MAPÚA INSTITUTE OF TECHNOLOGY

Lecture 4: Silicon Oxidation

Topics covered:

Thermal Oxidation process to form SiO_2.
Impurity redistribution during oxidation.
Material properties and thickness measurement techniques for SiO_2.

MOSFET

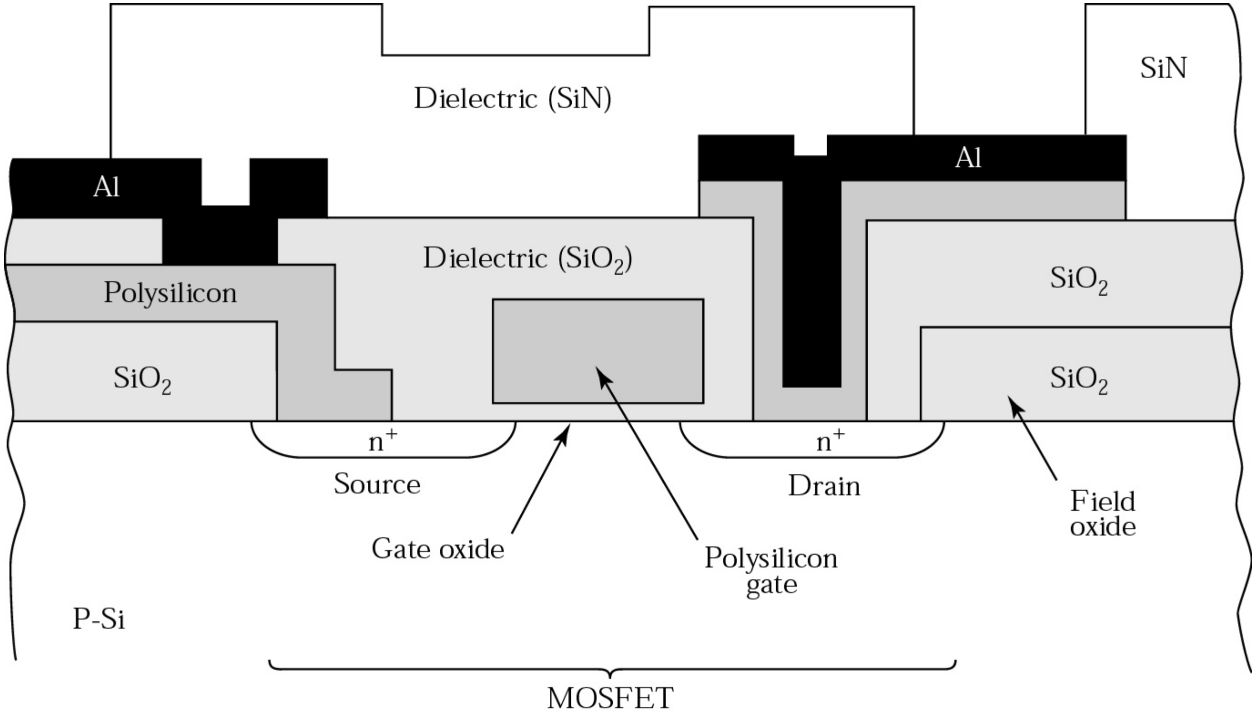


Fig 1. Schematic cross section of a metal-oxide-semiconductor field-effect transistor (MOSFET).

Thermal Oxidation Process

- Semiconductors can be oxidized by various methods such as thermal oxidation, electrochemical anodization and plasma-enhanced chemical vapor deposition (PECVD).
- Among these methods, *thermal oxidation is by far most important for silicon devices.* It is the key process in modern silicon integrated circuit technology. For GaAs, however, thermal oxidation results in generally nonstoichiometric films – which provide poor electrical insulation and semiconductor surface protection; hence, these oxides are rarely used in GaAs technology.

Thermal Oxidation Apparatus

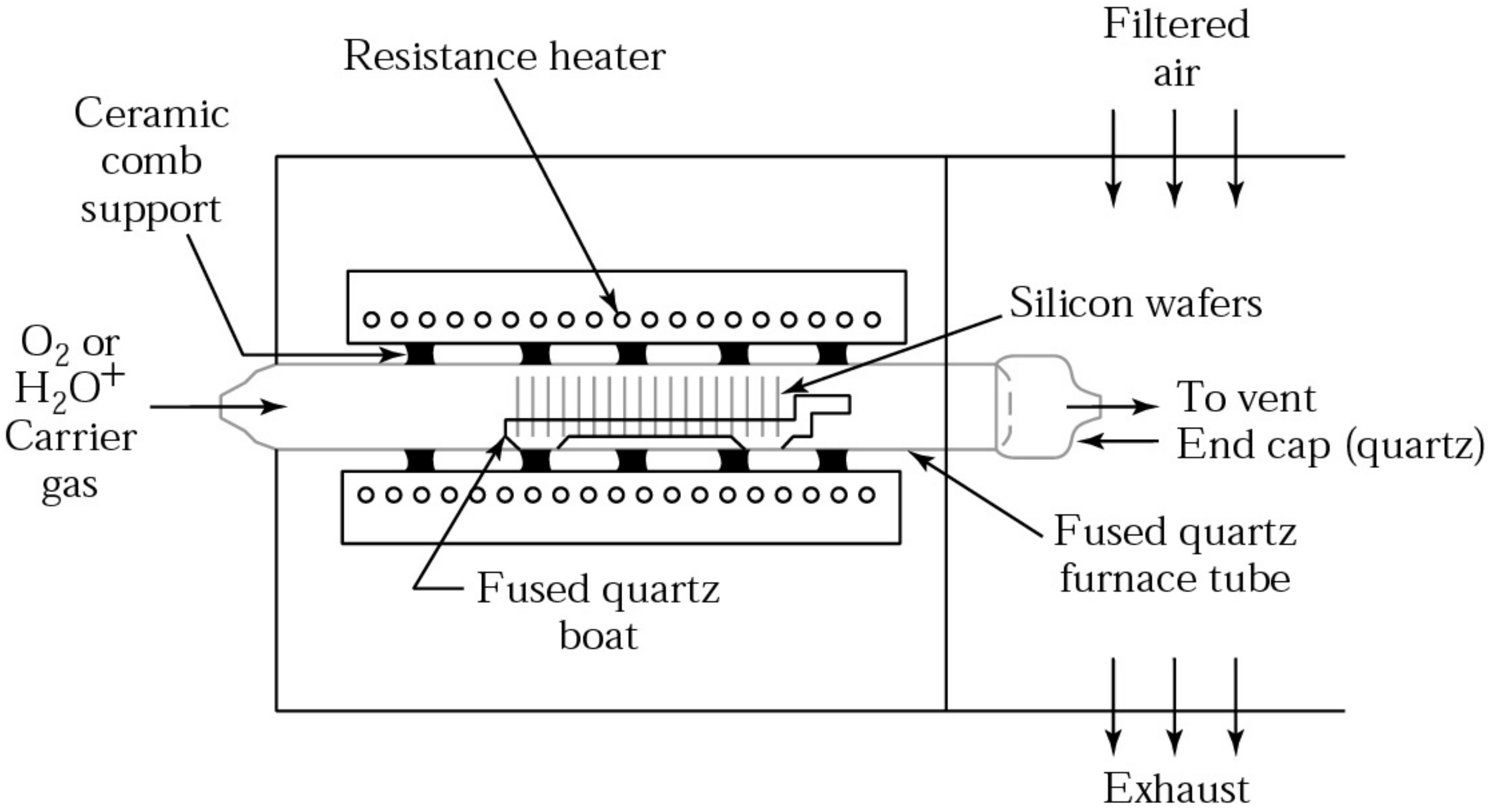


Fig 2. Schematic cross section of a resistance-heated oxidation furnace.

Kinetics of Growth

- Thermal oxidation of silicon in oxygen (dry oxidation) or water vapor (wet oxidation):

$$Si(solid) + O_2(gas) \rightarrow SiO_2(solid) \qquad (1)$$

$$Si(solid) + 2H_2O(gas) \rightarrow SiO_2(solid) + 2H_2(gas) \qquad (2)$$

Thermal Oxidation

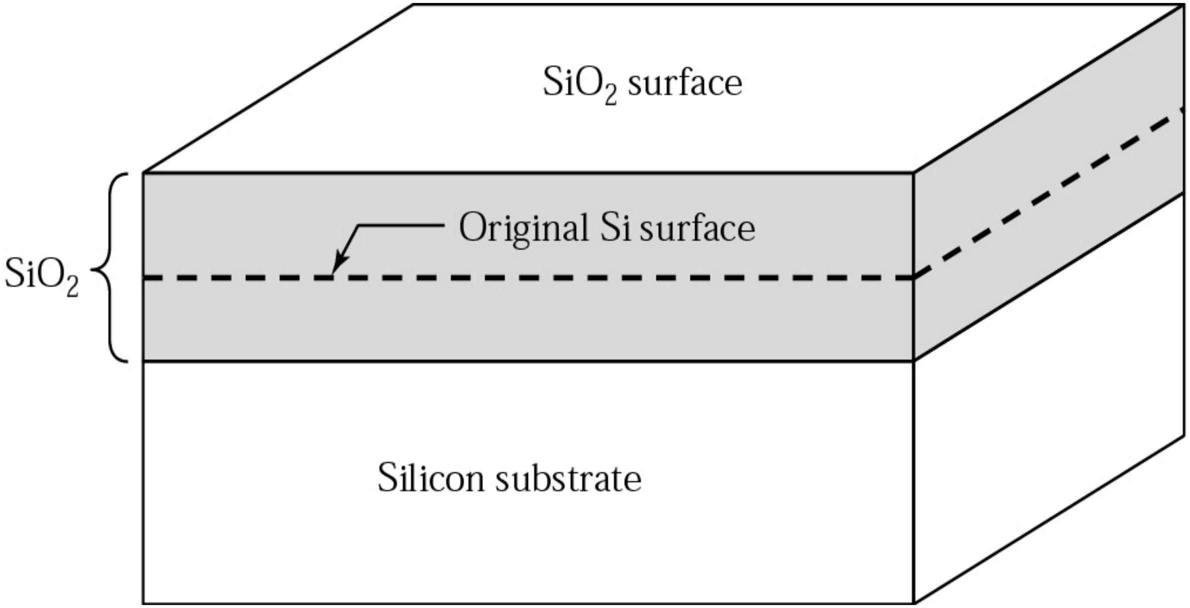


Fig 3. Growth of silicon dioxide by thermal oxidation.

- Growing an oxide of thickness x consumes a layer of silicon $0.44x$ thick.

Example 1

- If the silicon oxide layer of thickness by thermal oxidation, what is the thickness of silicon being consumed? The molecular weight of Si is 28.9 g/mol, and the density of Si is 2.33 g/cm^3. The corresponding values for SiO_2 are 60.08 g/mol and 2.21 g/cm^3.

Quartz Crystal Lattice

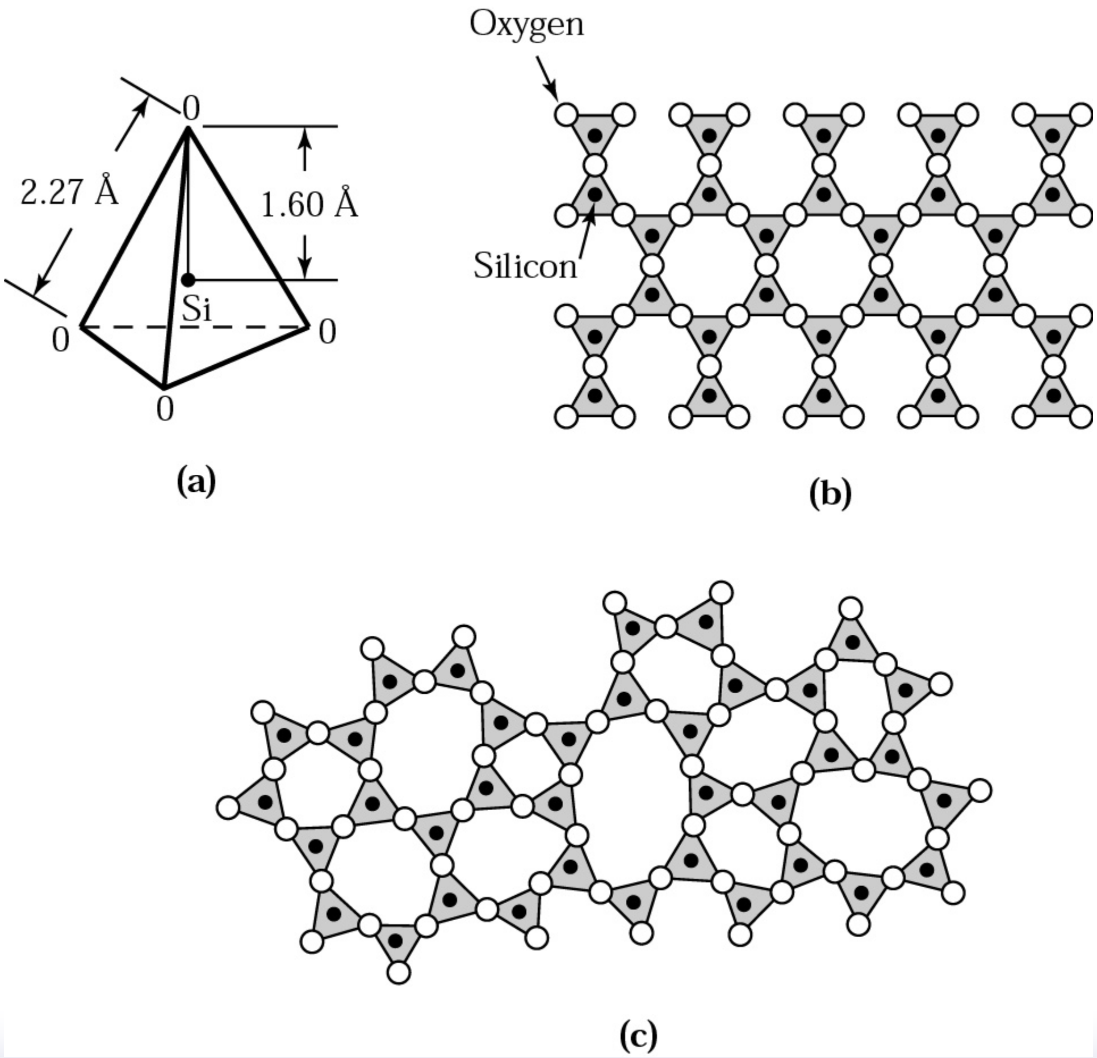


Fig 4. Quartz Crystal Lattice
(a) Basic structural unit of silicon dioxide.
(b) Two-dimensional representation of a quartz crystal lattice.
(c) Two-dimensional representation of the amorphous structure of silicon dioxide.

Basic Model for Silicon Thermal Oxidation

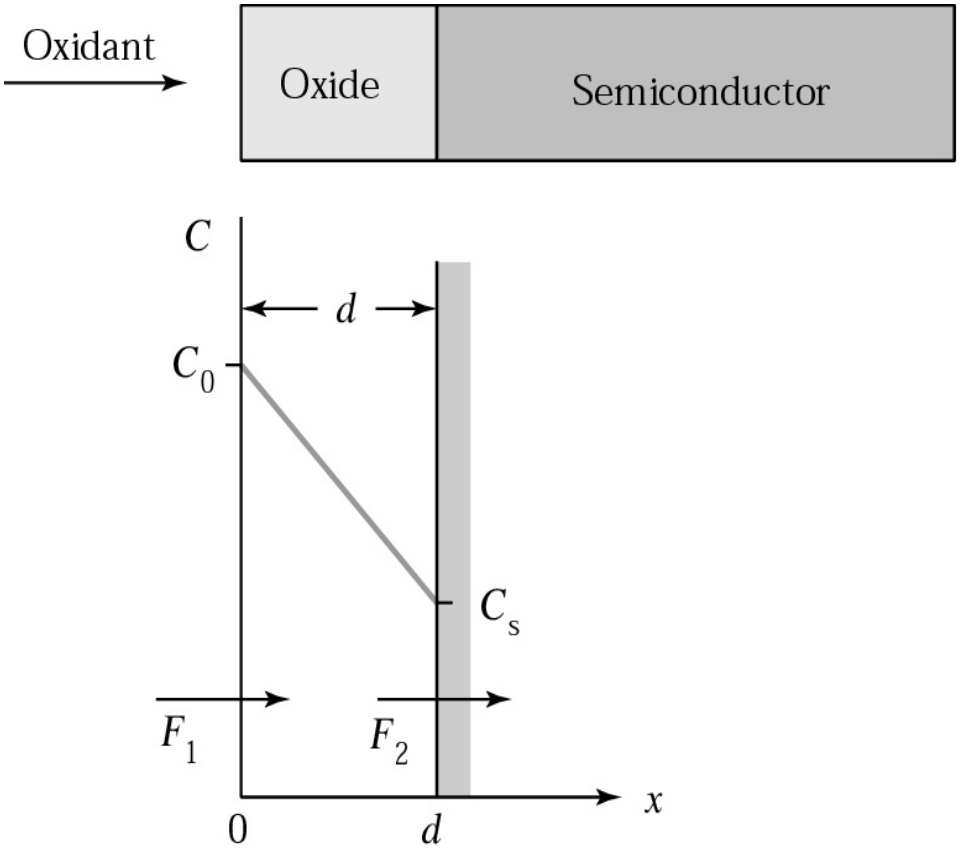
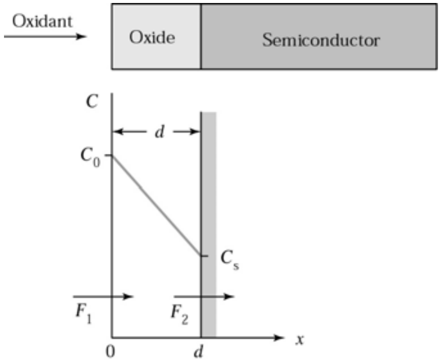
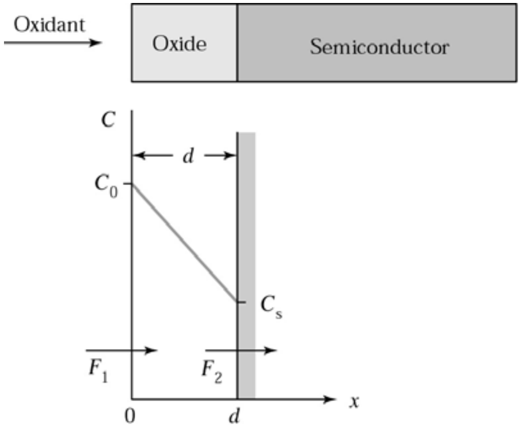


Fig 5. Thermal oxidation Model

Basic Model for Silicon Thermal Oxidation



- A silicon slice contacts the oxidizing species (oxygen and water vapor), resulting in a surface concentration of C_o molecules/cm^3 for these species.
- The magnitude of C_o equals the equilibrium bulk concentration of the species in the oxidation temperature. The equilibrium concentration generally is proportional to the partial pressure of the oxidant adjacent to the oxide surface. At 1000°C and at a pressure of 1 atm, the concentration C_o is 5.2×10^{16} molecules/cm^3 for dry oxygen and 3×10^{19} molecules/cm^3 for water vapor.



- The oxidizing species diffuses through the silicon dioxide layer, resulting in a concentration ***C_s*** at the surface of silicon. The flux ***F_1*** can be written as:

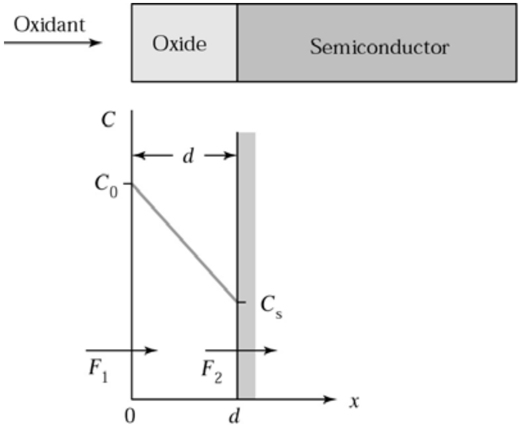
$$F_1 = D\frac{dC}{dx} \cong \frac{D(C_0 - C_s)}{x} \qquad (3)$$

where ***D*** is the diffusion coeeficient of the oxidizing species, and ***x*** is the thickness of the oxide layer already present.

- At silicon surface, ***F_2*** is given by:

$$F_2 = \kappa C_s \qquad (4)$$

where κ is the surface reaction rate constant oxidation.



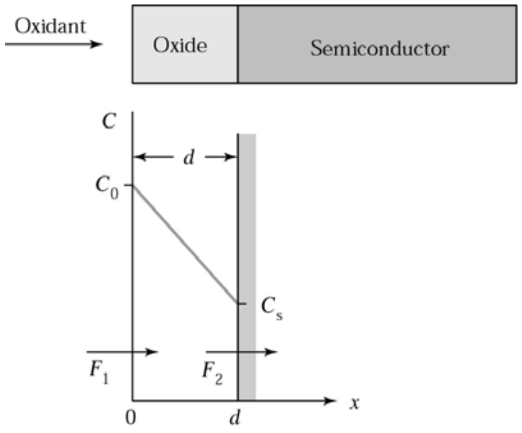
- Combining equation (3) and (4) gives

$$F = \frac{DC_0}{x + (D/\kappa)} \qquad (5)$$

- The growth rate of the oxide layer thickness is given by

$$\frac{dx}{dt} = \frac{F}{C_1} = \frac{DC_0/C_1}{x + (D/\kappa)} \qquad (6)$$

- Solve this differential with initial condition, ***$x(0)=d_0$***, where ***d_0*** is the initial oxide thickness.



- Equation (6) yields the general relationship for the oxidation of silicon,

$$x^2 + \frac{2D}{\kappa}x = \frac{2DC_0}{C_1}(t+\tau) \qquad (7)$$

where $\tau \equiv (d^2{}_0 + 2Dd_0/\kappa)C_1/2DC_0$, which represents a time coordinate shift to account for the initial oxide layer ***d_0***.

- The oxide thickness, x after an oxidizing time ***t*** is given by

$$x = \frac{D}{\kappa}\left[\sqrt{1+\frac{2C_0\kappa^2(t+\tau)}{DC_1}} - 1\right] \qquad (8)$$

- For small values of t, Eq. 8 reduces to $x \cong \dfrac{C_0\kappa(t+\tau)}{C_1}$ (9)

- For large values of t, Eq. 8 reduces to $x = \sqrt{\dfrac{2DC_0}{C_1}(t+\tau)}$ (10)

- During the early stages of oxide growth, when *surface reaction is the rate-limiting factor*, the oxide thickness varies linearly with time. As the oxide layer becomes thicker, the oxidant must diffuse though the oxide layer to react at the silicon-silicon dioxide interface, and the reaction becomes diffusion limited. The oxide growth then becomes proportional to the square root of the oxidizing time, which results into parabolic growth rate.

- Equation (7) is often written in a more compact form.

$$x^2 + Ax = B(t+\tau) \qquad (11)$$

where A=2D/κ, B=2DC$_0$/C$_1$, and B/A = κC$_0$/C$_1$.

Eqs. (9) and (10) can be written as

$$x \cong \frac{B}{A}(t+\tau) \quad \text{(linear region)} \qquad (12)$$

$$x^2 = B(t+\tau) \quad \text{(parabolic region)} \qquad (13)$$

where B/A is referred to as linear rate constant
B is the parabolic rate constant

Rate of Constants for Wet Oxidation of Silicon

Oxidation Temperature (^oC)	A (um)	Parabolic Rate Constant B (um^2/h)	Linear Rate Constant B/A (um/h)	τ (h)
1200	0.05	0.720	14.40	0
1100	0.11	0.510	4.64	0
1000	0.226	0.287	1.27	0
920	0.50	0.203	0.406	0

Rate of Constants for Dry Oxidation of Silicon

Oxidation Temperature (^oC)	A (um)	Parabolic Rate Constant B (um^2/h)	Linear Rate Constant B/A (um/h)	τ (h)
1200	0.040	0.0450	1.120	0.027
1100	0.090	0.0270	0.300	0.076
1000	0.165	0.0117	0.071	0.370
920	0.235	0.0049	0.0208	1.400
800	0.370	0.0011	0.0030	9.000
700	---	---	0.00026	81.00

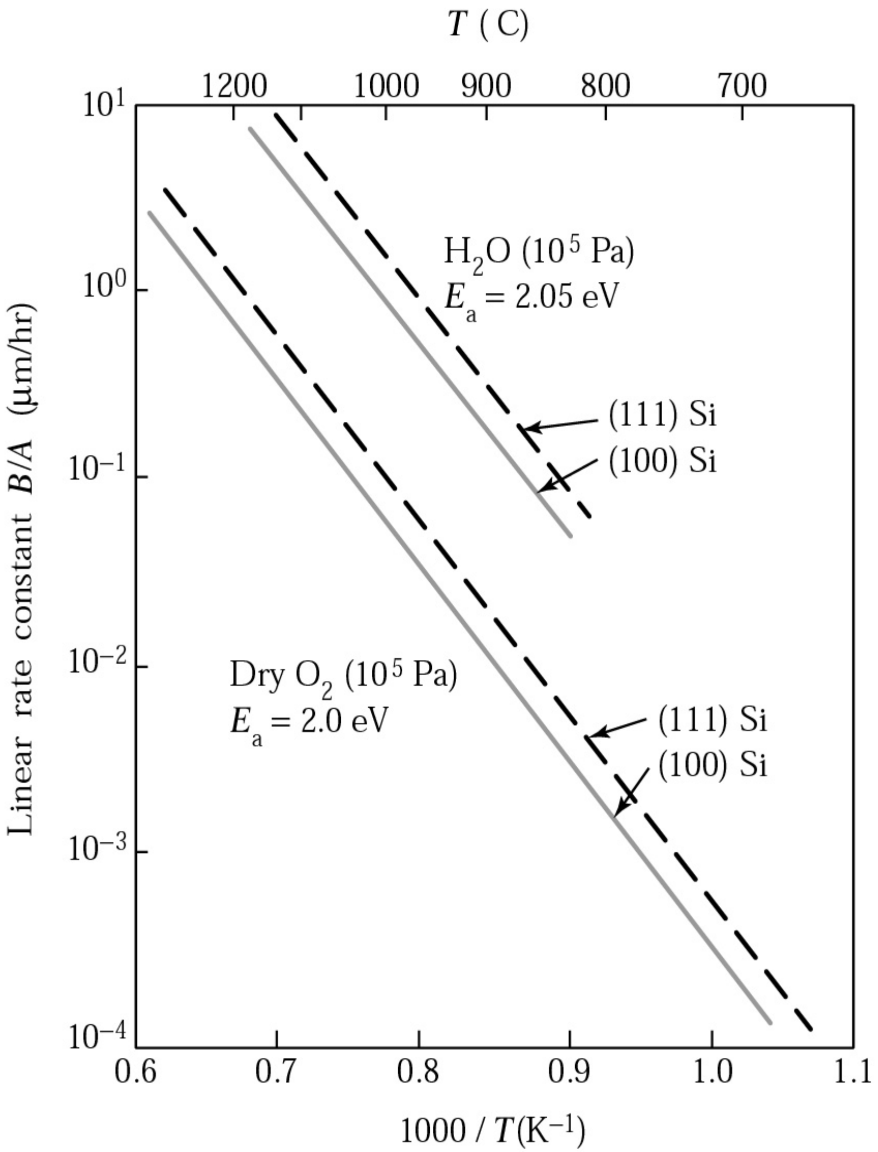


Fig 6. Linear rate constant versus temperature.

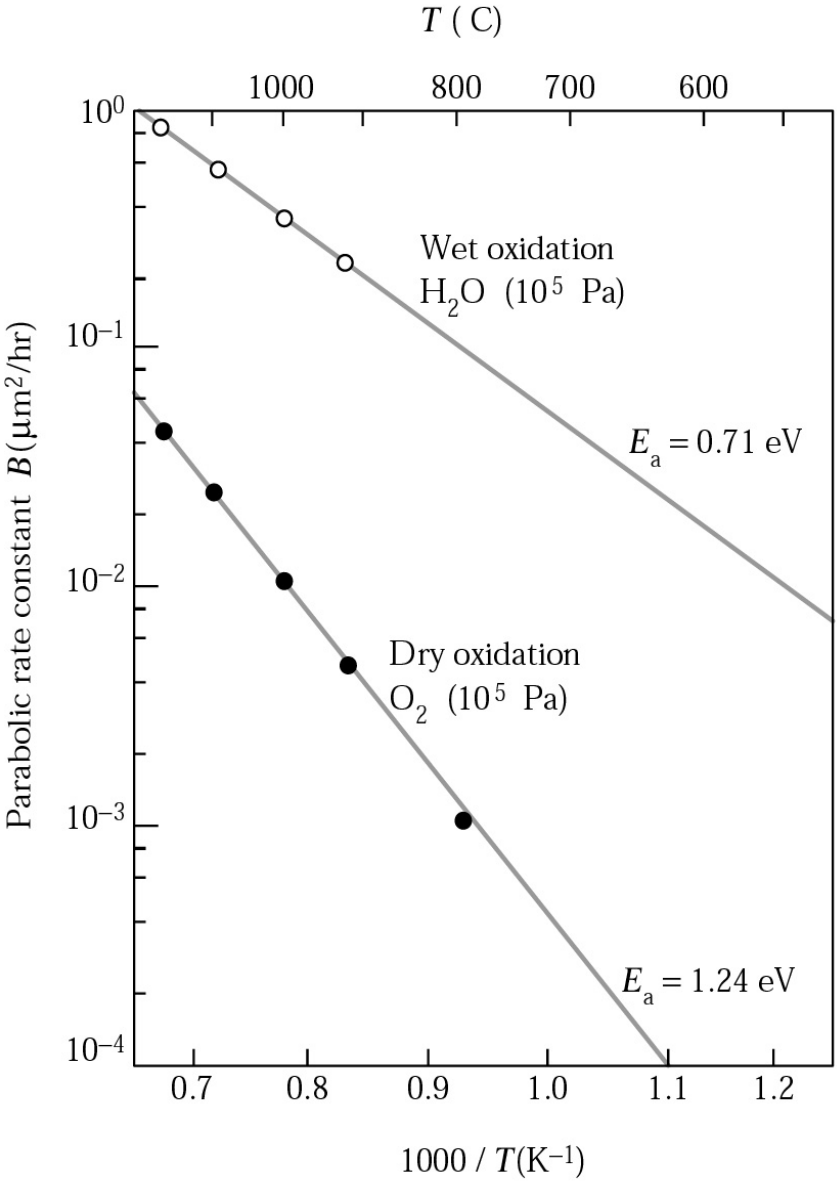
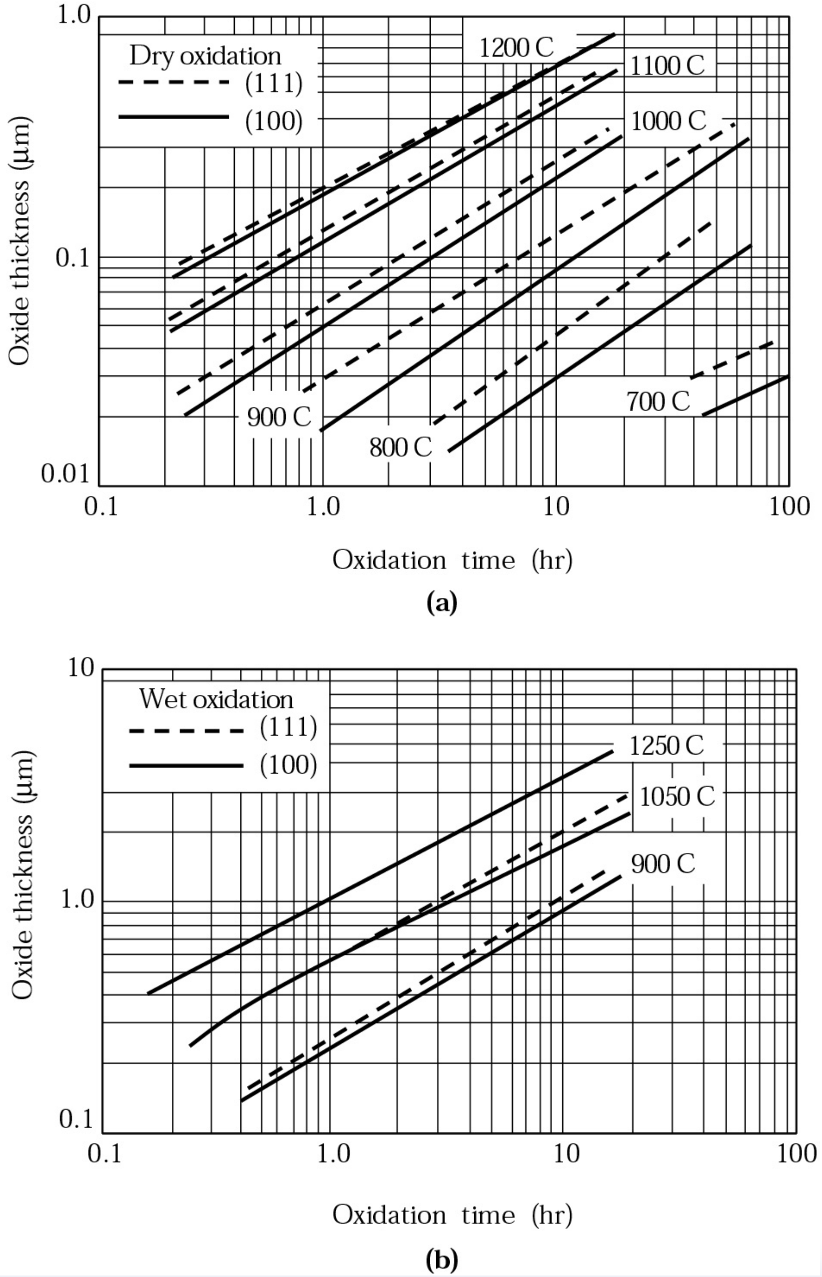


Fig 7. Parabolic rate constant versus temperature.

Experimental Results

Fig 8.
Silicon dioxide thickness as a function of reaction time and temperature for two substrate orientations.
(*a*) Growth in dry oxygen.
(*b*) Growth in steam.



Example 2

- A silicon is oxidized in dry O_2 at 1200^{o}C for 1 hour. (a) What is the thickness of the oxide grown? (b) How much additional time is required to grow 0.1um more oxide in wet O_2 at 1200^{o}C?

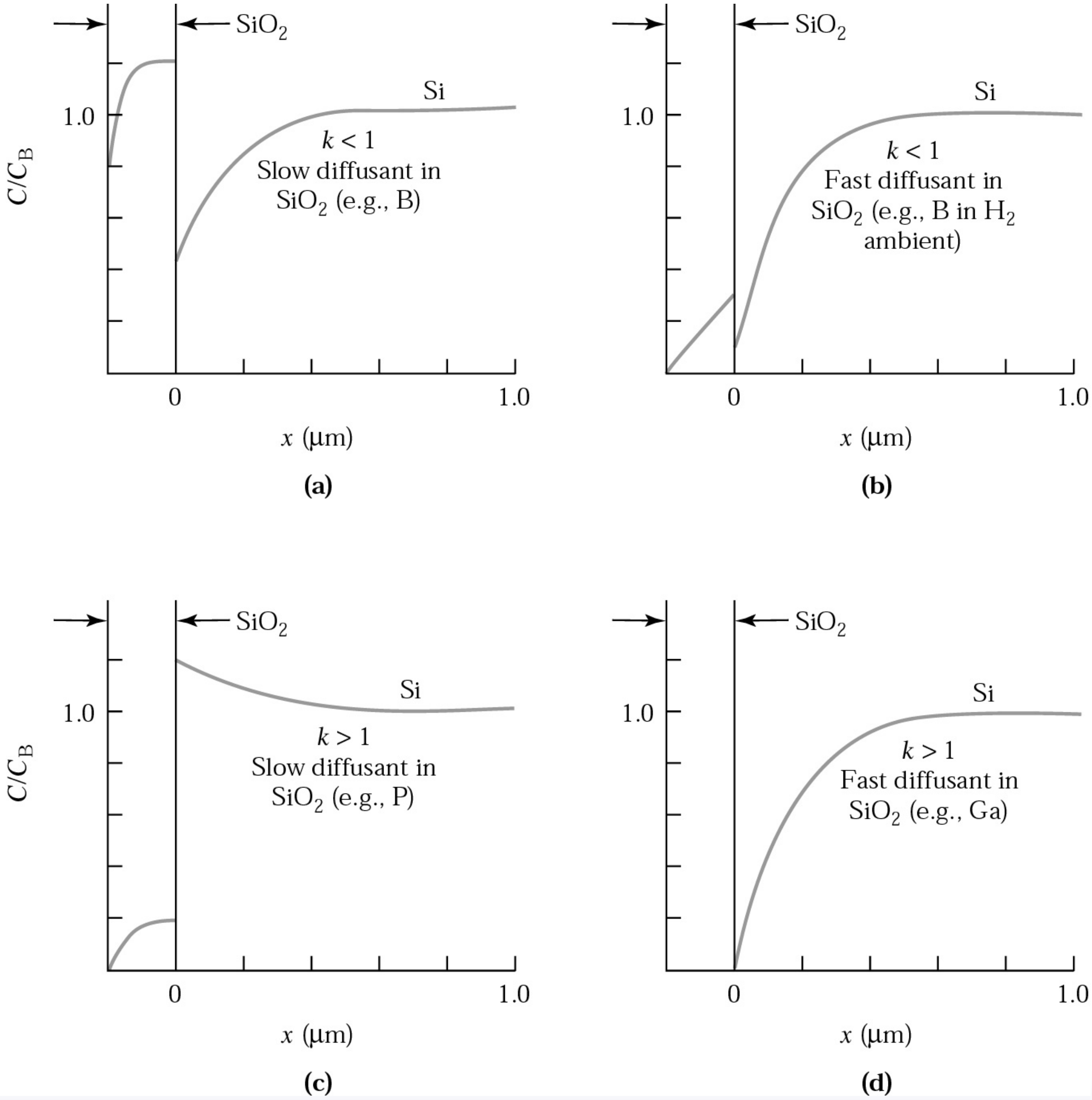
Impurity Distribution During Oxidation

- The distribution depends on several factors:
  - When two solid phases brought together, an impurity in one solid will distribute between solids until it reaches equilibrium. The ratio of the equilibrium concentration of the impurity in the silicon to that of the dioxide is called the segregation coefficient, denoted as *k*.

$$k = \frac{Equil.\_concentration\_of\_impurity\_in\_Si}{Equil.\_concentration\_of\_impurity\_in\_SiO_2}$$

  - Impurity may diffuse rapidly through the silicon dioxide and escape to the gaseous ambient.
  - The oxide is growing, thus the boundary between the silicon and the oxide is advancing into the silicon as a function of time.

Fig 9. Four different cases of impurity redistribution in silicon due to thermal oxidation.

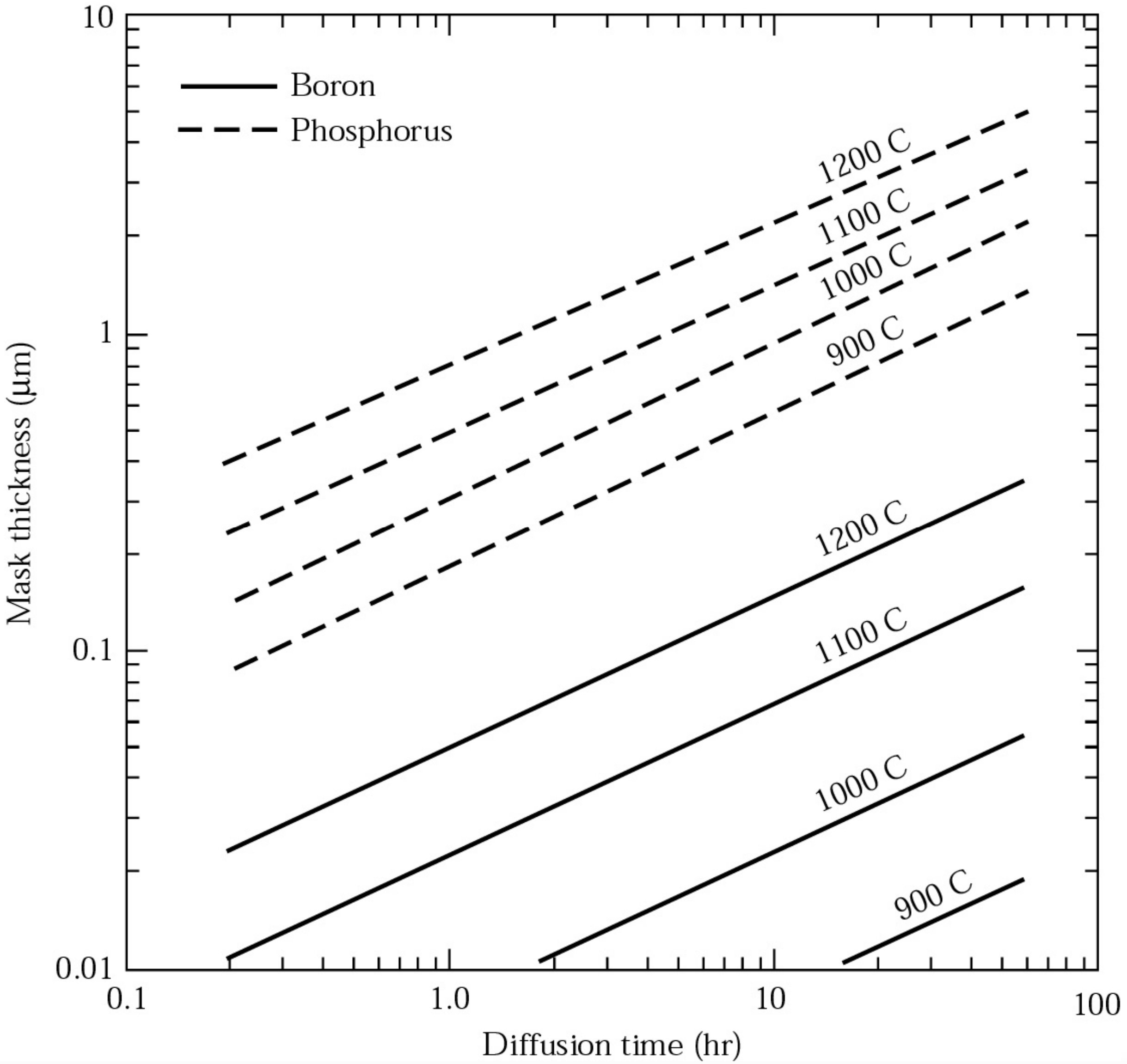


Masking Properties of SiO_2

- A silicon dioxide layer can also provide selective mask against the diffusion of dopants at elevated temperatures, a very useful property in IC fabrication.
- Predeposition of dopants, whether it be by ion implantation, chemical diffusion, or spin-on techniques, typically results in a dopant source at or near the surface of the oxides. During subsequent high-temperature drive-in step, diffusion in oxide masked-regions must be slow enough with respect to diffusion in silicon to prevent dopants from diffusing through the oxide mask to the silicon surface.
- The required thickness may be determined experimentally by measuring oxide thickness necessary to prevent inversion of a lightly doped silicon substrate of opposite conductivity at a particular temperature and time.

Experimental Results

Fig 10.
Thickness of silicon dioxide needed to mask boron and phosphorus diffusions as a function of diffusion time and temperature.



Oxide Quality

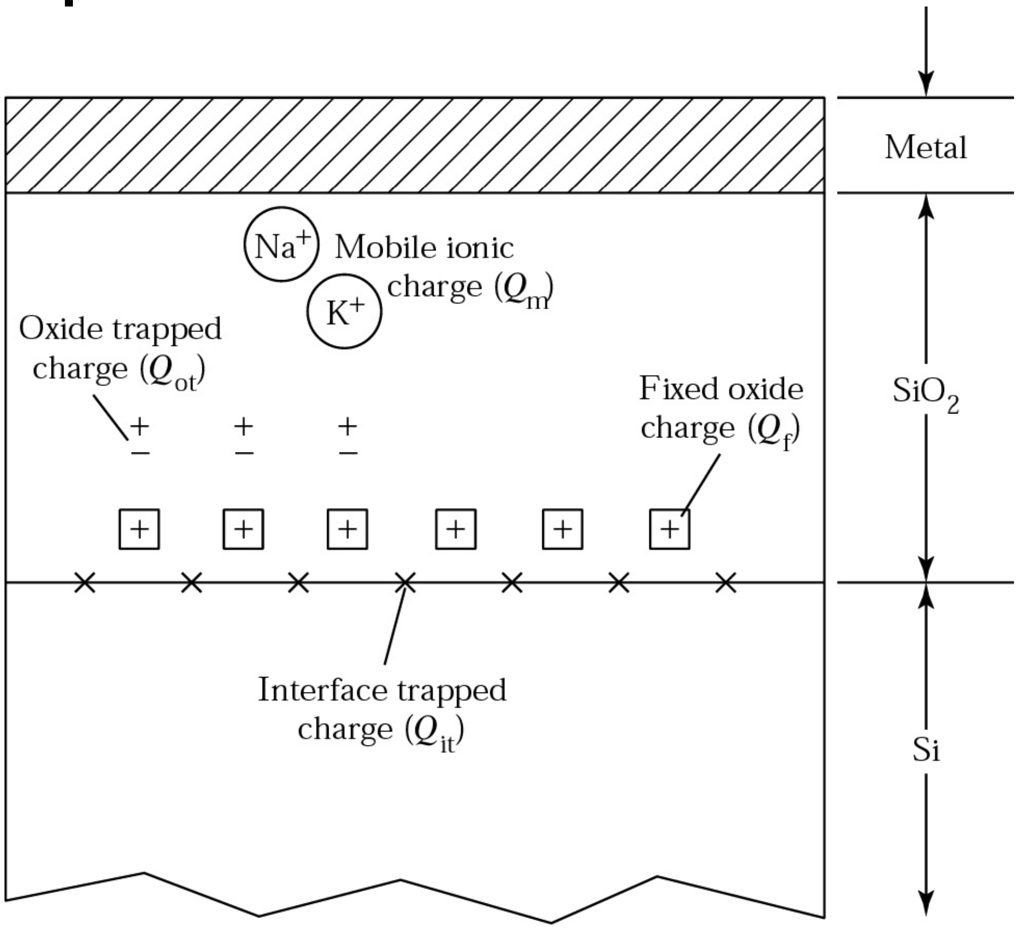


Fig 11.
Terminology for the charges associated with thermally oxidized silicon.

Oxide Thickness Characterization

- Profilometry
  - In this technique, a step feature in the grown or deposited film is first created, either by masking or during deposition or by etching aferward. The profilometer drags a fine stylus across the film surface. When a stylus encounters a step, a signal variation indicates a step height. This information is then dsplayed on achart recorder or CRTscreen. Applicable to less than 100nm thick up to greater than 5um.
- Ellipsometry
  - Based on polarization changes that occur when light is reflected from or transmitted through a medium. Measured are changes in polarization as a function of optical properties of the material, its thickness, and the wavelength and angle of incidence of light beam relative to the surface normal. Then, the oxide thickness are calculated.

Profilometer

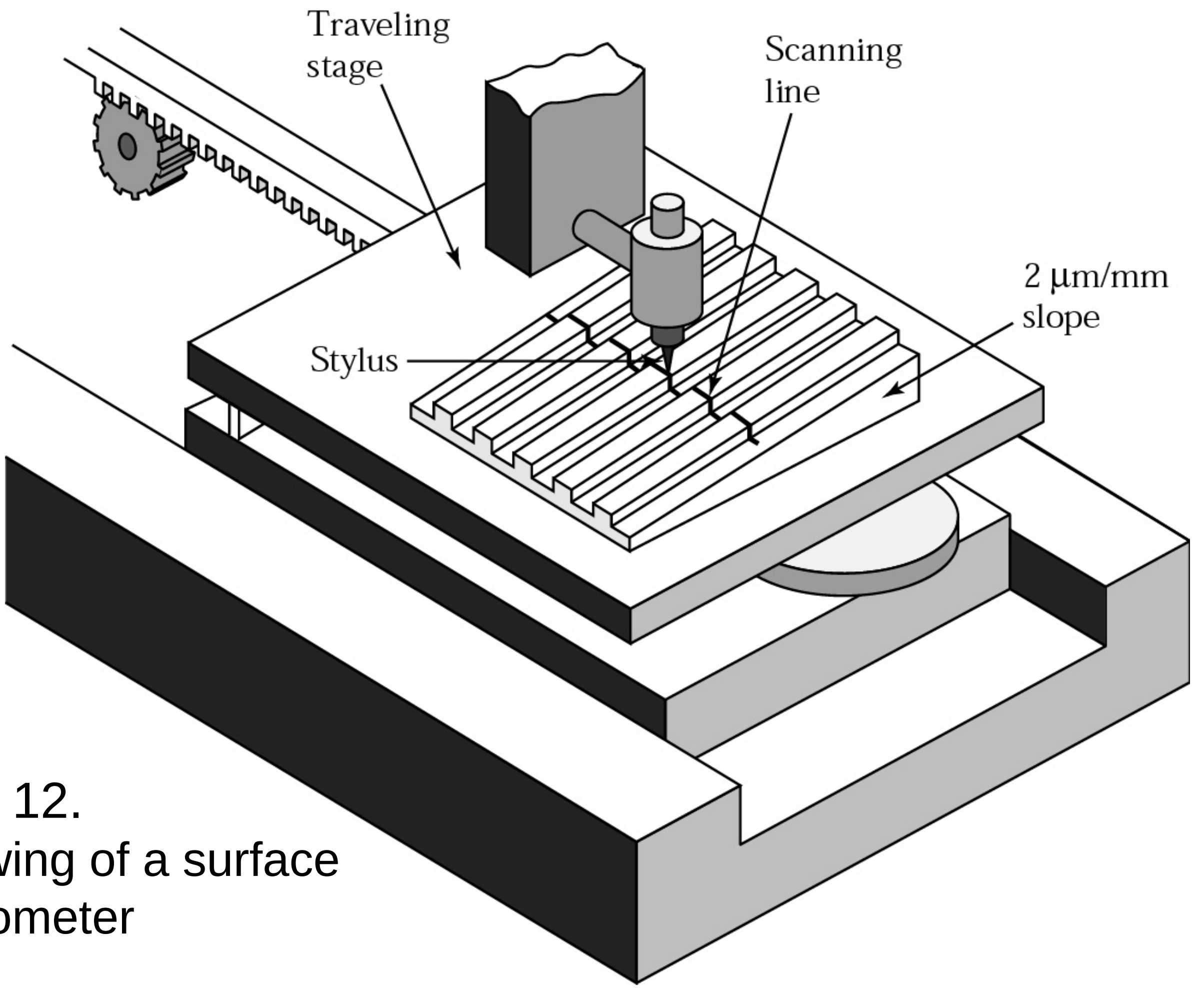
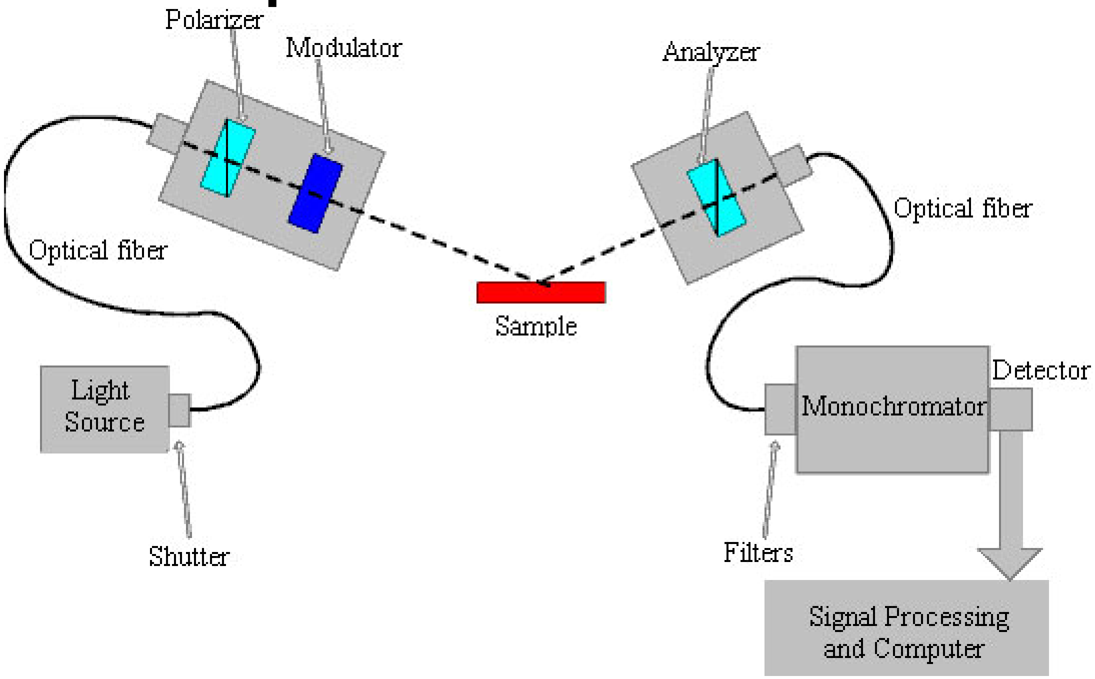


Fig 12.
Schematic drawing of a surface Profilometer

Ellipsometer



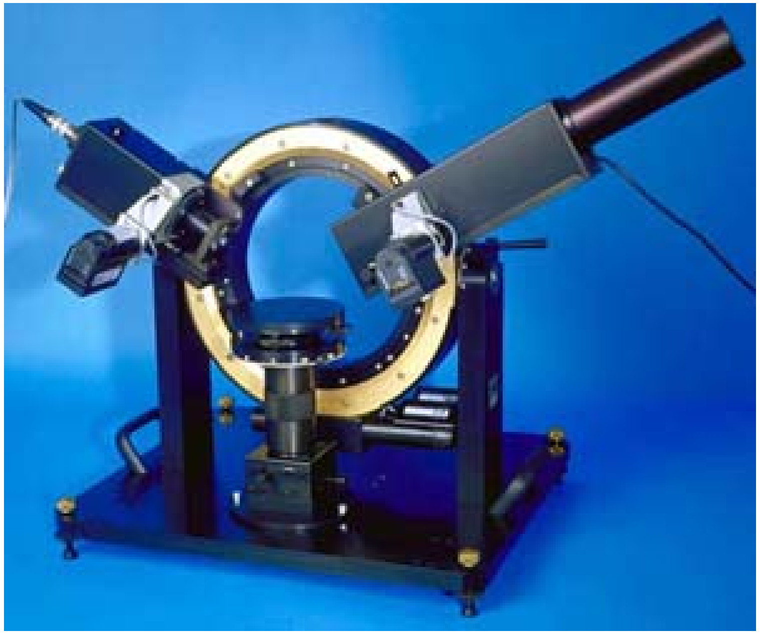


Fig 13. Ellipsometer Equipment

Oxidation Simulation

- Computer simulation is an important tool for investigating ULSI fabrication process. The most widely used example of such process simulation software is the Stanford University Process Engineering Modeling (SUPREM) program.
- SUPREM performs oxidation simulations based on the kinetic growth model. Included is the Arrhenius functions to describe the linear and parabolic rate coefficients for wet and dry oxidation. Oxidation is simulated using the command DIFFUSION, with either WETO2 or DRYO2 included as parameters indicating wet or dry oxidation.
- SUPREM uses an empirical model of the form

$$\frac{dx}{dt} = \frac{B}{2x + A} + Ce^{-x/L}$$

where B and A are the oxidation rate coefficients, and C and L are empirical constants

Example 3: Simulation Problem

Suppose we want to perform a dry-wet-dry oxidation sequence on a <100> silicon wafer at 1100°C for 5 minutes in a dry O_2, 2 hours in wet O_2,and finally, for 5 more minutes in dry O_2. If the silicon substrate is doped with phosphorous at a level of 10^{16} cm^{-3}, use SUPREM to determine the final oxidation thickness and the phosphorous doping profile in the oxide and silicon layers.

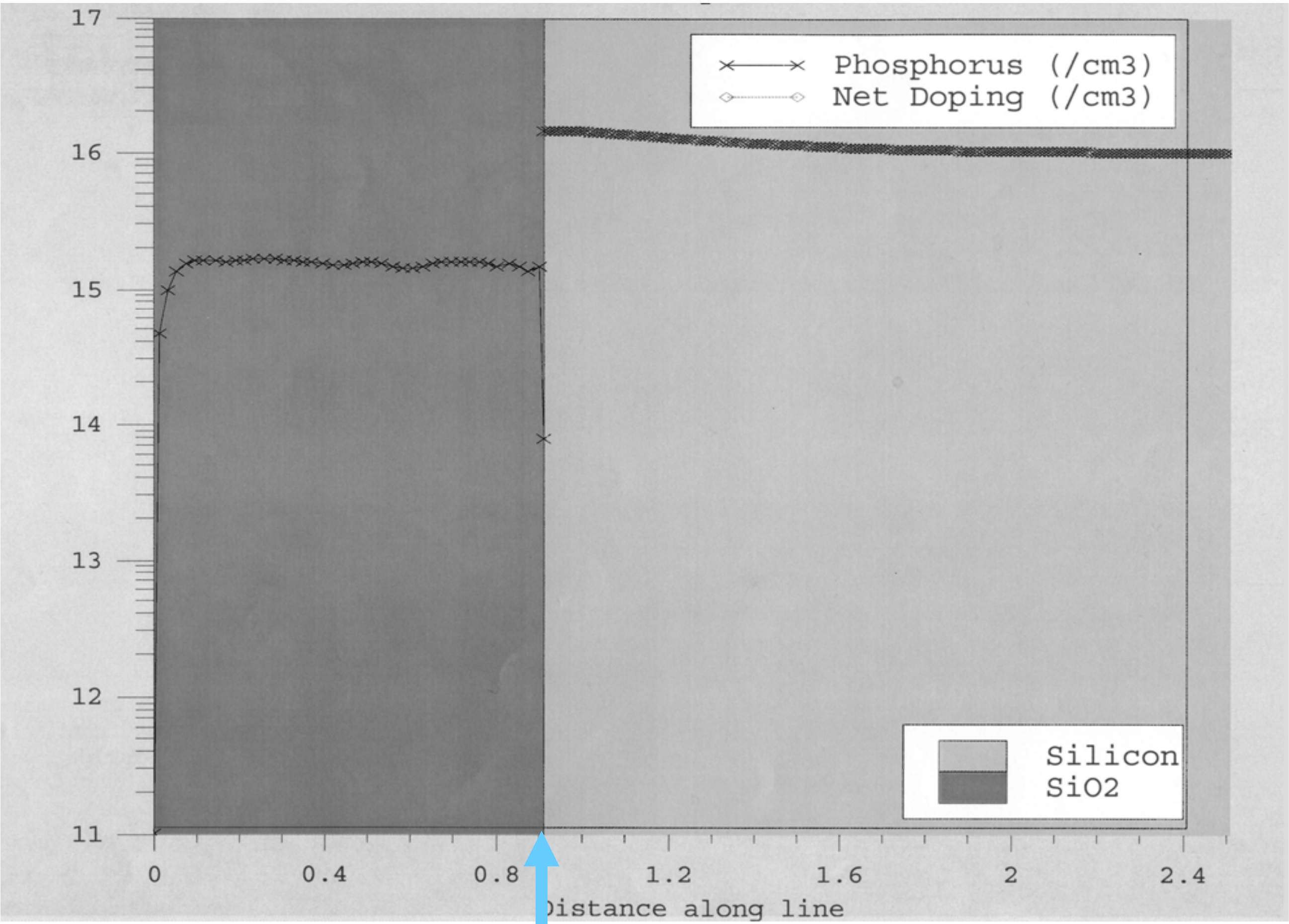
Assumptions:

Furnace idle temperature is 900°C.

Temperature ramp up and down is 20°C / minute in Nitrogen ambient.

SUPREM Input Listing

TITLE	**Oxidation Example**
COMMENT	Initialize silicon substrate
INITIALIZE	**<100> Silicon Phosphor Concentration = 1e^{16}**
COMMENT	Ramp furnace up to 1100 C over 10minutes in N2
DIFFUSION	**Time=10 Temperature=900 Nitrogen T.rate=20**
COMMENT	Oxidize wafers for 5 minutes at 1100 C in dry O2
DIFFUSION	**Time=5 Temperature=1100 DRY02**
COMMENT	Oxidize wafers for 120 minutes at 1100 C in wet O2
DIFFUSION	**Time=120 Temperature=1100 WET02**
COMMENT	Oxidize wafers for 5 minutes at 1100 C in dry O2
DIFFUSION	**Time=5 Temperature=1100 DRY02**
COMMENT	Ramp furnace down to 900 C over 10minutes in N2
DIFFUSION	**Time=10 Temperature=900 Nitrogen T.rate=-20**
PRINT	**Layers Chemical Concentration Phospor**
STOP	**End Oxidation example**



Oxide thickness = 0.9um

Fig 14. Plot of phosphorus concentration as a function of depth into the silicon substrate, using SUPREM software.

Additional Problems

- A p-type <100> oriented silicon wafer with a resistivity of 10 Ω-cm is placed in a wet oxidation system to grow a field oxide of 0.45um at 1050^{o}C. Determine the time required to grow the oxide.

- Determine the diffusion coefficient D for dry oxidation <100> oriented samples at 980^{o}C and 1 atm.