

13. Single-Crystal Silicon: Growth and Properties

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It is clear that silicon, which has been the dominant material in the semiconductor industry for some time, will carry us into the coming ultra-large-scale integration (ULSI) and system-on-a-chip (SOC) eras, even though silicon is not the optimum choice for every electronic device. Semiconductor devices and circuits are fabricated through many mechanical, chemical, physical, and thermal processes. The preparation of silicon single-crystal substrates with mechanically and chemically polished surfaces is the first step in the long and complex device fabrication process. In this chapter, the approaches currently used to prepare silicon materials (from raw materials to single-crystalline silicon) are discussed.

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Silicon, which has been and will continue to be the dominant material in the semiconductor industry for some time to come [13.1], will carry us into the ultra-large-scale integration (ULSI) era and the system-on-a-chip (SOC) era.

As electronic devices have become more advanced, device performance has become more sensitive to the quality and the properties of the materials used to construct them.

Germanium (Ge) was originally utilized as a semiconductor material for solid state electronic devices. However, the narrow bandgap (0.66 eV) of Ge limits the operation of germanium-based devices to temperatures of approximately 90 °C because of the considerable leakage currents observed at higher temperatures. The wider bandgap of silicon (1.12 eV), on the other hand, results in electronic devices that are capable of operating at up to ≈ 200 °C. However, there is a more serious problem than the narrow bandgap: germanium does not readily provide a stable passivation layer on the surface. For example, germanium dioxide (GeO₂) is water-soluble and dissociates at approximately 800 °C. Silicon, in contrast to germanium, readily accommo-

dates surface passivation by forming silicon dioxide (SiO₂), which provides a high degree of protection to the underlying device. This stable SiO₂ layer results in a decisive advantage for silicon over germanium as the basic semiconductor material used for electronic device fabrication. This advantage has led to a number of new technologies, including processes for diffusion doping and defining intricate patterns. Other advantages of silicon are that it is completely nontoxic, and that silica (SiO₂), the raw material from which silicon is obtained, comprises approximately 60% of the mineral content of the Earth's crust. This implies that the raw material from which silicon is obtained is available in plentiful supply to the integrated circuit (IC) industry. Moreover, electronic-grade silicon can be obtained at less than one-tenth the cost of germanium. All of these advantages have caused silicon to almost completely replace germanium in the semiconductor industry.

Although silicon is not the optimum choice for every electronic device, its advantages mean that it will almost certainly dominate the semiconductor industry for some time yet.

13.1 Overview

Very fruitful interactions have occurred between the users and manufacturers of semiconductor material since the invention of the point-contact transistor in 1947, when the necessity for *perfect and pure* crystals was recognized. The competition was often such that the crystal quality demanded by new devices could only be met by controlling crystal growth using electronic equipment built with these new devices. Since dislocation-free silicon crystals were grown as early as the 1960s using the *Dash technique* [13.2], semiconductor material research and developmental efforts have concentrated on material purity, production yields, and problems related to device manufacture.

Semiconductor devices and circuits are fabricated using a wide variety of mechanical, chemical, physical and thermal processes. A flow diagram for typical semiconductor silicon preparation processes is shown

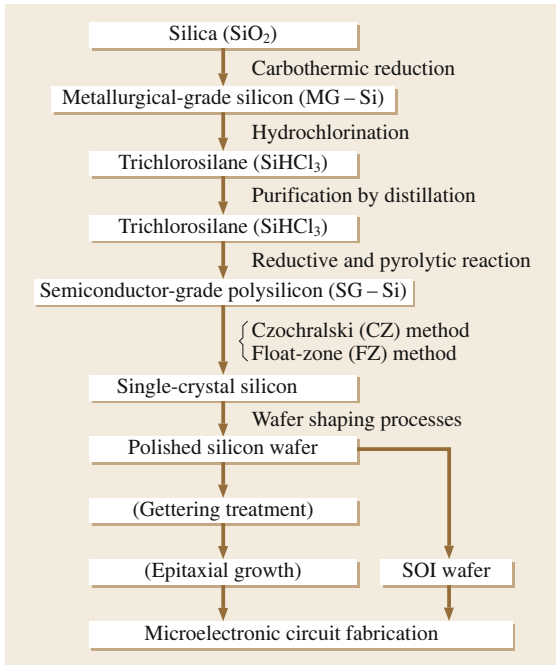


Fig. 13.1 Flow diagram for typical semiconductor silicon preparation processes. (After [13.1])

in Fig. 13.1. The preparation of silicon single-crystal substrates with mechanically and chemically polished surfaces is the first step in the long and complex process of device fabrication.

As noted above, silicon is the second most abundant element on Earth; more than 90% of the Earth's crust is composed of silica and silicates. Given this boundless supply of raw material, the problem is then to transform silicon into the usable state required by the semiconductor technology. The first and main requirement is that the silicon used for electronic devices must be extremely pure, since very small amounts of some impurities have a strong influence on the electronic characteristics of silicon, and therefore the performance of the electronic device. The second requirement is for large-diameter crystals, since the chip yield per wafer increases substantially with larger diameters, as shown in Fig. 13.2 for the case of DRAM [13.3], one of the most common electronic devices. Besides the purity and the diameter, the cost of production and the specifications of the material, including the grown-in defect density and the resistive homogeneity, must meet current industrial demands.

In this chapter, current approaches to the preparation of silicon – converting the raw material into single-crystalline silicon (see Fig. 13.1) – are discussed.

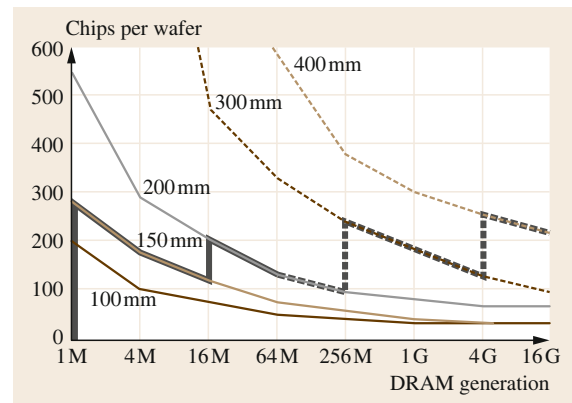


Fig. 13.2 Chips per wafer as a function of DRAM generation. (After [13.3])

13.2 Starting Materials

13.2.1 Metallurgical-Grade Silicon

The starting material for high-purity silicon single crystals is silica (SiO_2). The first step in silicon manufacture is the melting and reduction of silica. This is accomplished by mixing silica and carbon in the form of coal, coke or wood chips and heating the mixture to high temperatures in a submerged electrode arc furnace. This carbothermic reduction of silica produces fused silicon



A complex series of reactions actually occur in the furnace at temperatures ranging from 1500 to 2000 °C. The lumps of silicon obtained from this process are called metallurgical-grade silicon (MG-Si), and its purity is about 98–99%.

13.2.2 Polycrystalline Silicon

Intermediate Chemical Compounds

The next step is to purify MG-Si to the level of semiconductor-grade silicon (SG-Si), which is used as the starting material for single-crystalline silicon. The basic concept is that powdered MG-Si is reacted with anhydrous HCl to form various chlorosilane compounds in a fluidized-bed reactor. Then the silanes are purified by distillation and chemical vapor deposition (CVD) to form SG-polysilicon.

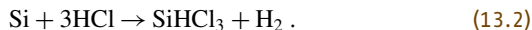
A number of intermediate chemical compounds have been considered, such as monosilane (SiH_4), silicon tetrachloride (SiCl_4), trichlorosilane (SiHCl_3) and dichlorosilane (SiH_2Cl_2). Among these, trichlorosilane is most commonly used for subsequent polysilicon deposition for the following reasons:

1. It can be easily formed by the reaction of anhydrous hydrogen chloride with MG-Si at reasonably low temperatures (200–400 °C).
2. It is liquid at room temperature, so purification can be accomplished using standard distillation techniques.
3. It is easy to handle and can be stored in carbon steel tanks when dry.
4. Liquid trichlorosilane is easily vaporized and, when mixed with hydrogen, it can be transported in steel lines.
5. It can be reduced at atmospheric pressure in the presence of hydrogen.
6. Its deposition can take place on heated silicon, eliminating the need for contact with any foreign surfaces that may contaminate the resulting silicon.

7. It reacts at lower temperatures (1000–1200 °C) and at faster rates than silicon tetrachloride.

Hydrochlorination of Silicon

Trichlorosilane is synthesized by heating powdered MG-Si at around 300 °C in a fluidized-bed reactor. That is, MG-Si is converted into SiHCl_3 according to the following reaction



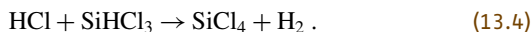
The reaction is highly exothermic and so heat must be removed to maximize the yield of trichlorosilane. While converting MG-Si into SiHCl_3 , various impurities such as Fe, Al, and B are removed by converting them into their halides (FeCl_3 , AlCl_3 , and BCl_3 , respectively), and byproducts such as SiCl_4 and H_2 are also produced.

Distillation and Decomposition of Trichlorosilane

Distillation has been widely used to purify trichlorosilane. The trichlorosilane, which has a low boiling point (31.8 °C), is fractionally distilled from the impure halides, resulting in greatly increased purity, with an electrically active impurity concentration of less than 1 ppba. The high-purity trichlorosilane is then vaporized, diluted with high-purity hydrogen, and introduced into the deposition reactor. In the reactor, thin silicon rods called slim rods supported by graphite electrodes are available for surface deposition of silicon according to the reaction



In addition this reaction, the following reaction also occurs during polysilicon deposition, resulting in the formation of silicon tetrachloride (the major byproduct of the process)



This silicon tetrachloride is used to produce high-purity quartz, for example.

Needless to say, the purity of the slim rods must be comparable to that of the deposited silicon. The slim rods are preheated to approximately 400 °C at the start of the silicon CVD process. This preheating is required in order to increase the conductivity of high-purity (high-resistance) slim rods sufficiently to allow for resistive heating. Depositing for 200–300 h at around 1100 °C results in high-purity polysilicon rods of 150–200 mm in diameter. The polysilicon rods are

shaped into various forms for subsequent crystal growth processes, such as chunks for Czochralski melt growth and long cylindrical rods for float-zone growth. The process for reducing trichlorosilane on a heated silicon rod using hydrogen was described in the late 1950s and early 1960s in a number of process patents assigned to Siemens; therefore, this process is often called the *Siemens method* [13.4].

The major disadvantages of the Siemens method are its poor silicon and chlorine conversion efficiencies, relatively small batch size, and high power consumption. The poor conversion efficiencies of silicon and chlorine are associated with the large volume of silicon tetrachloride produced as the byproduct in the CVD process. Only about 30% of the silicon provided in the CVD reaction is converted into high-purity polysilicon. Also, the cost of producing high-purity polysilicon may depend on the usefulness of the byproduct, SiCl_4 .

Monosilane Process

A polysilicon production technology based on the production and pyrolysis of monosilane was established in the late 1960s. Monosilane potentially saves energy because it deposits polysilicon at a lower temperature and produces purer polysilicon than the trichlorosilane process; however, it has hardly been used due to the lack of an economical route to monosilane and due to processing problems in the deposition step [13.5]. However, with the recent development of economical routes to high-purity silane and the successful operation of a large-scale plant, this technology has attracted the attention of the semiconductor industry, which requires higher purity silicon.

In current industrial monosilane processes, magnesium and Mg-Si powder are heated to 500°C under a hydrogen atmosphere in order to synthesize magnesium silicide (Mg_2Si), which is then made to react with ammonium chloride (NH_4Cl) in liquid ammonia (NH_3) below 0°C to form monosilane (SiH_4). High-purity polysilicon is then produced via the pyrolysis of the monosilane on resistively heated polysilicon filaments at $700\text{--}800^\circ\text{C}$. In the monosilane generation process, most of the boron impurities are removed from silane via chemical reaction with NH_3 . A boron content of $0.01\text{--}0.02$ ppba in polysilicon has been achieved using a monosilane process. This con-

centration is very low compared to that observed in polysilicon prepared from trichlorosilane. Moreover, the resulting polysilicon is less contaminated with metals picked up through chemical transport processes because monosilane decomposition does not cause any corrosion problems.

Granular Polysilicon Deposition

A significantly different process, which uses the decomposition of monosilane in a fluidized-bed deposition reactor to produce free-flowing granular polysilicon, has been developed [13.5]. Tiny silicon seed particles are fluidized in a monosilane/hydrogen mix, and polysilicon is deposited to form free-flowing spherical particles that are an average of $700\ \mu\text{m}$ in diameter with a size distribution of $100\text{--}1500\ \mu\text{m}$. The fluidized-bed seeds were originally made by grinding SG-Si in a ball or hammer mill and leaching the product with acid, hydrogen peroxide and water. This process was time-consuming and costly, and tended to introduce undesirable impurities into the system through the metal grinders. However, in a new method, large SG-Si particles are fired at each other by a high-speed stream of gas causing them to break into particles of a suitable size for the fluidized bed. This process introduces no foreign materials and requires no leaching.

Because of the greater surface area of granular polysilicon, fluidized-bed reactors are much more efficient than traditional Siemens-type rod reactors. The quality of fluidized-bed polysilicon has been shown to be equivalent to polysilicon produced by the more conventional Siemens method. Moreover, granular polysilicon of a free-flowing form and high bulk density enables crystal growers to obtain the most from of each production run. That is, in the Czochralski crystal growth process (see the following section), crucibles can be quickly and easily filled to uniform loadings which typically exceed those of randomly stacked polysilicon chunks produced by the Siemens method. If we also consider the potential of the technique to move from batch operation to continuous pulling (discussed later), we can see that free-flowing polysilicon granules could provide the advantageous route of a uniform feed into a steady-state melt. This product appears to be a revolutionary starting material of great promise for silicon crystal growth.

13.3 Single-Crystal Growth

Although various techniques have been utilized to convert polysilicon into single crystals of silicon, two techniques have dominated the production of them

for electronics because they meet the requirements of the microelectronics device industry. One is a zone-melting method commonly called the *floating-zone*

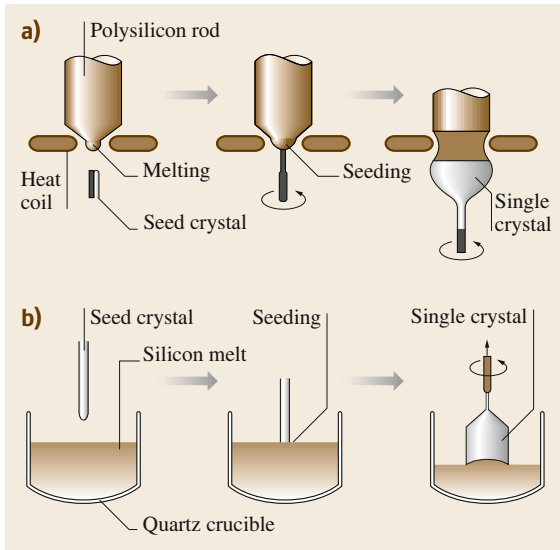


Fig. 13.3a,b Principles of single-crystal growth by (a) floating-zone method and (b) Czochralski method. (After [13.1])

(FZ) method, and the other is a pulling method traditionally called the *Czochralski (CZ) method*, although it should actually be called the *Teal–Little method*. The principles behind these two crystal growth methods are depicted in Fig. 13.3. In the FZ method, a molten zone is passed through a polysilicon rod to convert it into a single-crystal ingot; in the CZ method, a single crystal is grown by pulling from a melt contained in a quartz crucible. In both cases, the *seed crystal* plays a very important role in obtaining a single crystal with a desired crystallographic orientation.

It is estimated that about 95% of all single-crystal silicon is produced by the CZ method and the rest mainly by the FZ method. The silicon semiconductor industry requires high purity and minimum defect concentrations in their silicon crystals to optimize device manufacturing yield and operational performance. These requirements are becoming increasingly stringent as the technology changes from LSI to VLSI/ULSI and then SOC. Besides the quality or perfection of silicon crystals, crystal diameter has also been steadily increasing in order to meet the demands of device manufacturers. Since microelectronic chips are produced via a *batch system*, the diameters of the silicon wafers used for device fabrication significantly affect the productivity (as shown in Fig. 13.2), and in turn the production cost.

In the following sections, we first discuss the FZ method and then move on to the CZ method. The latter will be discussed in more detail due to its extreme importance to the microelectronics industry.

13.3.1 Floating-Zone Method

General Remarks

The FZ method originated from zone melting, which was used to refine binary alloys [13.6] and was invented by *Theurer* [13.7]. The reactivity of liquid silicon with the material used for the crucible led to the development of the FZ method [13.8], which permits the crystallization of silicon without the need for any contact with the crucible material, which is needed to be able to grow crystals of the required semiconductor purity.

Outline of the Process

In the FZ process, a polysilicon rod is converted into a single-crystal ingot by passing a molten zone heated by a needle-eye coil from one end of the rod to the other, as shown in Fig. 13.3a. First, the tip of the polysilicon rod is contacted and fused with a seed crystal with the desired crystal orientation. This process is called *seeding*. The seeded molten zone is passed through the polysilicon rod by simultaneously moving the single crystal seed down the rod. When the molten zone of silicon solidifies, polysilicon is converted into single-crystalline silicon with the help of the seed crystal. As the zone travels along the polysilicon rod, single-crystal silicon freezes at its end and grows as an extension of the seed crystal.

After seeding, a thin neck about 2 or 3 mm in diameter and 10–20 mm long is formed. This process is called *necking*. Growing a neck eliminates dislocations that can be introduced into newly grown single-crystal silicon during the seeding operation due to thermal shock. This necking process, called the *Dash technique* [13.2], is therefore fundamental to growing dislocation-free crystals and is used universally in both the FZ and the CZ methods. An x-ray topograph of the seed, neck and conical part of a silicon single-crystal grown by the FZ method is shown in Fig. 13.4. It is apparent that dislocations generated at the melt contact are completely eliminated by necking. After the conical part is formed, the main body with the full target diameter is grown. During the entire FZ growth process, the shape of the molten zone and the ingot diameter are determined by adjusting the power to the coil and the travel rate, both of which are under computer control. The technique most commonly used to automatically control the diameter in both the FZ and CZ methods employs an infrared sensor focused on the meniscus. The shape of the meniscus on a growing crystal depends on its angle of contact at the three-phase boundary, the crystal diameter, and the magnitude of the surface tension. A change in meniscus angle (and therefore crystal diameter) is sensed, and the information is fed back in order to automatically adjust the growth conditions.

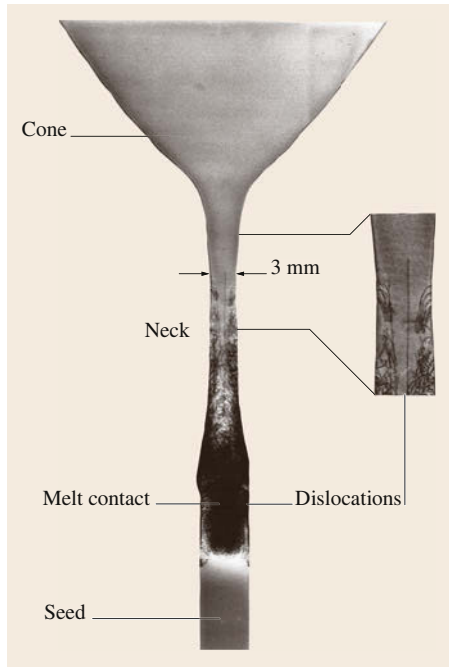


Fig. 13.4 X-ray topography of seed, neck and conical part of floating-zone silicon. (Courtesy of Dr. T. Abe)

In contrast with CZ crystal growth, in which the seed crystal is dipped into the silicon melt and the growing crystal is pulled upward, in the FZ method the thin seed crystal sustains the growing crystal, as does the polysilicon rod from the bottom (Fig. 13.3). As a result, the rod is balanced precariously on the thin seed and neck during the entire growth process. The seed and neck can support a crystal of up to a 20 kg so long as the center of gravity of the growing crystal remains at the center of the growth system. If the center of gravity moves away from the center line, the seed will easily fracture. Hence, it was necessary to invent a crystal stabilizing and supporting technique before long and heavy FZ silicon crystals could be grown. For large crystals, it is necessary to support the growing crystal in the way shown in Fig. 13.5 [13.9], particularly in the case of recent FZ crystals with large diameters (150–200 mm), since their weights easily exceed 20 kg.

Doping

In order to obtain n- or p-type silicon single-crystals of the required resistivity, either the polysilicon or the growing crystal must be doped with the appropriate donor or acceptor impurities, respectively. For FZ silicon growth, although several doping techniques have been tried, the crystals are typically doped by blowing a dopant gas such as phosphine (PH_3) for n-type silicon or diborane (B_2H_6) for p-type silicon onto the molten

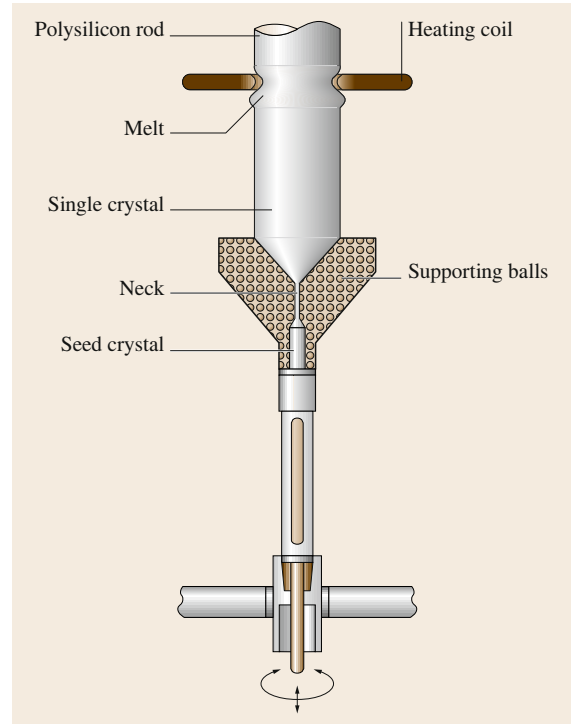
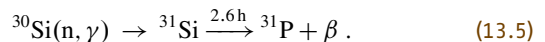


Fig. 13.5 Supporting system for floating-zone silicon crystal. (After [13.9])

zone. The dopant gas is usually diluted with a carrier gas, such as argon. The great advantage of this method is that the silicon crystal manufacturer does not need to store polysilicon sources with different resistivities.

Since the segregation (discussed in the next subsection) of elemental dopants for n-type silicon is much less than unity, FZ crystals doped by the traditional method have radial dopant gradients. Moreover, since the crystallization rate varies in the radial direction on the microscopic scale, the dopant concentrations distribute cyclically and give rise to so-called *dopant striations*, resulting in radial resistivity inhomogeneities. In order to obtain more homogeneously doped n-type silicon, neutron transmutation doping (NTD) has been applied to FZ silicon crystals [13.10]. This procedure involves the nuclear transmutation of silicon to phosphorus by bombarding the crystal with thermal neutrons according to the reaction



The radioactive isotope ^{31}Si is formed when ^{30}Si captures a neutron and then decays into the stable isotope ^{31}P (donor atoms), whose distribution is not dependent on crystal growth parameters. Immediately after irradiation the crystals exhibit high resistivity, which

is attributed to the large number of lattice defects arising from radiation damage. The irradiated crystal, therefore, must be annealed in an inert ambient at temperatures of around 700 °C in order to annihilate the defects and to restore the resistivity to that derived from the phosphorus doping. Under the NTD scheme, crystals are grown without doping and are then irradiated in a nuclear reactor with a large ratio of thermal to fast neutrons in order to enhance neutron capture and to minimize damage to the crystal lattice.

The application of NTD has been almost exclusively limited to FZ crystals because of their higher purity compared to CZ crystals. When the NTD technique was applied to CZ silicon crystals, it was found that oxygen donor formation during the annealing process after irradiation changed the resistivity from that expected, even though phosphorus donor homogeneity was achieved [13.11]. NTD has the additional shortcoming that no process is available for p-type dopants and that an excessively long period of irradiation is required for low resistivities (in the range of 1–10 Ω cm).

Properties of FZ-Silicon Crystal

During FZ crystal growth, the molten silicon does not come into contact with any substance other than the ambient gas in the growth chamber. Therefore, an FZ silicon crystal is inherently distinguished by its higher purity compared to a CZ crystal which is grown from the melt – involving contact with a quartz crucible. This contact gives rise to high oxygen impurity concentrations of around 10^{18} atoms/cm³ in CZ crystals, while FZ silicon contains less than 10^{16} atoms/cm³. This higher purity allows FZ silicon to achieve high resistivities not obtainable using CZ silicon. Most of the FZ silicon consumed has a resistivity of between 10 and 200 Ω cm, while CZ silicon is usually prepared to resistivities of 50 Ω cm or less due to the contamination from the quartz crucible. FZ silicon is therefore mainly used to fabricate semiconductor power devices that support reverse voltages in excess of 750–1000 V. The high-purity crystal growth and the precision doping characteristics of NTD FZ-Si have also led to its use in infrared detectors [13.12], for example.

However, if we consider mechanical strength, it has been recognized for many years that FZ silicon, which contains fewer oxygen impurities than CZ silicon, is mechanically weaker and more vulnerable to thermal stress during device fabrication [13.13, 14]. High-temperature processing of silicon wafers during electronic device manufacturing often produces enough thermal stress to generate slip dislocations and warpage. These effects bring about yield loss due to leaky junctions, dielectric defects, and reduced lifetime, as well as reduced photolithographic yields due to the degradation

of wafer flatness. Loss of geometrical planarity due to warpage can be so severe that the wafers are not processed any further. Because of this, CZ silicon wafers have been used much more widely in IC device fabrication than FZ wafers have. This difference in mechanical stability against thermal stresses is the dominant reason why CZ silicon crystals are exclusively used for the fabrication of ICs that require a large number of thermal process steps.

In order to overcome these shortcomings of FZ silicon, the growth of FZ silicon crystals with doping impurities such as oxygen [13.15] and nitrogen [13.16] has been attempted. It was found that doping FZ silicon crystals with oxygen or nitrogen at concentrations of $1\text{--}1.5 \times 10^{17}$ atoms/cm³ or 1.5×10^{15} atoms/cm³, respectively, results in a remarkable increase in mechanical strength.

13.3.2 Czochralski Method

General Remarks

This method was named after J. Czochralski, who established a technique for determining the crystallization velocities of metals [13.17]. However, the actual pulling method that has been widely applied to single-crystal growth was developed by *Teal* and *Little* [13.18], who modified Czochralski's basic principle. They were the first to successfully grow single-crystals of germanium, 8 inches in length and 0.75 inches in diameter, in 1950. They subsequently designed another apparatus for the growth of silicon at higher temperatures. Although the basic production process for single-crystal silicon has changed little since it was pioneered by Teal and coworkers, large-diameter (up to 400 mm) silicon single-crystals with a high degree of perfection that meet state-of-the-art device demands have been grown by incorporating the Dash technique and successive technological innovations into the apparatus.

Today's research and development efforts concerning silicon crystals are directed toward achieving microscopic uniformity of crystal properties such as the resistivity and the concentrations of impurities and microdefects, as well as microscopic control of them, which will be discussed elsewhere in this Handbook.

Outline of the Process

The three most important steps in CZ crystal growth are shown schematically in Fig. 13.3b. In principle, the process of CZ growth is similar to that of FZ growth: (1) melting polysilicon, (2) seeding and (3) growing. The CZ pulling procedure, however, is more complicated than that of FZ growth and is distinguished from it by the use of a quartz crucible to contain the molten

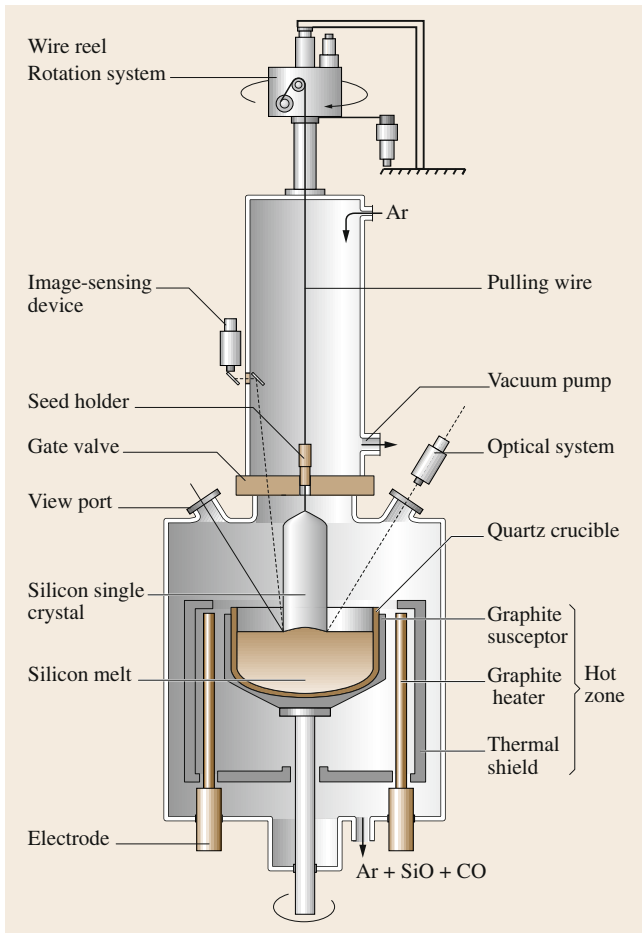


Fig. 13.6 Schematic view of typical Czochralski silicon crystal growing system. (After [13.1])

silicon. Figure 13.6 shows a schematic view of typical modern CZ crystal growth equipment. Important steps in the actual or standard CZ silicon crystal growth sequence are as follows:

1. Polysilicon chunks or grains are placed in a quartz crucible and melted at temperatures higher than the melting point of silicon (1420°C) in an inert ambient gas.
2. The melt is kept at a high temperature for a while in order to ensure complete melting and ejection of tiny bubbles, which may cause voids or negative crystal defects, from the melt.
3. A seed crystal with the desired crystal orientation is dipped into the melt until it begins to melt itself. The seed is then withdrawn from the melt so that the neck is formed by gradually reducing the diameter; this is the most delicate step. During the entire crystal growth process, inert gas (usually argon) flows

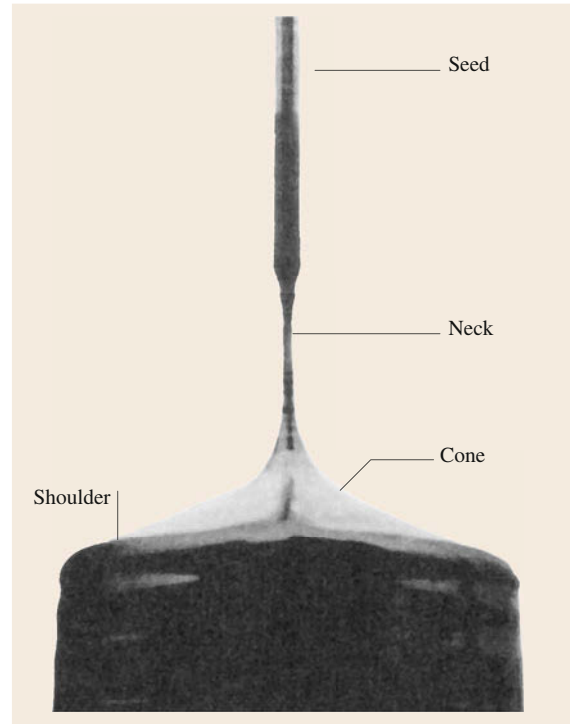


Fig. 13.7 Seed-end part of as-grown Czochralski silicon crystal

downward through the pulling chamber in order to carry off reaction products such as SiO and CO .

4. By gradually increasing the crystal diameter, the conical part and shoulder are grown. The diameter is increased up to the target diameter by decreasing the pulling rate and/or the melt temperature.
5. Finally, the cylindrical part of the body with a constant diameter is grown by controlling the pulling rate and the melt temperature while compensating for the drop in the melt level as the crystal grows. The pulling rate is generally reduced toward the tail end of a growing crystal, mainly due to increasing heat radiation from the crucible wall as the melt level drops and exposes more crucible wall to the growing crystal. Near the end of the growth process, but before the crucible is completely drained of molten silicon, the crystal diameter must be gradually reduced to form an end-cone in order to minimize thermal shock, which can cause slip dislocations at the tail end. When the diameter becomes small enough, the crystal can be separated from the melt without the generation of dislocations.

Figure 13.7 shows the seed-end part of an as-grown CZ silicon crystal. Although a seed-corn, which is the



Fig. 13.8 Extra-large as-grown Czochralski silicon ingot 400 mm in diameter and 1800 mm in length. (Courtesy of Super Silicon Crystal Research Institute Corporation, Japan)

transition region from the seed to the cylindrical part, is usually formed to be rather flat for economic reasons, a more tapered shape might be desirable from a crystal quality point of view. The shoulder part and its vicinity should not be used for device fabrication because this part is considered a transition region in many senses and it exhibits inhomogeneous crystal characteristics due to the abrupt change in growth conditions.

Figure 13.8 shows an extra-large as-grown CZ silicon crystal ingot 400 mm in diameter and 1800 mm in length grown by the Super Silicon Crystal Research Institute Corporation in Japan [13.3].

Influence of Spatial Location in a Grown Crystal

As Fig. 13.9 clearly depicts, each portion of a CZ crystal is grown at a different time with different growth conditions [13.19]. Thus, it is important to understand that each portion has a different set of crystal characteristics and a different thermal history due to its different position along the crystal length. For example, the seed-end portion has a longer thermal history, ranging from the melting point of 1420 to around 400 °C in a puller, while the tail-end portion has a shorter history and is cooled down rather rapidly from the melting point. Ultimately, each silicon wafer prepared from a different portion of a grown crystal could exhibit different physico-chemical characteristics depending on its location in the ingot. In fact, it has been reported that the oxygen precipitation behavior exhibits the greatest location dependence, which, in turn, affects the generation of bulk defects [13.20].

Also, a nonuniform distribution of both crystal defects and impurities occurs across the transverse section of a flat wafer prepared from a CZ crystal silicon melt crystallized or solidified successively at the crystal–melt interface, which is generally curved in the CZ

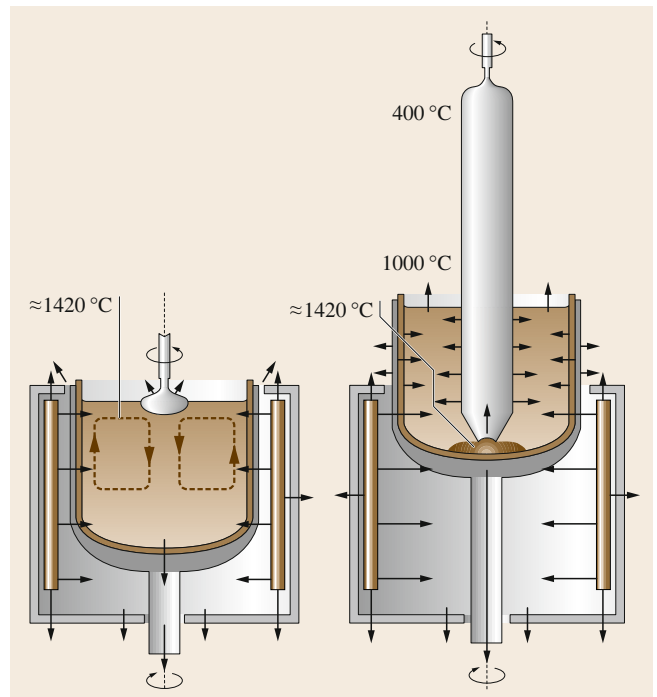


Fig. 13.9 Thermal environment during Czochralski crystal growth at initial and final stages. *Arrows* indicate approximate directions of heat flow. (After [13.19])

crystal growth process. Such inhomogeneities can be observed as *striations*, which are discussed later.

13.3.3 Impurities in Czochralski Silicon

The properties of the silicon semiconductors used in electronic devices are very sensitive to impurities. Because of this sensitivity, the electrical/electronic properties of silicon can be precisely controlled by adding a small amount of dopant. In addition to this dopant sensitivity, contamination by impurities (particularly transition metals) negatively affects the properties of silicon and results in the serious degradation of device performance. Moreover, oxygen is incorporated at levels of tens of atoms per million into CZ silicon crystals due to the reaction between the silicon melt and the quartz crucible. Regardless of how much oxygen is in the crystal, the characteristics of silicon crystals are greatly affected by the concentration and the behavior of oxygen [13.21]. In addition, carbon is also incorporated into CZ silicon crystals either from polysilicon raw materials or during the growth process, due to the graphite parts used in the CZ pulling equipment. Although the concentration of carbon in commercial CZ silicon crystals is normally less than 0.1 ppma, carbon is an impurity that greatly affects the behavior

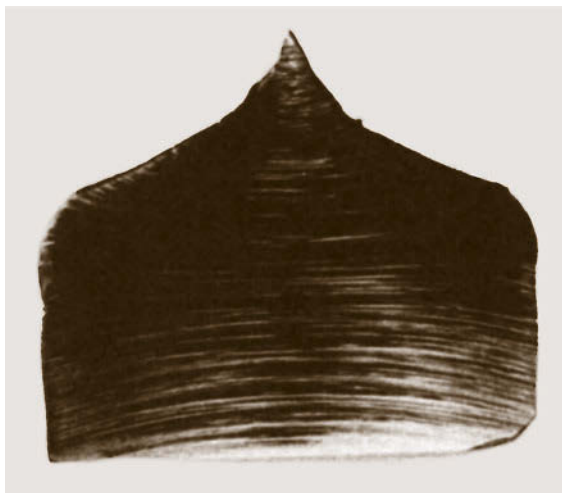


Fig. 13.10 Growth striations, revealed by chemical etching, in a shoulder of Czochralski silicon

of oxygen [13.22, 23]. Also, nitrogen-doped CZ silicon crystals [13.24, 25] have recently attracted much attention due to their high microscopic crystal quality, which may meet the requirements for state-of-the-art electronic devices [13.26, 27].

Impurity Inhomogeneity

During crystallization from a melt, various impurities (including dopants) contained in the melt are incorporated into the growing crystal. The impurity concentration of the solid phase generally differs from that of the liquid phase due to a phenomenon known as *segregation*.

Segregation. The equilibrium segregation behavior associated with the solidification of multicomponent systems can be determined from the corresponding phase diagram of a binary system with a *solute* (the impurity) and a *solvent* (the host material) as components.

The ratio of the solubility of impurity A in solid silicon $[C_A]_s$ to that in liquid silicon $[C_A]_L$

$$k_0 = \frac{[C_A]_s}{[C_A]_L} \quad (13.6)$$

is referred to as the *equilibrium segregation coefficient*. The impurity solubility in liquid silicon is always higher than that in solid silicon; that is, $k_0 < 1$.

The equilibrium segregation coefficient k_0 is only applicable to solidification at negligibly slow growth rates. For finite or higher solidification rates, impurity atoms with $k_0 < 1$ are rejected by the advancing solid at a greater rate than they can diffuse into the melt. In the CZ crystal growth process, segregation takes place at

the start of solidification at a given seed–melt interface, and the rejected impurity atoms begin to accumulate in the melt layer near the growth interface and diffuse in the direction of the bulk of the melt. In this situation, an *effective segregation coefficient* k_{eff} can be defined at any moment during CZ crystal growth, and the impurity concentration $[C]_s$ in a CZ crystal can be derived by

$$[C]_s = k_{\text{eff}}[C_0](1 - g)^{k_{\text{eff}} - 1}, \quad (13.7)$$

where $[C_0]$ is the initial impurity concentration in the melt and g is the fraction solidified.

Consequently, it is clear that a macroscopic longitudinal variation in the impurity level, which causes a variation in resistivity due to the variation in the dopant concentration, is inherent to the CZ batch growth process; this is due to the segregation phenomenon. Moreover, the longitudinal distribution of impurities is influenced by changes in the magnitude and the nature of melt convection that occur as the melt aspect ratio is decreased during crystal growth.

Striations. In most crystal growth processes, there are transients in the parameters such as instantaneous microscopic growth rate and the diffusion boundary layer thickness which result in variations in the effective segregation coefficient k_{eff} . These variations give rise to microscopic compositional inhomogeneities in the form of *striations* parallel to the crystal–melt interface. Striations can be easily delineated with several techniques, such as preferential chemical etching and x-ray topography. Figure 13.10 shows the striations revealed by chemical etching in the shoulder part of a longitudinal cross-section of a CZ silicon crystal. The gradual change in the shape of the growth interface is also clearly observed.

Striations are physically caused by the segregation of impurities and also point defects; however, the striations are practically caused by temperature fluctuations near the crystal–melt interface, induced by unstable thermal convection in the melt and crystal rotation in an asymmetric thermal environment. In addition, mechanical vibrations due to poor pulling control mechanisms in the growth equipment can also cause temperature fluctuations.

Figure 13.11 schematically illustrates a CZ-grown crystal cross-section containing a curved crystal–melt interface, which results in inhomogeneities on the surface of a slice. As each planar wafer is sliced, it contains different portions of several curved striations. Different *phonograph rings*, referred to as *swirl*, can then occur in each wafer, which can be observed across the wafer using the techniques mentioned above.

Doping

In order to obtain the desired resistivity, a certain amount of dopant (either donor or acceptor atoms) is added to a silicon melt according to the resistivity–concentration relation. It is common practice to add dopants in the form of highly doped silicon particles or chunks of about $0.01 \Omega \text{ cm}$ resistivity, which are called the dopant fixture, since the amount of pure dopant needed is unmanageably small, except for heavily doped silicon materials (n^+ or p^+ silicon).

The criteria for selecting a dopant for a semiconductor material are that it has the following properties:

1. Suitable energy levels
2. High solubility
3. Suitable or low diffusivity
4. Low vapor pressure.

A high diffusivity or high vapor pressure leads to undesirable diffusion or vaporization of dopants, which results in unstable device operation and difficulties in achieving precise resistivity control. A solubility that is too small limits the resistivity that can be obtained. In addition to those criteria, the chemical properties (the toxicity for example) must be considered. A further consideration from the viewpoint of crystal growth is that the dopant has a segregation coefficient that is close to unity in order to make the resistivity as uniform as possible from the seed-end to the tail-end of the CZ crystal ingot. Consequently, phosphorus (P) and boron (B) are the most commonly used donor and acceptor dopants for silicon, respectively. For n^+ silicon, in which donor atoms are heavily doped, antimony (Sb) is usually used instead of phosphorus because of its smaller diffusivity, in spite of its small segregation coefficient and high vapor pressure, which lead to large variations in concentration in both the axial and the radial directions.

Oxygen and Carbon

As shown schematically in Figs. 13.3b and 13.6, a quartz (SiO_2) crucible and graphite heating elements are used in the CZ-Si crystal growth method. The surface of the crucible that contacts the silicon melt is gradually dissolved due to the reaction



This reaction enriches the silicon melt with oxygen. Most of the oxygen atoms evaporate from the melt surface as volatile silicon mono-oxide (SiO), but some of them are incorporated into a silicon crystal through the crystal–melt interface.

However, the carbon in CZ silicon crystals originates mainly from the polycrystalline starting material. Levels of carbon ranging from 0.1 to 1 ppm, depending on the manufacturer, are found in the polysilicon. Sources of carbon in polysilicon are assumed to be mainly carbon-containing impurities found in the trichlorosilane used in the production of polysilicon. Graphite parts in CZ pulling equipment can also contribute to carbon contamination by reacting with oxygen, which is always present during the ambient growth. The resulting products of CO and CO_2 are dissolved into the silicon melt and account for the carbon impurities in silicon crystals. Thus, oxygen and

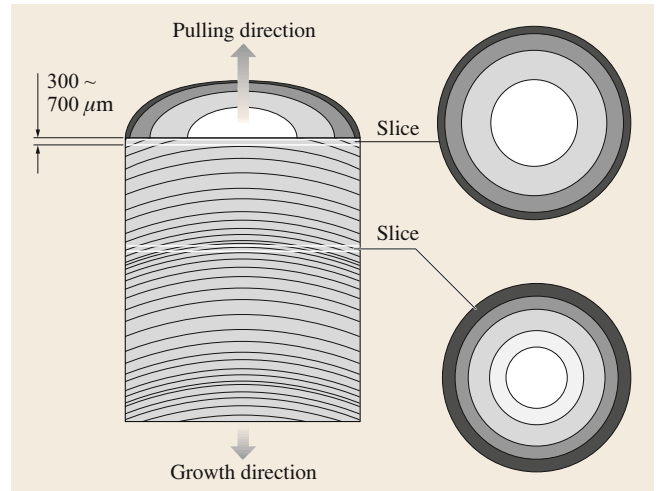


Fig. 13.11 Schematic illustration of Czochralski crystal cross-section containing a curved crystal–melt interface and planar wafers sliced into different portions. (After [13.1])

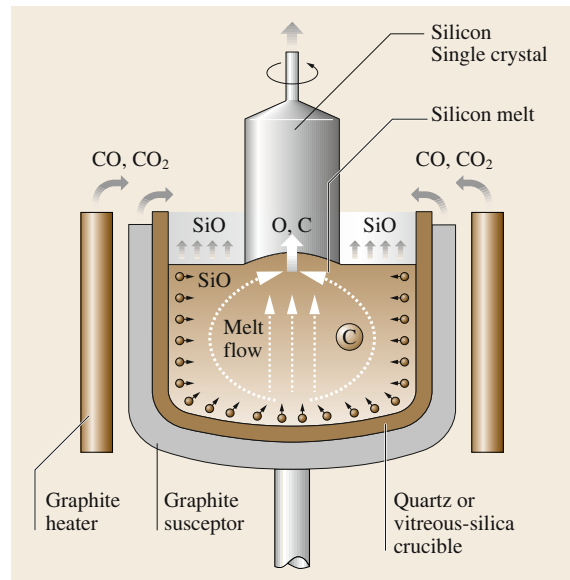


Fig. 13.12 Incorporation of oxygen and carbon into Czochralski silicon crystal. (After [13.1])

depending on the manufacturer, are found in the polysilicon. Sources of carbon in polysilicon are assumed to be mainly carbon-containing impurities found in the trichlorosilane used in the production of polysilicon. Graphite parts in CZ pulling equipment can also contribute to carbon contamination by reacting with oxygen, which is always present during the ambient growth. The resulting products of CO and CO_2 are dissolved into the silicon melt and account for the carbon impurities in silicon crystals. Thus, oxygen and

carbon are the two major nondoping impurities that are incorporated into CZ silicon crystals in the way shown schematically in Fig. 13.12. The behavior of

these impurities in silicon, which affect a number of the properties of CZ silicon crystals, has been the subject of intensive study since the late 1950s [13.21].

13.4 New Crystal Growth Methods

Silicon crystals used for microelectronic device fabrication must meet a variety of requirements set by device manufacturers. In addition to the requirements for silicon *wafers*, the following crystallographic demands have become more common due to high-yield and high-performance microelectronic device manufacturing:

1. Large diameter
2. Low or controlled defect density
3. Uniform and low radial resistivity gradient
4. Optimum initial oxygen concentration and its precipitation.

It is clear that silicon crystal manufacturers must not only meet the above requirements but also produce those crystals economically and with high manufacturing yields. The main concerns of silicon crystal growers are the crystallographic perfection and the axial distribution of dopants in CZ silicon. In order to overcome some problems with the conventional CZ crystal growth method, several new crystal growth methods have been developed.

13.4.1 Czochralski Growth with an Applied Magnetic Field (MCZ)

The melt convection flow in the crucible strongly affects the crystal quality of CZ silicon. In particular, unfavorable growth striations are induced by unsteady melt convection resulting in temperature fluctuations at the growth interface. The ability of a magnetic field to inhibit thermal convection in electrically conducting fluid was first applied to the crystal growth of indium antimonide via the horizontal boat technique [13.28] and the horizontal zone-melting technique [13.29]. Through these investigations, it was confirmed that a magnetic field of sufficient strength can suppress the temperature fluctuations that accompany melt convection, and can dramatically reduce growth striations.

The effect of the magnetic field on growth striations is explained by its ability to decrease the turbulent thermal convection of a melt and in turn decrease the temperature fluctuations at the crystal–melt interface. The fluid flow damping caused by the magnetic field is due to the induced magnetomotive force when the flow is orthogonal to the magnetic flux lines, which results

in an increase in the effective kinematic viscosity of the conducting melt.

Silicon crystal growth by the magnetic field applied CZ (MCZ) method was reported for the first time in 1980 [13.30]. Originally MCZ was intended for the growth of CZ silicon crystals that contain low oxygen concentrations and therefore have high resistivities with low radial variations. In other words, MCZ silicon was expected to replace the FZ silicon almost exclusively used for power device fabrication. Since then, various magnetic field configurations, in terms of the magnetic field direction (horizontal or vertical) and the type of magnets used (normal conductive or superconductive), have been developed [13.31]. MCZ silicon produced with a wide range of desired oxygen concentrations (from low to high) has been of great interest for different device applications. The value of MCZ silicon lies in its high quality and its ability to control the oxygen concentration over a wide range, which cannot be achieved using the conventional CZ method [13.32], as well as its enhanced growth rate [13.33].

As far as the crystal quality is concerned, there is no doubt that the MCZ method provides the silicon crystals most favorable to the semiconductor device industry. The production cost of MCZ silicon may be higher than that of conventional CZ silicon because the MCZ method consumes more electrical power and re-

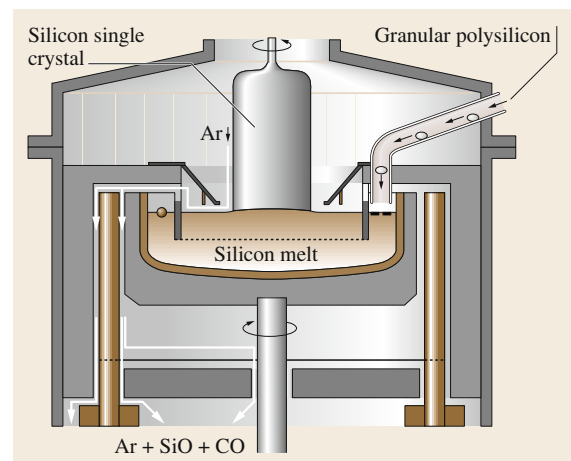


Fig. 13.13 Schematic illustration of the continuous-charging Czochralski method. (After [13.34])

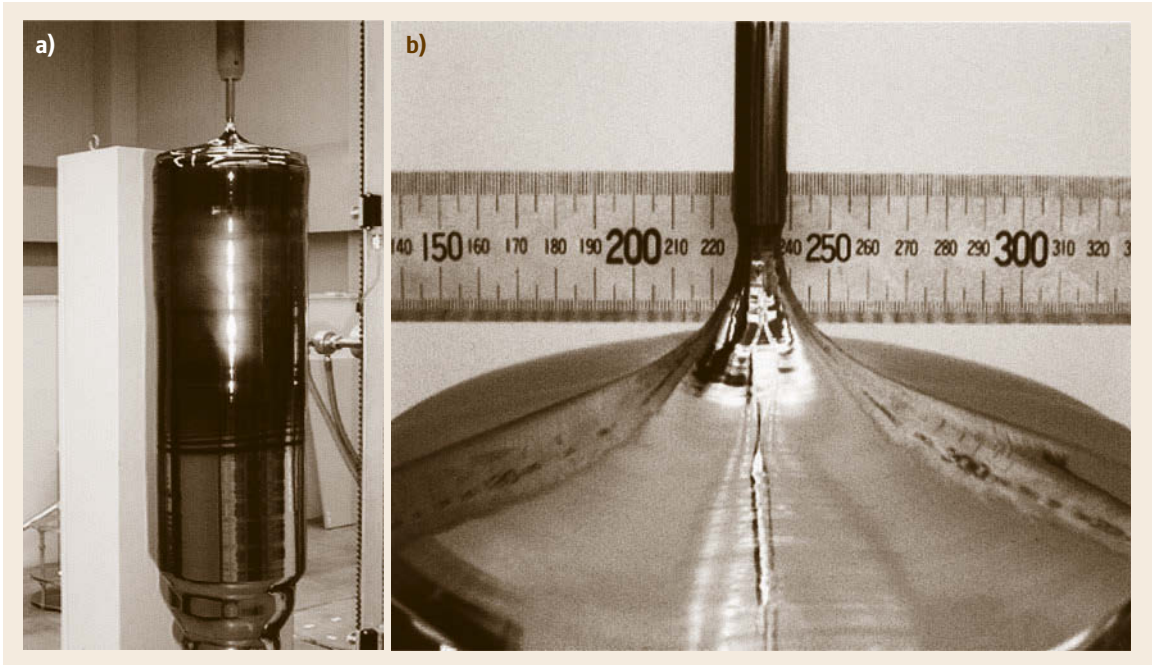


Fig. 13.14a,b 200 mm-diameter dislocation-free Czochralski silicon crystal grown without the Dash necking process. (a) Whole body, (b) seed and cone. (Courtesy of Prof. K. Hoshikawa)

quires additional equipment and operating space for the electromagnets; however, taking into account the higher growth rate of MCZ, and when superconductive magnets that need smaller space and consume less electrical power compared with conductive magnets are used, the production cost of MCZ silicon crystals may become comparable to that of conventional CZ silicon crystals. In addition, the improved crystal quality of MCZ silicon may increase production yields and lower the production cost.

13.4.2 Continuous Czochralski Method (CCZ)

Crystal production costs depend to a large extent on the cost of materials, in particular the cost of those used for quartz crucibles. In the conventional CZ process, called a *batch process*, a crystal is pulled from a single crucible charge, and the quartz crucible is used only once and is then discarded. This is because the small amount of remaining silicon cracks the crucible as it cools from a high temperature during each growth run.

One strategy for replenishing a quartz crucible with melt economically is to continuously add feed as the crystal is grown and thereby maintain the melt at a constant volume. In addition to saving crucible costs, the continuous-charging Czochralski (CCZ) method provides an ideal environment for silicon crystal growth. As already mentioned, many of the inhomogeneities in

crystals grown by the conventional CZ batch process are a direct result of the unsteady kinetics arising from the change in melt volume during crystal growth. The CCZ method aims not only to reduce production costs but also to grow crystals under steady conditions. By maintaining the melt volume at a constant level, steady thermal and melt flow conditions can be achieved (see Fig. 13.9, which shows the change in thermal environments during conventional CZ growth).

Continuous charging is commonly performed by polysilicon feeding, as shown in Fig. 13.13 [13.34]. This system consists of a hopper for storing the polysilicon raw material and a vibratory feeder that transfers the polysilicon to the crucible. In the crucible that contains the silicon melt, a quartz baffle is required to prevent the melt turbulence caused by feeding in the solid material around the growth interface. Free-flowing polysilicon granules such as those mentioned previously are obviously advantageous for the CCZ method.

The CCZ method certainly solves most of the problems related to inhomogeneities in crystal grown by the conventional CZ method. Moreover, the combination of MCZ and CCZ (the magnetic-field-applied continuous CZ (MCCZ) method) is expected to provide the ultimate crystal growth method, giving ideal silicon crystals for a wide variety of microelectronic applications [13.1]. Indeed, it has been used to grow

high-quality silicon crystals intended for microelectronic devices [13.35].

However, it should be emphasized that the different thermal histories of different parts of the crystal (from the seed to the tail ends, as shown in Fig. 13.9) must be considered even when the crystal is grown by the ideal growth method. In order to homogenize the grown crystal or to obtain axial uniformity in the thermal history, some form of post-treatment, such as high-temperature annealing [13.36], is required for the crystal.

13.4.3 Neckingless Growth Method

As mentioned previously, Dash's necking process (which grows a thin neck 3–5 mm in diameter, Fig. 13.7) is a critical step during CZ crystal growth because it eliminates grown-in dislocations. This technique has been the industry standard for more than 40 years. However, recent demands for large crystal

diameters (> 300 mm, weighing over 300 kg) have resulted in the need for larger diameter necks that do not introduce dislocations into the growing crystal, since a thin neck 3–5 mm in diameter can not support such large crystals.

Large diameter seeds that are typically 170 mm long, with a minimum diameter of > 10 mm and an average of 12 mm grown from silicon melt heavily doped with boron (> 10^{19} atoms/cm³) have been used to grow dislocation-free 200 mm-diameter CZ silicon crystals [13.37, 38]. It is estimated that large diameter necks 12 mm in diameter can CZ support crystals as heavy as 2000 kg [13.39]. Figure 13.14a shows a 200 mm-diameter dislocation-free CZ silicon crystal grown without the Dash necking process, and Fig. 13.14b shows its enlarged seed (compare with Fig. 13.7). The mechanism by which dislocations are not incorporated into the growing crystal has been primarily attributed to hardening effect of the heavy doping of boron in the silicon.

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