Defects

19

19.1 Introduction

An ideal crystalline solid has a periodic structure that is based on the chemical properties of its constituent atoms (see Chap. 3). However, real crystals are not perfect. They always have imperfections such as extra/missing atoms or impurities, which are called defects.

The periodicity characterizes the crystals as we learned in previous chapters. For example, the periodic potential of the lattice modulates the wavefunction, and we can establish relationships between the energy and wavevector using the Bloch theorem as shown by the Kronig-Penney model (Chap. 5). The existence of defects perturbs the potential of the lattice, and this modifies the band diagram in the crystals.

While many properties of crystalline systems depend upon the periodic lattice arrangement, many additional properties can be manipulated by adding defects or dopants to the crystal. These properties enable us to fabricate various devices in the modern world of semiconductor technology. On the other hand, unintentionally introduced defects can also have a profound impact on the properties of materials or on the performance of these devices. Therefore, it is a challenging goal to have precise control of defects in crystals.

The defects can determine the color of the crystal and its electric conductivity, and they can also introduce modifications in the lattice vibrations. For example, silicon becomes *p*-type with boron doping. Al_2O_3 has red color as a ruby when a small amount of Cr^{3+} substitutes Al^{3+}, but Al_2O_3 has blue color as a sapphire when a small amount of Ti^{3+} is substituted for Al^{3+}.

In this chapter, we will discuss how defects are introduced in crystals and the possible reasons or sources of such imperfections, which may be roughly summarized as follows:

M. Razeghi, *Fundamentals of Solid State Engineering*,
https://doi.org/10.1007/978-3-319-75708-7_19

(i) *Defects from fundamental physical laws*
There are defects that must exist due to fundamental physical laws. One example is a vacancy. At any finite temperature, the atoms undergo a degree of vibrational displacements. As the temperature is raised, the displacements may become so large that atoms are permanently moved from their normal sites. These atoms leave their sites and vacancies are formed.

(ii) *Defects from natural minerals*
Materials are never 100% pure. Therefore, all crystals have certain foreign atoms; impurities as defects. Silicon wafers used in modern semiconductor technology are purified to a very high degree (better than 99.999999%).

(iii) *Defects from crystal growth* (see Chap. 17 for details)
Intrinsic defects can be introduced during crystal growth. For example, typical concentrations of intrinsic defects in Si are on the order of 10^{13}–10^{14} cm^{-3}. Extrinsic defects (impurities) can also be introduced in the crystallization process. The species of the impurities depends on the growth method and on the constituent materials of the growth system.

(iv) *Defects from strain*
Deformation of metals or any strain added to crystals generates defects (mainly dislocations). Especially in semiconductor technology, the defects caused by strain are of great interest for heteroepitaxial thin film growth. For example, semiconductor lasers and integrated-optics devices are usually designed from multilayer structures which have similar lattice constant because the mismatch of lattice parameters accumulates strain and results in the creation of undesirable defects. The defects caused by lattice mismatch are efficient non-radiative recombination channels and therefore should be avoided since they degrade the performance of optical devices. However, the recent increasing demand for wide bandgap materials such as GaN has confronted the growers with exactly this difficulty. Since GaN has no readily available native lattice matched substrate, and the lattice mismatch depends on the substrate, these materials cannot be obtained without lattice mismatch. In addition, there also exist devices which positively make use of the effect of strain, such as high-electron-mobility transistors (HEMT) and self-organized strain-relaxed islands (quantum dots) made in the Stranski-Krastanov growth mode (Chap. 17). For these applications, the defects caused by strain constitute the active layer.

There are several categorizations of defects. One of the common classifications is based on the dimension of the defect structure. Defects may be classified into four groups: point defects (0D), line defects (1D), planar defects (2D), and volume defects (3D). Table 19.1 displays examples of these four types of defects.

Table 19.1 Table of dislocation dimension classifications

Dimension	Examples
0D: Point defects	Vacancies, self-interstitials, impurities
1D: Line defects	Edge dislocations, screw dislocations, mixed dislocations
2D: Planar defects	Stacking faults, grain boundaries, twin boundaries, interphase boundaries, external surfaces
3D: Volume defects	Precipitates, voids

19.2 Point Defects

Point defects, or 0-dimensional defects, refer to missing, additional, or misplaced atoms within the crystalline lattice. Figure 19.1 shows examples of substitutional, interstitial, and vacancy point defects, each of which will be discussed in more detail in the following sections.

19.2.1 Intrinsic Point Defects

The presence of intrinsic point defects is related to the nature of the atom. Atoms in a solid are subject to thermal vibrations at any temperature. The average amplitude of the atomic displacements increases with increasing temperature. Therefore, it is easy to imagine a localized area within the crystal where the vibrations are intense enough to cause a single atom to jump to a different location, either to the surface of the crystal or to an intermediate or interstitial position within the crystal. If the atom moves to the surface of the crystal, a Schottky defect is said to have formed, leaving a vacancy as the defect. However, if the atom jumps to an interstitial position within the crystal lattice, it is said to have formed a Frenkel defect, creating both a vacancy and a self-interstitial. A vacancy is a missing atom within the crystal lattice. A self-interstitial is an atom of the same type as the bulk material that is located at a non-lattice site. A Schottky defect is shown schematically in Fig. 19.2a, while a Frenkel defect is shown schematically in Fig. 19.2b.

It has been shown experimentally that at thermal equilibrium, all crystals contain intrinsic point defects. This leads to the conclusion that the imperfect crystal has a lower free energy than a perfect crystal. From thermodynamics, we know that the change in the free energy of a system, ΔG, is related to the changes in enthalpy, ΔH, and entropy, ΔS, as shown in Eq. (19.1), where T is absolute temperature:

$$\Delta G = \Delta H - T\Delta S \tag{19.1}$$

The energy to form a defect, E_D, is a positive contribution to the enthalpy term, thus *increasing* the free energy of the system. However, the creation of the defect increases

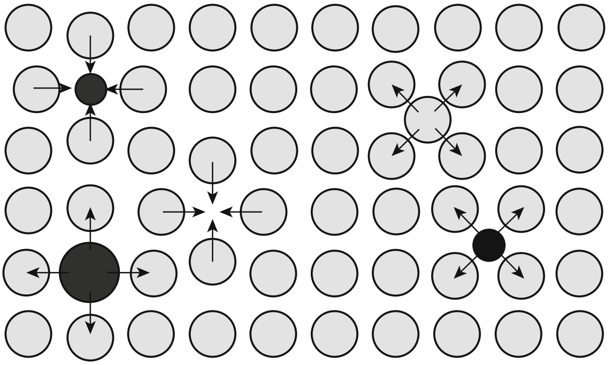


Fig. 19.1 Examples of point defects

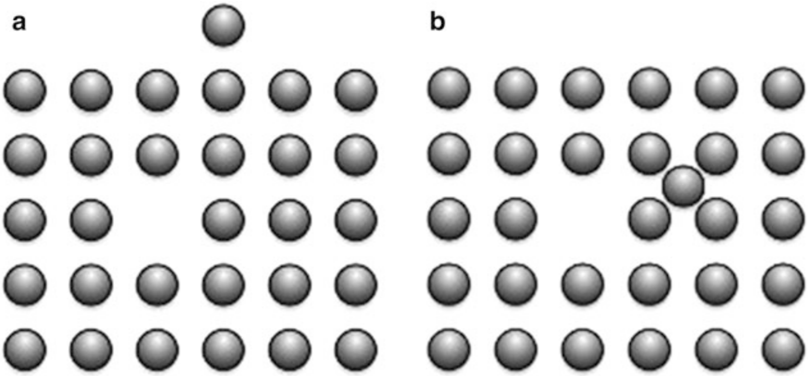


Fig. 19.2 Schematic diagrams of a: (**a**) Schottky defect and (**b**) Frenkel defect

the disorder of the crystal, thus increasing the entropy of the system and causing a *decrease* in the free energy of the system. The balance of these two factors leads to an equilibrium number of defects naturally occurring within the crystalline lattice. Through calculating the minimum free energy condition as a function of temperature, Boltzmann determined that the equilibrium number of defects, n_e, can be written according to Eq. (19.2), where N is the number of atoms in the crystal, A is a constant often taken as unity, T is the absolute temperature, and k_b is the Boltzmann constant. By dividing n_e by N, the equilibrium concentration of defects, n_e, may be found.

$$n_e = NA\exp\left(\frac{-E_D}{k_bT}\right) \tag{19.2}$$

One key process that affects both semiconductor device performance and some fabrication techniques is chemical diffusion. Chemical diffusion occurs when atoms of the same type or a different type are able to move through the crystalline lattice over time. The presence of vacancies in a solid enhances the rate at which chemical

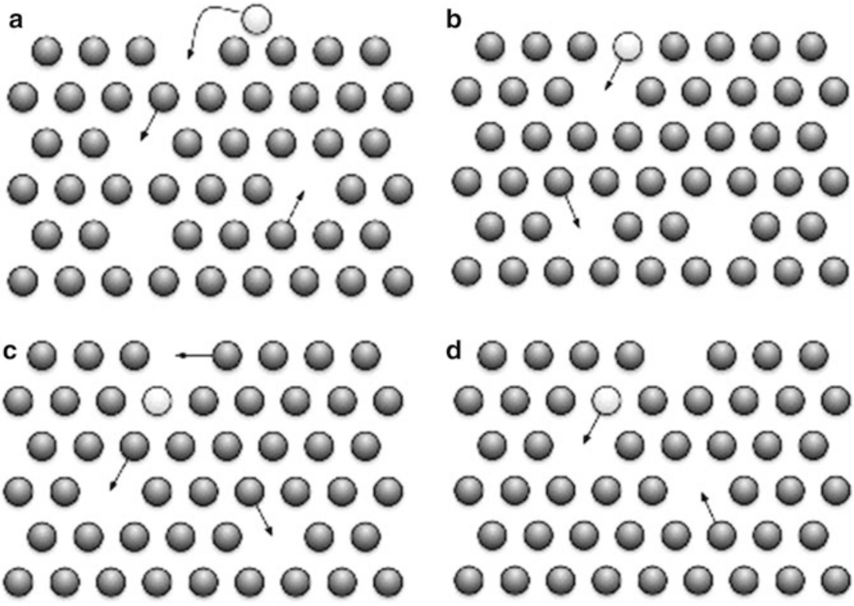


Fig. 19.3 Schematic of chemical diffusion showing how a foreign atom may diffuse into a crystal with time assisted by the presence of voids (increasing time from (**a**) to (**d**))

diffusion takes place. It is easy to imagine, for example, oxygen atoms diffusing from the surface of silicon into the silicon crystalline lattice through vacancies, as shown in Fig. 19.3.

Furthermore, it is also expected that at higher temperatures, when there are more vacancies in the network, the diffusion through the vacancy sites of the lattice takes place at a higher rate. The oxygen atom reaches a deeper site within the crystal more rapidly.

Another type of intrinsic point defect is an anti-site defect, shown in Fig. 19.3. An anti-site defect can occur when the crystalline lattice contains at least two kinds of atoms. Given enough energy, it is possible for two atoms to trade positions in the lattice. This is another diffusion mechanism, termed rotation about a midpoint.

19.2.2 Extrinsic Point Defects

Extrinsic point defects, shown schematically in Fig. 19.4, are caused by an outside source, such as growth conditions or processing factors. They are created when a foreign atom embeds itself within the crystal. If the atom is located on a lattice site, i.e., replacing the native atom, then it is called a substitutional impurity. The foreign atom may also be located at an interstitial site and is thus termed an interstitial impurity.

It is virtually impossible to control all environmental factors in order to have a 100% pure material, although for some applications this is highly desirable. The type

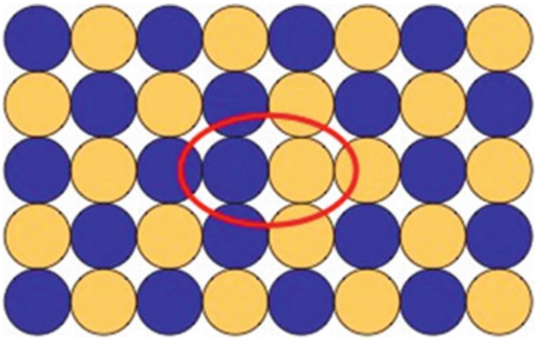


Fig. 19.4 Schematic diagram of an anti-site defect

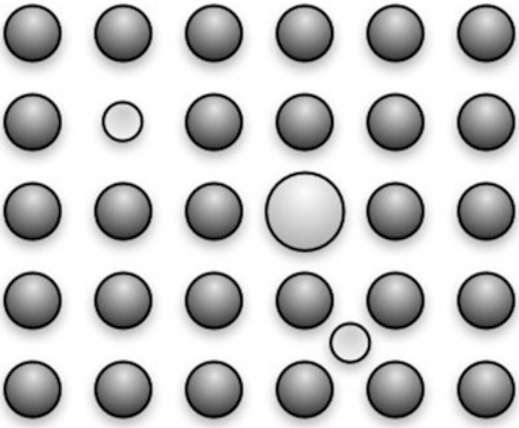


Fig. 19.5 Diagram of extrinsic point defects of substitutional impurities and an interstitial impurity

of the impurity depends on each growth method and the materials used in the system. For example, one of the major contaminations in MOCVD growth is carbon from group III sources. With respect to silicon technology, from the many possible impurities, it is the incorporation of metallic impurities that must be reduced to extremely low levels. This is because most metals have low solubility in silicon, and this results in metal silicides forming near the surface during device processing. Furthermore, many metals form deep traps in the energy bandgap of semiconductor materials, and this shortens the minority carrier lifetime considerably (Fig. 19.5).

There are also cases where impurities are desirable. In those cases, the challenge is the control of the type of impurity to be incorporated at well- defined lattice sites or specific regions within the crystal with precise concentration.

The most important application of extrinsic defects, especially with respect to semiconductors, is doping. While in many cases it is undesirable to have foreign atoms located within a crystal, doping purposely creates substitutional impurities in order to give the crystal certain properties. For example, GaN is doped with magnesium ions in order to create *p*-type GaN. Without achieving controlled doping, semiconductor devices would not exist. For more detailed information on doping, see Chap. 9.

Table 19.2 Impurity ionization energy (in meV) for several semiconductors (Wolfe et al. 1989)

Si		Ge		GaAs		GaP	
Li^{+}	32.81	Li^{+}	9.89	Si^{+}	5.854	Si^{+}	82.1
P^{+}	45.31	P^{+}	12.76	Ge^{+}	5.908	Ge^{+}	201.5
As^{+}	53.51	As^{+}	14.04	Sn^{+}	5.817	Sn^{+}	65.5
Sb^{+}	42.51	Sb^{+}	10.19	S^{+}	5.89	S^{+}	104.2
Bi^{+}	70.47	Bi^{+}	12.68	Se^{+}	5.808	Se^{+}	102.6
B^{-}	45	B^{-}	10.47	Te^{+}	5.892	Te^{+}	89.5
Al^{-}	57	Al^{-}	10.80	Be^{-}	30	Be^{-}	48.7
Ga^{-}	65	Ga^{-}	10.97	Mg^{-}	30	Mg^{-}	53.5
In^{-}	160	In^{-}	11.61	Zn^{-}	31.4	Zn^{-}	64
		Ti^{-}	13.10	Cd^{-}	35.4	Cd^{-}	96.5
				C^{-}	26.7	C^{-}	48
				Si^{-}	35.2	Si^{-}	203
				Ge^{-}	41.2	Ge^{-}	257
				Sn^{-}	171		

For doping to add carrier concentration or change the carrier type, impurities with shallow activation or ionization energies are used. For *p*-type silicon, boron is usually the preferred dopant, while phosphorus, arsenic, and antimony are used for *n*-type. Some of the activation energies are listed below in Table 19.2 (note: data about the most common dopants in Si, Ge, and GaAs was already listed in Table 19.1).

19.3 Line Defects

Line defects, or one-dimensional defects, refer exclusively to dislocations. Although there are two main types of dislocations, edge or screw, these two types typically combine to form several complicated mixed dislocations.

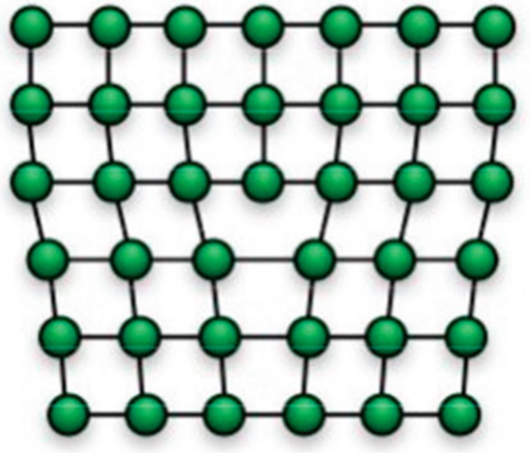
Edge dislocations may be described as an extra plane of atoms inserted into the crystalline lattice, causing a localized strain to be introduced into the lattice, as shown in Fig. 19.6.

Screw dislocations are formed when one side of the crystal undergoes a shear stress and is displaced at least one lattice plane, while the other side is held fixed. A schematic diagram of a screw dislocation is shown in Fig. 19.7.

Mixed dislocations are any combination of edge and screw dislocations and are the most typical ones that one finds in bulk crystals. An example of a simple mixed dislocation is shown in Fig. 19.8.

Burgers' vectors are used to classify and describe dislocations. In order to construct a Burgers' vector, a closed loop should be drawn around the dislocation by traveling the same amount of lattice points in all directions. If the loop does not close, it is surrounding a dislocation, and the vector that would close the circuit is the Burgers' vector. The starting point, the circuit direction, and the size of the loop are arbitrary. Independent of these factors, the Burgers' vector will always be perpendicular to the

Fig. 19.6 Illustration of an edge dislocation



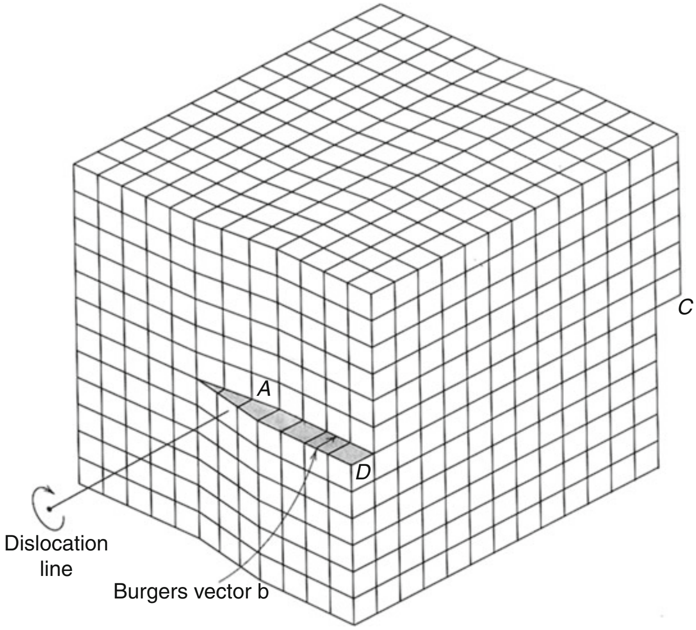


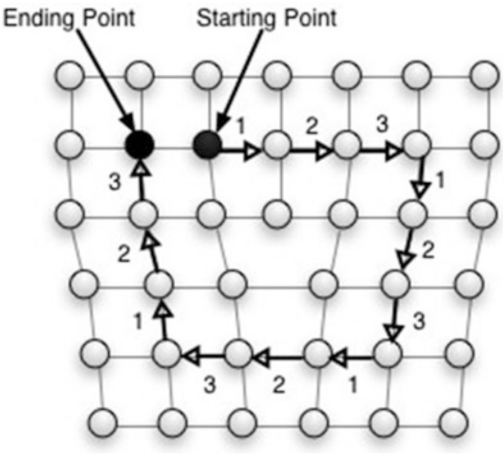
Fig. 19.7 Illustration of a screw dislocation. (Materials science and engineering: an introduction, Callister WD, p. 76, Fig. 4.4(a) Copyright © 2000 by John Wiley & Sons, Inc. Reprinted with permission of Wiley-Liss Inc., a subsidiary of John Wiley & Sons, Inc.)

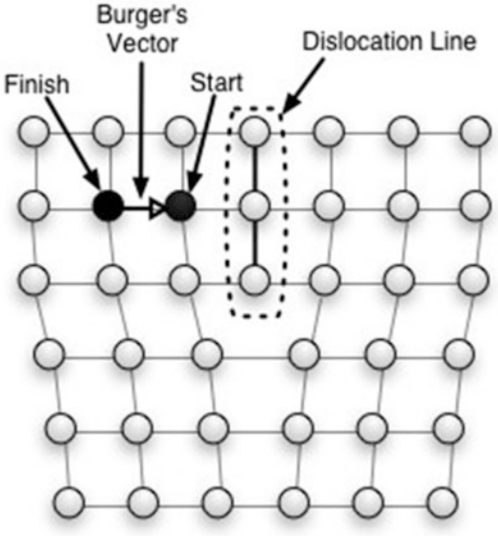
line of an edge dislocation and parallel to the line of a screw dislocation. It is often very complicated to find the Burgers' vector for a mixed dislocation.

Example

Q: Draw the Burgers' circuit to show that the Burgers' vector for an edge dislocation is perpendicular to the line of the dislocation.

A: Choose a starting point, a direction, and a side length that will be sure to enclose the edge dislocation. In the figure below, a clockwise direction and a side length of three were chosen. Then draw a vector from the end point of your circuit to the starting point of your circuit. This is the Burgers' vector.





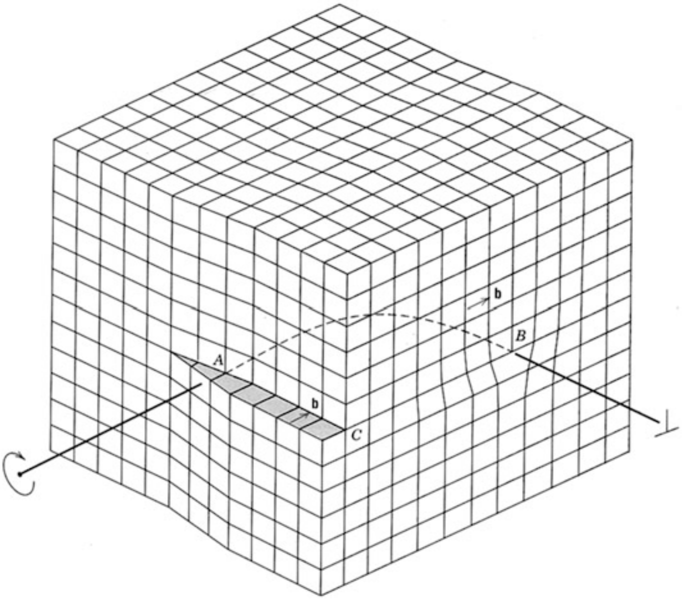


Fig. 19.8 Illustration of a mixed dislocation comprised of one edge dislocation and one screw dislocation. (Materials science and engineering: an introduction, Callister WD, p. 77, Fig. 4.5 (a) Copyright © 2000 by John Wiley & Sons, Inc. Reprinted with permission of Wiley-Liss Inc., a subsidiary of John Wiley & Sons, Inc.)

19.4 Planar Defects

Planar defects, or two-dimensional defects, refer to irregularities in the crystalline lattice that occur across a planar surface of the crystal. These may be due to an internal error in the crystal structure, or interfaces between two different materials, including interfaces with different phases of matter. Internal planar defects include stacking faults, twin boundaries, grain boundaries, and interphase boundaries, while external planar defects refer to surface defects caused by an interaction of the crystal with a gas or liquid environment.

Stacking faults occur when a single plane of atoms within the crystalline lattice is misoriented or out of order. For example, the cubic close-packed structure follows an ABCABC stacking order; however, an error in this order such as a stacking of ABCABABC produces a stacking fault. Figure 19.9 shows an example of a stacking fault.

Twin boundaries occur when a stacking fault reorients the rest of the crystal, forming a mirror plane within the crystal. For example, in the ABCABC stacking order of the cubic close-packed structure, a new stacking order of ABCABACBA would cause a twin boundary, where the center “B” plane would be a mirror plane. A schematic of a twin boundary is shown in Fig. 19.10 .

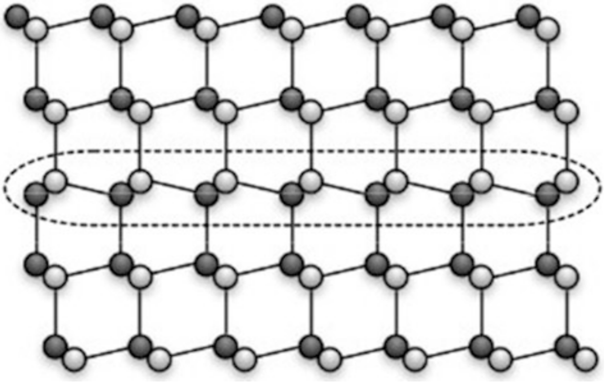
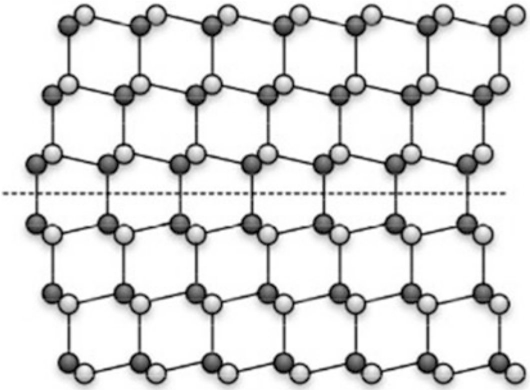


Fig. 19.9 Schematic diagram of a stacking fault

Fig. 19.10 Schematic diagram of a twin boundary



When two or more single crystals of different orientation meet, grain boundaries are formed. Two types of grain boundaries are pure tilt boundaries and pure twist boundaries. Pure tilt boundaries occur when the axis of rotation is parallel to the plane of the grain boundary, as shown in Fig. 19.10.

Pure twist boundaries, on the other hand, occur when the axis of rotation is perpendicular to the plane of the grain boundary, as shown in Figs. 19.11 and 19.12.

If the angle of rotation is small enough for these two cases, usually less than 10°–15°, the grain boundary is referred to as small angle. A small angle pure tilt boundary can be viewed as a series of parallel edge dislocations, while a small angle pure twist boundary may be viewed as an array of screw dislocations. The spacing between the dislocations, D, of low-angle grain boundaries is given in Eq. (19.3), where b is the magnitude of the Burgers' vector, which measures the degree of the misalignment introduced into the lattice due to one dislocation, and θ is the rotation angle.

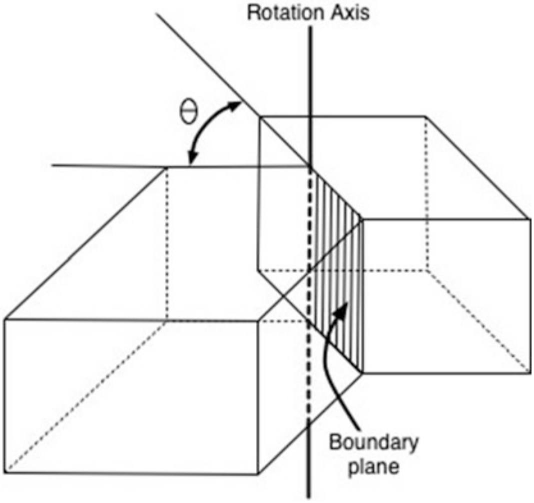


Fig. 19.11 Schematic diagram of a tilt boundary

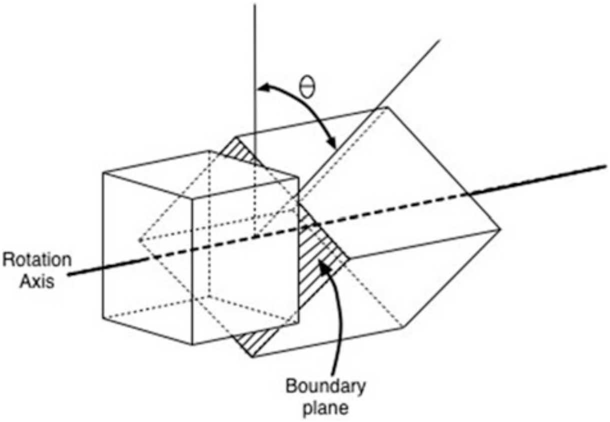


Fig. 19.12 Schematic diagram of a twist boundary

$$D = \frac{b}{\sin\theta} \approx \frac{b}{\theta} \tag{19.3}$$

Large-angle grain boundaries and combinations of twist and tilt boundaries lead to much more complicated structures for grain boundaries. Polycrystalline materials generally contain many grains of single crystalline material of random orientations with their neighbors. The size of the grains and the orientation between neighboring grains have an effect on properties of the polycrystalline material. For instance, a material with large grains and only a small misorientation between grains would have properties closer to a single crystalline material than a material with small, highly disordered grains.

Interphase boundaries occur when one crystalline material shares an interface with another crystalline material. Depending on the properties of each material, the interface will be either coherent, semi-coherent, or incoherent.

Coherent interphase boundaries will form when the two materials have similar geometries and a layer thickness less than the critical thickness for that material interface. The critical thickness, d_{crit}, is approximated by Eq. (19.4) where b is the magnitude of the Burgers' vector for a dislocation and f is the lattice mismatch between the two materials. Since the critical thickness is indirectly proportional to the lattice mismatch of the two materials, in order to have a coherent interface, it is necessary to have a small enough lattice mismatch in order to have a reasonable critical thickness (thicker than a few monolayers):

$$d_{\text{crit}} = \frac{b}{10 \cdot f} \tag{19.4}$$

While a small amount of strain may be introduced at a coherent boundary, no defects will be introduced due to the material change. A coherent boundary is shown in Fig. 19.13.

Semi-coherent interphase boundaries will form when the two materials have similar geometries but a larger lattice mismatch or the layer thickness exceeds the critical thickness. In this case, edge dislocations tend to form due to increased strain within the material. A semi-coherent boundary is shown in Fig. 19.14.

Incoherent interphase boundaries have a highly disordered structure that lack orientation relationships and have high energies. Little is known about the detailed structure of this type of interface.

External planar defects occur when the crystal periodicity is interrupted and bonds are broken, leading to dangling bonds. This occurs at the surface of the crystal and affects the outermost atomic layers or surface region. When this occurs, the atoms on the surface have a smaller coordination number, or number of nearest neighbors, than the atoms in the bulk crystal, and therefore have significantly different properties than the bulk crystal. The dangling bonds cause the surface to be more chemically and electrically active.

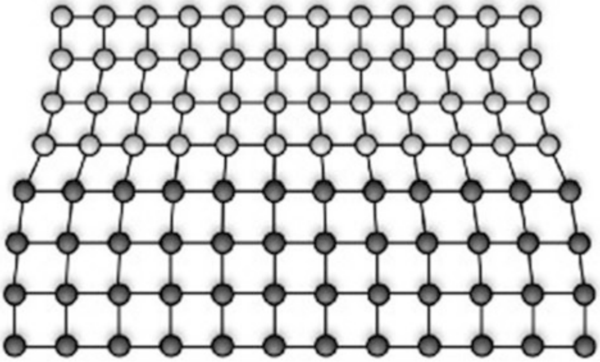


Fig. 19.13 Schematic of a coherent interphase boundary

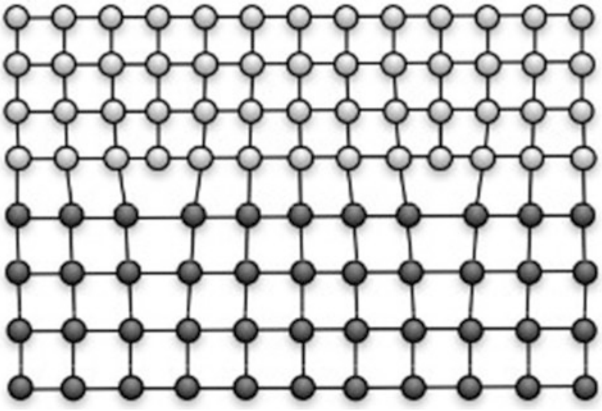


Fig. 19.14 Schematic of a semi-coherent interphase boundary

Since it takes energy to break the bonds, creating a surface takes energy, referred to as surface energy, which is always a positive amount. The surface wants to minimize its energy by reducing the number of dangling bonds, which it may do through surface relaxation or surface reconstruction. Surface relaxation is achieved by a change in the distance between the first and second layers of atoms at the surface. Typically, the distance is reduced, but there are a few cases where it is increased. Surface reconstruction occurs when the surface forms a different structure than the bulk structure. The silicon (001) surface relies on surface reconstruction in order to minimize its surface energy.

19.5 Volume Defects

Volume defects, also known as bulk defects, are clusters of point defects. Clusters of defects are produced when the crystal become supersaturated.

Each point defect introduced into a crystal has a certain level of solubility, which defines the maximum concentration of the impurity in the host crystal. In general, solubility is temperature dependent and decreases as the crystal is cooled down. When the concentrations of defects exceed their solubility limit or the crystal is cooled down after it gets saturated, it becomes supersaturated with that defect. The crystal under a supersaturated condition tries to achieve an equilibrium condition by condensing the excess defects into clusters with different phase regions.

Clusters of vacancies forming small regions where there are no atoms are called voids. High concentration of point defects in semiconductors results in formation of microvoids. The aggregation of vacancies is increasingly harmful to device performance as the size shrinking of devices continues in Si wafers Fig. 19.15 shows an SEM image of voids in AlGaN.

Clusters of foreign atoms forming small regions of different phase are often called precipitates. For example, Zn in InP at a doping level exceeding 1×10^{18} cm^{-3}

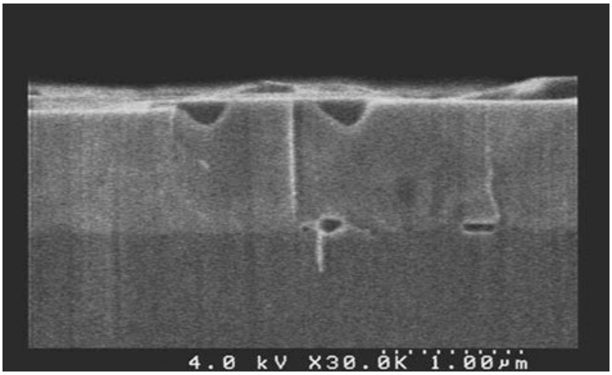


Fig. 19.15 SEM image of voids in AlGaN

forms precipitates. Another example is precipitates in silicon which occurs during the processing of wafers into integrated circuits. There are two foreign particle formation mechanisms: precipitates and inclusion incorporation. Precipitates are formed due to the retrograde solubility of native point defects. When the grown crystal is cooling down, the solidus line is crossed, and nucleation of the second phase takes place. In contrast to precipitates, inclusions are formed by capturing melt solution droplet from the diffusion boundary layer adjacent to the growing interface and enriched by the rejected excess component.

19.6 Defect Characterization

Characterization and analysis of defects is one of the biggest experimental challenges. There are conventional characterization methods to examine the overall quality or electrical features of the material such as Hall measurement and x-ray measurement (see Chap. 18). However, observing and identifying the type of each defect and the status in the material or devices is not easy because the defects are usually of atomic size unless they aggregate and form clusters.

When the defects are revealed by special etching techniques, they can be observed by optical microscopy. This method is called preferential etching. The basic idea of the method is to make defects visible in a microscope by marking the surface with small pits or grooves. This happens due to the differing physical and chemical properties near the defects. The surface is polished and etched with proper etching solutions that dissolve the material much more quickly around defects than in perfect regions.

Scanning electron microscope (SEM) has been used for observing large defects in devices in research and industry. For smaller features, transmission electron microscope (TEM) is now a better choice. Scanning probe microscope (SPM) and atomic force microscope (AFM) are capable of imaging single atoms. There are also several analytical methods for detecting impurities such as atomic absorption spectroscopy

(AAS), spark source mass spectrometry (SSMS), secondary ion mass spectrometry, and local mode infrared absorption.

19.7 Defects Generated During Semiconductor Crystal Growth

As previously mentioned, intrinsic defects will always exist at temperatures above the absolute zero. In reality, however, the actual defect concentrations in crystals are much higher than the equilibrium values at room temperature. This is because the finite defect diffusion rate leads to the freezing-in of a large fraction of the high-temperature defects produced as the crystal cools down. Therefore, pulling rate and cooling rate from the melting point are important parameters for crystal growth.

The development of crystal growth technology has been motivated by two major goals: achieve higher quality of bulk crystals and larger wafer diameters. Higher quality is necessary because as device sizes continue to shrink, the presence of defects in crystals becomes more significant. In particular, the aggregation of vacancies which results in the formation of microvoids is increasingly harmful to device performance. Large-diameter wafer development is driven by the demand of cost reduction in the device industry, since larger wafer diameter leads to higher throughput.

The growth of compound semiconductor single crystals is more complicated and less studied compared to Si, for instance. In III-V and II-VI semiconductors, the intrinsic point defect concentration is even greater than the intrinsic carrier concentration and can therefore influence the position of the Fermi level. The details of crystal growth were discussed in Chap. 17.

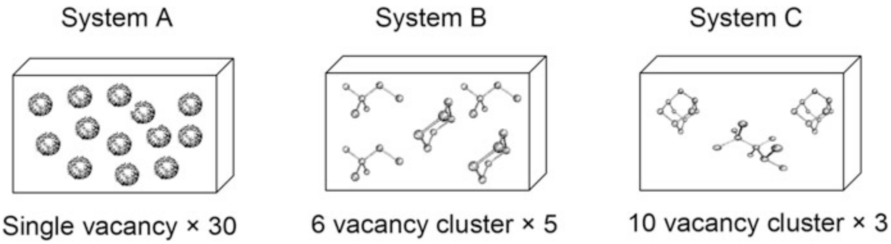
19.8 Summary

In this chapter, we discussed defects as imperfections that disturb the periodic structure of the crystal. The defects were classified into four groups according to their structural dimension. Point defects (0D), line defects (1D), planar defects (2D), and volume defects (3D) were explained. Several characterization techniques were introduced, and some issues regarding semiconductor single crystal growth were also discussed.

Problems

1. Give some examples of physical properties that defects can change.
2. Identify the types of point defects shown in Fig. 19.1. Please re-sketch the figure.
3. Calculate the number of vacancies per cubic meter in iron at 750 °C. The energy for vacancy formation is 1.08 eV/atom. Also, the density and atomic weight for Fe are 7.65 $\mathrm{g{\cdot}cm^{-3}}$ and 55.85 $\mathrm{g{\cdot}mol^{-1}}$, respectively. Assume A is unity.

4. Find the equilibrium concentration of defects for $T = 0$, 200, 400, 600, 800, 1000, and 1200 K if the energy to form a defect is 1 eV/atom. Assume A is unity. Graph your results. For T = 1200 K, how many atoms per single vacancy are present?
5. The formation energies of vacancy clusters in Si are listed below. Calculate the formation energy of (i) system a (30 single vacancies), (ii) system B (five 6-vacancy clusters), and (iii) system C (three 10-vacancy clusters). Which system has the lowest formation energy? Why?



(Cluster shapes reprinted with permission from Europhys Lett Vol. 43, p. 697, Fig. 1, Bongiorno A, Colombo L, and Diaz de la Rubia T, "Structural and binding properties of vacancy clusters in silicon," p. 697. Copyright 1998, EPD Sciences.)

Size	1	6	10
Energy (eV)	3.4	11.4	15.6

6. Briefly describe the difference between an edge dislocation and a screw dislocation.
7. Show how to find the Burgers' vector for a screw dislocation.
8. GaAs/InAs have a 7.2% lattice mismatch. How many monolayers of InAs may be grown on GaAs before a semi-coherent boundary is formed? ($a_{\mathrm{GaAs}} = 0.565$ nm $a_{\mathrm{InAs}} = 0.606$ nm, assume $b = a_{\mathrm{InAs}}/\sqrt{2}$).
9. What is preferential etching?
10. What have been the goals of the semiconductor industry in silicon crystal growth technology? Why?

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