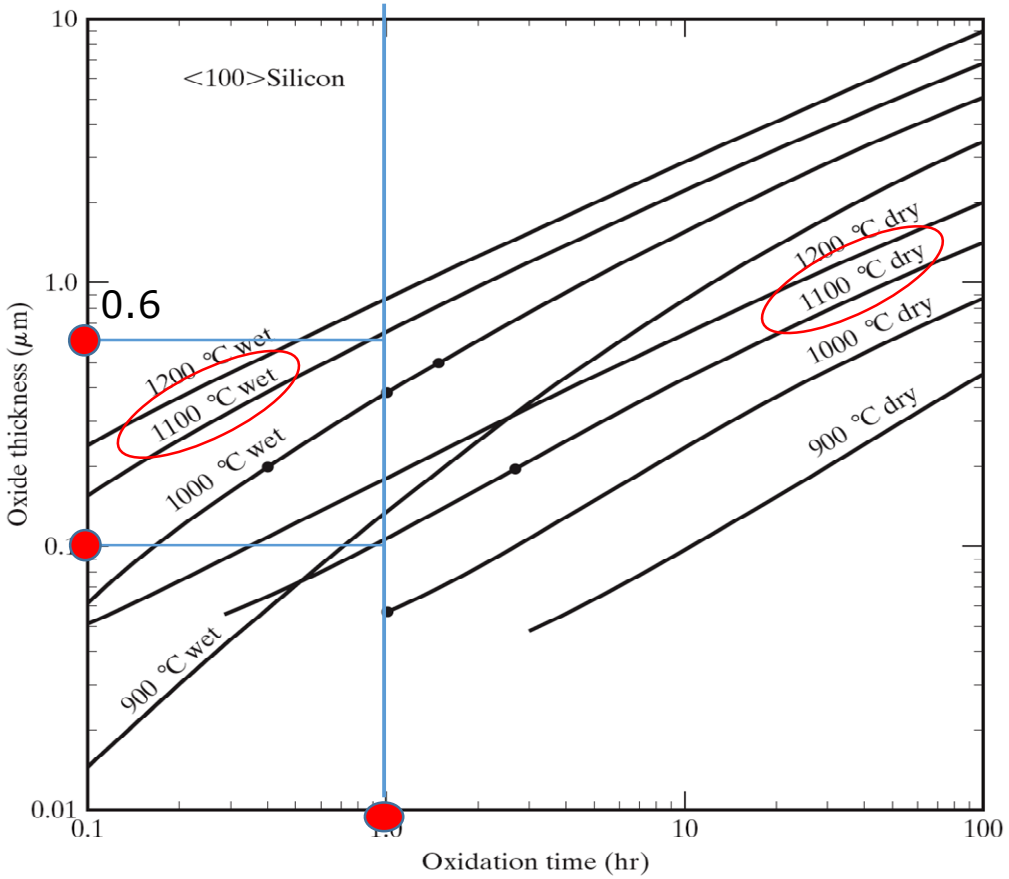


Figure 4.9

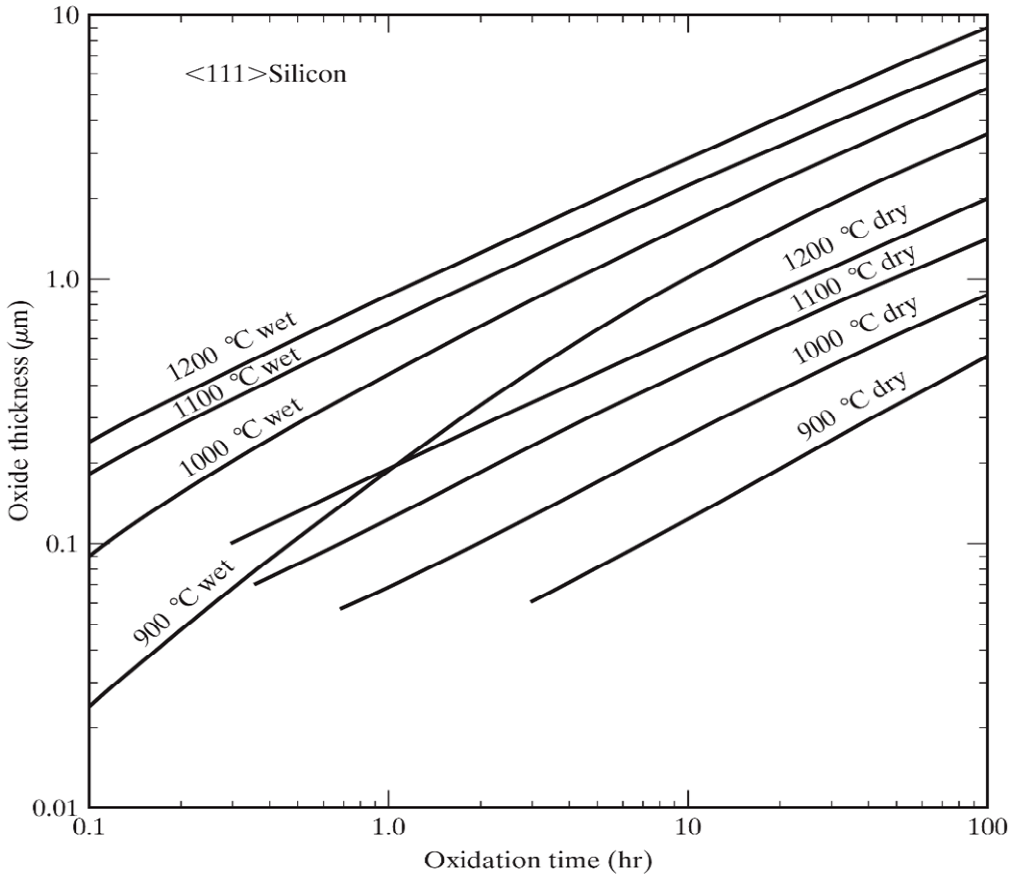


Figure 4.10

Factors Affecting Oxidation Rate (Cont'd.)

2. Growth temperature

- Oxidation rate increases with increasing temperature for both wet and dry processes.

- Recall for long time oxidation: $t_{ox} = \sqrt{Bt}$ *(Equation 4.10)*

Table 4.2 Oxidation Coefficients for Silicon

Temp (^oC)	**Dry**		**Wet (640 torr)**	
	$A\ (\mu m)$	$B\ (\mu m^2/hr)$	$A\ (\mu m)$	$B\ (\mu m^2/hr)$
800	0.370	0.0011	-	-
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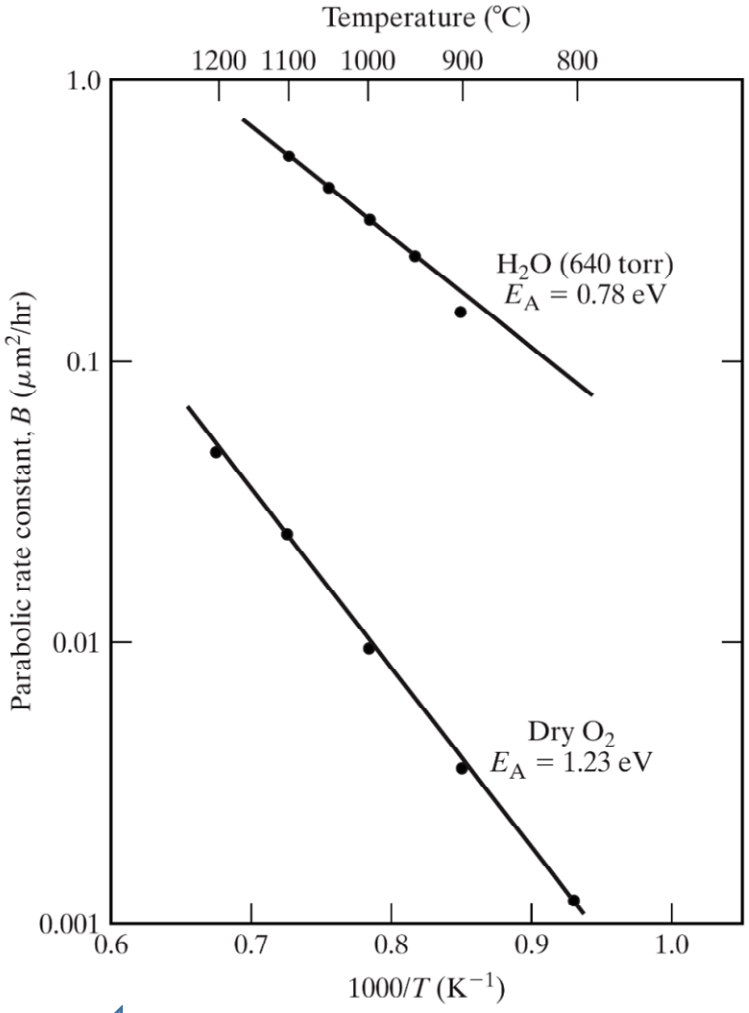


increasing temperature

Figure 4.11

Factors Affecting Oxidation Rate (Cont'd.)

3. Pressure

- Oxidation rate increases with increasing pressure.

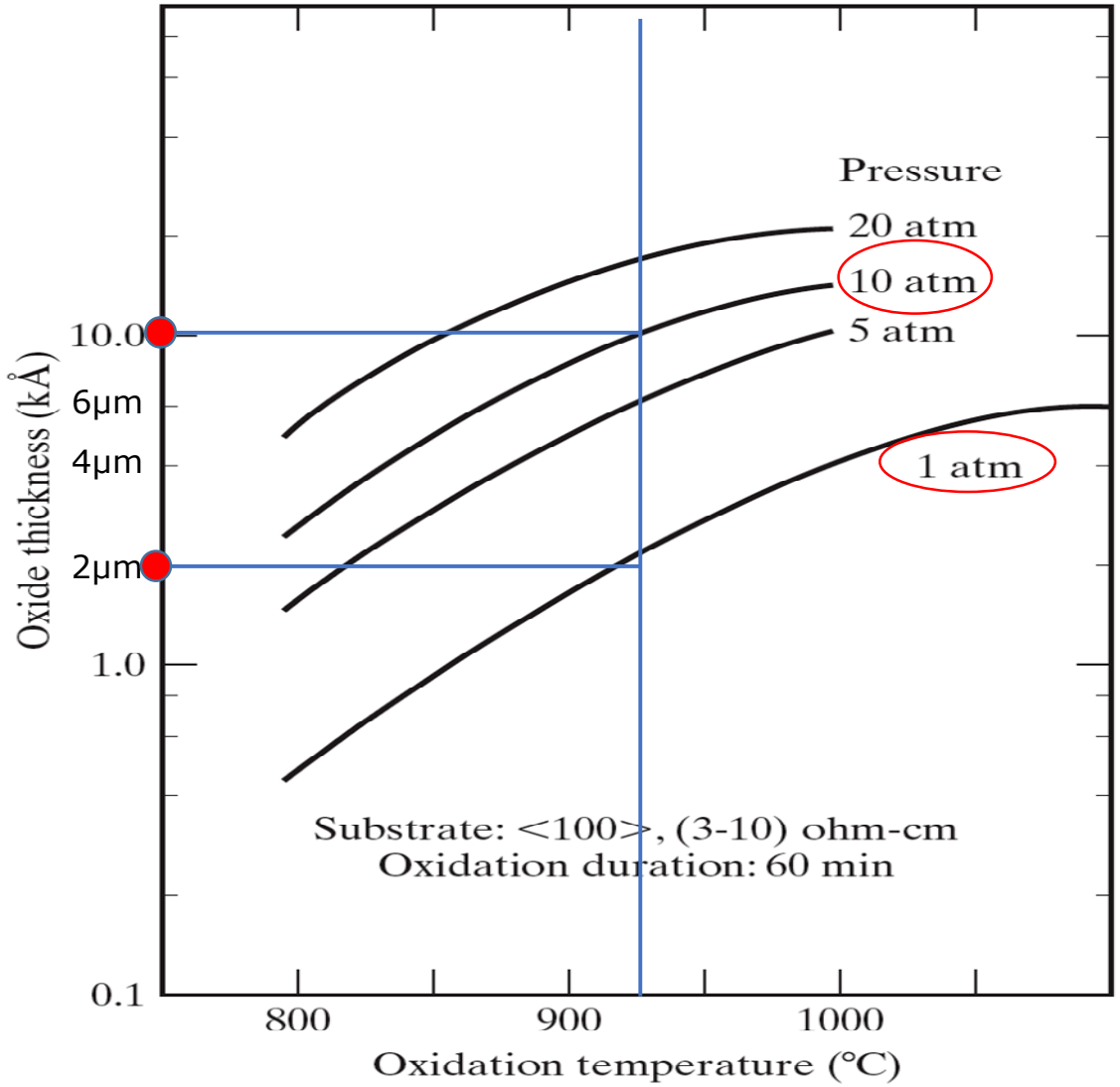


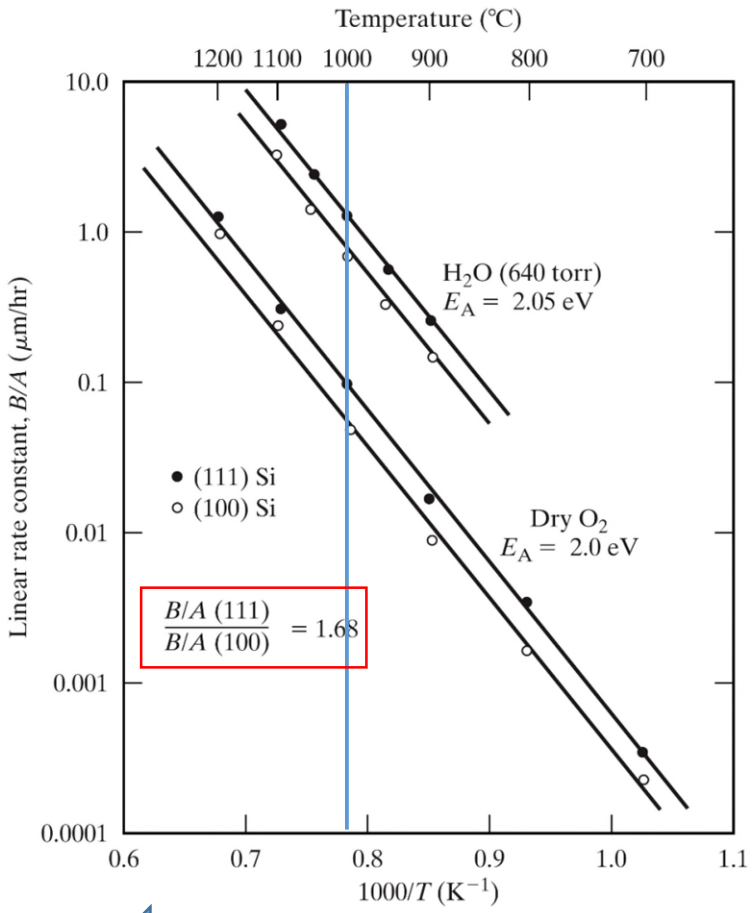
Figure 4.12

Factors Affecting Oxidation Rate (Cont'd.)

4. Crystal orientation: (100) versus (111)

- Oxidation rate is different for different crystal orientation irrespective of wet or dry process.
- Oxidation rate is faster in (111) than in (100) plane.

Recall: B/A called linear rate coefficient. (Growth rate is limited by the reaction at the silicon interface; it depends on Si-Si bond strength and not by diffusivity.)



increasing temperature

Figure 4.13

Factors Affecting Oxidation Rate (Cont'd.)

5. Dopant Effect on Oxidation Rate

- All dopants in Si enhance oxidation rate when the doping concentration is high.

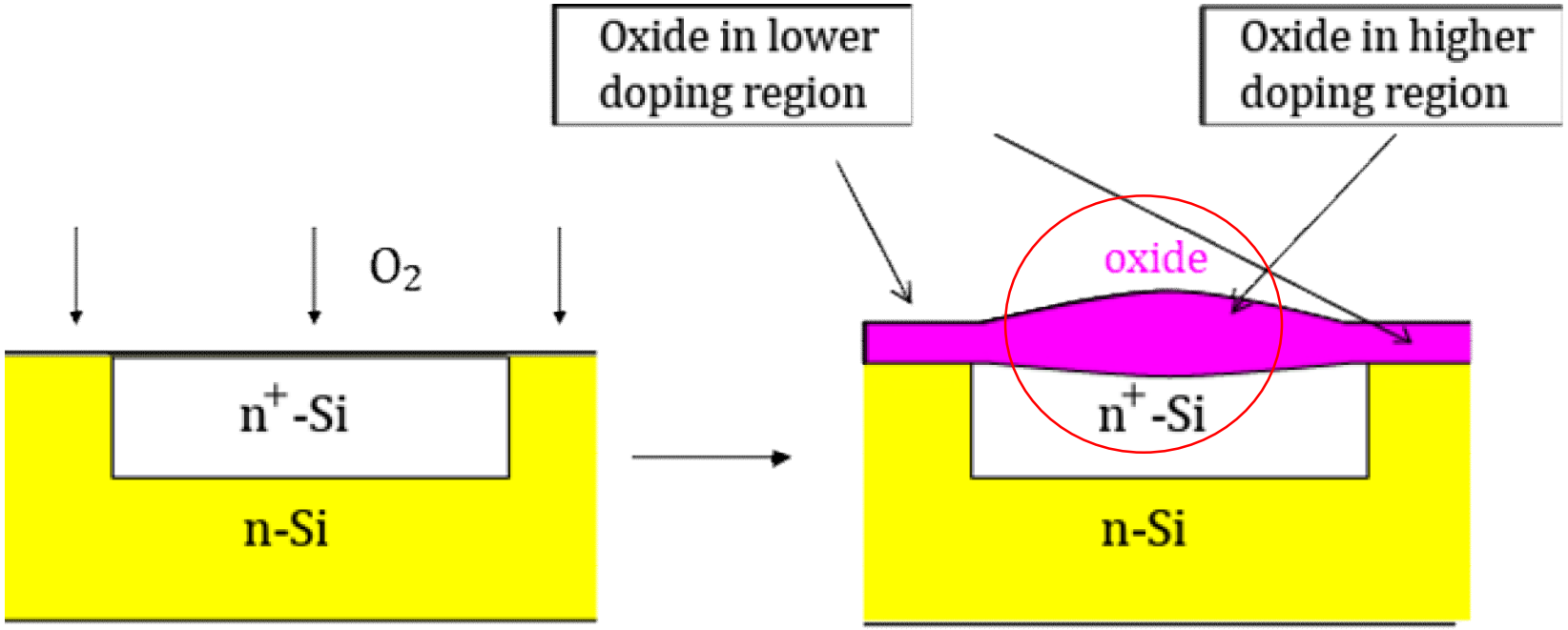


Figure 4.13 (a) **Figure 4.13 (a)**

Effect of Phosphorus

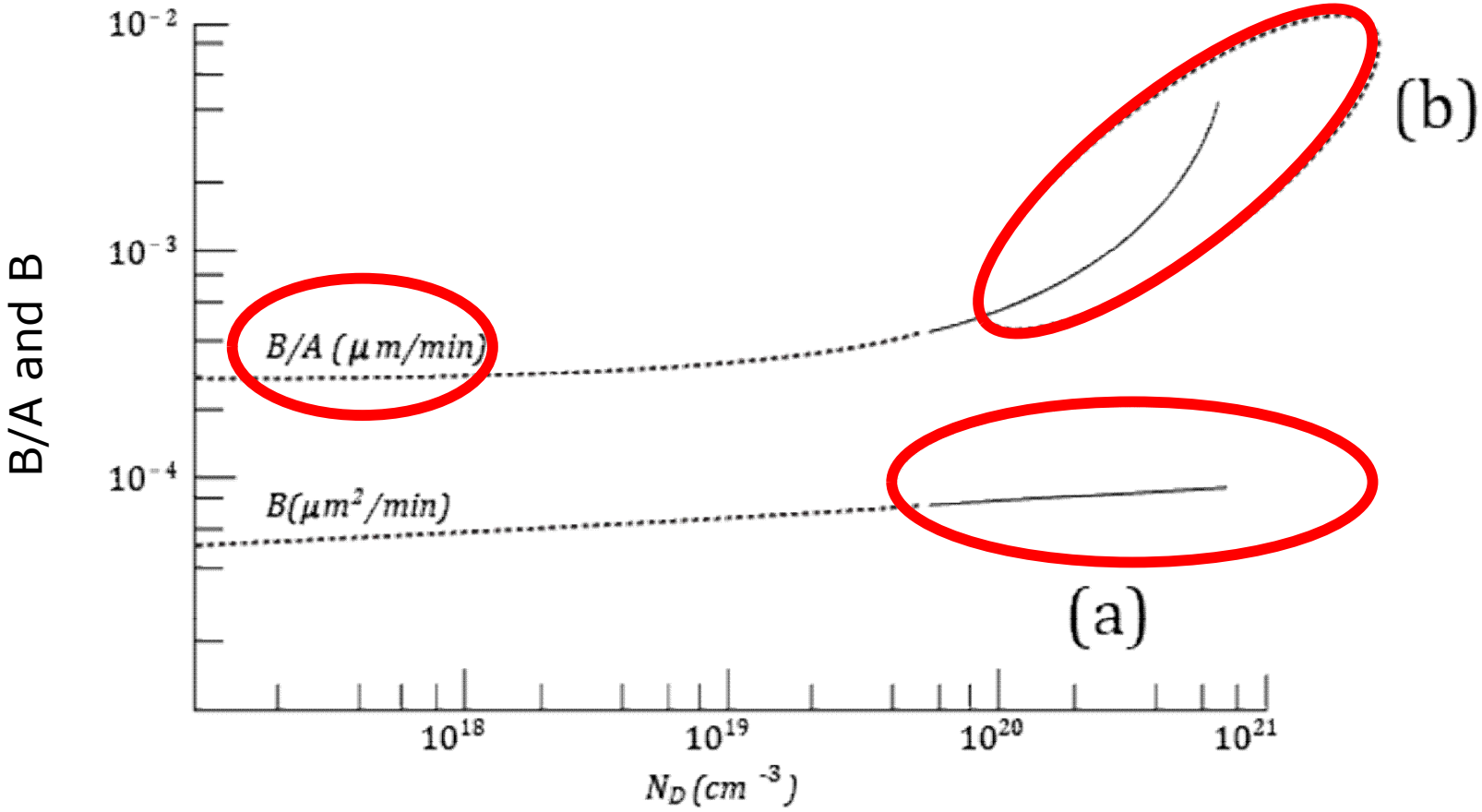


Figure 4.14

a) Parabolic rate coefficient (B) shows modest increase at high doping.

b) Linear rate coefficient (B/A) shows significant increase at high doping.

Effect of Boron

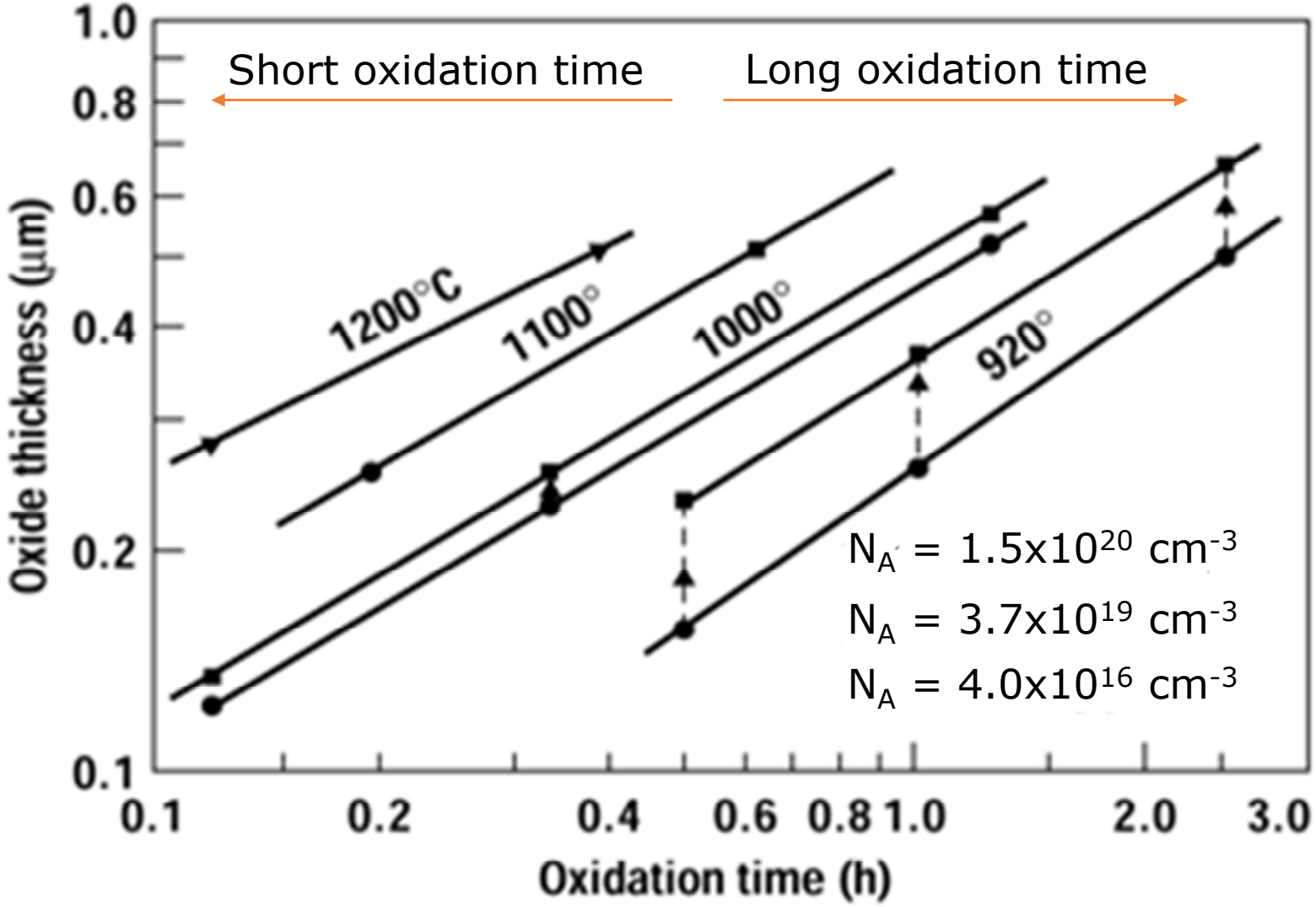


Figure 4.15

- Boron doping increases parabolic rate constant (B), but has little effect in B/A.

Oxide Masking

- Masking impurities takes place during ion-implantation and high-temperature diffusion.
- Diffusivities of impurities (e.g. Sb, As, B, P) in silicon oxide are orders of magnitude smaller than their corresponding values in silicon.
- Oxidation environment will affect the diffusivity of the impurity (e.g. presence of H_2 will greatly increase the boron diffusivity) such as during wet oxidation.

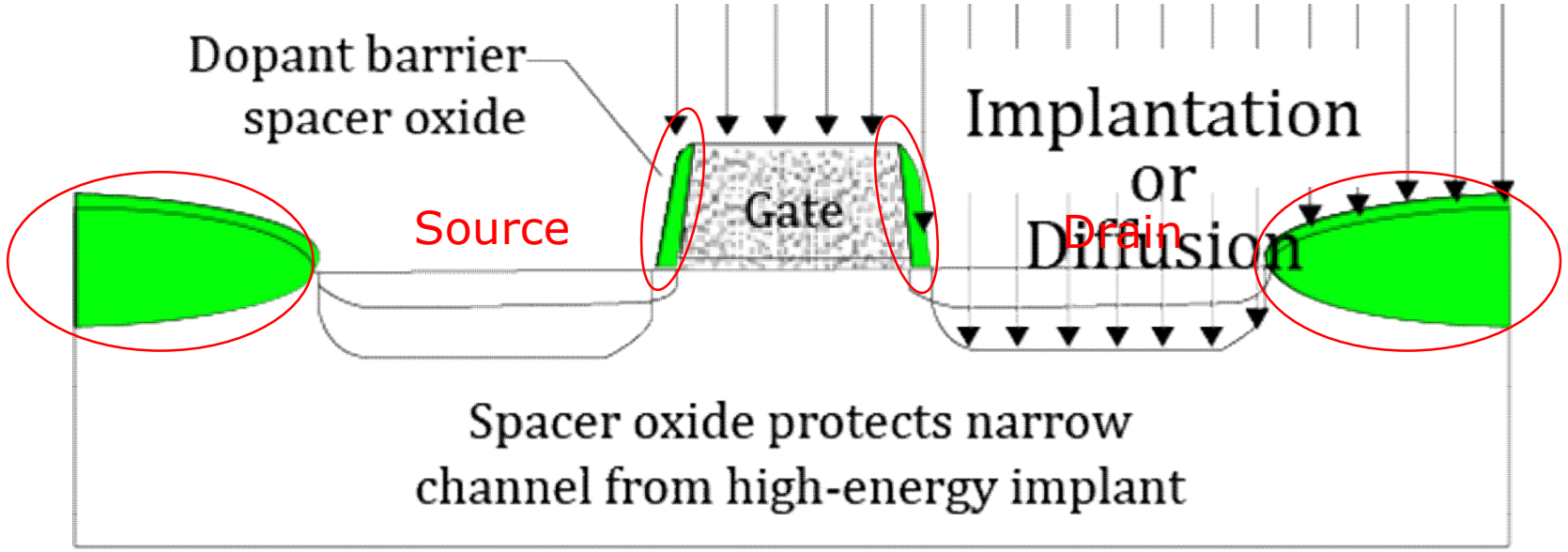


Figure 4.16

Oxide Masking (Cont'd.)

- Some impurities (e.g. Ga and Al) diffuses rapidly through SiO_2. Hence, it needs other type of masking material such as silicon nitride.
- **Example:**
  - For phosphorus diffusion at $1100°C$ with a diffusion time of $5\ hrs$, need an oxide mask thickness of $> 1\mu m$

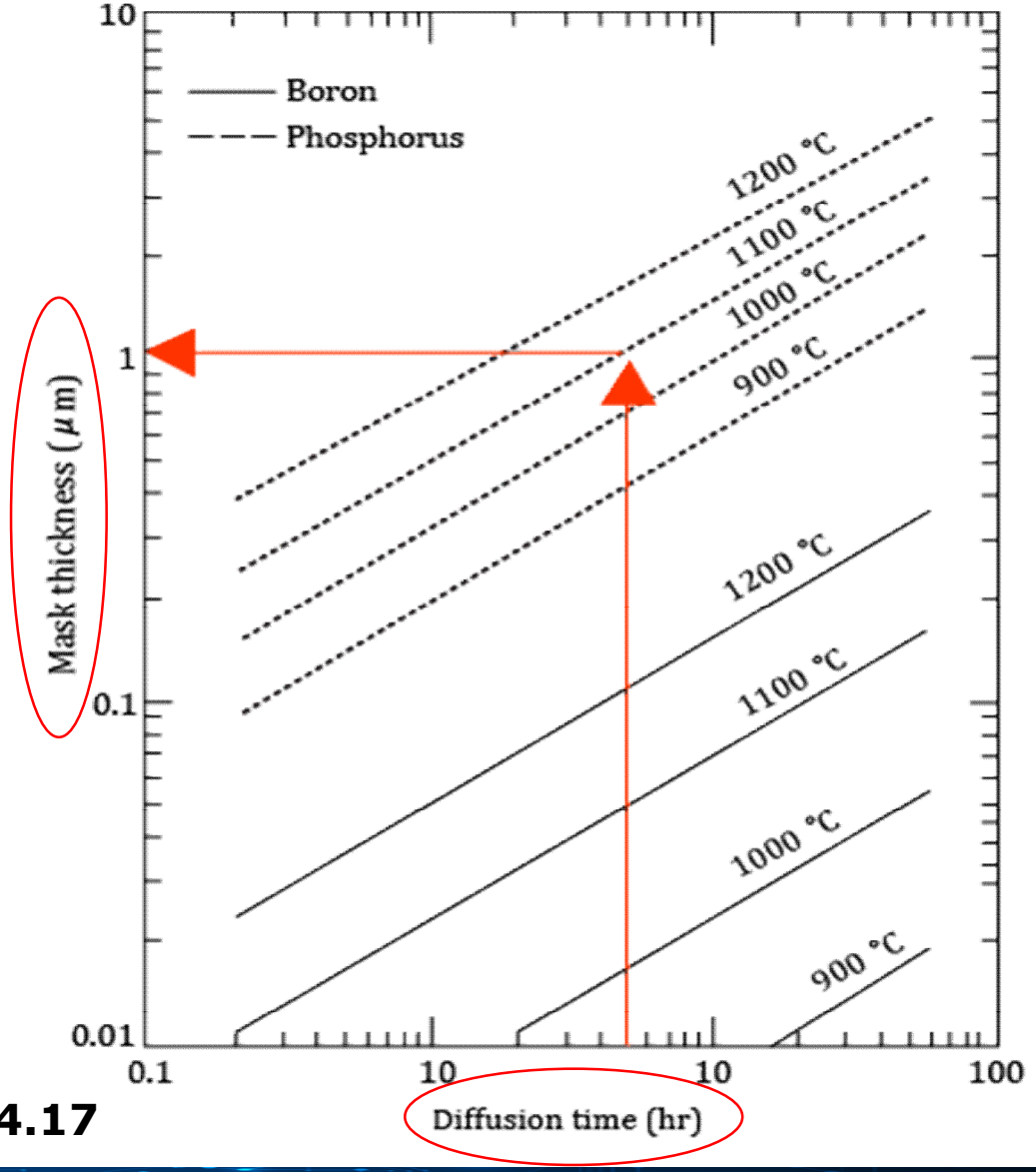


Figure 4.17

Examples of Oxidation in Semiconductor Processes

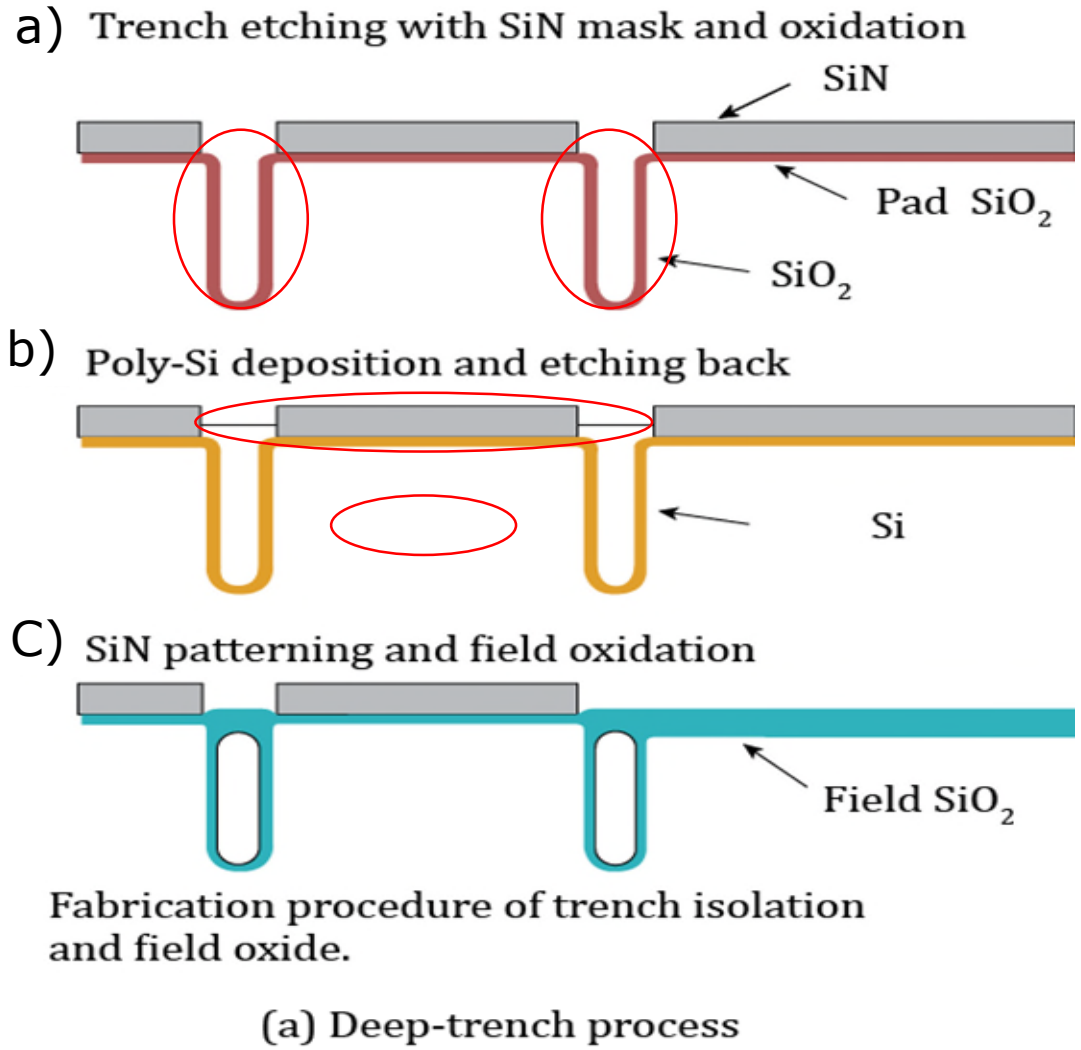


Figure 4.18

Thermal Oxidation for Deep Trench Isolation

- Often used in dynamic memory chips (DRAMS)
- Deep trenches used in high performance bipolar processes
- Deep trench isolation

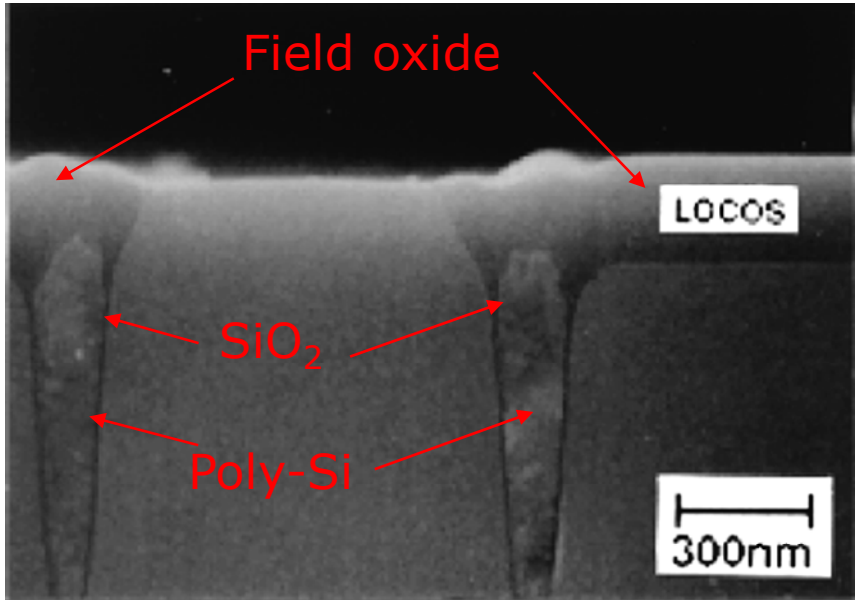


Figure 4.19

Examples of Oxidation in Semiconductor Processes

Thermal Oxidation for Shallow Trench Isolation (STI)

- Used for isolation between devices and to minimise device capacitance
- Shallow trench isolation

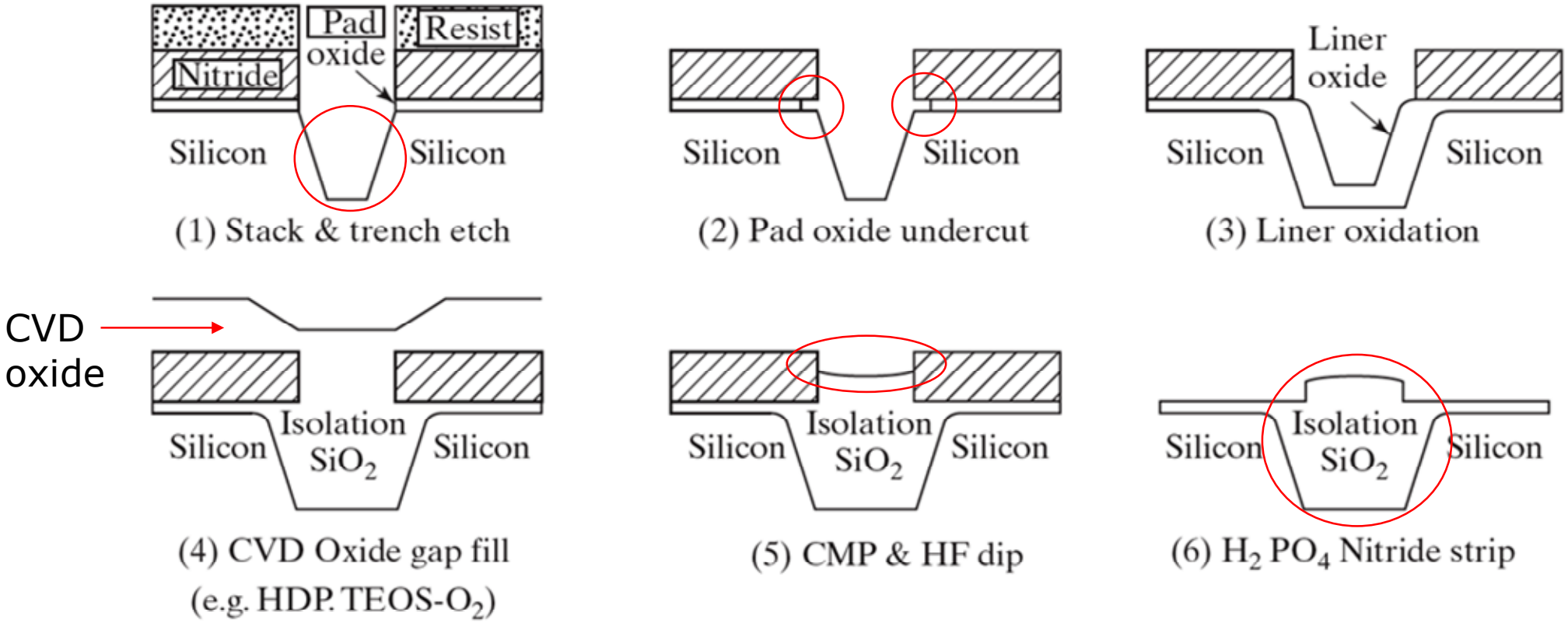


Figure 4.20 Steps in a typical STI process flow

Examples of Oxidation in Semiconductor Processes

Microphotography of actual deep and shallow trench isolation applied to SiGe HBT technology

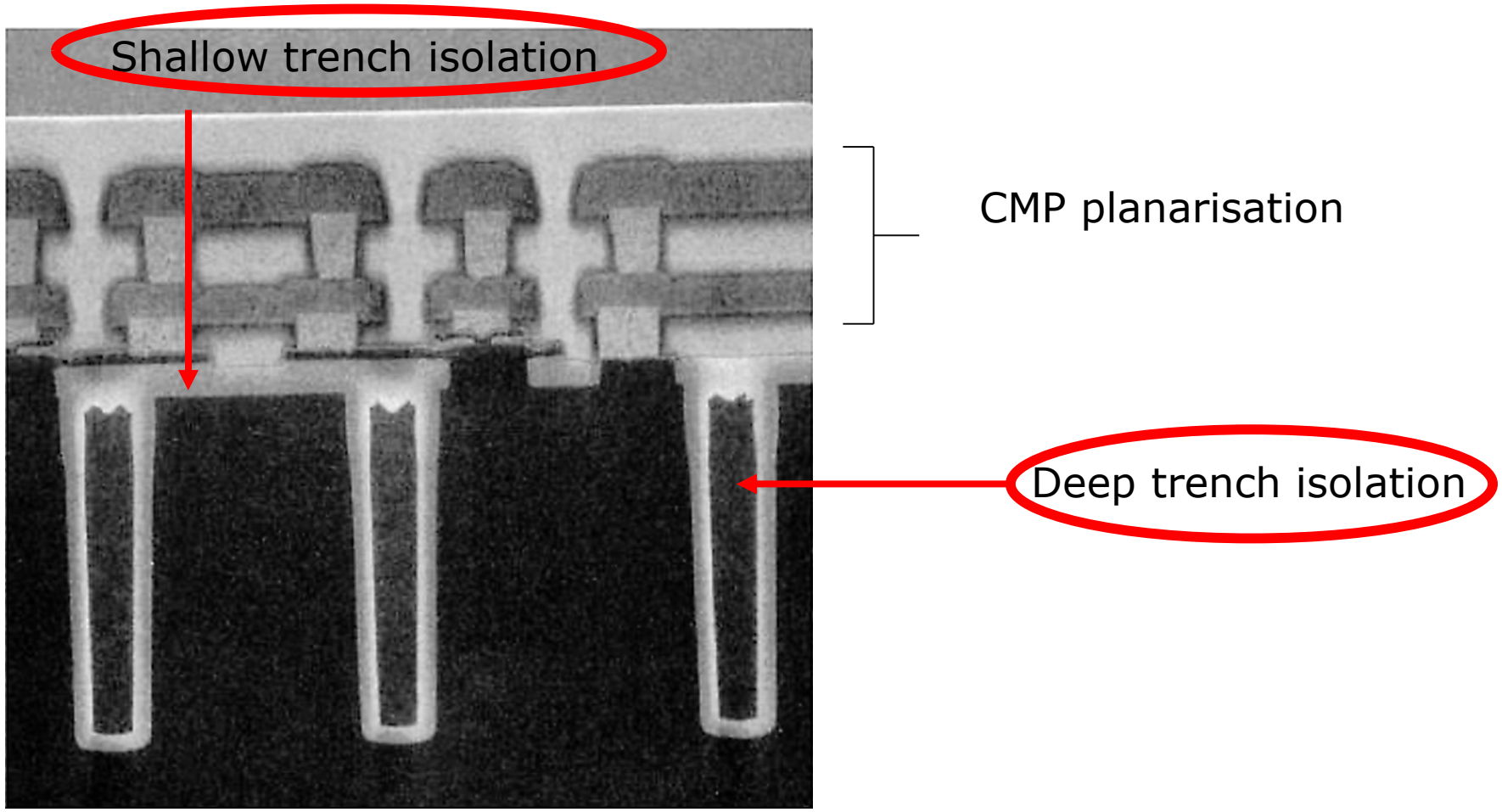


Figure 4.21

Thermal Oxidation Process Flow Chart

Wet Clean

- Chemicals
- % solution
- Time

Oxidation Furnace

- Gases: O_2, H_2, N_2
- Controllers for:
  - Flow rate
  - Temperature
  - Time
  - Exhaust

Inspection

- Film thickness
- Uniformity
- Particles
- Defects

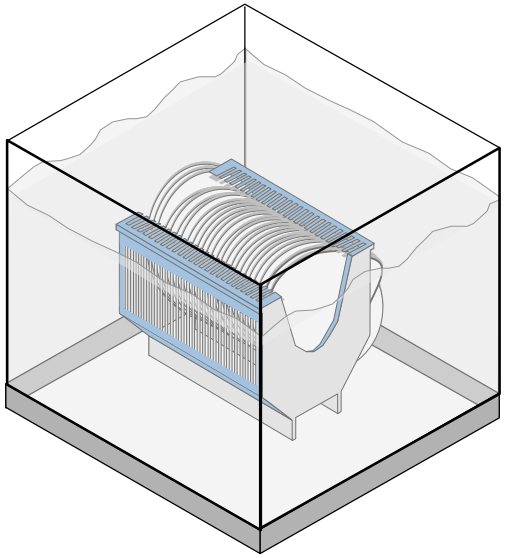
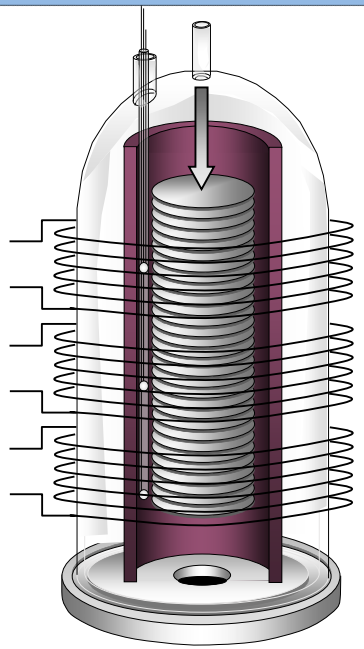
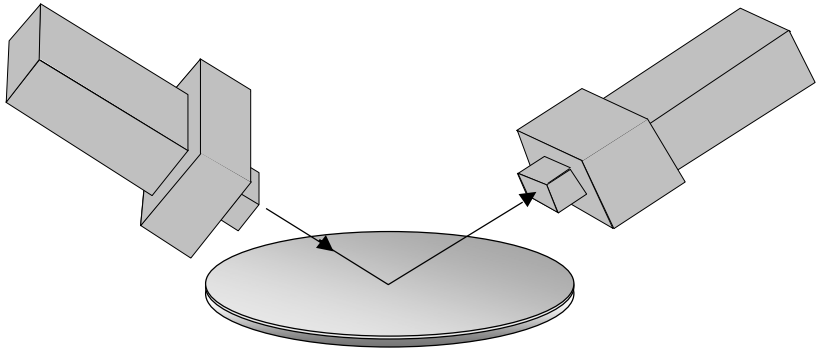


Figure 4.22





Thermal Oxidation Systems

A Horizontal Furnace for Dry or Wet oxidation

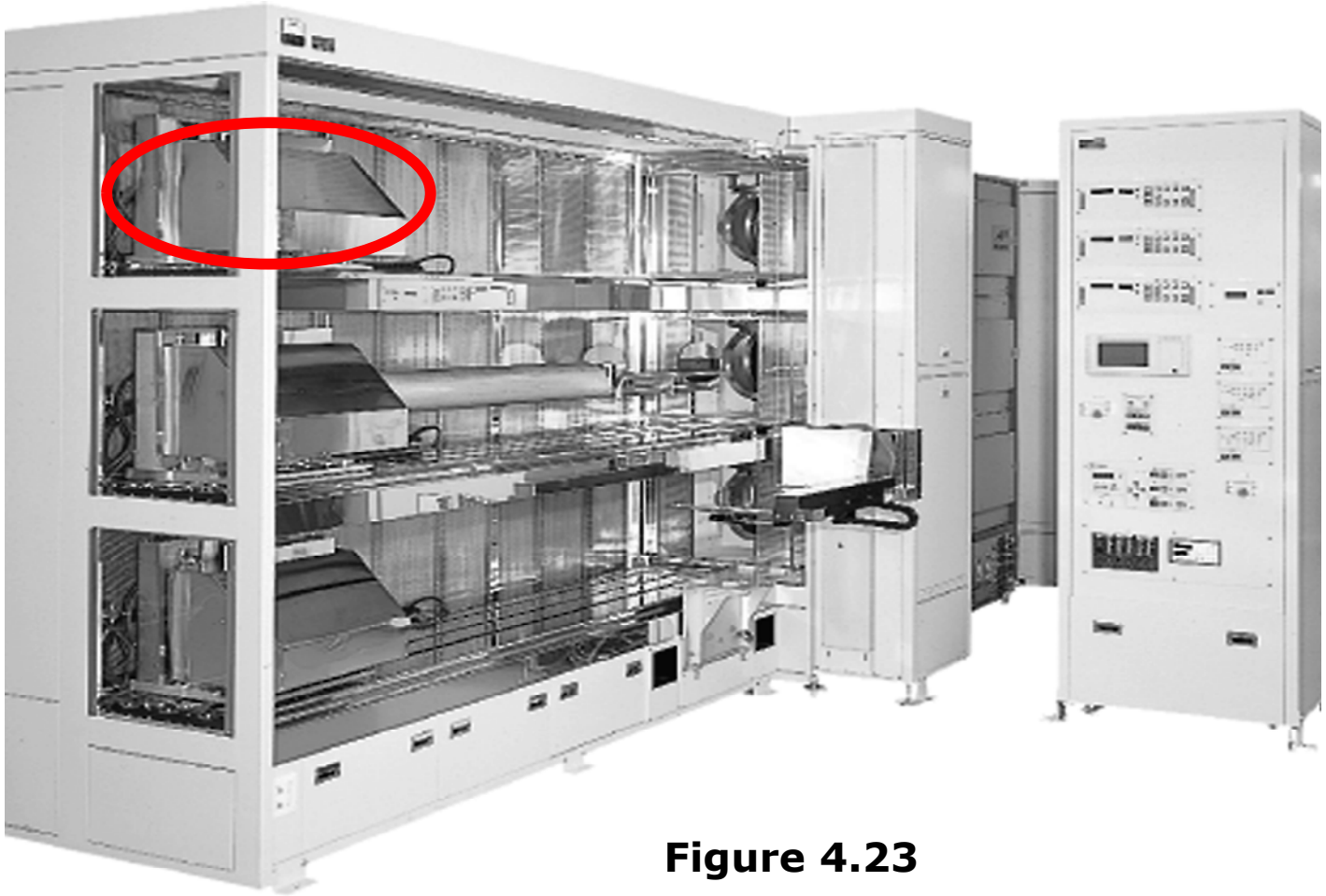
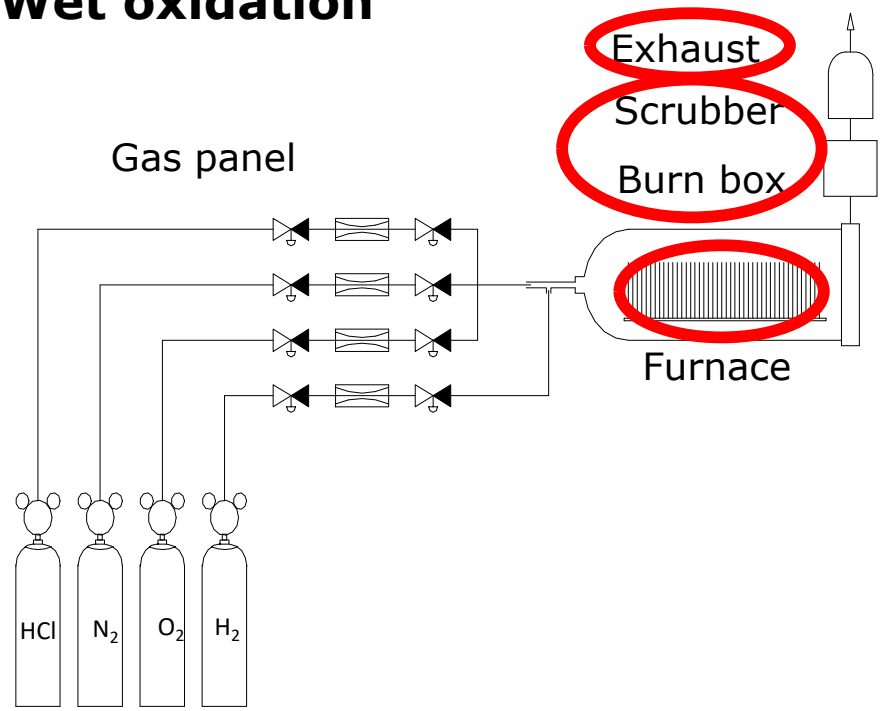


Figure 4.23



- Three-zone resistance heated furnace
- Temperature 800-1200°C
- The centre zone is over 0.5 m
- Furnace wall: quartz, polysilicon or SiC (no sodium contamination)

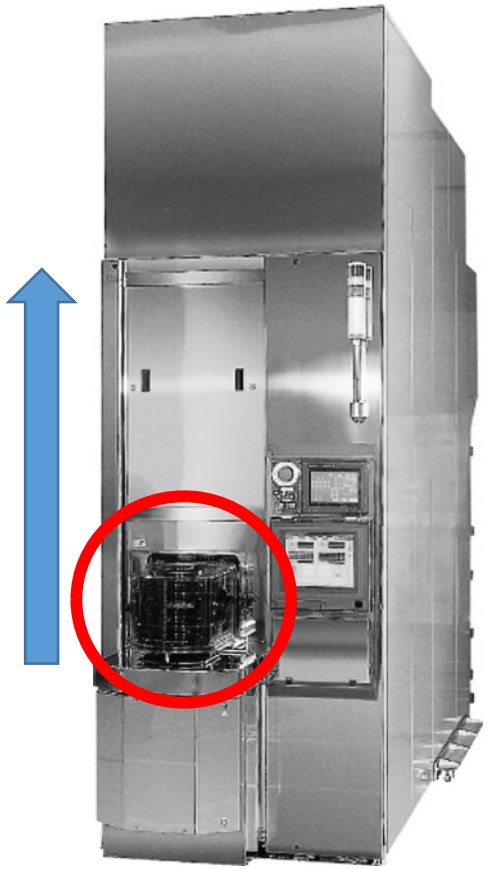
- Water vapor can be introduced by passing O_2 through a bubbler containing deionised water heated to 900^oC.

Thermal Oxidation Systems (Cont'd.)

Vertical Furnace

- For wafers with diameter $\geq 150\ mm$

Wafers are transferred vertically



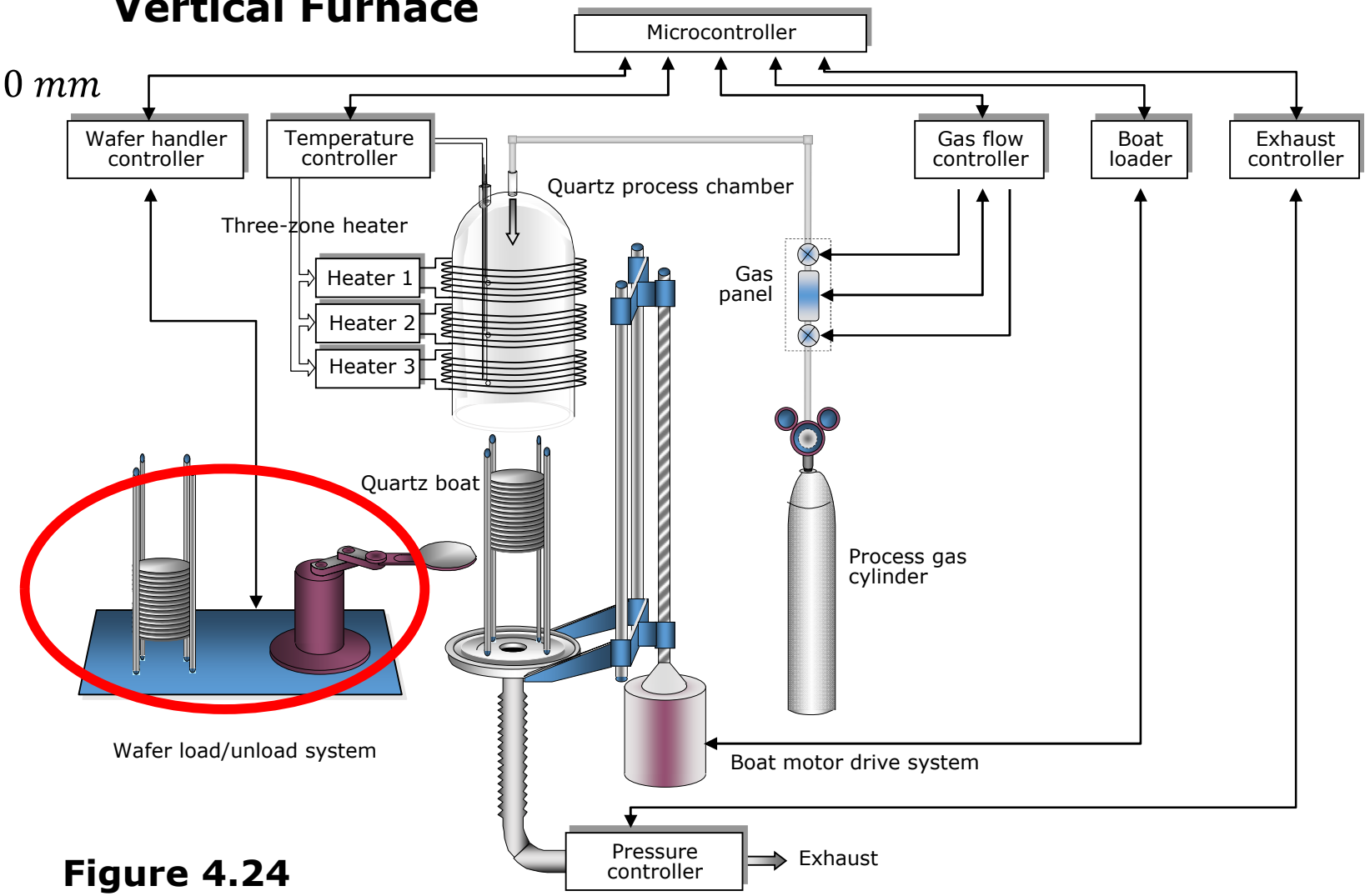


Figure 4.24

Rapid Thermal Processor for Ultrathin Gate Oxide

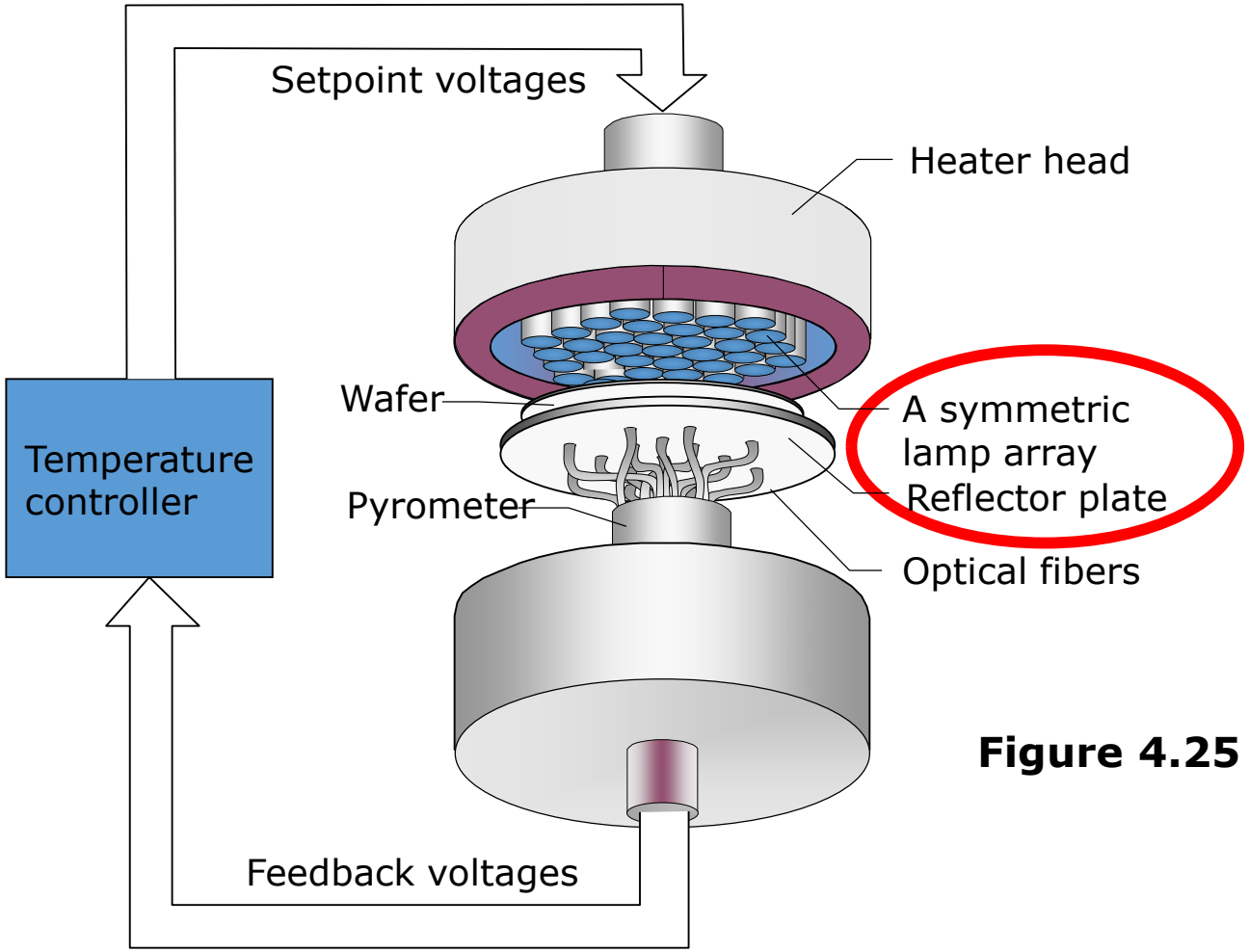
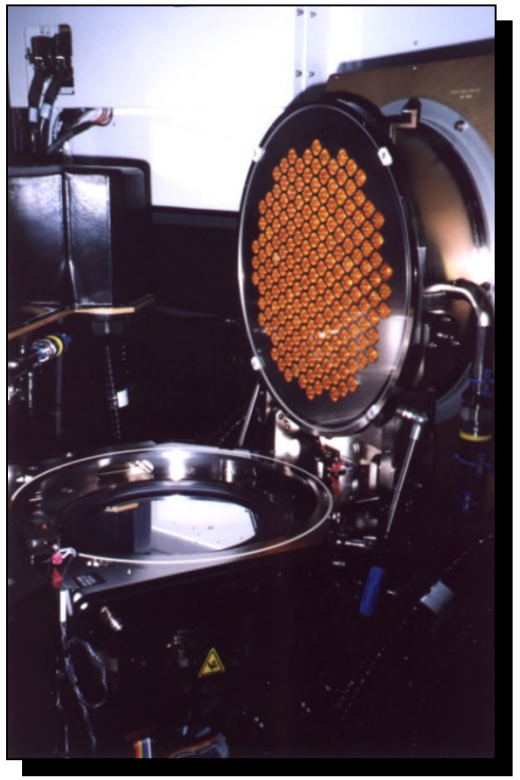


Figure 4.25



Oxide Thickness Measurement

Table 4.3

Color Chart for Thermally Grown SiO_2 Films Observed Perpendicularly Under Daylight Fluorescent Lighting. Copyright 1964 by International Business Machines Corporation; reprinted with permission from Ref. [11].

Film Thickness (μm)	Color and Comments	Film Thickness (μm)	Color and Comments
0.05	Tan	0.58	Light orange or yellow to pink
0.07	Brown	0.60	Carnation pink
0.10	Dark violet to red violet	0.63	Violet red
0.12	Royal blue	0.68	"Bluish" (not blue but borderline between violet and blue green; appears more like a mixture between violet red and blue green and looks grayish)
0.15	Light blue to metallic blue		
0.17	Metallic to very light yellow green		
0.20	Light gold or yellow; slightly metallic	0.72	Blue green to green (quite broad)
		0.77	"Yellowish"
0.22	Gold with slight yellow orange	0.80	Orange (rather broad for orange)
		0.82	Salmon
0.25	Orange to melon	0.85	Dull, light red violet
0.27	Red violet	0.86	Violet
0.30	Blue to violet blue	0.87	Blue violet
0.31	Blue	0.89	Blue
0.32	Blue to blue green	0.92	Blue green
0.34	Light green	0.95	Dull yellow green
0.35	Green to yellow green	0.97	Yellow to "yellowish"
0.36	Yellow green	0.99	Orange
0.37	Green yellow	1.00	Carnation pink
0.39	Yellow	1.02	Violet red
0.41	Light orange	1.05	Red violet
0.42	Carnation pink	1.06	Violet
0.44	Violet red	1.07	Blue violet
0.46	Red violet	1.10	Green
0.47	Violet	1.11	Yellow green
0.48	Blue violet	1.12	Green
0.49	Blue	1.18	Violet
0.50	Blue green	1.19	Red violet
0.52	Green (broad)	1.21	Violet red
0.44	Violet red	1.24	Carnation pink to salmon
0.46	Red violet	1.25	Orange
0.47	Violet	1.28	"Yellowish"
0.48	Blue violet	1.32	Sky blue to green blue
0.49	Blue	1.40	Orange
0.50	Blue green	1.45	Violet
0.52	Green (broad)	1.46	Blue violet
0.54	Yellow green	1.50	Blue
0.56	Green yellow	1.54	Dull yellow green
0.57	Yellow to "yellowish" (not yellow but is in the position where yellow is to be expected; at times appears to be light creamy gray or metallic)		

Color Chart

- When a white light illuminates a wafer perpendicular to surface, the light penetrates oxide, and is reflected by Si wafer.
- The reflected light is enhanced at a wavelength due to interference.
- **Is not very accurate.**

Accurate Oxide Thickness Measurement

Ellipsometry

- Polarisation changes occur when light is reflected from or transmitted through a medium.
- Polarisation changes are a function of optical properties, thickness, and wavelength and angle of incidence of the light beam.
- The oxide thickness can be calculated from the differences in polarisation measured by an *ellipsometer*.
- Is capable to measure thin films down to 10 nm.

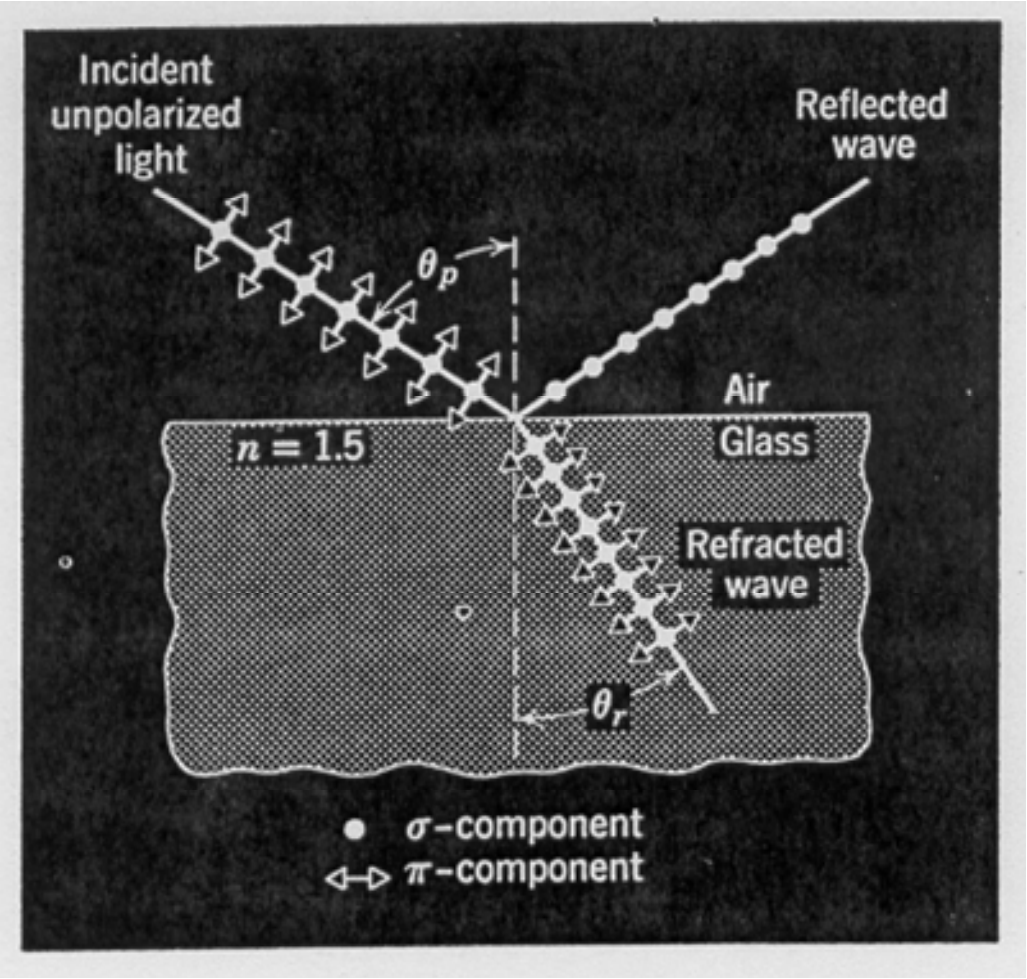
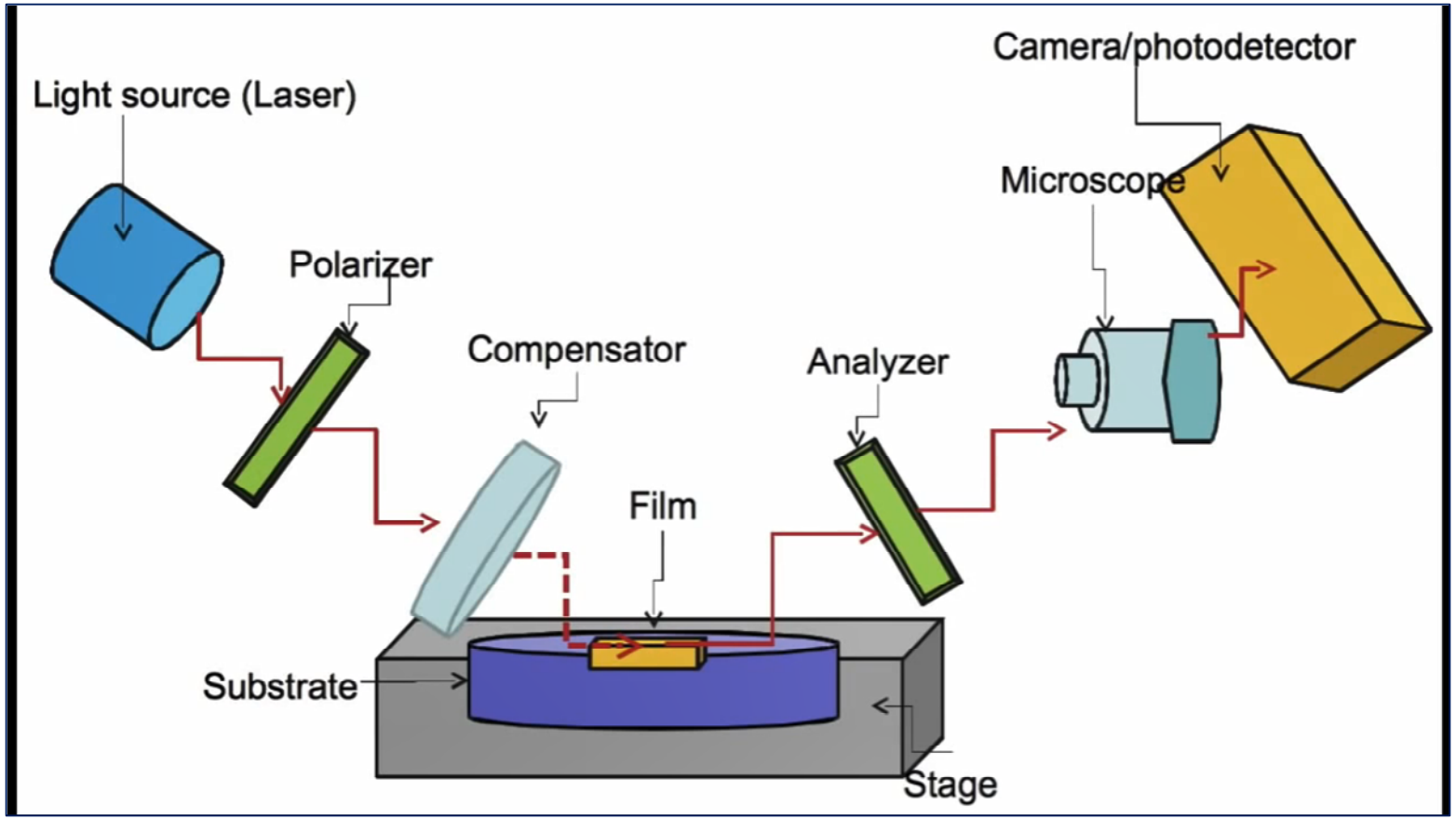


Figure 4.26

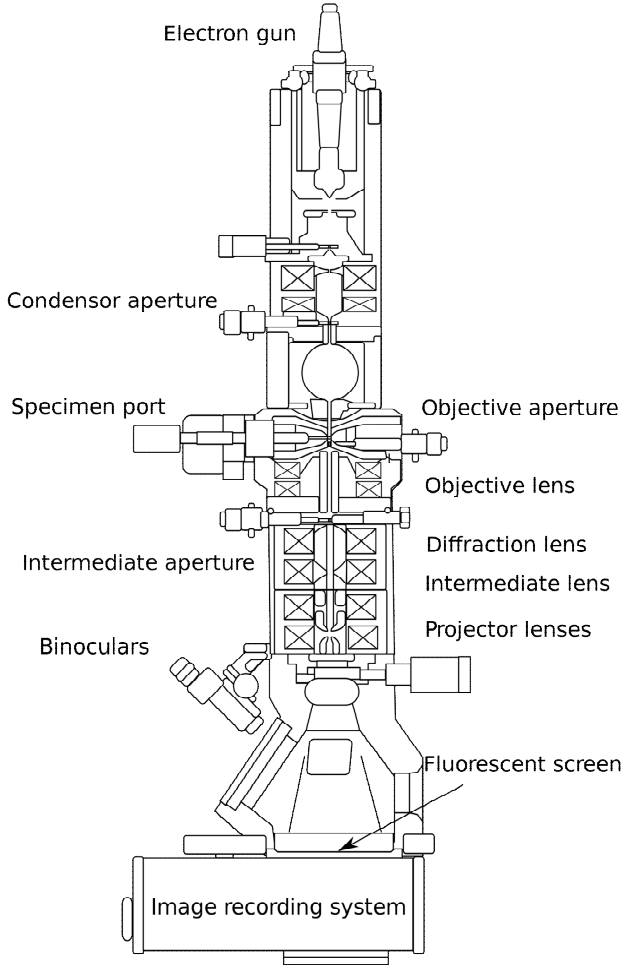
Working Principle of an Ellipsometer



S. (2011, December 01). ELLIPSOMETRY. Retrieved May 25, 2017, from https://www.youtube.com/watch?v=7dahtgGffhk&t=420s

Thickness Measurement for Ultrathin Gate Oxide

TEM (Transmission Electron Microscopy)



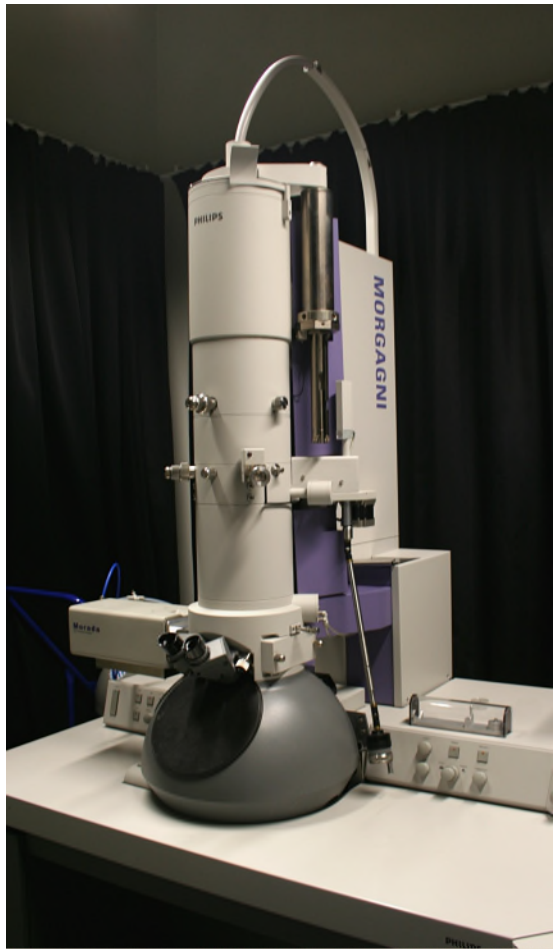
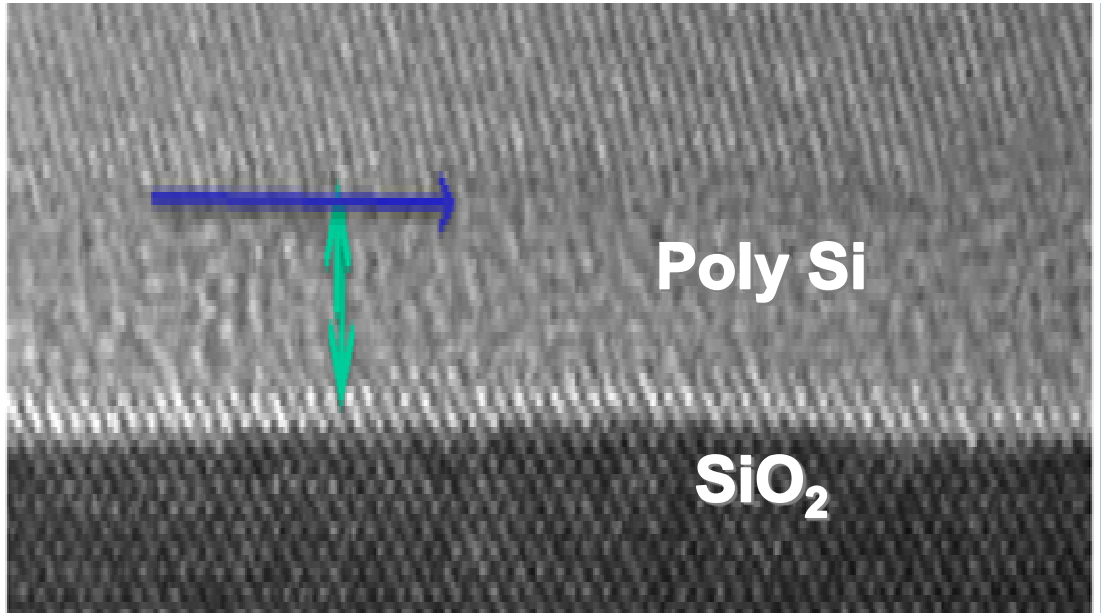


Figure 4.27



Si sub

Figure 4.28

Lesson Summary

1. **Properties of Silicon dioxide:** amorphous, high resistivity, very large band, good insulator, low interface trap density, low diffusivity for dopants ➔ good for isolation, gate dielectric and masking in semiconductor devices and processes
2. **Dry oxidation (Low oxidation rate):** higher quality, denser, higher breakdown voltage and low leakage current. Suitable for thin gate oxides in MOS devices and surface passivation

   Wet oxidation (High oxidation rate): poorer quality oxide, thick. Suitable for masking purpose and field oxide.
3. Oxide thickness is given by: $t_{ox} = \frac{-A+\sqrt{A^2+4B(t+\tau)}}{2}$ where $A = \frac{2D}{k_s}$, $B = \frac{2DN_0}{M}$ and $\tau = \frac{t^2{}_{ox}}{B} + \frac{t_{oxi}}{B/A}$
4. Short time with $t + \tau << \frac{A^2}{4B}$ ➔ $\Longrightarrow$ $t_{ox} = \frac{B}{A}(t+\tau)$ where $\boldsymbol{B/A}$ is called linear rate coefficient

   Long time with $t + \tau >> A^2/4B$, $t > \tau$ ➔ $t_{ox} = \sqrt{Bt}$ where $\boldsymbol{B}$ is called parabolic rate coefficient

Lesson Summary

5. **Factors affecting oxidation rate:** Growth techniques, Growth temperature, Pressure, Crystal orientation and Impurity doping
6. **Examples of oxidation in semiconductor processes:** masking, deep trench isolation, shallow trench isolation
7. **Types of thermal oxidation systems:** horizontal furnace, vertical furnace and rapid thermal processor
8. **Types of thickness measurement techniques**: colour chart, ellipsometry and Transmission Electron Microscopy