

about one part per 10^9 or less. The group I, II and VI atoms in a semiconductor such as Si are known as **recombination impurities** and frequently called the **lifetime killers**. They will change the electron and hole concentrations only very slightly unless their concentration is so high that it is comparable to or exceeds the concentration of the group III and V impurities. In all Si integrated circuits, these recombination impurities are avoided, by purification and careful control of the manufacturing processing steps. Their presence would increase leakage current and standby power. They are not used for lifetime control in high speed integrated circuits since it is not possible to control their densities under the best manufacturing conditions. However, recombination impurities are still used in some discrete (discrete means one transistor or diode on a chip) Si power and switching transistors and diodes to speed up switching in order to decrease power dissipation and increase power conversion efficiency in power control and ac-dc power conversion applications.

In summary, the semiconductor crystal used in electron device or integrated circuit applications must have low defect density and a controlled concentration of selected impurities to control the magnitude and type of the electrical conductivity.

130 CRYSTAL LATTICES AND PERIODIC STRUCTURES

The preceding discussion on physical defects shows that position periodicity of the host atoms have an important effect on the electrical properties of the solid and the performance of the transistors and integrated circuits. Deviation from periodicity due to a displacement of the atoms from their periodic position gives rise to randomness which reduces electron and hole lifetimes and mobilities or conductivities. The **topology** or **geometry** of the periodicity of the host atoms has another important effect on all the properties (electrical, chemical, optical, mechanical) of a solid. For example, the **shape** and **size** of the periodicity, known as the **unit cell** of atoms, are the key factors that distinguish an insulator and a semiconductor from a conductor or metal; a Si semiconductor from a Ge or GaAs semiconductor. In fact, the shape and the size are determined by a more fundamental factor, the number of protons in the nucleus of the host atom of the crystal. The force that determines the arrangement and the distance between the atoms is the Coulomb force between the positively charged protons in the nucleus and the negatively charged electrons around each atom and at neighboring atoms.

In order to understand and analyze the relationships between the geometrical shape and size of the periodic unit cell and the electrical and other properties of solids, some universal crystallographer's notations and rules will be discussed in the following subsections. These notations and rules are used to catalog and characterize the large number of fundamental crystal lattice structures in terms of the symmetry properties of the geometrical shape and size. Such a systematic approach is necessary since these fundamental structures are the basic building blocks of the infinite varieties of solid materials in the universe.

For example, the three-dimensional crystalline solids found in nature can be grouped into 7 crystal systems, 14 lattices known as Bravais lattice, 32 crystal point groups each with a different point symmetry (such as the rotation symmetry operations about a point), and a total of 230 space groups each with a different space symmetry (or three-dimensional extended symmetry such as mirror reflection in contrast to the point symmetry). To make sense from this large number of groups requires a consensus approach to facilitate analysis and inter-researcher communication. These notations and rules are arrived at from a systematic exploration of the symmetry properties of the shape and size. They can be rigorously derived mathematically using linear algebra and group theory which are given in advanced courses on group theory, solid state physics and solid state chemistry. We shall only give a summary of the several elementary properties which will help us to begin an understanding of the physics underlying the differences in the electrical properties of several semiconductors such as Si, $\text{Ge}_x\text{Si}_{1-x}$ and GaAs.

131 Description of Crystal Lattice by Vectors

A crystal or crystalline solid is a material whose atoms are situated **periodically** on one or more interpenetrating arrays of points known as a **crystal lattice** which is frequently called the physical lattice, the real lattice or the **direct lattice**. The term, direct lattice, is particularly useful in the mathematical (Fourier) analysis of the position-dependent crystal properties in the **position or physical space**. This Fourier analysis uses the **space harmonics**, $\exp(ik_n \cdot r)$ where n is the index of the n -th space harmonic. The twin of space harmonics is the familiar **time harmonics** used in the Fourier analysis of time-dependent signals in electrical circuit analysis. The time harmonics is $\exp(i\omega_m t)$ where m is the index of the m -th time harmonic.

The unique physical, chemical and electronic properties of crystals are intimately related and in fact determined by their geometrical features which are **periodic** or repetitive in the physical space. In order to describe these periodic properties quantitatively or mathematically, the following list of concepts and terms have been introduced and universally used by scientists and engineers. They are used to describe both the direct and the reciprocal lattices and we shall give many illustrations.

| | |
|---|-------------------------------|
| Unit Cell | (not unique) |
| Primitive Unit Cell | (not unique) |
| Basis Vectors a, b, c | (not unique) |
| Primitive Basis Vectors | (not unique) |
| Translation Vector of the Lattice | $R_n = n_1 a + n_2 b + n_3 c$ |
| Primitive Translation of the Lattice | |
| Miller Indices | |

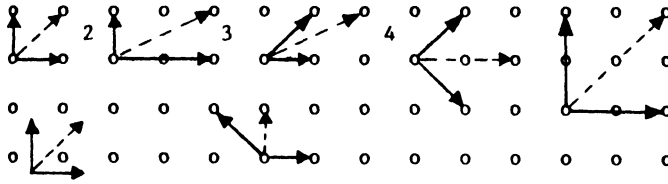


Fig.131.1 Basis vectors and lattice translation vectors of a two-dimensional square lattice.

The variety of **unit cell** is unlimited. The concept and selection of a **unit cell** is illustrated by the seven examples in a two-dimensional square lattice shown in Fig.131.1. The only requirement on constructing or discovering the **unit cell** of a given three-dimensional crystal is that when the unit cell is translated by all the combinations of three integers (positive, negative and zero for n_1 , n_2 and n_3) of a corresponding **lattice translation vector**, \mathbf{R}_n , of the periodic lattice, the many (infinitely many in the infinitely large crystal) translation operations of the unit cell will precisely fill up all the space occupied by the crystal. The unit cell is obviously **not unique** as the seven alternatives in Fig.131.1 indicate. The unit cell, having the smallest volume in 3-d, smallest area in 2-d, or smallest length in 1-d crystals, is known as the **primitive cell**. The corresponding lattice translation vector is known as the **primitive lattice translation vector**. Obviously from Fig.131.1, the primitive cell is also not unique - four of the seven are primitive, having the same and smallest area of 1 square. Some of the primitive and non-primitive cells offer **higher geometrical symmetry** than others and are preferred when a mathematical analysis of the crystal properties is carried out using Fourier series expansion. For example, the primitive unit cell with the atom located at the center of the cell (Exercise: sketch this in Fig.131.1.) was selected by Wigner and Seitz in 1933 in the one of the historical-first mathematical analysis of the electronic properties of a solid, the metallic sodium. [E. Wigner and F. Seitz, "On the constitution of metallic sodium," *Physical Review* 43, 804 (1933) and 46, 509 (1934).]

The lattice translation vectors of the crystal can be mathematically represented by one, two or three **basis vectors**, \mathbf{a} , \mathbf{b} , and \mathbf{c} , in the one-, two- and three-dimensional crystals. This is

$$\mathbf{R}_n = n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c}. \quad (131.1)$$

The coefficients, n_1 , n_2 , and n_3 are positive and negative integers including zero. Examples of the the basis vectors (solid arrows) and lattice translation vectors (dash arrows) of the two-dimensional unit cells are shown in Fig.131.1.

Once the crystal structure of a solid is determined, the unit cell and basis vectors can readily be obtained by inspection of the geometry. For example, the simplest primitive basis vectors of the two-dimensional square lattice in Fig.131.1 are \mathbf{a}_x and \mathbf{a}_y and the primitive unit cell is a square. The primitive lattice translation vectors are given by $\mathbf{R}_n = n_x \mathbf{a}_x + n_y \mathbf{a}_y$.

The face center cubic (fcc) lattice is now described as a three-dimensional example. Three unit cells are shown in Fig.131.2.

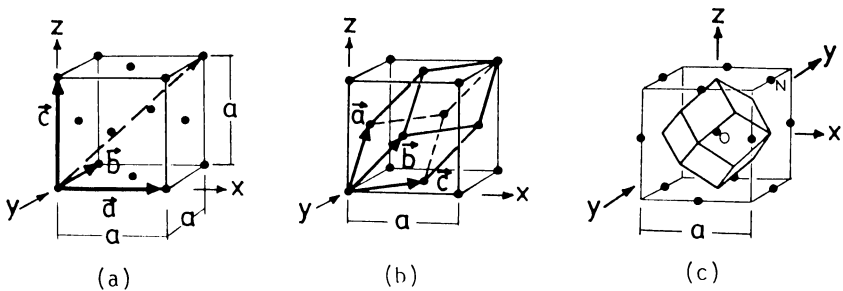


Fig.131.2 Unit cells and basis vectors of the face-centered cubic lattice. (a) The non-primitive cubic unit cell. (b) The primitive parallelepiped unit cell. (c) The primitive Wigner-Seitz unit cell.

The first is the cubic unit cell shown in Fig.131.2(a). It shows that there is one lattice point (or atom if the solid is monoatomic) at each of the eight corners of the cube and one lattice point (or atom) at center of each of the six square faces. The basis vectors of this cubic unit cell are \mathbf{a}_x , \mathbf{a}_y and \mathbf{a}_z , and the lattice translation vectors are given by $\mathbf{R}_n = n_x \mathbf{a}_x + n_y \mathbf{a}_y + n_z \mathbf{a}_z$. It is not primitive, that is, it is not the smallest volume unit cell as proved below.

The second unit cell of the fcc lattice is the non-cubic but primitive parallelepiped unit cell shown in Fig.131.2(b). The three basis vectors are labeled \mathbf{a} , \mathbf{b} , and \mathbf{c} whose cartesian (x,y,z) components can be readily written down by inspection and is left as an exercise for the students.

The third unit cell of the fcc lattice is the primitive octahedron (eight faces) cell shown in Fig.131.2(c). It has a lattice point (or atom) at the center of the unit cell. A sphere can be inscribed inside this cell. It is known as the **Wigner-Seitz** cell which was employed by Profs. Eugene Wigner and Frederic Seitz in 1933 when Seitz did his doctoral thesis at Princeton to ease the calculation of the electronic properties of solids. They discovered this unit cell geometry in order to use the spherical coordinate system and the spherical functions to compute the electronic properties of metallic sodium crystal. [See E. Wigner and F. Seitz, "On the constitution of metallic sodium," *Physical Review* 43, 804 (1933) and 46, 509 (1934).]

Miller Indices

Special sets of notations and symbols have been used by solid state physicists, chemists and material scientists to denote the **crystal directions and planes** for the three-dimensional crystals. These are known as the **Miller Indices** whose symbols and notations are listed as follows.

| | |
|-----------------|-----------------------------|
| Plane (hkl) | Equivalent planes {hkl} |
| Direction [hkl] | Equivalent directions <hkl> |

The (100), (110) and (111) planes for the cubic lattices are shown in Figs.131.3(a), (b) and (c).

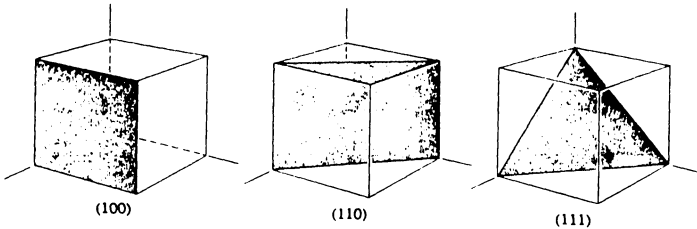


Fig.131.3 Miller indices of the three important planes in a cubic lattice. (a) The (100) plane. (b) The (110) plane. (c) The (111) plane.

The procedure to determine the Miller indices is as follows. The three Miller indices are the smallest set of integers computed from the reciprocal of the intercept of the plane with the three axes. Thus, the (100) plane has the intercepts of (1,∞,∞) whose reciprocals are (1,0,0) so that the Miller index of this plane is (100). Similarly, the cube face with x=0 in the y-z plane would have intercepts of (0,∞,∞) so that its Miller index would be (∞,0,0). The equivalent (100) planes of the faces of a cubic unit cell whose center is located at the origin of the coordinate are the (-100), (010), (0-10), (001) and the (00-1). These equivalent planes are represented by the symbol {100} and known as the set of equivalent {100} planes.

The crystal directions are denoted by [hkl]. For example, the x-axis is the [100] direction while the negative x-axis is the [-100] direction. The group of equivalent (parallel) [100] directions is denoted by <100>.

The Miller indices for directions can also be used for the two-dimensional lattices. However, the Miller indices for crystal planes are not needed in 2-d and 1-d crystals since there is only one plane in the two-dimensional lattice and no planes in the one-dimensional lattice. Using the square lattice given in Fig.131.1, the x-

axis is then the [10] direction while the y-axis is the [01] direction. A 45 degree arrow pointing at 1:30pm would be pointing in the [11] direction.

132 Three-Dimensional Crystal Structures

We shall focus on the three-dimensional solids and crystal lattices since the practical semiconductor, Si, and some of the potentially useful semiconductors (SiC, unstrained $\text{Ge}_x\text{Si}_{1-x}$, and GaAs) crystallize in three-dimensional structures. However, there have been a great deal of research activities during the 1980's on electrical conduction in two-dimensional and one-dimensional solids, for examples, the commensurately strained $\text{Ge}_x\text{Si}_{1-x}$ films, the organic semiconductors, and the high-temperature superconductors. So two- and one-dimensional crystals could find significant applications in the future. The three-dimensional analyses can be applied to the reduced dimension (1-d and 2-d) solids with considerable simplifications.

In the three-dimensional solids (3-d) there are

| | | |
|--------------------|-------|----------------------------|
| Seven | (7) | 3-d crystal systems. |
| Fourteen | (14) | Bravais or space lattices. |
| Thirty-two | (32) | crystal point groups, and |
| Two-hundred-thirty | (230) | space groups. |

The seven 3-d crystal systems are (1) triclinic, (2) monoclinic, (3) orthorhombic, (4) hexagonal, (5) rhombohedral, (6) tetragonal and (7) cubic systems. The fourteen 3-d space lattices are known as Bravais lattices and are shown in Fig.132.1. The name of each lattice is given, showing which crystal system it belongs to. For example, there is only one Bravis lattice for the triclinic, trigonal and hexagonal systems; two for the monoclinic and tetragonal systems; three for the cubic system; and four for the orthorhombic system.

The three cubic lattices in the cubic system of the seven 3-d crystal systems are of particular interest since the covalent monoatomic semiconductors, silicon and germanium, the covalent compound semiconductors, SiC and GeSi, and the partially ionic polar compound semiconductors, GaAs, GaP, InP and $\text{Ga}_x\text{Al}_y\text{As}_z$, all crystallize with cubic symmetry. The hexagonal crystal system is briefly described since some potentially useful compound semiconductors crystallize in the wurzite structure which has hexagonal symmetry. The three basic cubic lattices are

| | | |
|-------------------------|-------------------------------------|-------|
| (1) Simple Cubic | P=Primitive | (SC) |
| (2) Body-Centered Cubic | I = Innenzentrierte = body-centered | (BCC) |
| (3) Face-Centered Cubic | F=Face-centered | (FCC) |

where the abbreviated one-letter and multi-letter acronyms are also given. The German notation came from a 1848 study by the German crystallographer and

scientist Adolph Bravais and a 1891-1923 systematic analysis by the German scientist Arnold Schoenflies. A more recent and popular notation is the symbols used in the International Table published in 1935. A comprehensive list was given by the late John C. Slater (former Institute Professor at M.I.T. and Graduate Research Professor at the University of Florida) in a two-volume textbook on solid state theory. The crystal structures of the elemental and compound semiconductors are described in the following paragraphs.

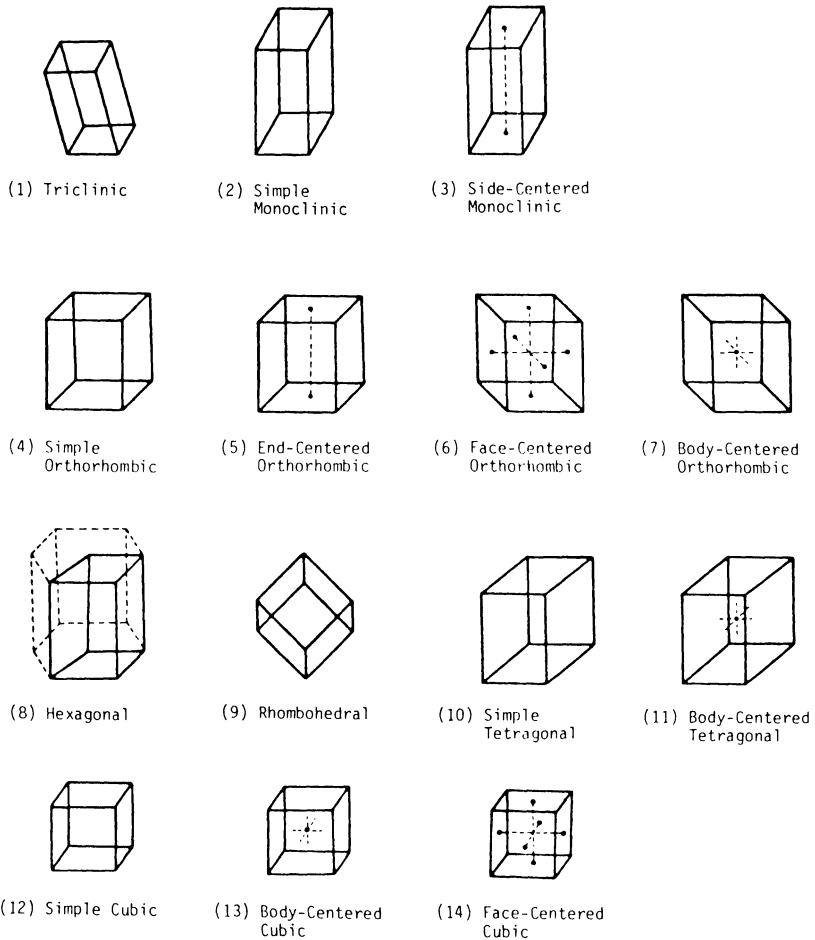


Fig.132.1 The fourteen three-dimensional Bravis space lattices.

Diamond Structure (Cubic System)

Elemental Semiconductors: C(diamond), Si, Ge, Sn

The space lattice of diamond is face-centered cubic. Its cubic unit cell is shown in Fig.132.2(a). It is composed of two fcc lattices displaced from each other by one quarter of a body diagonal, $(1/4,1/4,1/4)a$. This is illustrated in Fig.132.2(b).

The diamond structure has tetrahedral point symmetry (which is one of the five crystal point groups in the cubic crystal system). The tetrahedral symmetry property is also possessed by the other two common crystal structures of semiconductors to be described, the zinc-blende (GaAs) and wurzite (ZnO, ZnS) structures.

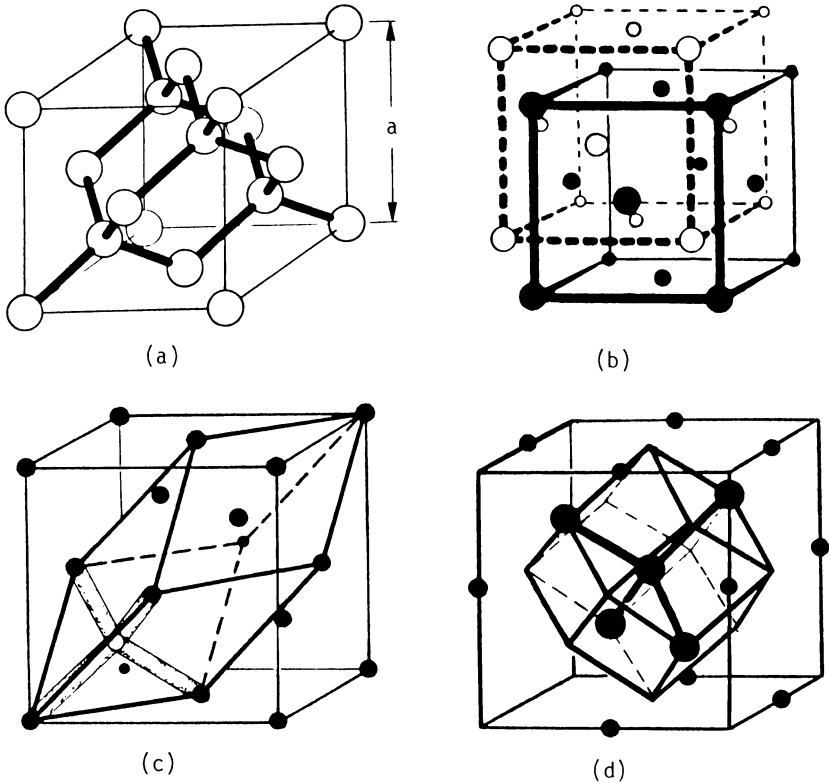


Fig.132.2 The cells of the diamond structure for C, Ge and Si. (a) The cubic unit cell. (b) Two interpenetrating face-centered cubic lattices. (c) The parallelepiped primitive unit cell. (d) The Wigner-Seitz primitive unit cell.

The tetrahedral symmetry is illustrated by the small 1/8 size cube inscribed in the cubic unit cell shown in Fig.132.2(a). For the central atom in this 1/8-size cube, there are four atoms located at the four tetrahedral positions relative to the center atom. The four atoms sit at the two opposite corners of the 1/8-size cube.

One particularly important general property of the cubic crystals is that its properties are **isotropic**, i.e., its reaction or response to an applied force is independent of the direction of the force, unless the force is so large that the cubic symmetry is destroyed by the displacement of the steady-state positions of the atoms. In contrast, the **anisotropic** symmetry of the wurzite structure gives very useful electrical and optical properties which are dependent on the direction of the force (mechanical or electrical) and are used to modulate light and to generate electric signals at very precise frequency (quartz oscillator used in electronic wrist watch).

Three examples of unit cells of the diamond crystal structure are shown in Figs.132.2(a), (c) and (d). The cubic unit cell of Fig.132.2(a) contains eight atoms and is not primitive. The parallelepiped unit cell in Fig.132.2(c) and the Wigner-Seitz unit cell in Fig.132.2(d) are primitive and contains two atoms per cell. These three unit cells are identical to those of the face-center cubic lattice shown in Fig.131.2 except that there are twice as many atoms per cell in the diamond structure because there are two interpenetrating fcc lattices in the diamond structure.

Zinc Blende Structure (Cubic System)

Compound Semiconductors

(SiC, SiGe, GaAs, GaP, InP, InAs, InSb, etc.)

Zinc blende crystal structure has the same geometry as the diamond crystal structure except that zinc blende crystals are binary or contains two different kinds of host atoms, such as Ga and As in GaAs. III-V compound semiconductors, such as GaAs, consist of a space array of Ga (or group-III) atoms on one fcc lattice and another space array of As (or group-V) atoms on the other fcc lattice of the diamond structure. This is shown in Fig.132.3(b). Note again the tetrahedral symmetry shown by the 1/8-size cube in the cubic unit cell of Fig.132.3(a). The distinction from diamond is that the four atoms tetrahedrally located with respect to the central atom in zinc blende are different. They may be Ga or group-III atoms while the central atoms would then be As or a group-V atom. Or the four corner atoms may be Si while the central atom is Ge in SiGe and C in SiC.

Wurzite Structure (Hexagonal System Hexagonal Close-Packed Structure)

Compound Semiconductors

(ZnO, GaN, AlN, ZnS, ZnTe,* CdS,* CdTe,* etc.)

(* These also crystallize in the zinc blende structure.)

The adjacent tetrahedrons in zinc blende structure are rotated 60° to give the wurzite structure. This distortion changes the symmetry from cubic to hexagonal and makes the crystal properties **anisotropic**, that is their properties are dependent on the direction of the applied force. The distortion also increases the periodic potential seen by the electrons, making the electron energy gap larger. (Energy gap is discussed later in this chapter.) Figure 132.4(a) shows a larger and nonprimitive hexagonal unit cell while Fig.132.4(b) shows a smaller and primitive unit cell. The white and black balls in Fig.132.4(a) represent the two types of host atoms such as Zn and S in ZnS. There has been a renewed research interest recently to grow and characterize several II-VI semiconductors because their larger energy gap offers the potential for solid state diode lasers, optical transistors and photonic devices operating in the deep blue or ultra-violet optical range with wavelength around and below 4000\AA or $0.4\mu\text{m}$. The anisotropy also gives large nonlinear optical properties useful in light modulation applications.

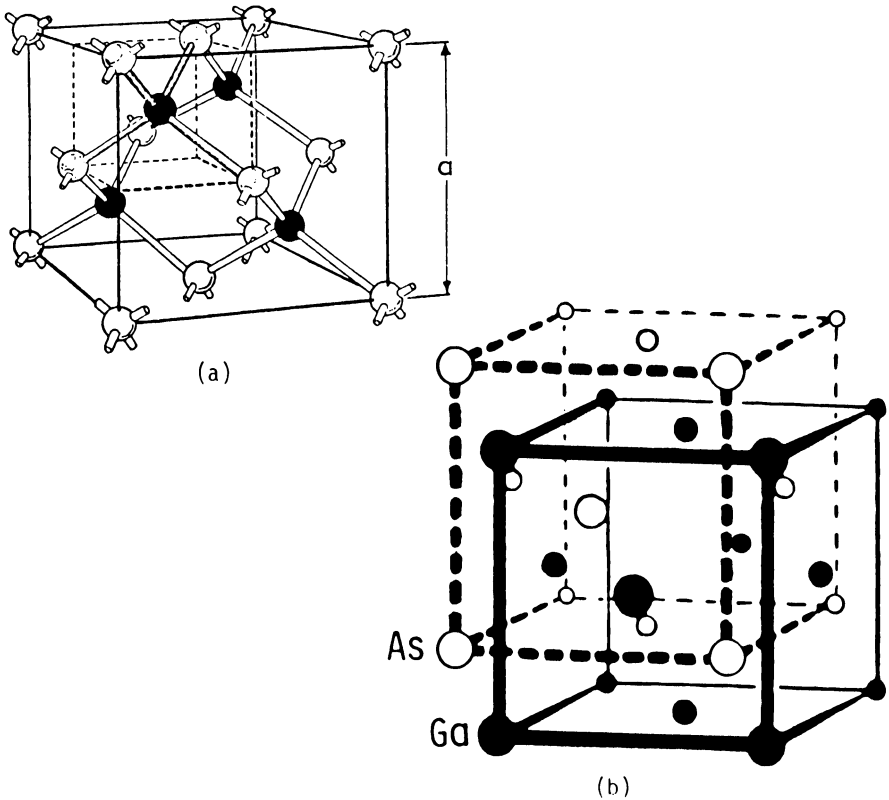


Fig.132.3 The cells of the zinc blende structure. The solid balls are Ga and the circles are As or vice versa. (a) The cubic unit cell. (b) Two interpenetrating face-centered cubic lattices.

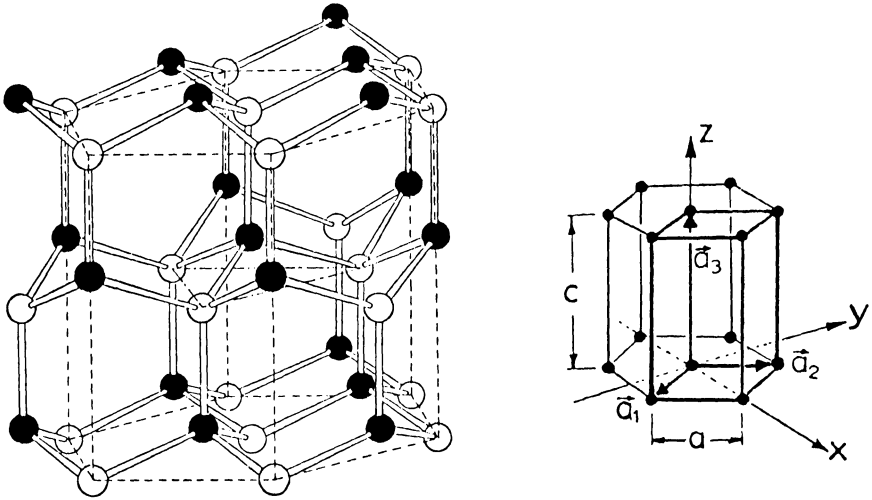


Fig.132.4 The cells of the wurzite structure.

133 Calculation of the Atomic Density

We now work out some examples on how to use the knowledge of crystal structures to compute some useful and important properties such as the number of atoms per unit cell and the atomic density or atoms per unit volume. For example, we will show that there are 8 silicon atoms per cubic unit cell. We shall first work out a simpler example, the two-dimensional square lattice shown in Fig.133.1. The small circle, o, is one atom. The circle with a dot is one enlarged atom which is used to illustrate that the composition of the atomic core also enters into the construction of a unit cell.

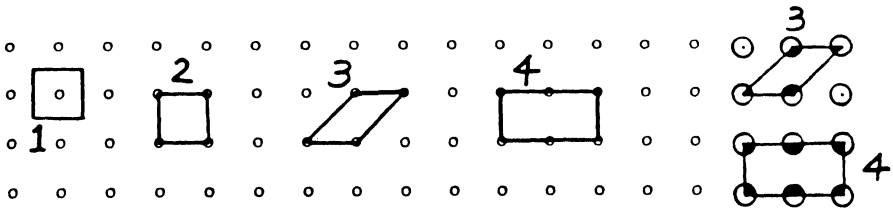


Fig.133.1 A two-dimensional square lattice used to illustrate the calculation of the atomic density of a crystal from a given atomic arrangement or lattice structure and type of host atom.

The following table illustrates the atomic density calculated using four different unit cells. As expected, they all give the same result: the atomic density is

$1/a^2$ where a is the lattice spacing, known as the lattice constant. It is the side of the primitive square unit cell labeled 1.

TABLE 133.1
CALCULATIONS OF THE ATOMIC DENSITY OF A SQUARE LATTICE

| <u>Unit Cell Type</u> | <u>Cell Area</u> | <u>Number of Atoms per Cell</u> | <u>Atomic Density</u> |
|-----------------------|------------------|--|-----------------------|
| 1 | a^2 | 1 | $1/a^2$ |
| 2 | a^2 | 1 = $4 \times (1/4)$ since each corner atom is shared by four adjacent square unit cells. | $1/a^2$ |
| 3 | a^2 | 1 by adding shaded areas | $1/a^2$ |
| 4 | $2a^2$ | $2 = 4 \times (1/4) + 2 \times (1/2)$ | $1/a^2 = 2/2a^2$ |

For the diamond lattice such as silicon, refer to the cubic unit cell shown in Fig.132.2(a). The following table illustrates the calculation steps. It gives 8 silicon atoms per cubic unit cell: $8 \times (1/8) + 6 \times (1/2) + 4 = 8$.

TABLE 133.2
Calculation of the Atomic Density of Silicon Crystal
 [Diamond Lattice, Cubic Unit Cell, Fig.132.2(a).]

| <u>Unit Cell Type</u> | <u>Cell Volume</u> | <u>Number of Atoms per Cell Calculation</u> |
|-----------------------|--------------------|--|
| Cubic | a^3 | 8 corner atoms each shared by 8 cells. 6 face-centered atoms each shared by two cells. 4 atoms inside the cubic unit cell. |

134 Growing Single Crystals

In the introduction, the reasons for needing a single crystal or crystalline semiconductor to fabricate transistors and integrated circuits were described. The growth of single crystal is briefly described in this section. Crystals are grown from a liquid or a gas of atoms. There are two essential ingredients to grow a single crystal: an oriented single crystal seed, and a growth condition (temperature gradient, stirring rate and growth rate) to give high mobility (or high velocity) to the atoms so that the atoms have enough time to find and be trapped at a lattice site on the surface of the solid seed before being immobilized by the decreasing solid temperature. The key to optimize the growth condition is to have few physical defects introduced and to have only predetermined and controlled amounts of doping impurity atom incorporated into the crystal to give a predetermined impurity concentration profile (impurity density versus position). The starting silicon can be

first purified by chemical means. For example, the elemental and highly pure silicon can be obtained from chemical vapor deposition (CVD) of silicon tetrachloride (SiCl_4), trichlorosilane (SiHCl_3), or silane (SiH_4) onto a clean substrate or mandril. The resulting Si rods or chunks are polycrystalline. The silicon rod can be further purified by the zone refining method and simultaneously grown into a single crystal. The chunks can also be grown into a single crystal using a horizontal-boat zone refiner or a vertical crystal puller by withdrawing a crystalline seed from a molten Si in a heated crucible (the Czochralski method). We shall briefly describe these two methods.

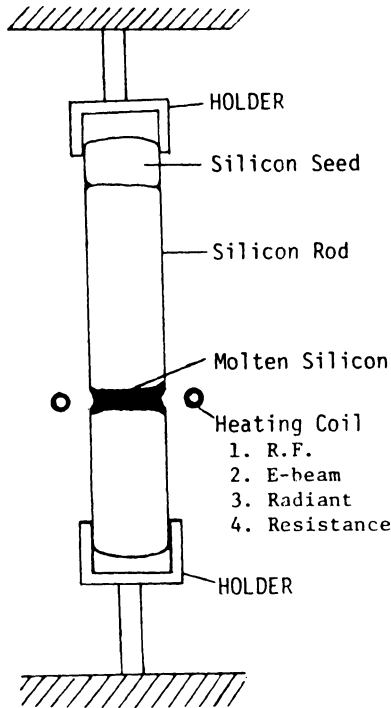


Fig.134.1 A schematic diagram of a vertical zone refining (float zone) apparatus for solid purification and crystal growth known as zone refiner.

The purification of a silicon rod or a boat of silicon chunks by the zone refining method is described first which can also give a single crystal if a crystal seed is placed at one end of the rod. A vertical Si zone refiner is sketched in Fig.134.1, known as the **float zone** refiner or grower. The whole apparatus is enclosed in a clean enclosure (not shown) and cooled by a water sleeve and/or air (not shown) to keep the interior wall and surface temperature low so that impurities will not outgas from the interior walls and surfaces. The ambient is an ultra pure inert gas, such as helium or argon from a liquid He or Ar tank, to prevent impurity

contamination. The purity requirement is so high (as we shall see the reason in chapter 2) that the grade of gases and chemicals used in the manufacturing of the Si transistors and integrated circuits is known as the MOS grade. The MOS grade is purer than the transistor grade, the electronic grade, and a million times purer than the reagent grade use in freshman chemistry laboratory. A crystalline seed is situated at the top (or the bottom) of the polycrystalline Si rod to give a single crystal. Without a seed, the Si rod would still be purified but would still be highly polycrystalline as the original poly Si rod. A thin disk-shaped molten zone of Si, shown in the figure, is created by one of the four heating methods: (1) radio frequency (r.f. at either 450kHz or 1.6MHz), (2) focused electron gun bombardment, (3) radiant focused IR light, or (4) resistance coil. The heating coil moves down, then up, and repeats many times in order to move the molten zone (disk) up and down the rod. One transit of the molten zone over the length of the rod is known as one pass.

This purification and crystal growth process is described as normal freezing or unidirectional solidification. Two key process mechanisms are involved in the first pass of the heating coil traveling down to the bottom from the top of the rod. (1) The polycrystalline rod is crystallized into one single crystal because when the molten zone moves downwards from the Si seed at the top, silicon atoms in the liquid are deposited onto the lattice sites of the cooler (below melting point of Si) Si seed above the molten zone, thereby increasing the length of the single crystal seed and crystallizing the entire poly Si rod into one single crystal rod when the molten zone reaches the bottom holder. (2) The impurities present in the original poly Si rod are swept out into the lower end because the impurities like the liquid better than the solid, namely, they have a higher solubility or are more soluble in the liquid than in the solid.

As the first mathematical example of this textbook, the impurity distribution in a semiconductor rod after one-pass of the molten-zone will be calculated. The analysis uses the coordinate system and symbols shown in Fig.134.2.

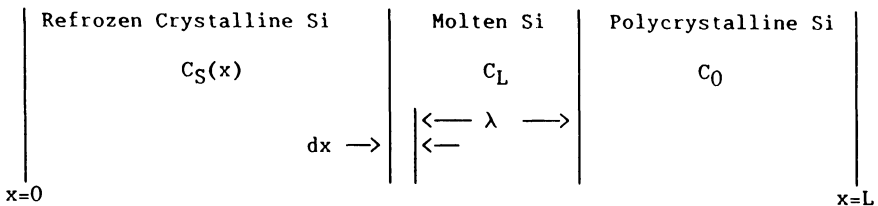


Fig.134.2 Schematic illustrating the calculation of the impurity distribution in a silicon rod after the molten-zone has passed through the rod once.

The following assumptions are made in order to obtain a simplified solution: (1) the thickness of the molten zone, λ , is a constant when it moves from the top end of the Si rod, $x=0$, to bottom end, $x=L$; (2) the cross-sectional areas of the

rod and the molten zone are equal, constant and given by A ; (3) the impurity concentration in the molten zone is spatially constant although it changes with time as the molten zone moves along the rod. Figure 134.1 shows the more realistic geometry of the molten zone.

The total number of impurity atoms in the molten zone of length λ is then $A\lambda C_L$ where C_L is impurity atomic concentration in the molten zone or liquid denoted by the subscript L. C_L is assumed to be spatially constant in the molten zone as stated in (3) above. Then, the change of the impurity atom number in the molten zone comes from two sources: it increases when some polysilicon is melted from the right and it decreases when some molten silicon solidifies onto the refrozen silicon on the left. Thus, material balance or conservation gives us

$$A\lambda dC_L = AC_0 dx - AC_S dx$$

where C_0 is the initial impurity atomic density in the polysilicon rod and is also assumed to be constant. $C_S = C_S(x)$ is the final impurity atomic density in the refrozen or resolidified part of the silicon rod.

C_S and C_L are proportional. The proportionality constant is known as the **impurity segregation coefficient** which measures the amount of segregation of an impurity species between a liquid and a solid solvent in this example. Generally, the impurity segregation coefficient measures the impurity concentration ratio at the interface between two solid solvents, two immiscible liquid solvents, a liquid and gas solvent, a liquid and solid solvent, or a gas and solid solvent. It is defined by

$$k = C_S(x)/C_L(x).$$

If the molten zone moves very slowly, (as compared with the product of the diffusion rate of the impurity atoms in the Si liquid and the attachment rate of the liquid Si atoms to the solidified Si lattice), then k approaches its thermal equilibrium value so it becomes an **equilibrium constant** sometime known as the **distribution coefficient**. Consequently, in the thermal equilibrium limit, it is a fundamental constant of the silicon material and the impurity in question. If the zone moves very fast or if the Si rod on one side of the molten zone rotates rather fast relative to the Si rod on the other side, k is no longer a constant and the mathematics becomes more complex. Rotation is used in crystal growth to produce a more uniform concentration of the impurity in the liquid hence more uniform concentration across the cross-sectional area of the crystal rod. In the float zone method described here, the zone is sufficiently thin so that rotation is not needed to homogenize the impurity in the liquid. In crystal growth by pulling a seed from a crucible of molten Si, to be described as a second example, rotation of the seed is essential to give better uniformity of impurity concentration.

A constant segregation coefficient is assumed in this analysis to simplify mathematics and focus on the basic phenomena. It can then be substituted into the

material balance equation above to eliminate one of the two variables, C_S and C_L . This gives

$$(\lambda/k)dC_S/dx = C_0 - C_S.$$

This simple first order differential equation can be integrated from $x=0$ to x , using the initial distribution: $C_S(0)=kC_L(0)=kC_0$. The result is

$$C_S(x) = C_0[1 - (1-k)\exp(-kx/\lambda)]. \quad (\text{Region I})$$

This solution is no longer valid in a layer of thickness λ at the end of the rod, labeled region II in Fig.134.3, since there is no solid Si on the far surface of the molten zone. The correct solution in region II is

$$C_S(y) = kC_0[1 - (y/\lambda)]^{k-1}. \quad (\text{Region II})$$

The solutions are graphed in Fig.134.3 for $k=0.1$, showing considerable variation of the impurity concentration over the length of the crystal. A nearly constant impurity concentration can be obtained by adding a minute concentration of the desired impurity to the inert ambient gas. The gaseous impurity atoms would rapidly saturate the molten Si zone. However, this gas phase impurity doping technique is controllable only down to about 0.1 atomic percent (one part per thousand) and hence cannot give the low impurity concentrations (one part per million or less) needed to build Si transistors.

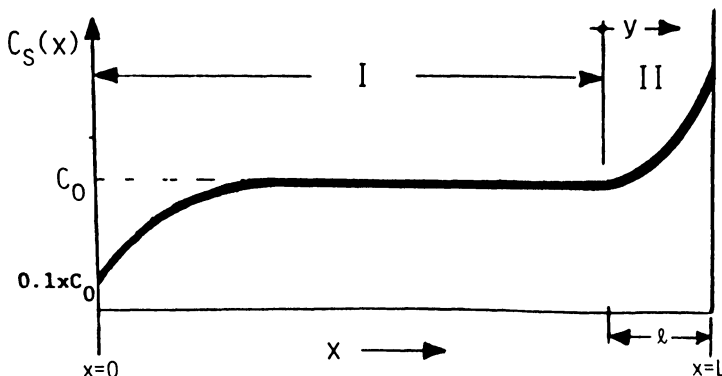


Fig.134.3 The variation of the impurity concentration in a Si rod after one float zone pass.

The second and one of the most common Si crystal growth methods is to pull a single crystalline seed slowly from an impurity-doped molten Si in a carbon crucible lined with a high purity silica (fused quartz). This is known as the

Czochralski technique and the apparatus is known as the crystal puller. A schematic diagram is shown in Fig.134.4. The parts are labeled and self-explanatory and will be briefly explained.

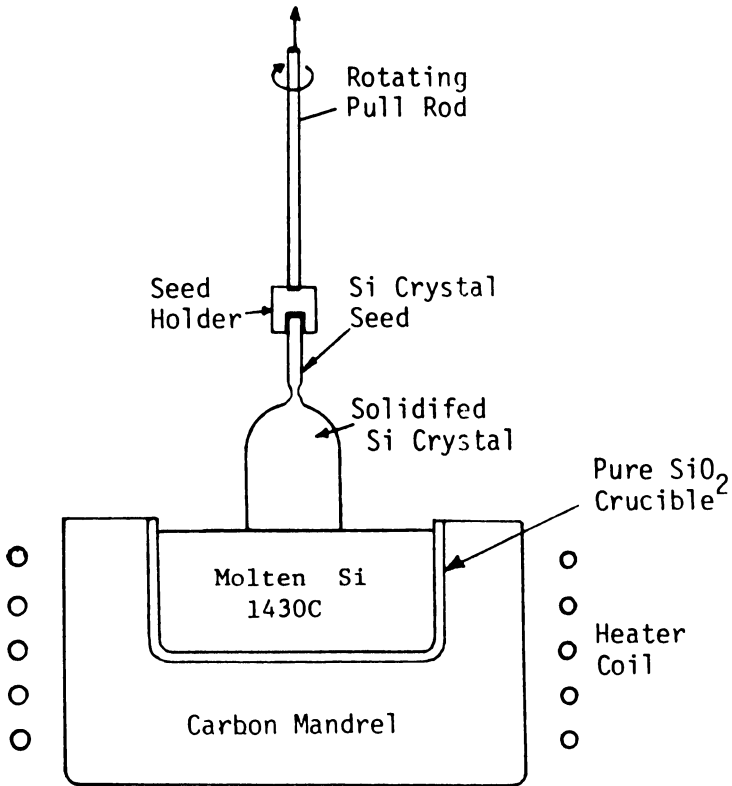


Fig.134.4 A Czochralski crystal puller for growing single crystals.

The entire crystal puller of Fig.134.4 is enclosed by a envelope container made of highly pure fused quartz in order to control the chemical composition of the gaseous ambient and prevent contamination from the laboratory ambient. A

high purity inert gas (He or Ar) is used inside of the envelope to surround the hot puller. High vacuum has been used to reduce oxygen contamination from the fused-quartz crucible (described later). In either case, the heated parts of the puller must have very low vapor pressure at high temperatures to prevent impurity evaporation from the hot surfaces which would contaminate the silicon crystal. To meet this purity requirement is quite an engineering feat due to the very high melting point of silicon, 1430°C.

A highly pure silicon crystal seed is rigidly attached to a pull-rod shown in Fig.134.4. The pull rod may be rotational or stationary depending on whether it is necessary to stir the melt in order to homogenize the impurity in the melt. The pulling and rotational motion of the pull rod is controlled by a servomechanism.

The molten silicon is contained in a mandrel made of highly pure carbon and lined with a highly pure fused quartz SiO_2 liner, usually in the shape of a cup. The carbon mandrel is then heated by a radio frequency or resistance power source via the heater coil shown in Fig.134.4. It is evident that the molten silicon is in contact with the SiO_2 crucible. Thus, a substantial amount of oxygen from the crucible is dissolved in the molten silicon via the reaction $\text{SiO}_2 + \text{Si}(\text{liquid}) \rightarrow \text{SiO} + \text{Si} + \text{O} \rightarrow 2\text{Si} + 2\text{O}$. Some of the reaction product (silicon mono-oxide SiO) will evaporate and deposit onto the cooler interior surfaces of the puller and the quartz envelope. The concentration of oxygen in the solid silicon is essentially equal to the solid solubility limit at the melting point of silicon, about 5×10^{18} oxygen/cm³. If oxygen is uniformly dispersed in the single crystal silicon, even such a high concentration will not affect the characteristics of transistors and integrated circuits since oxygen is not electrically active, that is, it does not trap electrons and holes. However, high concentrations of oxygen atoms will form SiO_2 particles and clusters around defects or nucleation centers if the crystalline silicon is heated to a high temperature (less than 1420°C) for a prolonged time, such as during transistor fabrication. During this heating, SiO_2 clusters are formed since at temperatures less than the melting point, the oxygen solubility in Si is lower than the maximum solubility at the melting point. Thus, the excess oxygen in the Si must precipitate out onto nucleation sites. Heating to a high temperature during oxidation or impurity diffusion will increase the mobility or diffusivity of the oxygen atoms and speed up their migration towards the nucleation sites.

The SiO_2 clusters are insulating regions which increase the local electrical field if they are situated in the high electric field regions of a Si p/n junction. This high electric field will cause high current to flow which degrades the electrical performance of transistors. The high current in the high electric field region can also charge and generate electron and hole traps. Electrical performance will degrade as traps are charged up or generated, causing transistors to age and integrated circuits to fail. Special heating cycles have been invented and incorporated into the oxidation and diffusion cycles of integrated circuit manufacturing processes. These heating cycles will deplete the oxygen in a thin

surface layer (about 10-micrometers and known as **denuded layer**) of the Si crystal wafer. The heating cycle will also cause oxygen to cluster and SiO₂ particles to form in the interior or bulk region of the Si wafer. The SiO₂ clusters are preferential sinks for metallic impurities which are detrimental to electron-hole lifetimes. Such a process has been widely employed to getter metallic impurities that are present or inadvertently introduced into the silicon wafers during transistor fabrication. Alternatively, oxygen can be avoided using the float-zone crystal grower since the molten zone is not in contact with an infinite source of oxygen (from the SiO₂ crucible liner in the Czochralski puller). Thus, any oxygen contamination will be swept to the end of the rod or evaporated from the molten zone and deposited onto the cooled wall during the float zone passes.

The basic principle of growth and impurity doping profile control of the Czochralski crystal pulling method are identical to those of the float zone technique. To start a crystal growth, the tip of the crystal seed is dipped into the molten Si and then withdrawn slowly by a servomechanism controlled stepping motor. The heater is also controlled to keep the molten Si at a constant temperature. The Si and impurity atoms in the molten Si are trapped onto the atomic sites at the Si-liquid/Si-solid interface of the seed.

The concentration of the impurity atoms on the solid Si surface is determined by the impurity segregation coefficient between the Si liquid and Si solid phases, $k = C_S(x,t)/C_L(x,t)$. The solid/liquid interface at $x=0$, and t is the time from the start of growth. The impurity concentration profile along the length of the crystal, $C_S(x)$ vs x , can be computed from the method just described for the float zone process whose results are shown in Fig.134.3. In the Czochralski or pulling method, as the seed is withdrawn from the melt (liquid), the volume of the melt decreases. Since k is usually less than 1 because impurities are more soluble in liquid than solid, the impurity concentration in the Si melt increases with time due to the decreasing volume of the Si melt. Thus, the impurity concentration in the Si solid will increase greatly with distance away from the seed end. However, it is immediately obvious that a constant impurity concentration in the Si melt and thereby also in the Si solid can be maintained to give a Si crystal rod with nearly constant impurity concentration over the entire length of the rod if pure Si chunks are continually added to the Si melt in the crucible.

There are several precautions: (1) mechanical disturbances of the molten Si due to adding Si to the melt must be minimized or eliminated, and (2) sufficient time must be allowed for the impurity in the melt to homogenize by diffusion when additional pure Si chunks are added. The chemical cleanliness and mechanical controls required to add Si chunks into a crucible of molten Si at 1420°C are not trivial. These factors have been successfully controlled to give production quantities of Si single crystals (8-inch diameter, several feet long) which are almost physically perfect and have nearly constant dopant impurity concentration. They have been used in megabit DRAMs (1, 4, 16Mb) manufacturing by IBM since 1988.