

CHAPTER 2: Crystal Growth and Wafer Preparation

Silicon is the most important semiconductor for the microelectronics industry. When compared to germanium, silicon excels for the following reasons:

- (1) Si has a larger bandgap (1.1 eV for Si versus 0.66 eV for Ge).
- (2) Si devices can operate at a higher temperature (150°C vs 100°C).
- (3) Intrinsic resistivity is higher ($2.3 \times 10^5 \Omega\text{-cm}$ vs $47 \Omega\text{-cm}$).
- (4) SiO_2 is more stable than GeO_2 which is also water soluble.
- (5) Si is less costly.

2.1 Crystal Structure

The processing characteristics and some material properties of silicon wafers depend on its orientation. The $\langle 111 \rangle$ planes have the highest density of atoms on the surface, so crystals grow most easily on these planes and oxidation occurs at a higher pace when compared to other crystal planes. Traditionally, bipolar devices are fabricated in $\langle 111 \rangle$ oriented crystals whereas $\langle 100 \rangle$ materials are preferred for MOS devices. Real crystals are imperfect and contain point defects, line defects or dislocations, area or plane defects, and volume defects.

Point defects manifest themselves in several forms, as shown in *Figure 2.1*. Any non-silicon atoms incorporated into the lattice at either a substitutional or interstitial site are considered point defects. Point defects are important in the kinetics of diffusion and oxidation. Moreover, to be electrically active, dopants must occupy substitutional sites in order to introduce an energy level in the bandgap.

Dislocations are line defects. *Figure 2.2* is a schematic representation of a line dislocation in a cubic lattice. Dislocations in a lattice are dynamic defects. That is, they can diffuse under applied stress, dissociate into two or more dislocations, or combine with other dislocations. Dislocations in devices are generally undesirable, because they act as sinks for metallic impurities and alter diffusion profiles.

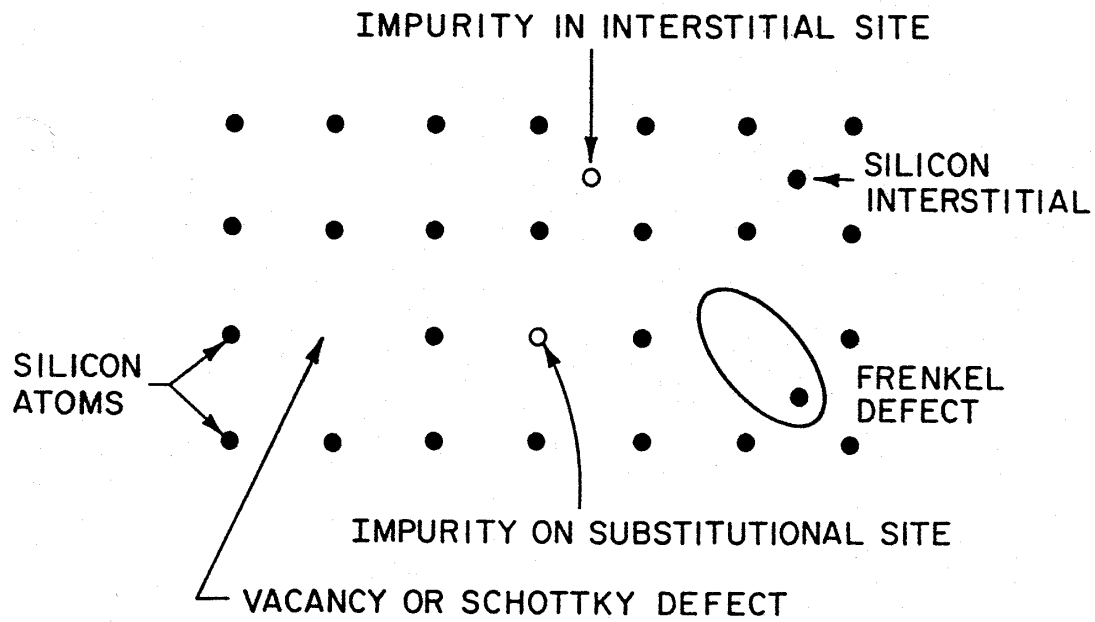


Figure 2.1: Location and types of point defects in a simple lattice.

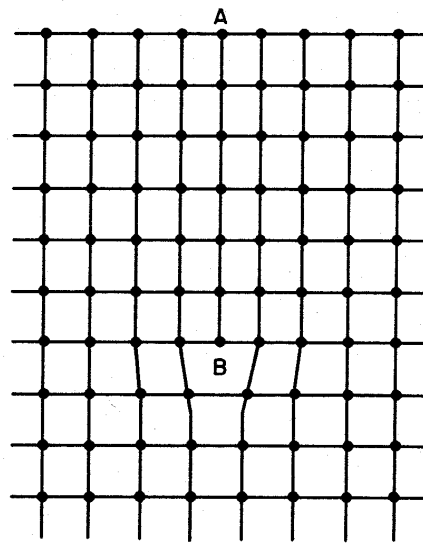


Figure 2.2: An edge dislocation in a cubic lattice created by an extra plane of atoms. The line of the dislocation is perpendicular to the page.

Two typical area or planar defects are twins and grain boundaries. Twinning represents a change in the crystal orientation across a twin plane, such that a mirror image exists across that plane. Grain boundaries are more disordered than twins and separate grains of single crystals in polycrystalline silicon. Planar defects appear during crystal growth, and crystals having such defects are not considered usable for IC manufacture and are discarded.

Precipitates of impurity or dopant atoms constitute the fourth class of defects. The solubility of dopants varies with temperature, as exhibited in *Figure 2.3*. Thus, if an impurity is introduced at the maximum concentration allowed by its solubility, a supersaturated condition will exist upon cooling. The crystal achieves an equilibrium state by precipitating the impurity atoms in excess of the solubility level as a second phase. Precipitates are generally undesirable as they act as sites for dislocation generation. Dislocations result from the volume mismatch between the precipitate and the lattice, inducing a strain that is relieved by the formation of dislocations.

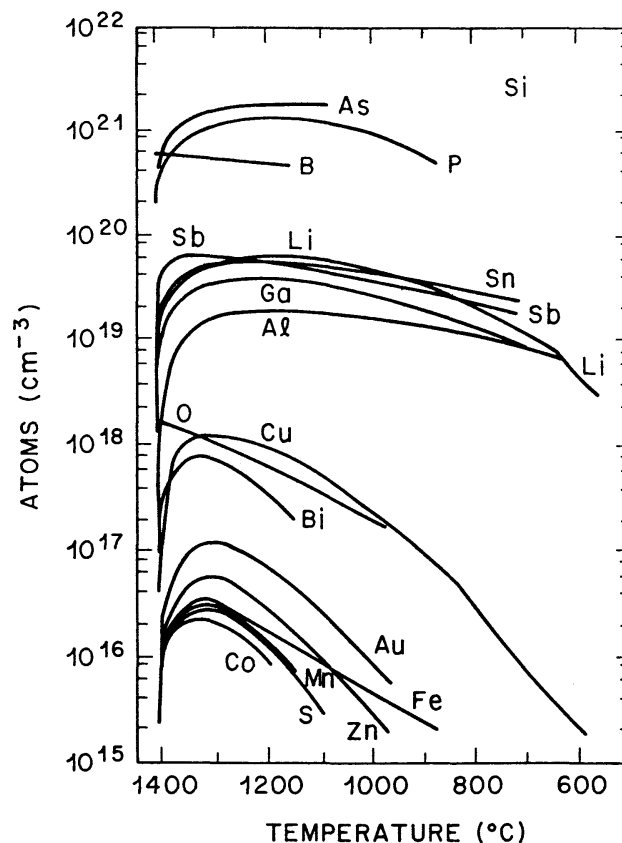


Figure 2.3: Solid solubility of impurity elements in silicon.

2.2 Electronic-Grade Silicon

Electronic-grade silicon (EGS), a polycrystalline material of high purity, is the starting material for the preparation of single crystal silicon. EGS is made from metallurgical-grade silicon (MGS) which in turn is made from quartzite, which is a relatively pure form of sand (*Table 2.1*). MGS is purified by the following reaction:



The boiling point of trichlorosilane (SiHCl_3) is 32°C and can be readily purified using fractional distillation. EGS is formed by reacting trichlorosilane with hydrogen:

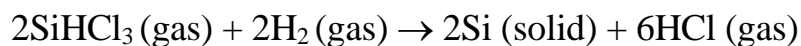


Table 2.1: Comparison of typical impurity contents in various materials (values in ppm except as noted).

Impurity	Quartzite	Carbon	MGS *	EGS #	Crucible quartz
Al	620	5500	1570
B	8	40	44	<1 ppb	...
Cu	<5	14	...	0.4	0.23
Au	0.07 ppb	...
Fe	75	1700	2070	4	5.9
P	10	140	28	<2 ppb	...
Ca
Cr	137	1	0.02
Co	0.2	0.01
Mn	70	0.7	...
Sb	0.001	0.003
Ni	4	6	0.9
As	0.01	0.005
Ti	163
La	1 ppb	...
V	100
Mo	1.0	5.1
C	80	0.6	...
W	0.02	0.048
O
Na	0.2	3.7

* Metallurgical-grade silicon

Electronic-grade silicon

2.3 Czochralski Crystal Growth

Crystal growth typically involves a phase change from a solid, liquid, or gas phase to a crystalline solid phase. The Czochralski (CZ) process, which accounts for 80% to 90% of worldwide silicon consumption, consists of dipping a small single-crystal seed into molten silicon and slowly withdrawing the seed while rotating it simultaneously. *Figure 2.4* is a schematic of a Czochralski crystal growing apparatus. The crucible is usually made of quartz or graphite with a fused silica lining. After the seed is dipped into the EGS melt, the crystal is pulled at a rate that minimizes defects and yields a constant ingot diameter.

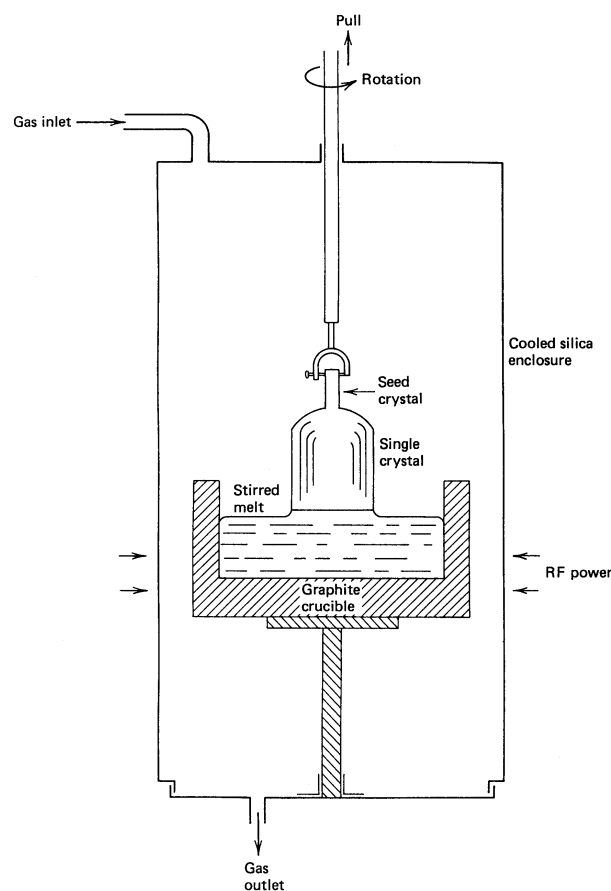


Figure 2.4: The Czochralski crystal growth apparatus.

Impurities, both intentional and unintentional, are introduced into the silicon ingot. Intentional dopants are mixed into the melt during crystal growth, while unintentional impurities originate from the crucible, ambient, etc. All common impurities have different solubilities in the solid and in the melt. An equilibrium segregation coefficient k_0 can be defined to be the ratio of the equilibrium

concentration of the impurity in the solid to that in the liquid at the interface, i.e. $k_o = C_s/C_l$. **Table 2.2** lists the equilibrium segregation coefficients for some common impurities and dopants. Note that all are below unity, implying that the impurities preferentially segregate to the melt and the melt becomes progressively enriched with these impurities as the crystal is being pulled.

Table 2.2: Segregation coefficients for common impurities in silicon.

Impurity	Al	As	B	C	Cu	Fe	O	P	Sb
k_o	0.002	0.3	0.8	0.07	4×10^{-6}	8×10^{-6}	0.25	0.35	0.023

The distribution of an impurity in the grown crystal can be described mathematically by the normal freezing relation:

$$C_s = k_o C_o (1 - X)^{k_o - 1} \quad (\text{Equation 2.1})$$

where X is the fraction of the melt solidified, C_o is the initial melt concentration, C_s is the solid concentration, and k_o is the segregation coefficient. **Figure 2.5** illustrates the segregation behavior for three segregation coefficients.

CZ-Si crystals are grown from a silicon melt contained in a fused silica (SiO_2) crucible. Fused silica reacts with hot silicon and releases oxygen into the melt. Hence, CZ-Si has an indigenous oxygen concentration of approximately 10^{18} atoms/cm³. Although the segregation coefficient of oxygen is <1 , the axial distribution of oxygen is governed by the amount of oxygen in the melt. Less dissolution of the crucible material occurs as the melt volume diminishes, and less oxygen is available for incorporation. **Figure 2.6** shows the variation in the oxygen content along a typical silicon ingot. Oxygen is an important element in CZ-Si on account of the following reasons:

- (1) Oxygen forms a thermal donor in silicon.
- (2) Oxygen increases the mechanical strength of silicon.
- (3) Oxygen precipitates provide gettering sites for unintentional impurities.

Thermal donors are formed by the polymerization of Si and O into complexes such as SiO_4 in interstitial sites at 400°C to 500°C. Careful quenching of the crystal annihilates these donors.

Under certain annealing cycles, oxygen atoms in the bulk of the crystal can be precipitated as SiO_x clusters that act as trapping sites to impurities. This process, which is illustrated in [Figure 2.7](#), is called internal gettering and is one of the most effective means to remove unintentional impurities from the near surface region where devices are fabricated.

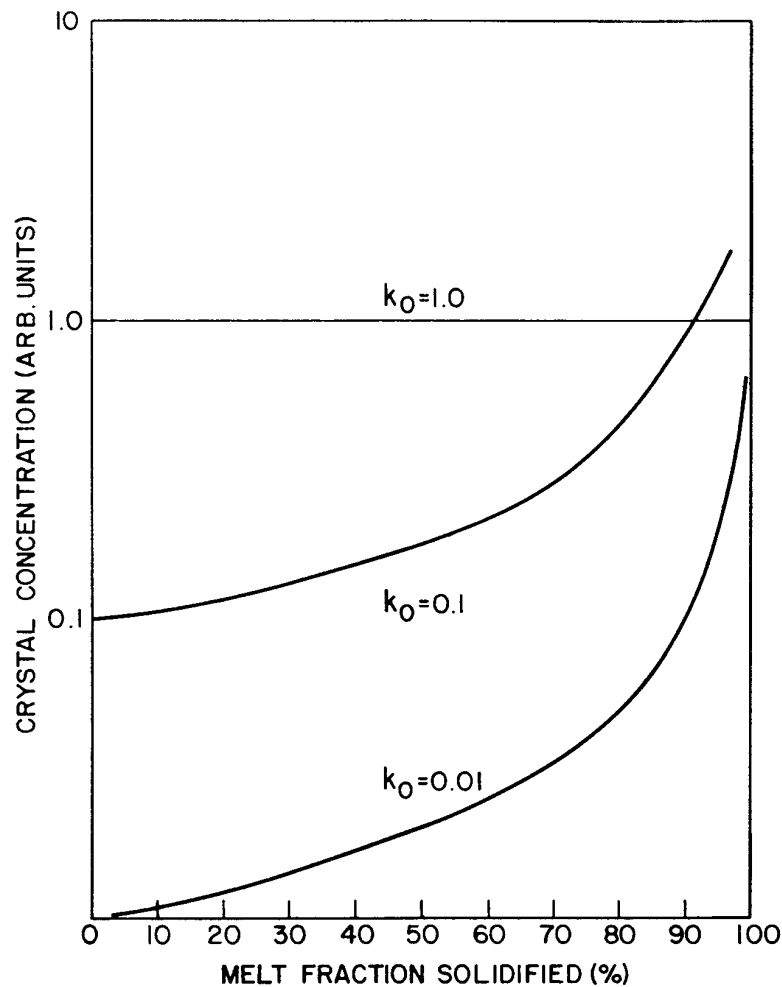


Figure 2.5: Impurity concentration profiles for different k_0 with $C_0 = 1$.

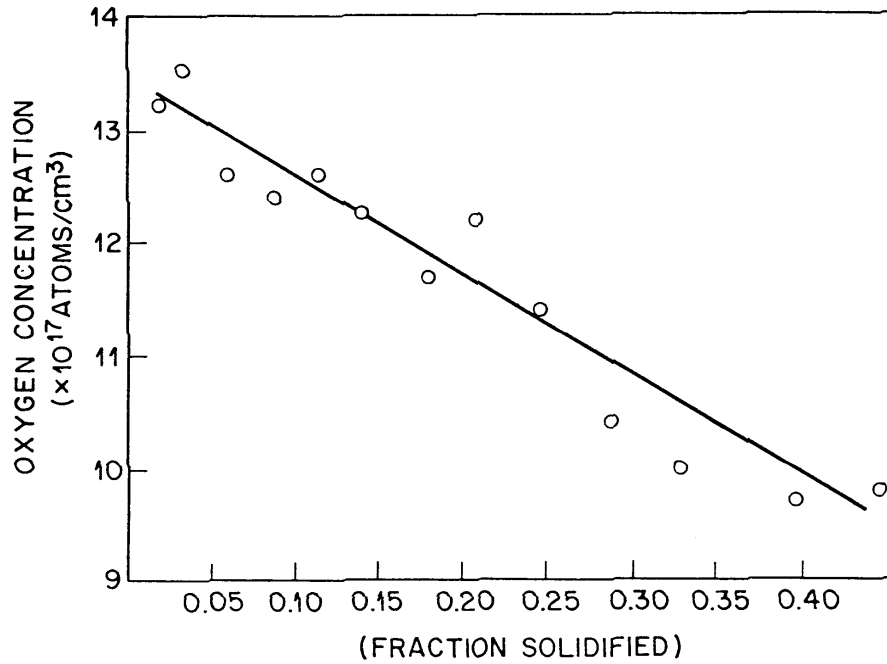


Figure 2.6: Axial distribution of oxygen in a typical CZ-Si ingot.

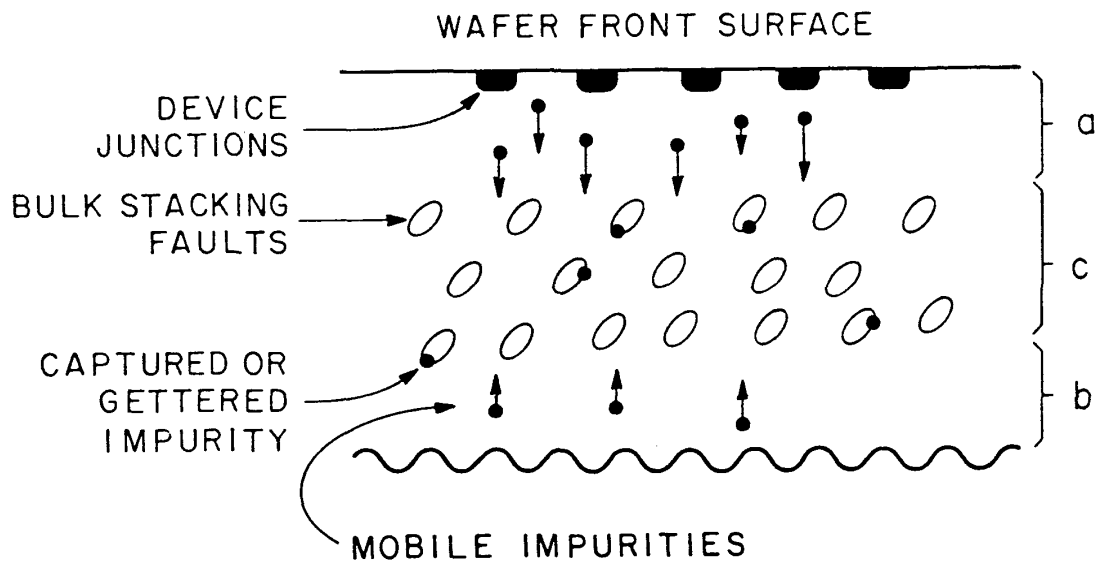
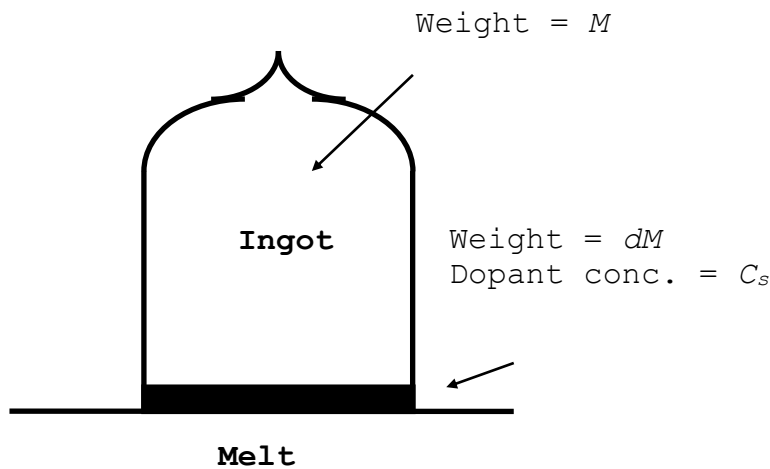


Figure 2.7: Schematic of a denuded zone in a wafer cross section illustrating the gettering sites (**a** and **b** are zones denuded of defects whereas **c** represents the region of intrinsic gettering).

Derivation of the normal freezing relation (Equation 2.1):

S = dopant remaining in melt

Consider a crystal being grown from a melt having an initial weight M_o with an initial doping concentration C_o in the melt (i.e., the weight of the dopant per 1 gram melt). At a given point of growth when a crystal of weight M has been grown, the amount of the dopant remaining in the melt (by weight) is S . For an incremental amount of the crystal with weight dM , the corresponding reduction of the dopant ($-dS$) from the melt is $C_s dM$, where C_s is the doping concentration in the crystal (by weight):

$$-dS = C_s dM \quad (1)$$

Now, the remaining weight of the melt is $M_o - M$, and the doping concentration in the liquid (by weight), C_l , is given by

$$C_l = \frac{S}{M_o - M} \quad (2)$$

Combining (1) and (2) and substituting $C_s/C_l = k_o$:

$$\frac{dS}{S} = -k_o \left[\frac{dM}{M_o - M} \right] \quad (3)$$

Given the initial weight of the dopant, $C_o M_o$, we can integrate (3):

$$\int_{C_o M_o}^S \frac{dS}{S} = k_o \int_0^M \frac{-dM}{M_o - M} \quad (4)$$

Solving (4) and combining with (2) give

$$C_s = k_o C_o \left[1 - \frac{M}{M_o} \right]^{k_o - 1} \quad (5)$$

Details on how to solve Eq. (4)

(1) Left hand side of Eq. (4): $\int_{C_o M_o}^S \frac{dS}{S} = \ln \left[\frac{S}{C_o M_o} \right]$

(2) Right hand side of Eq. (4): Let $m = M_o - M$, $dm = -dM$;

$$k_o \int_0^M \frac{-dM}{M_o - M} = k_o \int_{M_o}^{M_o - M} \frac{dm}{m} = k_o \ln \left[\frac{M_o - M}{M_o} \right]$$

Eq. (4) becomes: $\ln \left[\frac{S}{C_o M_o} \right] = k_o \ln \left[\frac{M_o - M}{M_o} \right]$

and so $\frac{S}{C_o M_o} = \left[\frac{M_o - M}{M_o} \right]^{k_o}$

From Eq. (2), $S = C_l (M_o - M)$

Therefore, $\frac{C_l (M_o - M)}{C_o M_o} = \left[\frac{M_o - M}{M_o} \right]^{k_o}$

$$\frac{C_s (M_o - M)}{k_o C_o M_o} = \left[\frac{M_o - M}{M_o} \right]^{k_o} \quad \text{or} \quad \frac{C_s}{k_o C_o} \left[1 - \frac{M}{M_o} \right] = \left[1 - \frac{M}{M_o} \right]^{k_o}$$

Finally, $C_s = k_o C_o \left[1 - \frac{M}{M_o} \right]^{k_o - 1} \quad (5)$

Example 2.1

Using *Equation 2.1* and the segregation coefficient for oxygen from *Table 2.2*, predict the concentration of oxygen in the crystal at a fraction solidified of 0.4 in *Figure 2.6*.

Solution

First, find the concentration of oxygen in the melt at the top of the crystal ($x = 0.05$) using *Equation 2.1*:

$$1.3 \times 10^{18} = 0.25 \times C_o(1-0.05)^{0.25-1}$$

$$C_o = 5.0 \times 10^{18} \text{ atoms/cm}^3$$

Second, calculate the expected value at a fraction solidified of 0.4:

$$C_s = 0.25 \times 5.0 \times 10^{18} (1-0.4)^{0.25-1}$$

$$C_s = 1.83 \times 10^{18} \text{ atoms/cm}^3$$

Since this is higher than the observed value of $1.0 \times 10^{18} \text{ atoms/cm}^3$, it indicates a loss of oxygen from the melt during growth and shows that *Equation 2.1* is not strictly applicable for this case.

2.4 Float-Zone Process

The float-zone process has some advantages over the Czochralski process for the growth of certain types of silicon crystals. The molten silicon in the float-zone apparatus (*Figure 2.8*) is not contained in a crucible, and is thus not subject to the oxygen contamination present in CZ-Si crystals. The float-zone process is also necessary to obtain crystals with a high resistivity ($\gg 25 \Omega\text{-cm}$).

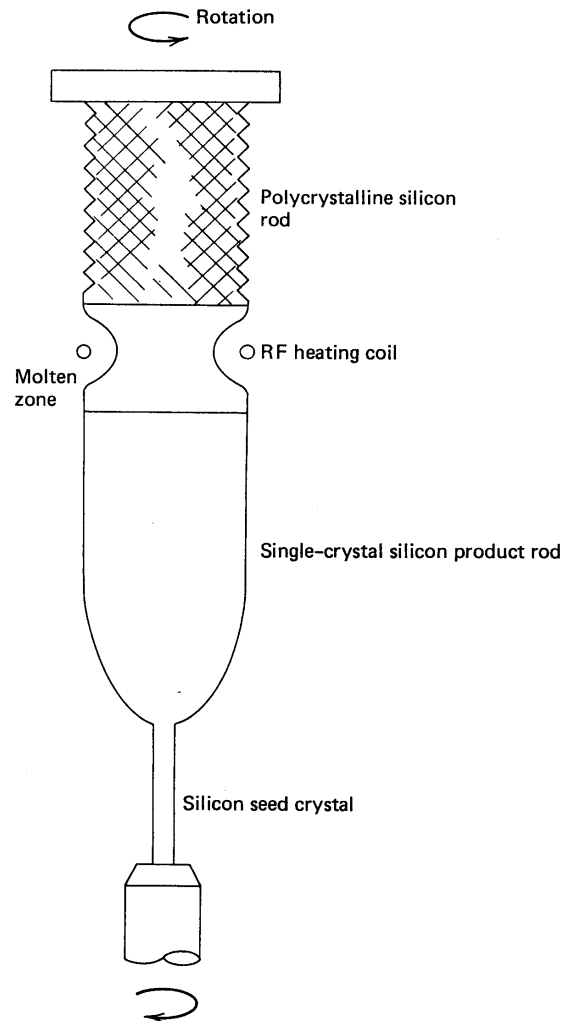


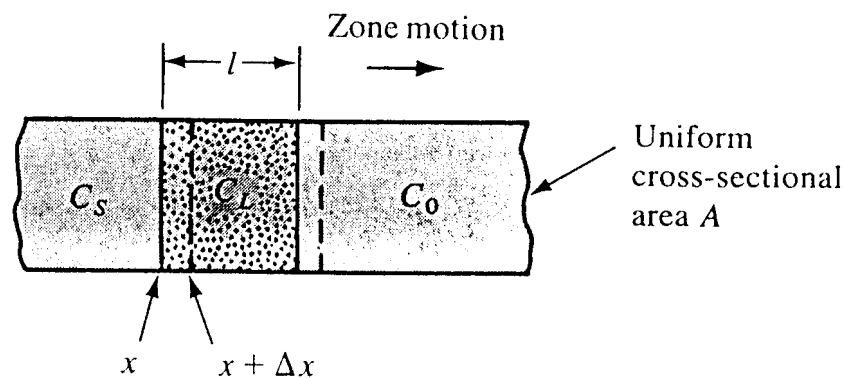
Figure 2.8: Float-zone crystal growth apparatus.

Example 2.2

Show that in the float-zone process, the impurity concentration at a distance x , $C_s(x)$, is given by the following relationship:

$$C_s(x) = C_o - C_o(1 - k) \exp\left[-\frac{k_o x}{l}\right]$$

where C_o is the original impurity concentration in the ingot, k_o is the impurity segregation coefficient, and l is the length of the molten zone.

Solution

Assume that the zone in the above figure moves a distance Δx to the right. Write the balance that the quantity of impurity in the zone after the shift of Δx is equal to that before the shift, minus the quantity solidified at the left, and plus that melted into the zone at the right. Obtain the standard derivative form and let Δx approach zero. Solve the differential equation for $C_L(x)$ using the boundary condition that $C_L(x = 0) = C_o$.

Therefore,

$$lAC_L(x + \Delta x) = lAC_L(x) - C_s(x)A\Delta x + C_oA\Delta x$$

Since $C_s(x) = k_o C_L(x)$,

$$\frac{C_L(x + \Delta x) - C_L(x)}{\Delta x} = \frac{C_o}{l} - \frac{k_o}{l} C_L(x)$$

Let $\Delta x \rightarrow 0$,

$$\frac{dC_L(x)}{dx} = \frac{C_0}{l} - \frac{k_o}{l} C_L(x)$$

The solution of this differential equation is:

$$C_L(x) = \frac{C_o}{k_o} + B e^{-k_o x/l}$$

At $x = 0$, $C_L(0) = C_o$, and $B = C_o (1 - 1/k_o)$. Thus,

$$C_L(x) = \frac{C_o}{k_o} + C_o \left(1 - \frac{1}{k_o}\right) e^{-\frac{k_o x}{l}}$$

$$C_s(x) = C_0 - C_o (1 - k_o) \exp\left[-\frac{k_o x}{l}\right]$$

2.5 Characterization

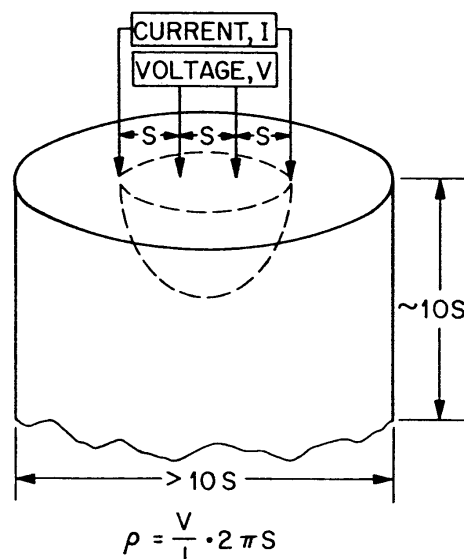
Routine evaluation of ingots or boules involves measuring the resistivity, evaluating their crystal perfection, and examining their mechanical properties, such as size and mass. Other less routine tests include the measurement of oxygen, carbon, and heavy metal contents.

Resistivity measurements are made on the flat ends of the crystal by the four-point probe technique. As depicted in [Figure 2.9](#), a current I passes through the outer probes and the voltage V is measured between the inner probes. The measured resistance (V/I) is converted to resistivity ($\Omega\text{-cm}$) using the relationship

$$\rho = (V/I)2\pi S \quad (\text{Equation 2.2})$$

where S is the probe spacing in centimeters. The calculated resistivity can be correlated with dopant concentration using a chart such as the one displayed in [Figure 2.10](#).

Gross crystalline imperfections are detected visually and defective crystals are cut from the boule. More subtle defects such as dislocations can be disclosed by preferential chemical etching. Chemical information can be acquired employing wet analytical techniques or more sophisticated solid-state and surface analytical methods.



[Figure 2.9](#): Four-point probe measurement on crystal end.

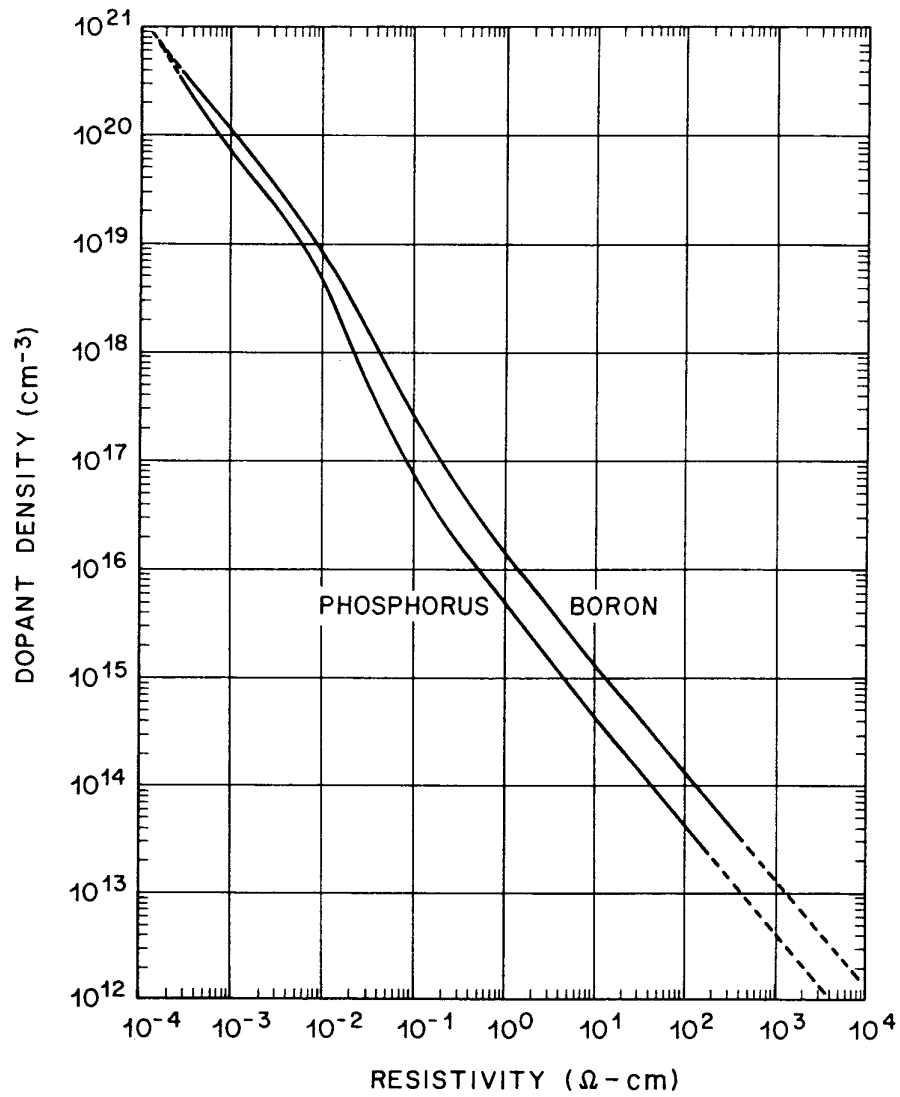


Figure 2.10: Conversion between resistivity and dopant density in silicon.

Example 2.3

A boron-doped crystal is measured at its seed end with a four-point probe of spacing 1 mm. The (V/I) reading is 10 ohms. What is the seed end doping and the expected reading at 0.95 fraction solidified?

Solution

First use *Equation 2.2* to find the seed end resistivity.

$$\rho = 10 \times 2 \times \pi \times 0.1$$

$$\rho = 6.3 \text{ } \Omega\text{-cm}$$

Figure 2.10 shows that this equates to a doping of 2×10^{15} atoms/cm³.

Next use *Equation 2.1* and *Table 2.2* to find the melt concentration:

$$2 \times 10^{15} = 0.8 C_o (1-0)^{0.8-1}$$

$$C_o = 2.5 \times 10^{15} \text{ atoms/cm}^3$$

At 0.95 fraction solidified, the solid concentration is:

$$C_s = 0.8 \times 2.5 \times 10^{15} (1-0.95)^{0.8-1}$$

$$C_s = 3.6 \times 10^{15} \text{ atoms/cm}^3$$

or about 5 $\Omega\text{-cm}$

Example 2.4

Resistivity is usually inversely proportional to dopant concentration in a silicon wafer. Suppose that in a Czochralski process, a chunk of undoped polysilicon is mixed with a small amount of heavily doped silicon with resistivity of 0.01 Ω -cm and the crystal is subsequently pulled. For one run, the resistivity of the grown crystal at the midsection is 1 Ω -cm. The amount of heavily doped silicon is to be changed in the next run to obtain a resistivity of 0.5 Ω -cm at the midsection of the new ingot. Determine the increase in the amount of heavily doped silicon that is needed. Assume that all operating conditions remain the same and the amount of the added heavily-doped polysilicon is small compared to the undoped polysilicon charge. Discuss whether your answer is correct only at the midpoint of the ingot or is universally true for all other axial positions on the ingot.

Solution

Based on the normal freezing relationship: $C_s = k_o C_o (1 - X)^{k_o - 1}$

At the midsection of the first ingot: $C_{0.5,1} = k_o C_1 (0.5)^{k_o - 1}$

At the midsection of the second ingot: $C_{0.5,2} = k_o C_2 (0.5)^{k_o - 1}$

$$\text{Therefore, } \frac{C_{0.5,1}}{C_{0.5,2}} = \frac{C_1}{C_2} = \frac{1}{2}$$

The concentration in the midsection depends only on the initial dopant concentration in the melt. If the volume change is neglected, one can simply double the amount of the heavily-doped polysilicon to achieve a two-fold decrease in the resistivity everywhere.

2.6 Wafer Preparation

Silicon, albeit brittle, is a hard material. The most suitable material for shaping and cutting silicon is industrial-grade diamond. Conversion of silicon ingots into polished wafers requires several machining, chemical, and polishing operations.

After a grinding operation to fix the diameter of the material (*Figure 2.11*), one or more flats are grounded along the length of the ingot. The largest flat, called the "major" or "primary" flat, is usually relative to a specific crystal orientation. The flat is located by x-ray diffraction techniques. The primary flat serves as a mechanical locator in automated processing equipment to position the wafer, and also serves to orient the IC device relative to the crystal. Other smaller flats are called "secondary" flats that serve to identify the orientation and conductivity type of the wafer. Secondary flats thus provide a means to quickly sort and identify wafers should mixing occur. The flat locations for the four common types of silicon wafers are exhibited in *Figure 2.12*.

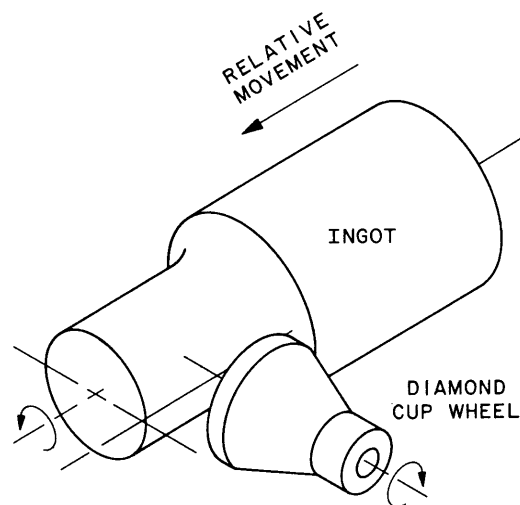


Figure 2.11: Schematic of the grinding process.

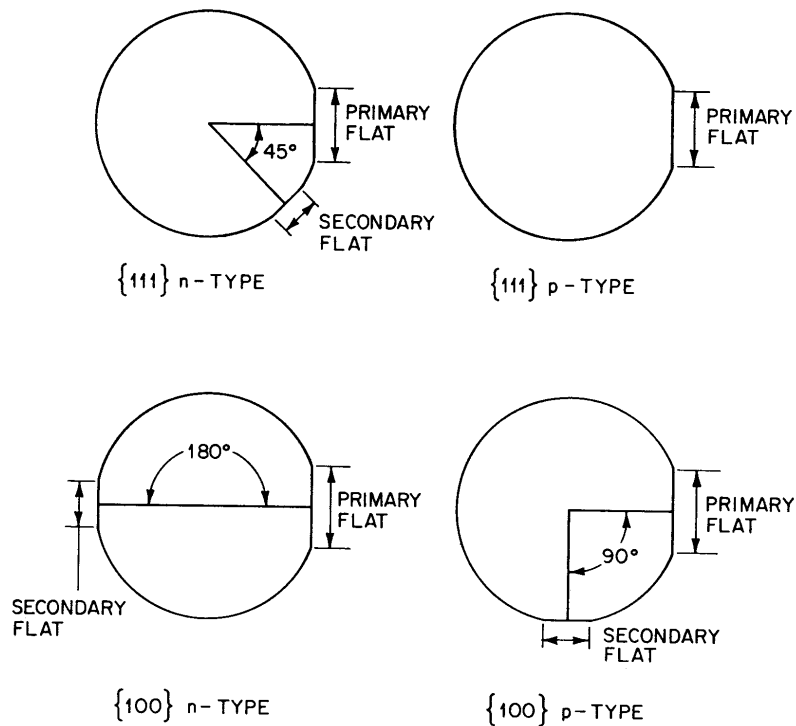


Figure 2.12: Identifying flats on silicon wafers.

The drawback of these flats is that the usable area on the wafer, i.e. the area on which microelectronic devices can be fabricated, is reduced. For some 200 mm and 300 mm diameter wafers, only a small notch is cut from the wafer to enable lithographic alignment but no dopant type or crystal orientation information is conveyed.

Once these operations have been completed, the ingot is ready to be sliced by diamond saw into wafers. Slicing determines four wafer parameters: surface orientation (e.g., $\langle 111 \rangle$ or $\langle 100 \rangle$); thickness (e.g., 0.5 – 0.7 mm, depending on wafer diameter); taper, which is the wafer thickness variations from one end to another; and bow, which is the surface curvature of the wafer measured from the center of the wafer to its edge. After slicing, the wafers undergo lapping operation that is performed under pressure using a mixture of Al_2O_3 and glycerine. Subsequent chemical etching removes any remaining damaged and contaminated regions. Historically, mixtures of hydrofluoric, nitric, and acetic acids have been employed, but alkaline etching, using potassium or sodium hydroxide, is also common.

Polishing is the final step. Its purpose is to provide a smooth, specular surface on which device features can be photoengraved. **Figure 2.13** depicts the schematic of a typical polishing machine and the process. **Figure 2.14** displays finished

silicon wafers of various dimensions. A finished wafer is subject to a myriad of physical tolerances, and examples of the specifications are shown in [Table 2.3](#).

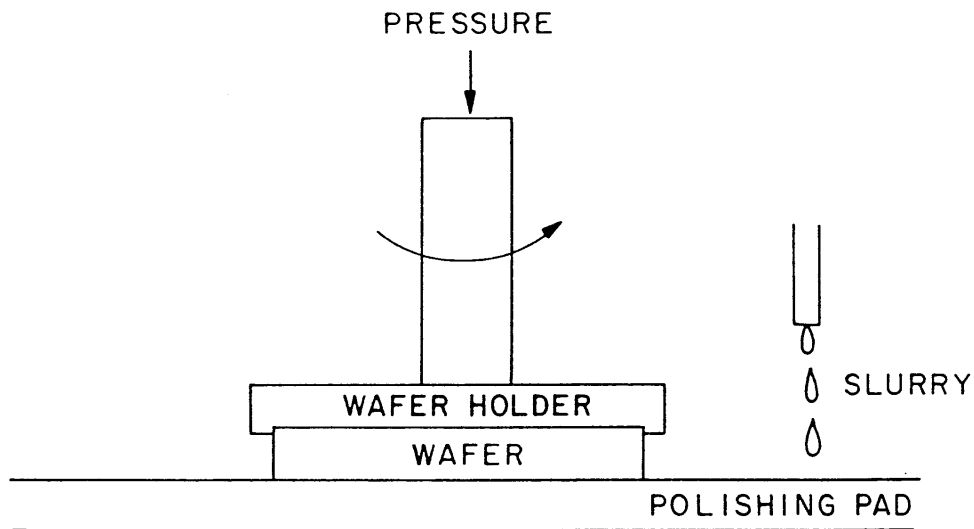


Figure 2.13: Schematic of the polishing process.



Figure 2.14: Finished silicon wafers of various sizes.

Table 2.3: Typical specifications for monocrystalline silicon wafers.

Parameter	125 mm	150 mm	200 mm	300 mm
Diameter (mm)	125 \pm 1	150 \pm 1	200 \pm 1	300 \pm 1
Thickness (mm)	0.6-0.65	0.65-0.7	0.715-0.735	0.755-0.775
Bow (μm)	70	60	30	<30
Total thickness variation (μm)	65	50	10	<10
Surface orientation	\pm 1 $^{\circ}$	\pm 1 $^{\circ}$	\pm 1 $^{\circ}$	\pm 1 $^{\circ}$