

OXIDATION

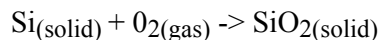
1.1 Introduction:

Silicon has become the dominant semiconductor material in IC technology because of the ease with which stable oxides can be grown. Silicon dioxide is the basis of the planar technology without which we would not have ICs as we know them today. In industrial practice, silicon dioxide layers are frequently formed by thermal oxidation of Si in the temperature range 900 - 1200°C. There are four important applications:

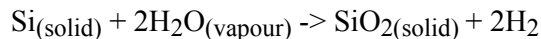
- * selective masking against dopant diffusion
- * passivation of device junctions
- * device isolation
- * gate insulator in MOSFET devices

There are two important growth methods:

- 1) Dry Oxidation Here the Si wafers are heated to $\approx 1,000^\circ\text{C}$ in an O_2 ambient. The chemical reaction is given as



- 2) Wet Oxidation Here the Si wafers are heated to $\approx 1,000^\circ\text{C}$ in a water vapour ambient and this permits a faster growth rate. The chemical reaction is



The SiO_2 layers grown by thermal oxidation have no long-range crystalline order, they are amorphous in structure.

1.2 Oxidation Rate

For $t \gg A^2/4B$ (large t)

$$x_o^2 = Bt \quad - \text{parabolic relationship}$$

For $(t + \tau) \ll A^2/4B$ (small t)

$$x_o = B/A (t + \tau) \quad - \text{linear relationship.}$$

B is referred to as the parabolic-rate constant and B/A is referred to as the linear-rate constant.

$$B = 2DC^*/N$$

Where D is the diffusion coefficient for the oxidizing species

C^* is the solubility of the oxidizing species and

N is the number of oxidizing species incorporated per unit volume

Ex 1 Calculate the parabolic rate constant B for a wafer oxidised in dry O₂ at 1100°C.

$$\sqrt{D} = 60 \text{ } \mu\text{m/hr}^{1/2}$$

$$C^* = 5 \times 10^{16} \text{ cm}^{-3}$$

$$N = 2.2 \times 10^{22} \text{ cm}^{-3}$$

Ex 2 Calculate the parabolic rate constant for a wafer oxidised in wet O₂ at 1100°C.

$$\sqrt{D} = 18 \text{ mm/hr}^{1/2}$$

$$C^* = 3 \times 10^{19} \text{ cm}^{-3}$$

$$N = 4.4 \times 10^{22} \text{ cm}^{-3}$$

Note N is twice that for dry O₂ as two water molecules are incorporated into each SiO₂ molecule.

These examples show that the parabolic rate constant B is significantly higher for oxidation in water vapour compared to oxidation in dry O₂. The reason for this is that the solubility of the H₂O molecule in oxide is nearly three orders of magnitude higher than the solubility of the oxygen molecule. So we can expect the oxidation of Si in dry O₂ to be much slower than in H₂O. However, the dry oxide is denser and of a much higher quality.

The principal effect of temperature on B is reflected in the diffusivity D where

$$D = D_0 \exp -E_a/kT.$$

Figure 11 of the process curves shows this temperature dependence.

Ex 3 Calculate the activation energies for oxidation in water vapour and in dry O₂ from Fig 13.

These values are in good agreement with the activation energies for diffusion of O₂ (1.16 eV) and H₂O (0.79 eV) in fused silica suggesting that the parabolic rate constant is associated with the diffusion of the oxidants. A similar analysis on Fig. 12 yields an activation energy of 2 eV for both O₂ and H₂O. This is close to the bond-breaking energy of silicon (1.83 eV) which suggests that B/A is associated with the interface reaction constant k_s .

Ex 4 (a) Use the value of B obtained in Ex 1 to calculate the oxide thickness following a 1 hour oxidation in dry O₂.

(b) Use the value of B obtained in Ex 2 to calculate the oxide thickness following a 2 hour oxidation in wet O₂.

Confirm that the results are in agreement with the data in Fig 8 /Fig. 13 of the process curves.

Ex 5 A <111> silicon wafer is subjected to the following oxidation schedule. Sixty minutes dry O₂ at 1100°C followed by 40 min wet O₂ at 920°C. Determine the resultant oxide thickness using Fig 13.

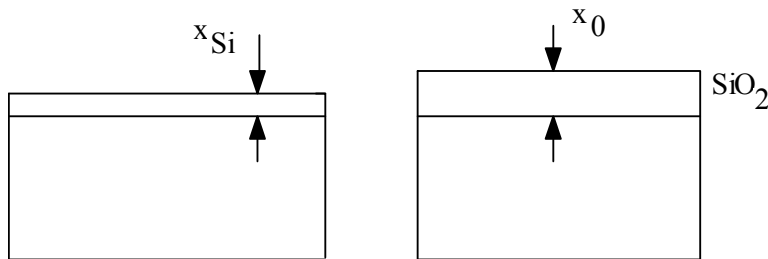
Verify the above result by calculation assuming the following:

	1100°C	920°C
B μ^2/hr	1.6×10^{-2}	.2
B/A $\mu\text{m}/\text{hr}$.35
A = B/(B/A)		.57

Ex. 6 Calculate the parabolic rate constant B for oxidation in water vapour at 1000°C assuming a values of 0.71 eV for the activation energy and a value of 18 $\mu\text{m}/\text{hr}$ for \sqrt{D} at 1100°C.

1.3 Silicon Consumption

Consider an oxidised Si wafer



During oxidation the thickness of the Si substrate is reduced by x cm. To find the resultant oxide thickness x_0 we look at the relative densities of the atoms/molecules in the Si/SiO₂.

Density of Si atoms $N_s = 5.0 \times 10^{22} \text{ cm}^{-3}$

Density of SiO₂ molecules $N_{ox} = 2.3 \times 10^{22} \text{ cm}^{-3}$

As a consequence of the lower number of SiO₂ molecules incorporated per cm³ in oxide there must be an expansion in volume to accommodate the oxidised Si atoms. Hence

$$x_{Si}/x_0 = 2.3 \times 10^{22} / 5.0 \times 10^{22} = 0.46$$

which means that for x_0 units of oxide formed, 0.46 x_0 units of Si are consumed.

Ex 7 Calculate the amount of silicon consumed when a an oxide of thickness 1.5 μm is grown.

1.4 Factors Affecting Oxidation Kinetics

Three factors affect the rate of oxidation of Si:

- * substrate orientation
- * pressure
- * impurities

Orientation dependence arises mainly from the total number of available Si atoms as a function of Si orientation.

Chlorine is an impurity which enhances the oxidation rate and it is often included, in small amounts, in the oxidising ambient. It is useful in the suppression of stacking faults which can have a detrimental effect on device performance. It is also beneficial in the passivation of sodium and other alkali ions which can move easily in SiO₂, even near room temperature.

1.5 Oxidation Methods

Dry oxides are produced by passing high-purity O₂ over the wafers in the temperature range 800 - 1200°C.

Wet oxides are produced by two methods:

- 1) N₂ or O₂ is passed through a high-purity water bath where the temperature is maintained ~95°C. This water vapour is then transported to the furnace tube via the carrier gas where it reacts with the Si wafers in the temperature range 800-1200°C.
- 2) A more common industrial practice is to use pyrogenic steam. This is produced by the reaction of O₂ and H₂ in the high-temperature furnace. Careful safety procedures must be adopted because of the explosive nature of the H₂ gas and a slight excess of O₂ is generally employed to avoid the presence of unreacted H₂ in the furnace.

High-pressure oxidation allows formation of a desired oxide thickness at the same temperature in a shorter time. The model of Deal and Grove still applies, with modified values of B and B/A.

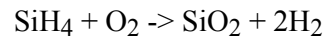
Plasma Oxidation

High-quality oxides can be grown at temperatures as low as 500 °C using the anodic plasma-oxidation process. This has all the advantages of low-temperature processing such as minimal movement of impurities from previous steps. Growth rates can be as high as 1µm/hr and oxides of 1µm thickness may be grown. The process is normally carried out in a pure oxygen discharge. The wafer is biased positively below the plasma potential allowing it to collect active charged oxygen species. Growth rate increases with substrate temperature, plasma density and dopant concentration. Properties of plasma oxides grown at 500°C compare favourably with thermal oxides grown at 1100 °C.

Deposition Methods

In addition to thermal oxidation of Si to form SiO₂, deposition techniques may also be used. These apply to other insulating layers, such as Si₃N₄, as well. There are three commonly used deposition methods: atmospheric-pressure chemical-vapour deposition (CVD), low-pressure CVD (LPCVD) and plasma-assisted CVD (PCVD). Considerations such as substrate temperature, deposition rate and film properties determine which process is used. We will look briefly at CVD only.

SiO₂ may be deposited from the vapour phase by the reaction of silane and oxygen at a temperature of 350°C.



A simplified sketch of the equipment is shown below. Silox is used for a final passivating layer after the metallisation has been patterned. It is mainly used where a low temperature process is required.

1.6 Masking properties of oxide

An oxide layer is only effective as a mask if it is sufficiently thick to prevent the impurity reaching the underlying silicon and forming a junction.

Revised April, 2004