6. Diffusion in Semiconductors

Atomic diffusion in semiconductors refers to the migration of atoms, including host, dopant and impurities. Diffusion occurs in all thermodynamic phases, but the solid phase is the most important in semiconductors. There are two types of semiconductor solid phase: amorphous (including organic) and crystalline. In this chapter we consider crystalline semiconductors and describe the processes by which atoms and defects move between lattice sites. The emphasis is on describing the various conditions under which diffusion can occur, as well as the atomic mechanisms that are involved, rather than on tabulating data. For brevity's sake, we also focus on the general features found in the principal semiconductors from Groups IV, III–V and II–VI; IV–VI and oxide semiconductors are excluded from consideration. It is not surprising that most of the data available in this field relate to the semiconductors that are technologically important – they are used to fabricate electronic and optoelectronic devices. One unavoidable consequence of this technological need is that diffusion data tend to be acquired in a piecemeal fashion.

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Diffusion describes the movement of atoms in space, primarily due to thermal motion, and it occurs in all forms of matter. This chapter focuses on atom diffusion in crystalline semiconductors, where diffusing atoms migrate from one lattice site to another in the semiconductor crystal. The diffusion of atoms and defects is at the heart of material processing, whether at the growth or post-growth stage, and control over diffusion is the basis of process simulation and defect engineering. Such control calls for an understanding of the diffusion processes involved in a given situation. The needs of device technology have provided the main impetus for investigations into the diffusion of atoms in semiconductors. As the physical dimensions of devices have shrunk, the barriers to understanding diffusion mechanisms and processes in complex structures have greatly multiplied.

6.1 Basic Concepts

Consider a particle in a three-dimensional isotropic lattice which migrates by making jumps from one lattice site to a nearest neighbor site. If the distance between nearest neighbor sites is a and the particle makes n jumps in time t, then, assuming each jump is random (so the directions of successive jumps are independent of each other), the mean square displacement $\langle R^2 \rangle$ is equal to na^2 [6.1]. Fick's first law defines the associated diffusivity D to be $na^2/6t = \langle R^2 \rangle/6t = \upsilon a^2/6$, where $\upsilon = n/t$ is the average jump rate of the particle. Taking the diffusion length as $2\sqrt{(Dt)}$, it follows that this is also equal to $2\sqrt{(\langle R^2 \rangle/6)}$. For $D = 10^{-12}\,\mathrm{cm^2/s}$, $t = 10^4\,\mathrm{s}$ and $a = 2 \times 10^{-8}\,\mathrm{cm}$, the diffusion length is $2\,\mu\mathrm{m}$, $n = 1.5 \times 10^8$ jumps and the total distance na traveled by the particle is 3 cm. However, it turns out that in most diffusion mechanisms successive jumps are correlated, not random. The effect of nonrandom jumps is to decrease the diffusivity of the particle relative to what it would be if the jumps were random. Taking this correlation into account leads to $D = f\upsilon a^2/6$, where $f(\leq 1)$ is the correlation factor [6.1], υ is temperature-dependent and f may or may not be, depending on the particular situation. Overall, the temperature dependence of D is found to obey the Arrhenius relation $D = D_0 \exp(-Q/kT)$.

6.2 Diffusion Mechanisms

Two categories of diffusion mechanism are recognized: defect and nondefect. A simple example of the latter class is the simultaneous jumps of two adjacent atoms in order to exchange sites. There is a general consensus, however, that nondefect mechanisms do not play any significant role in semiconductor diffusion, although recently nondefect contributions have been proposed for self- and dopant diffusions in Si [6.2]. In the elemental semiconductors Si and Ge, vacancies and interstitials are the primary defects. In binary compound semiconductors (such as GaAs and ZnSe) there are two sublattices, the anion and cation, so there are vacancies and interstitials for each sublattice together with antisite defects on each sublattice. Further complexity arises due to the various states of ionization of the defects: the mobility of a defect depends on its charge state. The relative concentrations of the different charge states will be determined by the position of the Fermi level.

6.2.1 Vacancy and Interstitial Diffusion Mechanisms

In the Si lattice, a vacancy V_{Si} can migrate by a nearest neighbor Si atom jumping into the vacancy (in other words, the Si atom and V_{Si} have exchanged sites so that the Si atom has also migrated). Equally, a substitutional dopant atom can migrate by jumping into a V_{Si} at a nearest neighbor site. Similarly, in a binary semiconductor such as GaAs, Ga atoms can migrate over the Ga sublattice via jumps into nearest neighbor Ga vacancies, as can dopant atoms substituting into the Ga sublattice. Anti-site defects can diffuse by jumping into vacancies in the same sublattice, such as the As anti-site defect in GaAs, As_{Ga}, diffusing by jumps into Ga vacancies. For self-interstitials, such as Si_i or Ga_i, their concentrations are sufficiently small for neighboring interstitial sites to always be empty, which means that the occupancy of nearest neighbor sites is not a factor when determining jump rates. If a self-interstitial, such as Si_i, pushes a Si atom on a normal lattice site into an interstitial site instead of jumping into a neighboring interstitial site, and therefore replaces the displaced Si atom, the process is known as the "interstitialcy mechanism". This concept extends to a substitutional dopant atom forming a pair with a self-interstitial, which then migrates with the dopant atom, alternating between substitutional and interstitial sites. It is also possible for point defects to form complexes which can diffuse as a single entity. Examples are the Frenkel pair $V_{Si}Si_i$, di-vacancies such as $V_{Ga}V_{Ga}$ or $V_{Ga}V_{As}$, and the defect pair formed between a substitutional dopant atom and an adjacent vacancy.

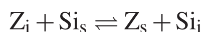
6.2.2 The Interstitial–Substitutional Mechanism: Dissociative and Kick-Out Mechanisms

The interstitial–substitutional diffusion mechanism arises when a dopant species Z occupies both interstitial and substitutional sites, represented by Z_i and Z_s respectively, and diffusion is restricted to jumps of Z_i. In this case, we may ask how the Z_s concentration $[Z_s]$ is linked to the Z_i migration. Consider the diffusion of Z in Si. The dissociative mechanism (also known as the Frank–Turnbull mechanism) is based on the defect

interaction

$$Z_i + V_{Si} \rightleftharpoons Z_s$$

and application of the law of mass action (LMA) leads to $[Z_i][V_{Si}] \propto [Z_s]$. In the kick-out mechanism, the defect interaction is



$$Z_i + Si_s \rightleftharpoons Z_s + Si_i$$

and therefore $[Z_i] \propto [Z_s][Si_i]$ ($[Si_s]$ is omitted because it is effectively constant). In order to sustain growth in $[Z_s]$ by either mechanism, it is clearly necessary to have either a supply of V_{Si} or a means of removing Si_i. For simplicity, neutral charge states have been assigned to all of the defects in these two interactions. A detailed treatment of the kick-out mechanism has been given by *Frank* et al. [6.3]. For in-diffusion of Z, the Frank–Turnbull mechanism consumes vacancies and will therefore tend to reduce the local vacancy concentration, whereas the local self-interstitial concentration will be enhanced by the kick-out mechanism. Out-diffusion of Z reverses the effects on the native defect concentrations.

6.2.3 The Percolation Mechanism

The percolation mechanism [6.4] was proposed to explain group V dopant diffusion in Si at high dopant concentrations (in excess of $\approx 1\%$). At low concentrations diffusion is via dopant-V_{Si} pairs. As the dopant concentration increases, regions occur in the Si lattice where the proximity of the dopant atoms enhances the mobility and concentration of the V_{Si}. Within this network the diffusivity of dopant-V_{Si} pairs is thereby also enhanced so that the dopant diffusivity increases overall. The percolation network only forms once the dopant concentration exceeds a certain critical value. In principle this mechanism could extend to other highly doped materials.

6.3 Diffusion Regimes

The mobility of a native defect and/or dopant atom reflects the physical and chemical environment under which diffusion is occurring. Two types of environment arise: conditions of chemical equilibrium and those of chemical nonequilibrium. Diffusion in temperature gradients is excluded – only isothermal conditions are considered.

6.3.1 Chemical Equilibrium: Self- and Isoconcentration Diffusion

Chemical equilibrium means that the concentrations of all chemical components, including native defects, are uniform throughout the semiconductor, and where appropriate (such as in a compound material), the solid is in equilibrium with the ambient vapor of the components so that the level of nonstoichiometry is defined. Experimentally this requires diffusion to be carried out in a sealed system. Self-diffusion refers to the diffusion of the host atoms, such as Si atoms diffusing in the Si lattice. Isoconcentration diffusion describes the diffusion of dopant atoms when the same dopant concentration is uniform throughout the sample, such as for As diffusion in Si for a constant As doping level. In either case, diffusion can only be observed if some of the particular diffusing atoms are tagged, such as by using a radioisotope or an isotopically enriched diffusion source. The diffusivity of a tagged or tracer species is related to the concentration of the native defect that provides the diffusion path, and the self-diffusivity (the diffusivity of the tracer) is always significantly smaller than the associated defect diffusivity. Specific relations can be found in *Shaw* [6.5]. A diffusion flux of the tracer arises from a tracer concentration gradient, which is not to be confused with a chemical concentration gradient.

6.3.2 Chemical Diffusion (or Diffusion Under Nonequilibrium Conditions)

This category contains all of the diffusion phenomena that are of technological interest and importance. In this case, diffusion occurs due to spatial gradients in the concentrations of the chemical components in the material, which are in turn caused by departures from equilibrium: the diffusion processes are attempting to either restore or achieve equilibrium.

Chemical Self-Diffusion

Chemical self-diffusion describes the process whereby a compound semiconductor changes from one level of nonstoichiometry to another through changes in the native defect populations. These changes can arise due to a change in the ambient partial pressure of one

of the components (that of As in the case of GaAs for example), or through a change in temperature under a defined or controlled component partial pressure. Good examples are provided by II–VI semiconductors [6.6] and in particular $Hg_{0.8}Cd_{0.2}Te$ [6.7], where p- to n-type conversion is used to form p–n junctions by annealing in Hg vapor. Changes in the native defect concentrations can also lead to an increased dopant diffusivity; an increase in the vacancy concentration will enhance any diffusivity based on a vacancy mechanism for instance.

Dopant Diffusion

Suppose we have a dopant diffusing into the semiconductor from a source located at an external surface (such as a surface layer) or in an external phase (such as a gas or vapor). The existence of the dopant concentration gradient can lead to various effects which can influence the dopant flux. For example, if a dopant diffuses via a vacancy mechanism, then at any position in the diffusion region the increase in the dopant concentration requires a supply of vacancies, so that to maintain local defect equilibrium there must also be an associated vacancy flux. If the dopant controls the position of the Fermi level, then the concentrations of ionized native defects will increase or decrease, depending on their charge state, relative to their intrinsic concentrations (the Fermi-level effect). This means that the concentrations of native defects of opposite (the same) polarity to the dopant will be increased (decreased). Increases in the concentrations of ionized native defects due to Zn, Si or Te diffusion into GaAs/GaAlAs superlattice structures explain the disordering of the superlattices [6.8]. Usually a substitutional dopant atom will have a different size to that of the host atom it replaces. This size difference creates a local mechanical strain which in turn can cause changes in the local concentrations of native defects as well as to jump rates and hence dopant diffusivity [6.9]. If the strain is large enough, misfit dislocations will be generated [6.10], otherwise there will be a strain energy gradient matching the dopant concentration gradient which can enhance or retard the dopant flux [6.11]. More recently a new scenario has emerged: dopant diffusion in strained epilayers. Whether diffusion is enhanced or retarded depends on several poorly understood parameters [6.12]. However, significant effects are found, such as the decrease in the B diffusivity in strained $Si_{1-x}Ge_x$ epilayers by a factor of ≈ 10 as the strain increased from zero to 0.64 [6.13].

Compositional Interdiffusion (CID)

Compositional interdiffusion describes diffusion across the interface separating two materials of different chemical composition. Chemical composition here refers to major components; dopants and deviations from stoichiometry are excluded. CID can be exploited when making graded bandgap structures and during material preparation, such as in $Hg_{1-x}Cd_xTe$, where an alternating sequence of HgTe and CdTe epilayers of appropriate thicknesses are first grown and then interdiffused. CID can also pose problems in the fabrication of multiple quantum wells and superlattice structures when sharp boundaries are necessary. In particular, donor or acceptor dopant diffusion into GaAs-based superlattices can cause essentially complete intermixing on the cation sublattice [6.8]. This phenomenon is also known as diffusion-induced disorder. B or As doping also results in rapid intermixing at a Si/Ge interface [6.14].

Transient Enhanced Diffusion (TED)

Ion implantation is often the preferred way to achieve a doped layer. The implantation process does however create a significant amount of lattice damage so that a subsequent anneal stage is needed in order to achieve full electrical activity of the implanted dopant and recovery of the lattice damage. During the implantation process, the implant ions create collision cascades of vacancies and self-interstitials (an excess of native defects). The post-implant anneal serves to remove or reduce this excess. In addition to vacancy/interstitial recombination, the excess native defects can interact to form clusters (which also may contain implant ions as well as residual impurities) and extended defects, such as dislocation loops. At the start of the post-implant anneal, the local concentrations of vacancies and self-interstitials in the implant region can greatly exceed equilibrium values and therefore enhance the implant ion diffusivity in the implant region. As annealing proceeds the excess concentrations will diminish and will be reflected in a diminishing dopant diffusivity until values appropriate to local equilibrium are reached. This temporary enhancement in the dopant diffusivity is known as TED. The topic is a complex one to analyze quantitatively and detailed consideration of the issues involved in the case of B implants in Si can be found in the review by *Jain* et al. [6.15]. In the fabrication of shallow p–n junctions using ion implants and rapid thermal annealing (RTA), TED can determine the lower limit to junction depth. TED of B in Si can be reduced with coimplants of Si prior to RTA [6.16]. TED of Be and Si

in GaAs has also been discussed [6.17]. Some workers use the term TED to describe the enhanced diffusivity of a dopant, incorporated during growth, which occurs when the structure is annealed at a higher temperature than the growth temperature, such that there is an initial supersaturation of the relevant native defects at the anneal temperature.

Segregation, Gettering, Precipitation and Clustering

A variety of important scenarios arise, involving many of the above regimes, during growth and/or thermal processing stages of materials and structures. The segregation of acceptor dopants in InP [6.18] and in III–V heterostructures [6.19, 20] has been observed and modeled. The segregation (or accumulation) due to diffusion of the dopant is in effect a partitioning process to preferred (higher solubility) regions within the layer structure. Gettering describes the segregation, or cleanup, of a fast-diffusing impurity from the active regions of a device structure. Such impurities are typically Group IB and transition metals and are incorporated either during growth or during subsequent processing. Gettering sites in Si are provided by O precipitates, self-ion implant damage layers and nanocavities [6.21]. In contrast, Group IB impurities are gettered in $Hg_{1-x}Cd_xTe$ by regions of high cation vacancy concentration [6.22].

Precipitation occurs when a species – whether native defect, dopant or impurity – becomes supersaturated, and in order to achieve its equilibrium concentration the species excess is removed by the formation of precipitates within the host lattice. A self-interstitial or vacancy excess can be removed through the nucleation of dislocation loops, stacking faults or voids, which then provide sites for the precipitation of the remaining excess. In the case of a dopant, impurity or nonstoichiometric excess, nucleation of a precipitate can be spontaneous (homogeneous) or heterogeneous. The latter occurs at the site of an impurity atom (for example, C atoms in Si serve as nucleation centers for the precipitation of O) or at dislocations, giving rise to the term "decoration". Growth of any precipitate proceeds via diffusion of the particular species from solution in the matrix to the precipitate and is generally diffusion-limited. Invariably local stress fields will be present which influence the diffusion and, if present initially, they may also play a role in the nucleation stage. The precipitation of O impurities in Si presents a unique case study because of the high [O], its technological importance and its complexity [6.23, 24]. The rather simpler case of B precipitation in Si has been described by *Solmi* et al. [6.25]. A cluster (or agglomerate) refers to a configuration of at least a few dopant atoms (with or without associated native point defects) or host species. *Solmi* and *Nobili* [6.26] have identified $(2As_{Si} - V_{Si})^0$ and $(4As_{Si} - V_{Si})^+$ clusters in heavily As-doped Si. Heavy C doping [6.27] and B implants [6.28] in Si give rise to self-interstitial clusters with C and B respectively. In Si, according to *Ortiz* et al. [6.29], if the number of self-interstitials in a cluster exceeds ≈ 10 there is a transition to a {113} defect.

6.3.3 Recombination-Enhanced Diffusion

The local energy released in the nonradiative recombination of excess free carriers can help a diffusing species to surmount the energy barrier separating it from an adjacent lattice site – in other words, the energy barrier facing a jump is effectively reduced. This situation is important in the degradation of performance of device structures which utilize high excess minority carrier concentrations, such as light-emitting and laser diodes.

6.3.4 Surface Effects

The concentrations of native point defects within the bulk can be altered by surface processes. In the case of Si it is well known that during surface oxidation or nitridation there is injection of Si interstitials or of vacancies respectively. All diffusants can therefore be affected during the duration of the process. Ion beam milling causes the injection of Hg interstitials into $Hg_{1-x}Cd_xTe$ in sufficient quantities to effect p- to n-type conversion.

6.3.5 Short Circuit Paths

The existence of dislocations and subgrain boundaries in single-crystal materials generally provides high diffusivity routes for all atomic species relative to the surrounding matrix. Care is always needed when evaluating experimental data to ensure that bulk diffusion is not being masked by short circuit paths [6.30]. In the case of polycrystalline Si, the grain boundaries may provide high diffusivity routes, as in the cases of As and B [6.31], or retard diffusion, as for Au [6.32]. The situation is a complex one, as grain growth also occurs during any anneal. *Kaur* et al. [6.33] have provided a comprehensive account of short circuit path diffusion.

6.4 Internal Electric Fields

When the dopant concentration is large enough to make the diffusion zone electrically extrinsic, free carriers from the dopant, due to their much higher mobility, will diffuse ahead of the parent dopant atoms. This separation creates a local electric field whose direction is such as to pull the dopant atoms after the free carriers (and also to pull the free carriers back). Provided that the diffusion length $>\approx$ six Debye screening lengths (typically $\approx 10^2$ nm), the diffusion zone can be regarded as electrically neutral (the space charge density is negligible) [6.34]. In this situation the local electric field E is given by $-(kT/en)(\partial n/\partial x)$ for an ionized donor dopant diffusing parallel to the x-axis, and nondegenerate conditions apply: k, T, e and n are Boltzmann's constant, the absolute temperature, the electronic charge and the free electron concentration respectively. E exerts a force on each ionized donor (D^+) parallel to the x-axis, creating a local donor flux $-(D(D^+)[D^+]/n)(\partial n/\partial x)$ due to drift in the electric field: $D(D^+)$ is the donor diffusivity [6.35]. This drift flux adds to the diffusion flux, $-D(D^+)\partial[D^+]/\partial x$, to give the total donor flux at any position in the diffusion region, so that the donor flux in this case is increased due to E. E will also cause drift of any other charged species.

Internal electric fields can arise in other circumstances such as in depletion layers where E must be calculated from Poisson's equation, in graded bandgap structures [6.11, 36], and at the interfaces of heterostructures. Cubic II–VI and III–V strained layer heterostructures grown on the $\{111\}$ direction are piezoelectric and typical strains from lattice mismatch of $\approx 1\%$ can give $E \approx 10^5$ V/cm in the absence of free carrier screening [6.37]. In wurtzite heterostructures based on the Ga, In nitrides, even higher fields are found ($E \approx 10^6$ V/cm) due to piezoelectric and spontaneous polarization [6.38]. These fields can be important in CID and chemical self-diffusion.

6.5 Measurement of Diffusion Coefficients

6.5.1 Anneal Conditions

Accurate control of sample temperature and ambient are essential if controlled and reproducible results are to be obtained in a diffusion anneal. Depending on the time spent at the anneal temperature, the warm-up and cool-down times may also be important. An appropriate choice of ambient is needed to preserve the sample surface (to avoid evaporation, surface melting or alloying with the dopant source for example). For compound semiconductors it is necessary to define the level of nonstoichiometry by controlling the ambient partial pressure of one of the components, such as As for GaAs or Hg for $Hg_{1-x}Cd_xTe$. If the dopant is in an external phase, knowledge of the phase diagram of all of the components is required [6.1, 35]. Control over partial pressure is best achieved in a sealed system, typically a fused silica ampoule. Annealing in a vertical or horizontal resistance-heated furnace requires a minimum anneal time of 30 to 60 min in order to avoid uncertainties due to warm-up and cool-down. The drive to shallow dopant profiles has been facilitated through rapid thermal annealing (RTA) techniques. These are based on radiant heating of the sample, and linear heating rates of 100–400 °C/s with cooling rates of up to 150 °C/s are available. RTA however precludes the use of a sealed system and, in this case, a popular means of preventing surface deterioration is to seal the sample with an inert, impervious capping layer, made of silicon nitride for example.

6.5.2 Diffusion Sources

Consideration is limited to planar samples with diffusion normal to a principal face. This is a common situation and diffusion of a dopant or tracer species can take place from: (i) a surrounding vapor or gas phase; (ii) a surface layer, which may be evaporated, chemically deposited (CVD) or a spun-on silicate glass, all incorporating the diffusant; (iii) epilayers containing the diffusant, which may provide the external surface or be buried within the epitaxial structure; (iv) ion implants of a dopant either directly into the sample surface or into a thin surface layer so as to avoid lattice damage. It is obviously desirable that negligible diffusion occurs prior to reaching the anneal temperature when the diffusant is incorporated into an epilayer. In self-diffusion experiments the tracer can be a radiotracer or an isotopically enriched species. A key requirement for either form of tracer is availability, and a radiotracer must have a half-life that is long enough for the experiments to be carried out.

6.5.3 Profiling Techniques

Determining the spatial distribution of a diffusant for various anneal times is fundamental to obtaining its diffusion coefficient or diffusivity. Most methods are destructive, as they generally require a bevel section through the diffusion zone or the sequential removal of layers. The two broad profiling categories are electrical and species-specific. Electrical methods are primarily the p–n junction method, spreading resistance and capacitance–voltage profiling. Limitations of the electrical methods are: (i) assumptions are needed to link the electrical data to the diffusant (for example, that the diffusant is the only electrically active center and that it is fully ionized); (ii) the assumption that the anneal temperature defect situation is "frozen-in" during cool-down. Electrical methods are the most direct means of measuring chemical self-diffusivities and can readily detect changes in host concentrations of < 1 part in 10^4. Species-specific (chemical element or isotope) profiling means that the chemical concentration of the diffusant is determined regardless of its location(s) in the lattice and of its electrical state. Profiling of the diffusant using a radiotracer has been widely used [6.39], but in the past decade or so secondary ion mass spectrometry (SIMS) has become what is essentially the standard procedure for diffusant profiling. This is because SIMS can measure diffusant concentrations within the range 10^{16} to $10^{22}\,\mathrm{cm}^{-3}$ with spatial resolutions at best of several nanometers per decade (of concentration). Primary factors determining the resolution are progressive roughening of the eroded surface and "knock-on" effects due to the probing ion beam displacing the diffusant to greater depths. A further problem may arise when the atomic mass of a dopant is close to that of the host species.

Nondestructive profiling techniques applicable to CID in quantum well and superlattice structures utilize either high-resolution X-ray diffraction (HRXRD) [6.40] or photoluminescence (PL). The detail in the X-ray diffraction patterns reflects the CID profiles at the interfaces and can also reveal the presence of strain in the structures. The use of PL requires the presence of optically active centers in the quantum well. CID changes the shape and depth of the quantum well, which in turn changes the photon energies in the luminescence spectra. HRXRD and PL can also be combined. A particular advantage of these techniques is that they allow successive anneals to be performed on the same sample.

6.5.4 Calculating the Diffusion Coefficient

Once a planar concentration profile has been obtained, the first step is to see if the profile can be fitted to a solution of Fick's second law. The simplest solution occurs for a diffusivity D independent of the diffusant concentration (c), for a constant surface concentration c_0 and a diffusion length $\ll$ the layer or sample thickness. The solution is $c = c_0 \mathrm{erfc}[x/2\sqrt{(Dt)}]$ [6.1]. If the profile is not erfc, it may be because D varies with c, and D (as a function of c) can be obtained by a Boltzmann–Matano analysis [6.35]. It is important to recognize that the erfc or Boltzmann–Matano solutions are only valid provided c_0 does not change with time and that c/c_0 versus $x/\sqrt{t}$ for profiles at various t reduce to a single profile. More complex situations and profiles require numerical integration of the appropriate diffusion equation(s) and matching to the experimental c versus x profile; in other words a suitable model with adjustable parameters is used to simulate the observed profiles. The interpretation of HRXRD and/or PL data provides a good example of a simulation scene in which an assumed D, either c-dependent or -independent, is used to calculate the resulting CID profile and its effect on the X-ray patterns and/or PL spectra. Whereas SIMS can observe diffusivities as low as $\approx 10^{-19}\,\mathrm{cm}^2/\mathrm{s}$, the HRXRD limit is $\approx 10^{-23}\,\mathrm{cm}^2/\mathrm{s}$.

6.6 Hydrogen in Semiconductors

Hydrogen is a ubiquitous element in semiconductor materials and can be incorporated either by deliberate doping or inadvertently, at significant concentrations, during growth and/or in subsequent surface treatments where organic solvents, acid or plasma etching are used. H is known to passivate electrically active centers by forming complexes with dopants and native defects as well as by bonding to the dangling bonds at extended defects. Such interactions may well affect the diffusivities of the dopant and native defect. This expectation is realized in the case of O in Si, where the presence of H can enhance O diffusivity by two to three orders of magnitude [6.41]. Ab initio calculations show that, at least in the Group IV and III–V semiconductors, H is incorporated interstitially in the three charge states, H^+, H^0 and H^-, with the Fermi level controlling

the relative concentrations. In addition to interactions with dopant atoms and native defects, H_2 molecules also form. *Mathiot* [6.42] has modeled H diffusion in terms of simultaneous diffusion by the three interstitial charge states with the formation of immobile neutral complexes. In polycrystalline Si, the grain boundaries retard H diffusion, so H diffuses faster in the surrounding lattice than in the grain boundary.

6.7 Diffusion in Group IV Semiconductors

Diffusants divide into one of five categories: self-, other Group IVs, slow diffusers (typically dopants from Groups III and V), intermediate diffusers and fast diffusers. The materials of interest are Ge, Si, Si/Ge alloys and SiC. A particular feature is that self-diffusion is always slower than the diffusion of other diffusants. With the exception of SiC, which has the zinc blende structure, as well as numerous polytypes (the simplest of which is the wurtzite, 2H − SiC, form), the other members of this group have the diamond lattice structure.

6.7.1 Germanium

The evidence to date identifies the dominant native defect in Ge as the singly ionized vacancy acceptor, V_{Ge}^- [6.43], which can account for the features found in self-diffusion and in the diffusivities of dopants from groups III and V. The self-diffusivity, relative to the electrically intrinsic value, is increased in n-type Ge and decreased in p-type as expected from the dependence of $[V_{Ge}^-]$ on the Fermi level. In intrinsic Ge the best parameters for the self-diffusivity are $D_0 = 13.6\,\mathrm{cm^2/s}$ and $Q = 3.09\,\mathrm{eV}$, from *Werner* et al. [6.44], because of the wide temperature range covered (535–904 °C). The diffusivities of donor dopants (P, As, Sb) are very similar in magnitude, as are those for acceptor dopants (Al, In, Ga). The acceptor group diffusivities, however, are very close to the intrinsic self-diffusivity, whereas those for the donor group are 10^2 to 10^3 times larger. Li is a fast (interstitial) diffuser with a diffusivity exceeding the donor group diffusivities by factors of 10^7 to 10^5 between 600 and 900 °C, whereas Cu [6.45] and Au [6.46] are intermediate (dissociative) diffusers.

6.7.2 Silicon

Si stands alone due to the intensive investigations that have been lavished on it over the past 50 years. In the early days diffusion data yielded many perplexing features. Today the broad aspects are understood along with considerable detail, depending on the topic. Diffusion in Si covers many more topics than arise in any other semiconductor and it is still a very active area of R & D. It is now recognised that, apart from foreign purely interstitial species, self-interstitials, Si_i, and vacancies, V_{Si}, are involved in all diffusion phenomena. So far the best self-diffusion parameters obtained for intrinsic Si are $D_0 = 530\,\mathrm{cm^2/s}$ and $Q = 4.75\,\mathrm{eV}$ in the temperature range 855–1388 °C [6.47]. Two distinct facets of self- and dopant diffusion in Si are: (a) the diffusivity has two or three components, each with differing defect charge states; (b) the diffusivity reflects contributions from both Si_i and V_{Si} [6.2, 43, 48, 49]. Thus the Si self-diffusivity is determined by Si_i and V_{Si} mechanisms and by three separate defect charge states: neutral (0), positive (+) and negative (−). Identifying which charge state goes with which defect remains a problem. For the common dopants (B, P, As and Sb), B and P diffuse primarily via the Si_i defect, As diffuses via both Si_i and V_{Si} defects, whereas Sb diffuses primarily via V_{Si}. Two defect charge states are involved for B (0, 1+), As (0, 1−) and Sb (0, 1−), and three for P (0, 1−, 2−). The situation for Al [6.50], Ga [6.9] and In [6.51] has Si_i dominant for Al and In diffusion whereas both Si_i and V_{Si} are involved for Ga. The associated charge states are Al (0, 1+), Ga (0, 1+) and In (0). The diffusivities of the Group V donor dopants (P, As, Sb) lie close to each other and are up to a factor of ≈ 10 greater than the self-diffusivity. The acceptor dopants (B, Al, Ga, In) also form a group with diffusivities that are up to a factor of $\approx 10^2$ greater than the donor dopants. A recently observed interesting feature is that the diffusivities of B and P in intrinsic material depend on the length of the anneal time, showing an initial change until reaching a final value [6.52]. This time effect is attributed to the time needed for equilibration of the V_{Si} and Si_i concentrations at the anneal temperature.

The data presented by *Tan* and *Gösele* [6.43] show that Au, Pt and Zn are intermediate (kick-out) diffusers and that H, Li, Cu, Ni and Fe are fast interstitial diffusers. Recent evidence shows that Ir diffusion occurs via both kick-out and dissociative mechanisms [6.53]. To provide some perspective: at 1000 °C the diffusivity of H is $\approx 10^{-4}\,\mathrm{cm^2/s}$ compared to a self-diffusivity

of $8\times10^{-17}\,cm^2/s$. C and O are important impurities because, though electrically neutral, they occur in high concentrations and can affect the electrical properties. Although O occupies interstitial sites and diffuses interstitially it should be classed as an intermediate diffuser because a diffusion jump entails the breaking of two Si–O bonds. C has a diffusivity that is a little larger than those of Group III dopants: its mechanism is unresolved between the "kick-out" mode or a diffusing complex comprising a Si_i and a substitutional C.

6.7.3 $Si_{1-x}Ge_x$ Alloys

Si and Ge form a continuous range of alloys in which there is a random distribution of either element as well as a continuous variation of bandgaps. The alloys have attracted considerable interest from a device perspective and are usually prepared as epilayers on Si substrates so that the epilayer will generally be in a strained state. Diffusivity data are sparse and, in the case of dopants, limited to B, P and Sb. One might expect that the diffusivity D(Z) of dopant Z would increase continuously as x goes from 0 to 1 at any given temperature below the melting point of Ge. However, in the case of B, D(B) hardly varies for $x \lesssim 0.4$; even so, D(B) increases by a factor $\approx 10^3$ from $\approx 10^{-15}\,cm^2/s$ in traversing the composition range at 900 °C [6.54, 55]. D(P) increases by a factor of ≈ 4 for x values between 0 and 0.24, only to show a decrease at $x = 0.40$ [6.55]. Limited data suggest that D(Sb) rises continuously across the composition range, increasing by a factor $\approx 10^6$ at 900 °C [6.56]. Surface oxidation enhances D(B) and D(P), indicating that the diffusivities are dominated by a self-interstitial mechanism, whereas D(Sb) is reduced by surface oxidation, pointing to a vacancy mechanism. Compressive strain retards D(B) whereas tensile strain gives a marginal enhancement [6.55]. Compressive strain enhances D(P) and D(Sb) [6.57]. Overall, some disagreement exists between different workers about the behavior of D(Z), which may well stem from difficulties with characterizing the experimental conditions. Compositional interdiffusion has been characterized at the interface between Si and layers with $x < 0.2$ [6.58].

6.7.4 Silicon Carbide

Its large bandgap, high melting point and high dielectric breakdown strength make SiC a suitable material for devices intended for operation at high temperatures and high powers. It also has potential optoelectronic applications. Characterizing the material is complicated, as SiC occurs in a range of polytypes (different stacking sequences of close packed layers). Common polytypes are the cubic zinc blende phase 3C–SiC and the hexagonal phases 2H–SiC (wurtzite), 4H–SiC and 6H–SiC. This combination of high melting point, polytypism and variations in stoichiometry makes it difficul to measure diffusivities. Typical diffusion anneal temperatures for acceptor (B, Al, Ga) and donor (N, P) dopants are in the range 1800–2100 °C. Ab initio calculations for single vacancies and anti-sites in 4H–SiC [6.59] found the Si_C and C_{Si} anti-sites to be both neutral and therefore generally inactive (electrically and optically).The C vacancy is amphoteric with charge states ranging from 2+ to 2−. The Si vacancy is also amphoteric with charge states ranging from 1+ to 3−. Similar calculations for self-interstitials in 3C–SiC [6.60] predict divalent donor behavior for both Si and C interstitials. *Bockstedte* et al. [6.61] have calculated, using ab initio methods, the activation energies Q for self-diffusion in 3C–SiC by vacancies and self-interstitials. Generally Q is smaller for self-interstitials but the defect charge state is also an important factor. The Si vacancy is predicted to be metastable, readily transforming to the stable complex $V_C{-}C_{Si}$: the complex $V_{Si}{-}Si_C$ is unstable, reverting to V_C.

The Si and C self-diffusivities, D(Si) and D(C), respectively, were measured between 1850 and 2300 °C by *Hong* et al. ([6.62] and references therein) in both 3C–SiC and 6H–SiC. The ratio D(C)/D(Si) was ≈ 650 in 3C–SiC and ≈ 130 in 6H–SiC. N doping increased D(Si) and reduced (marginally) D(C). This behavior suggests that native acceptors are important for Si self-diffusion and that native donors are only marginally involved in determining D(C). Of particular interest is that, between the two polytypes, the self-diffusivities in 6H-SiC exceeded those in 3C–SiC by less than a factor of ≈ 3. This suggests that diffusivities are insensitive to the particular polytype. More recent measurements of D(C), between 2100 and 2350 °C, in 4H–SiC found diffusivities that were $\approx 10^5$ times smaller than the earlier results for 3C–SiC and 6H–SiC, mainly because of differences in D_0 [6.63]. There is currently no explanation for these huge differences and the question of the reliability of self-diffusivity data must be considered.

Earlier work by *Vodakov* et al. [6.64] found that the diffusivity of B in six different polytypes of SiC, excluding 3C-SiC, varied by $\leq 30\%$, not only for diffusion along the c-axis but also perpendicular to it. The diffusivities of some common dopants have been sum-

marized by *Vodakov* and *Mokhov* [6.65]. B diffusion mechanisms in 4H and 6H-SiC have been discussed by *Usov* et al. [6.66]. A recent finding is that an SiO_2 layer on the surface of 6H-SiC greatly enhances B diffusion [6.67], yielding a diffusivity of $\approx 6\times10^{-16}\,cm^2/s$ at 900 °C. This compares to a temperature of ≈ 1400 °C (extrapolated) for the same diffusivity without an SiO_2 layer. Electric fields of $\approx 10^6$ V/cm have been found in 4H/3C/4H-SiC quantum wells due to spontaneous polarization in the 4H-SiC matrix [6.68].

6.8 Diffusion in III–V Compounds

The III–V binary compounds are formed between the cations B, Al, Ga, In and the anions N, P, As and Sb. Mutual solubility gives rise to the ternaries, such as $Al_{1-x}Ga_xAs$, and to the quaternaries, such as $In_{1-x}Ga_xAs_{1-y}P_y$. The B compounds offer little more than academic interest, whereas the rest of the III–V family are important materials in both electronic and optoelectronic devices. The nitrides all have the wurtzite structure, with the remaining compounds possessing the zinc blende structure. In view of the wide range of binaries, ternaries, and so on, it is not surprising that diffusivity measurements have focused mainly on those compounds relevant to devices: essentially GaAs and GaAs-based materials. An important characteristic of these compounds is the high vapor pressures of the anion components; it is the variations in these components that lead to significant changes in levels of nonstoichiometry. This means that a proper characterization, at a given temperature, of any diffusivity must specify the doping level and the ambient anion vapor pressure during the anneal: the latter determines native defect concentrations in intrinsic samples, and both factors have equal importance in controlling the concentrations under extrinsic conditions. On both the anion and the cation sublattices, the possible native point defects are the vacancy, the self-interstitial and the anti-site and all can occur in one or more charge states.

6.8.1 Self-Diffusion

Self-diffusivity data are limited to the Ga and In compounds [6.35, 69], and even here systematic measurements are restricted to GaAs [6.43, 69] and GaSb ([6.70] and references therein). For GaAs, early evidence (based largely on CID in AlGaAs structures) concluded that the Ga self-diffusivity D(Ga) was determined by the triply ionized Ga vacancy V_{Ga}^{3-} and doubly ionized Ga interstitial Ga_i^{2+}. More recent and direct measurements of D(Ga) in Ga isotope heterostructures identified the three vacancy charge states V_{Ga}^{2-}, V_{Ga}^{1-} and V_{Ga}^{0} as being responsible for D(Ga) in intrinsic and lightly doped GaAs; the possibility remains that V_{Ga}^{3-} and Ga_i^{2+} could dominate at high doping levels. Between 800 and 1200 °C the Arrhenius parameters for D(Ga) are $D_0 = 0.64\,cm^2/s$ and $Q = 3.71$ eV in intrinsic GaAs under a partial As_4 vapor pressure of ≈ 1 atm. The situation for As self-diffusion is less clear, but the evidence points to the dominance (in the diffusion process) of the neutral As interstitial over the As vacancy (the supposedly dominant native defect, the As anti-site, is not involved). Data have been obtained for both Ga and Sb self-diffusion in intrinsic GaSb under Ga- and Sb-rich conditions. There is a conflict between the results obtained with bulk material and those from isotope heterostructures (see [6.70] and references therein). *Shaw* [6.70] concluded that the defects involved in Ga self-diffusion were the Frenkel pair Ga_iV_{Ga} and V_{Ga} even though the Ga anti-site Ga_{Sb} appears to be the dominant native defect. Two parallel mechanisms were also identified for Sb self-diffusion, namely one due to the defect pair Sb_iV_{Ga} and the second due to either to the mixed vacancy pair $V_{Ga}V_{Sb}$ or to the triple defect $V_{Ga}Ga_{Sb}V_{Ga}$. Reliable results for D(Ga) in intrinsic GaP under a partial vapor pressure (P_4) of ≈ 1 atm are also available [6.71]: between 1000 and 1190 °C the Arrhenius parameters for D(Ga) are $D_0 = 2.0\,cm^2/s$ and $Q = 4.5$ eV. Data on the effects of doping and changing partial pressure are lacking.

6.8.2 Dopant Diffusion

Most of the data on dopant diffusion in the III–Vs refer to GaAs [6.35], notably for Be [6.72], Cd [6.69], C, Si, S, Zn and Cr [6.43]. The singly ionized acceptors Be, Zn and Cd (which occupy Ga sites) and the singly ionized donors C and S (which occupy As sites) all diffuse via the kick-out mechanism. The native interstitials involved are Ga_i^{2+} and As_i^0, apart from Be where the data are best accounted for in terms of the singly ionized interstitial Ga_i^{1+}. Si is an amphoteric dopant and at low concentrations it predominantly occupies Ga sites as a singly ionized donor Si_{Ga}^{1+}. At high concentrations compensation starts to occur due to increasing occupancy as a singly ionized acceptor on As sites. At low

concentrations Si_{Ga}^{1+} diffusion is attributed to a vacancy mechanism (V_{Ga}^{3-}). Cr sits on Ga sites and is a deep-level acceptor dopant important in the growth of high resistivity GaAs. Depending on circumstances, it can diffuse by either the kick-out or the Frank–Turnbull mechanism. The creation of extended defects in the diffusion zone by Zn in-diffusion in GaAs is a well-established feature. The same feature has also been found by *Pöpping* et al. [6.73] for Zn in-diffusion in GaP. They further concluded that Zn diffuses via the kick-out process in GaP through the involvement of either Ga_i^{1+} or Ga_i^{2+}.

6.8.3 Compositional Interdiffusion

The III–V binaries, ternaries and quaternaries are the bases for the fabrication of numerous quantum well and superlattice structures. CID is clearly an issue in the integrity of such structures. The general situation in which the cation and anion sublattices in each layer can contain up to four different components with concentrations ranging from 0 to 100% presents an impossibly complex problem for characterizing diffusion behavior with any rigour. The role of strain in the layers must also be considered a parameter. As a consequence, CID studies have been limited to simpler structures, primarily GaAs-AlAs and GaAs-AlGaAs with interpretations in terms of known diffusion features in GaAs [6.43]. Doping is an important ingredient of these multilayer structures and it was soon discovered that the acceptors Be, C, Mg, Zn and the donors Si, Sn, S, Se and Te could all cause complete disorder of the structure through enhancement of the CID process on either or both sublattices [6.43, 74]. An interesting exception, however, is found in GaAs-GaAsSb, where either Si or Be reduce CID. Two generally accepted reasons for these dopant effects are: (i) the Fermi-level effect in which the dopant (acceptor/donor) concentration is high enough to make the semiconductor extrinsic so that the concentrations of native (donor/acceptor) defects are increased; (ii) if the dopant diffuses by the kick-out mechanism then in-diffusion will generate a local excess of the native self-interstitial. Clearly (i) operates for dopants incorporated during growth or by subsequent in-diffusion, whereas (ii) is restricted to in-diffusion. Either way the increase in the local native defect concentration(s) leads to a direct enhancement of CID. In the case of GaAs-GaAsSb, cited above, Si will also decrease the concentrations of native donors such as native anion vacancies, which would have a direct impact on and reduction of CID on the anion sublattice. On the other hand, Be should increase native donor concentrations and therefore give enhanced CID of the anions, contrary to observation. Overall, the general features of the dopant-induced disordering process seem to be understood but problems still remain. *Harrison* [6.74] has commented on the approximations commonly made when extracting quantitative information from CID data. The demands of III–V device technology present increasing complexity when attempting to understand the physical processes involved, so that recourse to empirical recipes is sometimes needed. This is illustrated by structures comprising GaInNAs quantum wells with GaAs barriers, all enclosed within AlAs outer layers, whose optoelectronic properties can be improved by the judicious choice of time/temperature anneals [6.75].

6.9 Diffusion in II–VI Compounds

Interest in II–VI materials pre-dates that in the III–Vs because of their luminescence properties in the visible spectrum, which, based on powder technology, resulted in the application of the bigger bandgap materials (such as ZnS) as phosphors in luminescent screens. The development of crystal growth techniques extended interest in the optoelectronic properties of the wider family of II–VI binary compounds formed between the group II cations Zn, Cd and Hg and the group VI anions S, Se and Te. As with the III–Vs, ternary and quaternary compounds are readily formed. The ternary range of compositions $Hg_{1-x}Cd_xTe$ has proved to be the most important family member because of their unique properties and consequent extensive exploitation in infra-red systems. ZnS, CdS and CdSe crystallize in the wurtzite structure, whereas the remaining binaries have the zinc blende structure. The native point defects that can occur are similar to the III–Vs; namely, vacancies, self-interstitials and anti-sites for the cation and anion sublattices. Recent interest has expanded to include the cations Be, Mg and Mn, usually in ternary or quaternary systems. A distinctive feature of atomic diffusion in the II–VI compounds is the much higher diffusivities relative to those in the Group IV and III–V semiconductors. The relative ease of measurement has ensured that much more self- and dopant diffusion data are available compared to the III–Vs. A further difference is that both cation and anion equilibrium vapor pressures are signif-

icant compared to the III–Vs, where the cation vapor pressures are negligible. Unless otherwise stated, the material in the following sections is drawn from the reviews by *Shaw* [6.6,76,77] and by *Capper* et al. [6.78].

6.9.1 Self-Diffusion

Where the anion self-diffusivity D_A has been measured as a function of the ambient anion or cation partial pressure in undoped material (ZnSe, CdS, CdSe, CdTe and $Hg_{0.8}Cd_{0.2}Te$), a consistent pattern of behavior has emerged: in traversing the composition range from anion-rich to cation-rich, D_A is inversely proportional to the rising cation vapor pressure, P_C, until close to cation saturation, when D_A starts to increase with P_C. Strong donor doping in anion-rich CdS and CdSe had no effect on D_A. This evidence points to either a neutral anion interstitial or a neutral anion antisite/anion vacancy complex as the diffusion mechanism over most of the composition range, changing to an anion vacancy mechanism as the cation-rich limit is approached.

The situation for cation self-diffusion proves to be more complicated due to the different variations of the cation self-diffusivity D_C with P_C across the compounds. In undoped ZnSe, ZnTe, CdTe and $Hg_{0.8}Cd_{0.2}Te$ (above $\approx 300\,°C$), D_C is largely independent of P_C across the composition range. Such an independence excludes native point defect diffusion mechanisms and (excluding nondefect mechanisms) points to self-diffusion via neutral complexes such as a cation interstitial/cation vacancy or a cation vacancy/anion vacancy pair. Donor or acceptor doping increases D_C, indicating the involvement of ionized native defects or complexes. The Arrhenius parameters for Zn self-diffusion in undoped ZnSe above 760 °C are $D_0 = 9.8\,cm^2/s$ $Q = 3.0\,eV$ and those for Hg in undoped $Hg_{0.8}Cd_{0.2}Te$ above 250 °C are $D_0 = 3.8 \times 10^{-3}\,cm^2/s$ and $Q = 1.22\,eV$. In the case of undoped ZnS, CdS, CdSe and HgTe, D_C generally varies with P_C across the composition range. The simplest variations are found in CdSe and HgTe. In CdSe, D_C can be attributed to the parallel diffusion of singly (1+) and doubly (2+) ionized Cd self-interstitials. D_C in HgTe initially falls with P_C and then increases when crossing from anion-rich to cation-rich material, corresponding to diffusion by a singly ionized (1−) Hg vacancy and by a singly ionized (1+) Hg interstitial respectively. The behavior patterns in ZnS and CdS, however, present substantial problems in their interpretation: donor doping can also enhance D_C, pointing to the participation of an ionized native acceptor mechanism.

6.9.2 Chemical Self-Diffusion

Changes in the electrical conductivity or conductivity type caused by step changes to P_C in sample anneals have been used to characterize the change in level of nonstoichiometry through the chemical self-diffusivity, D_Δ, in CdS, CdTe and $Hg_{0.8}Cd_{0.2}Te$. D_Δ obviously describes the diffusion of one or more ionized native defects, but in itself it does not identify the defect(s). In CdS and CdTe, D_Δ is attributed to the singly ionized (1+) and/or doubly ionized (2+) Cd interstitial; in CdTe, depending on the temperature, D_Δ exceeds D_C by a factor 10^5 to 10^6. Modeling based on the simultaneous in-diffusion and out-diffusion of doubly ionized cation interstitials (2+) and vacancies (2−) gives a satisfactory quantitative account of type conversion (p → n) in $Hg_{0.8}Cd_{0.2}Te$ [6.7].

6.9.3 Dopant Diffusion

Although much information on dopant diffusion is available, it is mainly empirical and it is not uncommon for a dopant diffusivity to be independent of dopant concentration (as revealed by an *erfc* profile – a constant diffusivity for a given diffusion profile) under one set of conditions only to give profiles which cannot be characterized by single diffusivities when the conditions are changed. Equally, the variation of a dopant diffusivity with P_C may differ at different temperatures. A further difficulty when attempting to identify a diffusion mechanism is that the local electroneutrality condition is usually not known with any certainty due to significant concentrations of various ionized native defects. A good illustration of the problems encountered is provided by In diffusion in $Hg_{0.8}Cd_{0.2}Te$, where diffusion of the singly ionized (1−) pair $In_{Hg}V_{Hg}$ can account for some of the diffusion features. Some dopants, however, can present clear-cut diffusion properties which permit a well-defined interpretation. The diffusion of As in $Hg_{0.8}Cd_{0.2}Te$ is one such case [6.79]. All of the observed features of D(As) are accounted for on the basis that: (i) As occupies both cation and anion lattice sites as singly ionized donors (1+) and acceptors (1−) respectively; (ii) only the ionized donor is mobile and diffuses by a vacancy mechanism on the cation sublattice; (iii) the diffusion sample is electrically intrinsic throughout, so the As concentration is always less than the intrinsic free carrier concentration.

6.9.4 Compositional Interdiffusion

Empirical information, based on bulk material, exists for CID in the following ternaries: (ZnCdHg)Te, (ZnCd)Se, (ZnCdHg)SeTe, (ZnCd)SSe, CdSeTe, ZnCdS, HgCdTe and CdMnTe. It might be expected that features evident in the binaries, such as donor doping enhancing the cation diffusivity but having no effect on that of the anion, and the anion diffusivity increasing (decreasing) with anion (cation) vapor pressure across most of the composition range, would continue to be seen. This means that in a ternary or quaternary system, donor doping will enhance CID on the cation sublattice, but not on the anion sublattice, and annealing under a high (low) anion (cation) vapor pressure will enhance CID on the anion sublattice. This effect of the anion vapor pressure has been confirmed in CdSSe and CdSeTe and more recently in ZnSSe/ZnSe superlattices [6.80]. In (donor) doping has also been found to enhance the CID of the cations in CdMnTe [6.81], as has N (acceptor) doping in ZnMgSSe/ZnSSE superlattices [6.82]. The consequences of doping on CID in the II–VIs are obviously very similar to the III–V situation.

6.10 Conclusions

The first step in a diffusion investigation is to collect empirical data, which then leads to the second step where experiments can be designed to study the effects of the Fermi level (through the background doping level), of the ambient atmosphere (such as oxidizing, inert or vapor pressure of a system component) and of the sample structure (such as an MBE layer or a quantum well). The third step is to identify the diffusion mechanism and the associated defects using the experimental results in conjunction with the results from first-principles calculations of defect formation energies and their activation energies for diffusion. Clarification of the active processes involved can be gained by numerical modeling (see *Noda* [6.83]). These data then provide the basis for the development of process simulators and defect engineering in which the concentrations and spatial distributions of host atoms, dopants and defects are organized according to requirement. Most progress towards achieving this ideal scenario has been made in Si and to a lesser extent in GaAs and $Hg_{0.8}Cd_{0.2}Te$. The reality elsewhere is that the boundaries between the steps are blurred, with the third step often being undertaken with inadequate experimental information. Much work remains to be done in order to master our understanding of diffusion processes in semiconductors.

6.11 General Reading and References

General background material for diffusion in semiconductors can be found in *Shaw* [6.5], *Tuck* [6.1], *Abdullaev* and *Dzhafarov* [6.11] and *Tan* et al. [6.8]. More specific accounts are given by *Fair* [6.9] and *Fahey* et al. [6.84] for Si, by *Frank* et al. [6.3] for Si and Ge, by *Tan* and *Gösele* [6.43] for Si, Ge and GaAs, by *Tuck* [6.35] for the III–Vs and by *Shaw* [6.6, 77] for the II–VIs. *H in Semiconductors II* (1999) ed. by N. H. Nickel (*Semiconductors and Semimetals*, 61, Academic, San Diego) provides a recent account of H in semiconductors. The volumes in the EMIS Datareviews Series (IEE, Stevenage, UK) cover all of the important semiconductors. The series *Defects and Diffusion in Semiconductors* ed. by D. J. Fisher (Trans Tech., Brandrain 6, Switzerland) offers an annual and selective retrospective of recent literature.

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