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FAST DIFFUSION IN SEMICONDUCTORS

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INTRODUCTION

Elements diffusing in semiconductors are frequently classified as "slow" or "fast" diffusers (1). Slow diffusers have diffusion coefficients reasonably close to those of self-diffusion, whereas fast diffusers have diffusion coefficients that are many orders of magnitude larger than those of slow diffusers for a given temperature. In Figure 1 this classification is exemplified for the diffusion of various elements in crystalline silicon. The large difference in the diffusion rates of fast and slow diffusers derives mainly from their different diffusion mechanisms, which in turn are closely related to their incorporation in the semiconductor lattice. Slow diffusers, such as the common group III and group V dopants, are substitutionally dissolved and require intrinsic point defects (vacancies and/or self-interstitials) for their diffusion process, whereas fast diffusers, such as Cu, Li, H, or Fe, are predominantly interstitially dissolved and move by jumping from interstitial site to interstitial site (Figure 2) without requiring the presence of intrinsic point defects. Since most interstitially dissolved elements are only weakly bound to the lattice, the jump process itself does not involve breaking bonds as in the case of substitutionally dissolved elements. There are also elements with diffusion coefficients between the extreme fast and slow diffusers, such as oxygen or gold in silicon. Oxygen is interstitially dissolved, but forms fairly strong bonds with the two neighboring silicon atoms. These bonds are broken during the jump from interstitial site to interstitial site (Figure 3), which slows down the diffusion process (2–4). Gold in silicon is an example of an element that is predominantly substitutionally dissolved but diffuses interstitially (5–6). The corresponding substitutional-interstitial diffusion mechanism (7, 8) also plays

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an important role in the diffusion of dopants and impurities in III–V compounds and is considered in the category of fast diffusion in this article.

An enormous amount of data on slow and fast diffusers has been compiled in the literature (1, 9–21) especially for the technologically important crystalline semiconductors: silicon (1, 9, 11–19), germanium (1, 11, 18), and the III–V compounds (10, 11, 14, 20, 21). These papers also contain ample information on experimental techniques for measuring diffusion profiles. The purpose of this article, rather than to give a summary

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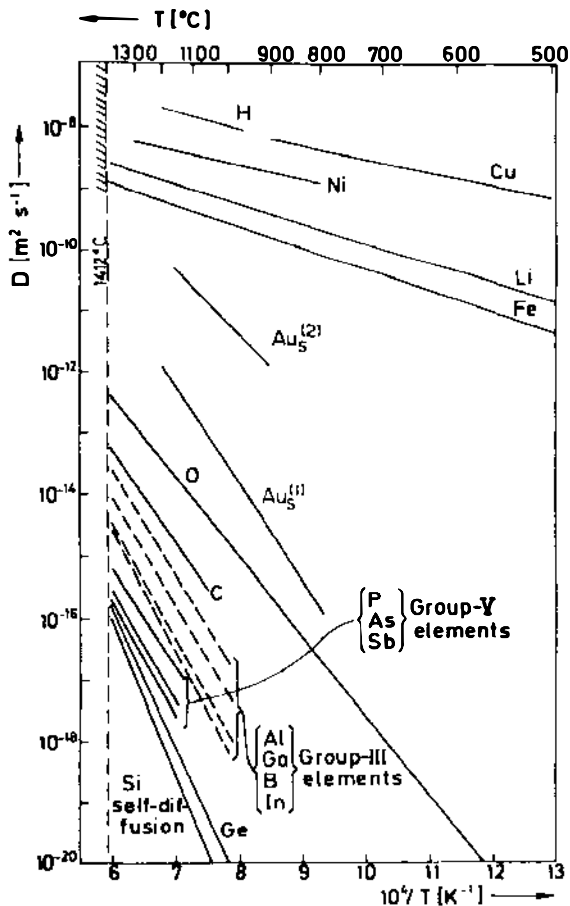

Figure 1 Diffusivities of various elements in silicon as a function of inverse absolute temperature [partly from (19)]. $Au_s^{(1)}$ and $Au_s^{(2)}$ refer to effective diffusivities of substitutional gold in dislocation-free and highly dislocated silicon, respectively.

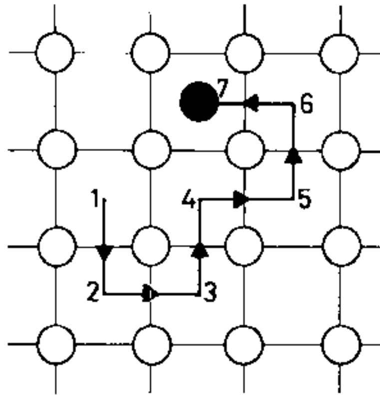

Figure 2 Direct interstitial diffusion mechanism, schematically; Foreign interstitial atom (●) jumps from interstitial site 1 to 2, from 2 to 3, etc (19).

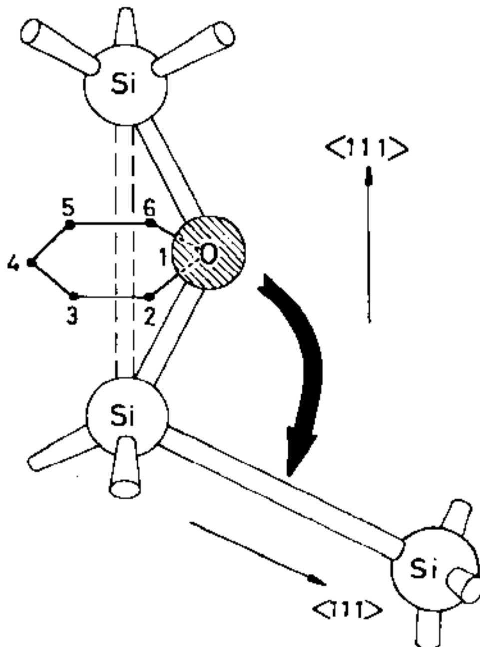

Figure 3 Bond-centered configuration of the oxygen interstitial in the silicon lattice. The points labeled 1–6 mark equivalent positions of the O atom (19).

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of all this easily accessible information, is to concentrate on specific examples of fast diffusion in crystalline semiconductors in which either significant progress has been made or obvious questions have emerged over the last few years. Discussion of examples is limited to silicon, germanium, and the III–V compounds GaAs and InP although many of the concepts discussed may—in an appropriately modified form—be applied to other semiconductors, such as the II–VI compounds.

In the elemental semiconductors silicon and germanium, the main technological interest concerning diffusion is the diffusion of group III and group V elements, which are used as p- and n-type dopants in the fabrication of electronic devices. Fast diffusers have been investigated mainly because of their role as deep-level contaminants that enter the semiconductor during device processing. These contaminants can either directly reduce the minority carrier lifetime or they can precipitate in the electrically active device region and hence influence the device behavior negatively and often catastrophically. Only a few fast diffusers have been used purposely for fabricating or improving devices. Examples are lithium-drifted detectors, the use of interstitial oxygen to induce gettering centers in silicon, and the use of hydrogen for passivating electrically active defects. Gold and platinum act as efficient electron-hole recombination centers in silicon and have therefore been diffused into devices to improve their frequency behavior.

In III–V semiconductors, not only do typical impurities, such as Cr or Fe in GaAs, diffuse via a substitutional-interstitial mechanism but also some of the most common dopants such as zinc (10, 22, 23) or beryllium (24, 25). All of them must be considered in the category of fast diffusers. Instead of discussing the rather well understood direct interstitial diffusion of Figure 2 (11), I first elaborate on the controversial role of interstitial molecules in the difusion of oxygen and hydrogen in silicon and then concentrate on fast diffusion via substitutional-interstitial mechanisms in silicon, germanium, and some III–V compounds.

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INTERSTITIAL DIFFUSION WITH MOLECULE FORMATION

Oxygen in Silicon

Oxygen precipitates are frequently used in Czochralski-grown silicon to induce gettering sites in the bulk region of wafers in order to remove undesirable metallic contaminants from the electrically active device area near the surface. [This is called intrinsic gettering (26–28).] Oxygen is dissolved interstitially in silicon and is electrically inactive in this position (Figure 3). Its diffusivity D_i under thermal equilibrium conditions is domi-

nated by the process of jumping from interstitial site to interstitial site. The corresponding diffusion coefficient, given in Figure 1 and Figure 4 from the melting point to 250°C (4, 29–32), spans one of the largest ranges in the diffusivity in the area of solid-state diffusion. The diffusivity at the lower temperatures was measured via the change in stress-induced dichroism due to the reorientation associated with single diffusion jumps (4, 30).

Around 450°C interstitial oxygen forms electrically active agglomerates, which have been termed "thermal donors" (33–35). It has been noticed frequently that D_i is much too low to account for the agglomeration process (36–39). Based on thermal donor measurements at the surface of

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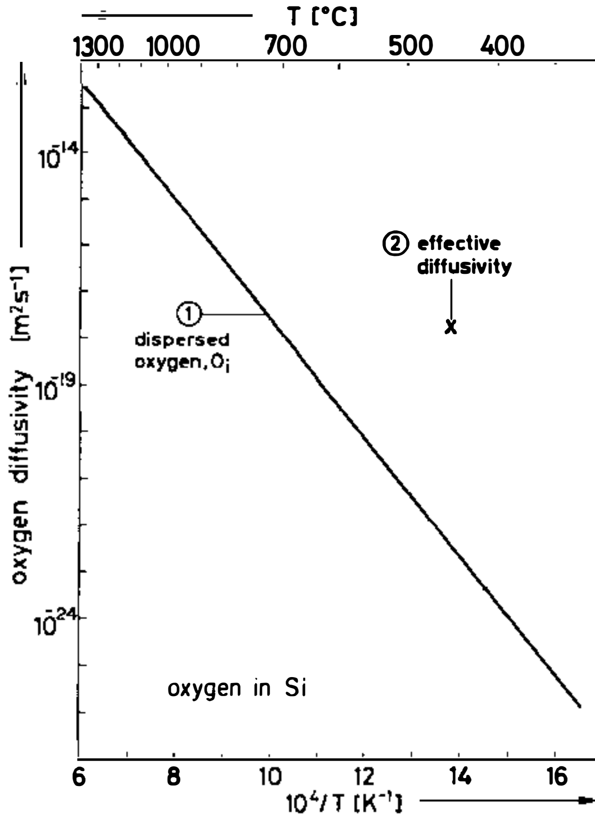

Figure 4 Diffusivity of oxygen in silicon as a function of inverse absolute temperature for isolated oxygen interstitials O_i. The cross indicates the high effective diffusivity found for out-diffusion (40, 47).

silicon wafers, Gaworzewski & Ritter (40) concluded that the diffusivity governing long-range transport of oxygen is several orders of magnitude higher than D_i derived from single reorientation/diffusion jumps as indicated in Figure 4. Precipitate growth experiments also required a strongly enhanced long-range oxygen diffusivity (41). Two types of diffusion models have been put forward to explain the fast long-range diffusion of oxygen. In the first model, fast diffusing complexes of intrinsic point defects (vacancies and/or self-interstitial) and interstitial oxygen are responsible for the high effective diffusivity (e.g. 38, 42). Specifically designed experiments could not confirm this suggestion although it cannot be ruled out conclusively (39, 43). The second model suggests the formation of O_2 molecules via the reaction (37)

$$O_i + O_i \underset{k_d}{\overset{k_a}{\rightleftarrows}} O_2, \qquad 1.$$

where O_i stands for interstitial oxygen and k_a and k_d for the appropriate association and dissociation constants, respectively. The O_2 molecules are assumed to diffuse extremely fast since they are not directly bound to the silicon lattice atoms as is O_i. The effective long-range diffusivity of oxygen is then expected to be

$$D_{eff} = (D_i C_i + 2D_2 C_2)/(C_i + 2C_2), \qquad 2.$$

where D_i is the O_i diffusivity, C_i its concentration, and D_2 and C_2 the corresponding quantities for the O_2 molecules. Equation 2 reduces for dynamical equilibrium according to Equation 1 and for sufficiently large D_2C_2 to $2D_2C_2/C_i$. If the association reaction is diffusion controlled, as indicated by experimental results on the loss of interstitial oxygen during thermal donor formation (44–46), D_{eff} may be expressed as

$$D_{eff} \approx 16\pi D_2 D_i r_i C_i / k_d, \qquad 3.$$

where k_a is assumed to be $8\pi D_i r_i$ and r_i is the reaction radius for the Equation 1.

Recent work using Secondary Ion Mass Spectroscopy (SIMS) by Lee & Fellinger (47) confirmed the existence of a fast long-range diffusion process of oxygen in silicon. An example of oxygen out-diffusion from a silicon wafer at 500°C is shown in Figure 5. The calculated effective diffusivity of about 3×10^{-14} cm^2 s^{-1} falls in the range determined by Gaworzewski & Ritter (40). Lee & Fellinger (47) also measured the diffusion of implanted oxygen isotopes and observed an unexpected diffusion tail that indicated strongly enhanced diffusion in the temperature range of thermal donor formation (Figure 6). The depth of the tail increased with decreasing temperature. The tail is due to the dissociation

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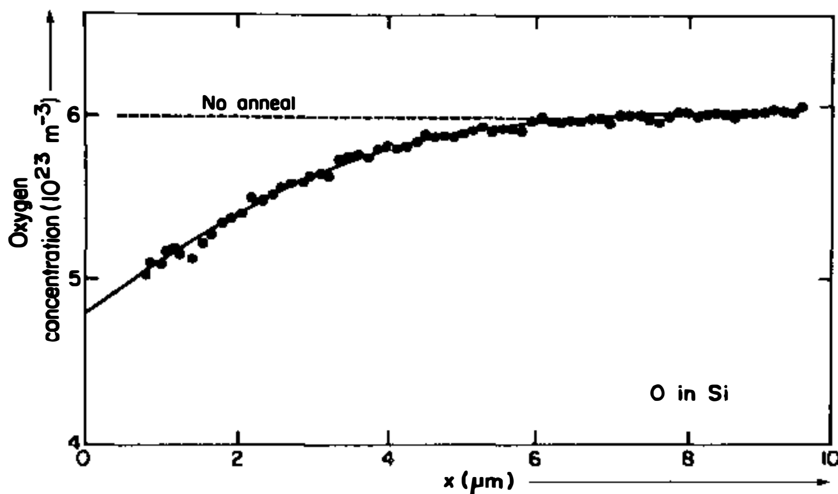

Figure 5 Oxygen concentration profile in silicon annealed at 500°C for 17 days. The solid curve is the best fit to data using a constant effective diffusivity (47).

of a fast-diffusing species containing oxygen. In terms of the O_2 model, the O_2 diffusion may be described by (47)

$$\partial C_2/dt = D_2\partial^2 C_2/\partial x^2 \quad k_d C_2 + k_a C_i^2. \qquad 4.$$

If outside the implanted region the association term is neglected and steady state is assumed, the equation

$$C_i = 2tC_2^0 k_d \exp[-(k_d/D_2)^{0.5}x] \qquad 5.$$

holds, where C_2^0 is the O_2 concentration in the implanted region. An equation analogous to Equation 5 may be derived for any fast-diffusing dissociating complex containing oxygen. The experimental data are well described by Equation 5. The measured k_d/D_2 values may be used to calculate D_{eff} according to Equation 3 and lead to a good agreement with the D_{eff} values measured in the actual out-diffusion experiments (47).

Equation 3 predicts that D_{eff} should linearly increase with the interstitial oxygen concentration C_i. Out-diffusion experiments of silicon wafers with different oxygen contents resulted in a rather unsystematic scatter of D_{eff} values with no noticeable correlation to the oxygen concentration (48, S.-T. Lee, private communication). Since during the out-diffusion experiments oxygen precipitation is occurring, which strongly depends on the thermal history of the sample, it may well be that the precipitation process influ-

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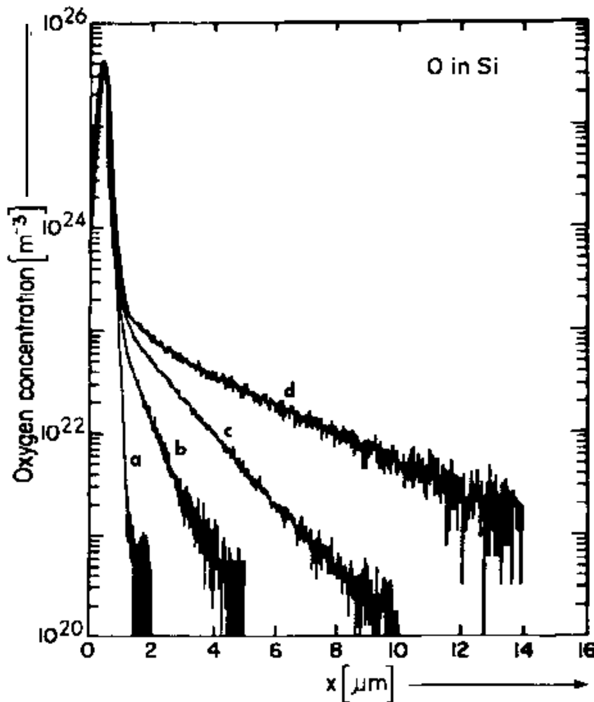

Figure 6 Oxygen-18 concentration profile in silicon: (*a*) as implanted, and annealed for 67 hours at (*b*) 525°C, (*c*) 480°C, and (*d*) 425°C (47).

ences D_{eff} by the absorption and incorporation of O_2 molecules into oxygen precipitates.

The presence of an effective long-range diffusivity of oxygen in silicon that is much higher than the diffusivity of single O_i is now well established (39, 47). An explanation in terms of fast-diffusing oxygen molecules is tempting, but further experiments are required to prove or disprove the O_2 model. This model may also hold for oxygen in germanium where similar thermal donor phenomena occur (49). Nitrogen diffusion in silicon has also been suggested to proceed via molecules (50), but only recently clear-cut experimental proof of their existence has become available (50a).

Hydrogen in Silicon

Hydrogen can be introduced into semiconductors during crystal growth, by direct implantation, by exposure to a hydrogen-containing plasma, or by chemical reaction at the surface (51). The principal interest in hydrogen in crystalline semiconductors results from its ability to passivate the elec-

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trical activity of dangling or defective bonds, although it can also deactivate shallow and deep donor and acceptor levels in elemental and compound semiconductors. Excellent review articles are available on hydrogen in semiconductors and its diffusion behavior (48, 52, 53). Therefore, I only comment briefly on the diffusion of hydrogen in silicon since it appears to involve molecules also but in a manner directly opposite to that of oxygen in silicon.

Hydrogen in silicon is assumed to diffuse in the form of unbound atomic hydrogen that may be present in a neutral or positively charged form. The diffusivity of hydrogen in silicon has been measured by Van Wieringen & Warmoltz (54) in the temperature range 970–1200°C. The results are included in Figure 1. At temperatures between room temperature and 700°C hydrogen diffusivities much lower than those extrapolated from the high temperature data have been measured. Corbett and coworkers (52, 55, 56) rationalized this observation by suggesting that atomic hydrogen, H_i, forms interstitially dissolved hydrogen molecules, H_2, according to a reaction analogous to Equation 1. Based on quantum mechanical calculations they assume that H_2 is essentially immobile, which is just opposite to what has been assumed for O_2 molecules (37). The resulting effective diffusivity of hydrogen is $D_i C_i / C_T$ where D_i is the diffusivity of interstitial atomic hydrogen, C_i its concentration, and C_T the total hydrogen concentration, which at low temperatures may essentially consist of immobile hydrogen molecules and also includes hydrogen trapped at various trapping centers. Analogous considerations hold for hydrogen diffusion in germanium (51, 52, 57). As in the case of oxygen the existence of hydrogen molecules in silicon and germanium has not been proven experimentally.

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SUBSTITUTIONAL-INTERSTITIAL DIFFUSION

Basic Mechanisms

GENERAL CONSIDERATIONS A number of elements in semiconductors are dissolved predominantly substitutionally (A_s), but their movement is accomplished by the fast diffusion of A-atoms in interstitial form (A_i) (1, 10, 22). The changeover of A-atoms from interstitial sites to substitutional sites requires either vacancies (V) or self-interstitials (I). If all species are uncharged then the changeover reaction involving vacancies is described by

$$A_i + V \rightleftarrows A_s \qquad 6.$$

and is termed the Frank-Turnbull mechanism (1, 7, 58). The analogous reaction involving self-interstitials,

$$A_i \rightleftarrows A_s + I, \qquad 7.$$

has been termed the kick-out mechanism (8). Both mechanisms are schematically indicated for an elemental semiconductor in Figure 7. In the case of silicon, the recognition that self-interstitials can be involved in a substitutional-interstitial diffusion mechanism led to a major advance in our understanding of the diffusion of these elements and also of the mechanism of self- and dopant diffusion (19).

The diffusion via Equation 6 may be described by three appropriate diffusion equations for A_i, A_s, and V. If necessary, the diffusion equation for vacancies should also include a term for the generation or absorption of vacancies at dislocations (8). Analogous differential equations hold for the kick-out mechanism (8, 15). Instead of discussing in detail the solution of these equations (19), I derive in a simplified manner (following the treatment in Ref. 59) the expressions for describing the diffusion behavior of elements migrating by the Frank-Turnbull or the kick-out mechanism and apply this knowledge to the diffusion of Au, Pt, Ni, Zn, S, and C in silicon, and Cu in germanium. For this purpose the most simple example of in-diffusion from a source of A at the surface into a dislocation-free crystal is considered.

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EFFECTIVE DIFFUSION COEFFICIENTS FOR THE FRANK-TURNBULL MECHANISM

The actual movement of the element A is accomplished by A_i moving with the diffusivity D_i. The diffusivity of A_s via a direct exchange with vacancies or self-interstitials is neglected. Within the framework of the

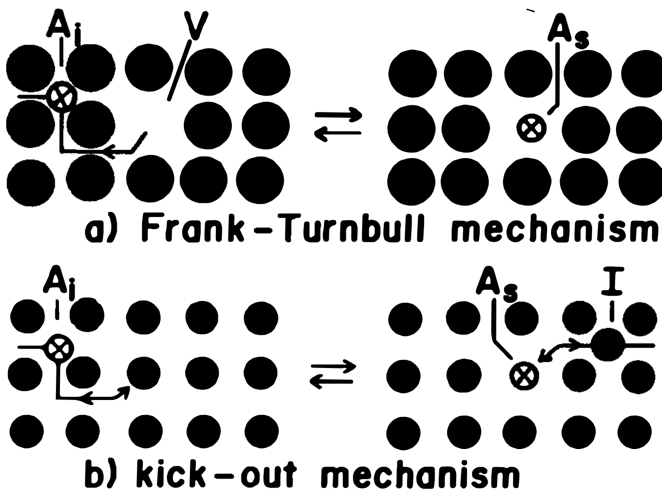

Figure 7 Frank-Turnbull and kick-out mechanism, according to (59).

Frank-Turnbull mechanism, the incorporation of an A atom as A_s is associated with the consumption of a vacancy. If local equilibrium prevails then the concentrations of the various species are related by

$$C_i C_V / C_s = C_i^{eq} C_V^{eq} / C_s^{eq}, \quad 8.$$

where C_i, C_V, and C_s refer to the actual concentrations of A_i, V, and A_s and C_i^{eq}, C_V^{eq}, and C_s^{eq} to their respective thermal equilibrium concentrations. Activity coefficients deviating from unity are not considered in this overview (23). The incorporation rate of A_s and consequently the effective diffusivity D_{eff} of A_s is determined by the slower process of either supplying A_i from the surface or establishing the thermal equilibrium concentration of vacancies. If the supply of A_i from the surface is the slower process, then the vacancy concentration C_V is close to its equilibrium value C_V^{eq}. Based on Equation 8 and with $C_i^{eq} \ll C_s^{eq}$, the effective A_s diffusivity is then approximately given by (5, 7, 12)

$$D_{eff}^{(i)} \simeq D_i C_i^{eq} / C_s^{eq}. \quad 9.$$

When the supply of vacancies from the surface (in dislocation-free material) limits the incorporation of A_s, then the in-diffusion of A_s with an effective diffusivity $D_{eff}^{(V)}$ is governed by the flux balance equation

$$D_{eff}^{(V)} \partial C_s / \partial x = D_V \partial C_V / \partial x, \quad 10.$$

where D_V is the vacancy diffusivity (59). With $C_i = C_i^{eq}$ the effective diffusivity becomes (5, 7, 19)

$$D_{eff}^{(V)} = D_V C_V^{eq} / C_s^{eq}. \quad 11.$$

Both effective diffusion coefficients do not depend on the concentration C_s itself. Therefore in both cases a complementary error function-(erfc) type profile is expected for constant surface concentration of A (case D = constant in Figure 8). The parameter R_V, which determines which of the two diffusion coefficients is applicable, reads $D_V C_V^{eq} / (D_i C_i^{eq})$. For $R_V \gg 1$ Equation 9 holds and for $R_V \ll 1$ Equation 11. For known C_s^{eq} the quantity $D_{eff}^{(V)} C_s^{eq}$ allows one to determine which of the two cases is realized by comparing this quantity with the self-diffusion coefficient, $D_V C_V^{eq}$, measured by other means (19). If it coincides with $D_V C_V^{eq}$ then the case of Equation 11 is fulfilled. For Equation 9 to hold, $D_{eff}^{(V)} C_s^{eq}$ must be smaller than $D_V C_V^{eq}$ in dislocation-free material. In highly dislocated material, $C_V = C_V^{eq}$ and therefore Equation 9 holds even if $R_V \ll 1$. Intermediate dislocation densities may lead to more complicated concentration profiles (60).

EFFECTIVE DIFFUSION COEFFICIENTS FOR THE KICK-OUT MECHANISM In the

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case of the kick-out mechanism, the incorporation of an A atom as A_s is associated with the generation of a self-interstitial. The equation analogous to Equation 8 now reads

$$C_i/(C_s C_I) = C_i^{eq}/(C_s^{eq} C_I^{eq}), \quad 12.$$

and the parameter R_I analogous to R_V is $D_I C_I^{eq}/(D_i C_i^{eq})$, where D_I denotes the diffusivity of self-interstitials (8, 19). For $R_I \gg 1$ the in-diffusion of A_i is much slower than the out-diffusion of the generated self-interstitials to the surface (in dislocation-free material) and Equation 9 also holds for this case. For $R_I \ll 1$ the incorporation of A_s is limited by the out-diffusion of self-interstitials to the surface. The corresponding effective diffusivity $D_{eff}^{(I)}$ of A_s follows from the flux balance equation

$$D_{eff}^{(I)} \partial C_s/\partial x = -D_I \partial C_I/\partial x, \quad 13.$$

and Equation 12 as

$$D_{eff}^{(I)} = [D_I C_I^{eq}/C_s^{eq}](C_s^{eq}/C_s)^2, \quad 14.$$

which, contrary to $D_{eff}^{(V)}$, strongly depends on the local A_s concentration C_s (8, 19). If this case is fulfilled in a particular material, it can easily be recognized by the specific profile shape, examples of which will be shown later for Au and Pt in silicon (case $D \propto C^{-2}$ in Figure 8). Again, for high dislocation densities local intrinsic point defect equilibrium ($C_I = C_I^{eq}$) is established and Equation 9 holds. For intermediate dislocation densities more complicated concentration profiles result. In this case the increase of C_s with time is different for the Frank-Turnbull and the kick-out

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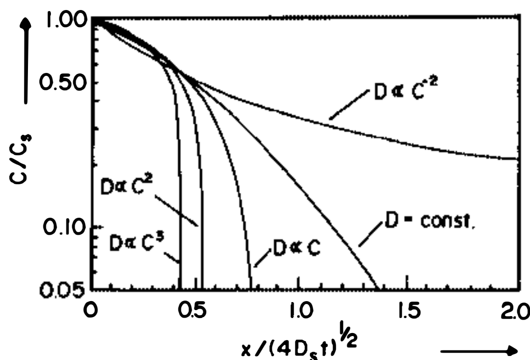

Figure 8 Normalized diffusion profiles for different concentration dependencies of the effective diffusivity D. C_s and D_s refer to the concentrations and diffusivities at the surface, respectively (59).

mechanism and also allows one to distinguish between the two mechanisms (8, 19).

If both vacancies and self-interstitials are present as in silicon and if the Frank-Turnbull and the kick-out mechanism are operating simultaneously, then the effective diffusivity (Equation 9) holds for $(R_I + R_V) \gg 1$, whereas for the opposite condition, an effective A_s diffusivity combined from Equations 11 and 14,

$$D_{eff}^{(I,V)} = D_{eff}^{(I)} + D_{eff}^{(V)}, \qquad 15.$$

can be derived (19, 61).

EFFECTIVE DIFFUSION COEFFICIENTS FOR CHARGED SPECIES For III–V compounds it must be assumed in many cases that the species involved in a substitutional-interstitial diffusion mechanism are charged (10, 22, 23). In general, the Frank-Turnbull mechanism may then be written as

$$A_i^{j+} + V^{k-} \rightleftarrows A_s^{m-} + (m+j-k)h, \qquad 16.$$

where j, k, and m are integers characterizing the charge state of the species and h stands for holes. The vacancy is assumed to be in the same sublattice in which A_s is substitutionally dissolved, e.g. a gallium vacancy in the case of zinc acceptors substitutionally dissolved on the gallium sublattice in GaAs (10, 22, 23). The first extension of the Frank-Turnbull mechanism to charged species has been given by Longini (22) for Zn in GaAs. In the literature on III–V compounds, substitutional-interstitial mechanisms of this form are, therefore, frequently termed Longini mechanism. The corresponding extension of the kick-out mechanism may be written as (62)

$$A_i^{j+} \rightleftarrows A_s^{m-} + I^{k+}(m+j-k)h. \qquad 17.$$

In general, the intrinsic point defects, as well as the interstitials A_i, may occur in more than one charge state. For the generalized Frank-Turnbull mechanism the mass-action law for local equilibrium between the different species reads

$$C_i C_V / (C_s p^{m+j-k}) = \mathrm{const(T)}, \qquad 18.$$

where p is the hole concentration. For completely ionized substitutional acceptor impurities ($m > 0$) of sufficiently high concentration (above the intrinsic electron concentration n_i), p may be replaced by mC_s. For donor impurities ($m < 0$), analogously the electron concentration n is given by $|m|C_s$. For dislocation-free material, considerations similar to those for uncharged species lead to

$$D_{eff}^{(i)} = (|m|+1)[D_i C_i^{eq}(C_s^{eq})/C_s^{eq}](C_s/C_s^{eq})^{|m|\pm j} \qquad 19.$$

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if the supply of A_i^{j+} limits the incorporation rate (22, 23, 60). The positive sign in the exponent holds for substitutional acceptors and the negative sign for substitutional donors. The factor $|m|+1$ accounts for the electric field set up by the concentration gradient of the charged substitutional atoms. Equation 19 is independent of the charge state k of the vacancies and also applies to the kick-out mechanism when the supply of A_i^{j+} limits the incorporation rate of A_s.

When the supply of vacancies from the surface limits the incorporation rate of A_s, then the effective diffusion coefficient for the A_s atoms is given by

$$D_{eff}^{(V)} = (|m|+1)[D_V C_V(C_s^{eq})/C_s^{eq}](C_s^{eq}/C_s)^{\pm k - |m|}, \quad 20.$$

where the same sign convention holds as for Equation 14. When the supply of self-interstitials from the surface limits the incorporation rate then

$$D_{eff}^{(I)} = (|m|+1)[D_I C_I^{eq}(C_s^{eq})/C_s^{eq}](C_s/C_s^{eq})^{\pm k - |m| - 2} \quad 21.$$

holds. The derivation of Equation 20 and 21 takes into account that C_i^{eq} of charged interstitials depends on the local electron or hole concentration and is not spatially constant as had erroneously been assumed in the literature (60, 62, 63). Equations 19–21 have not been derived for uncharged substitutional atoms A_s ($m = 0$); however, they do hold in this case provided all species are uncharged, and then they reduce to Equations 9, 11, and 14, respectively.

The quantities $D_V C_V^{eq}(C_s^{eq})$ and $D_I C_I^{eq}(C_s^{eq})$ refer to the self-diffusion transport coefficients of V^{k-} and I^{k+} under the doping conditions $C_s = C_s^{eq}$ and not necessarily to the intrinsic self-diffusion coefficient. It is worthwhile to mention that even for charged species, constant effective diffusivities may be obtained. For example, for singly charged acceptor dopants ($m = 1$), V^- ($k = 1$) or I^{3+} ($k = 3$) lead to constant effective diffusivities $D_{eff}^{(V)}$ or $D_{eff}^{(I)}$, respectively, with corresponding simple diffusion profiles. Since the applicable effective diffusion coefficient may change with the depth of the profile, complicated concentration profiles may result, especially if p-n junctions are present which, due to the large electric fields involved, may lead to locally strongly enhanced diffusion coefficients (64, 65).

Diffusion in Silicon

In-diffusion profiles of Au at and above 800°C (19, 66–68), of Pt (69, 70) at all temperatures investigated ($T > 700°C$), as well as of Zn (71) and sulphur (H. Mehrer and N. Stolwijk, private communication), are dominated by the kick-out mechanism, and their concentration profiles may be described by the effective concentration-dependent diffusivity equation

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(Equation 14). A typical gold concentration profile is shown in Figure 9 from the work of Stolwijk et al (67, 68). The platinum concentration profiles in Figure 10 are from the work of Mantovani et al (70). From the known C_s^{eq} values of Au and Pt the self-interstitial contribution $D_I C_I^{eq}$ to the self-diffusion coefficient D^{SD} has been determined. The concentration-independent part of $D_{eff}^{(I)}$ for $C_s = C_s^{eq}$ is plotted as $Au_s^{(1)}$ in Figure 1.

In heavily dislocated silicon the dislocations act as efficient sinks for self-interstitials and keep C_I close to C_I^{eq} so that Equation 9 holds. This has been shown for gold and zinc in silicon (68, 71). An example is the upper zinc diffusion profile in Figure 11. The $D_i C_i^{eq}$ value determined for Au in silicon is actually much larger than $D_I C_I^{eq}$, as required for the kick-out mechanism to yield the concentration-dependent diffusivity equation (see $Au_s^{(2)}$ in Figure 1). In the case of zinc, $D_i C_i^{eq}$ is not much larger than

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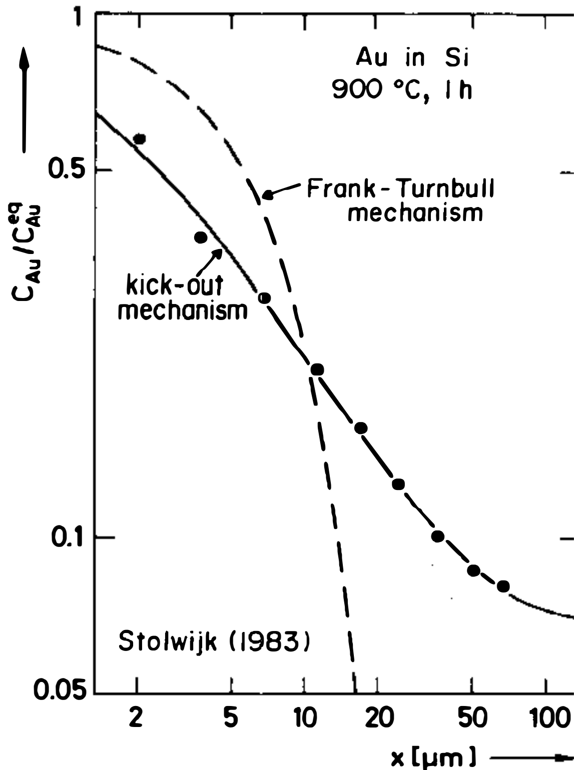

Figure 9 Gold concentration profile in dislocation-free silicon, according to (67, 68).

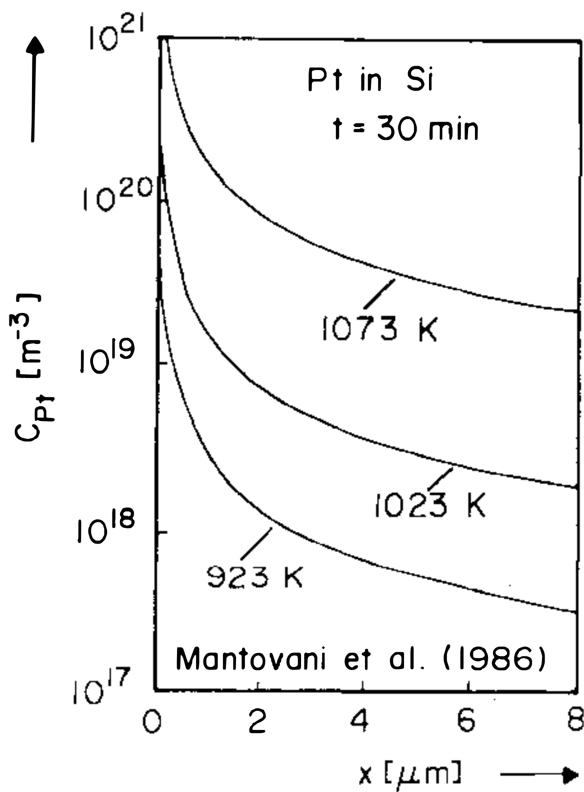

Figure 10 Platinum concentration profiles in dislocation-free silicon (70).

$D_I C_I^{eq}$ so that even in dislocation-free silicon only the profile close to the surface is governed by $D_{eff}^{(I)}$ of Equation 14, which strongly increases with depth. For larger penetration depths $D_{eff}^{(I)}$ finally exceeds $D_{eff}^{(i)}$, and a constant effective diffusivity begins to determine the concentration profile, as shown in Figure 11.

The diffusion of Au in silicon is very sensitive to the presence of dislocations since dislocations may act as sinks for self-interstitials and therefore enhance the local incorporation rate of Au_s. Even in dislocation-free silicon the self-interstitials created in supersaturation by the indiffusion of Au may agglomerate and form interstitial-type dislocation loops that further absorb self-interstitials and lead to W-shaped [instead of the usual U-shaped (67, 68)] concentration profiles in gold-diffused silicon wafers (72).

A detailed analysis of gold profiles at 1000°C showed the presence of a

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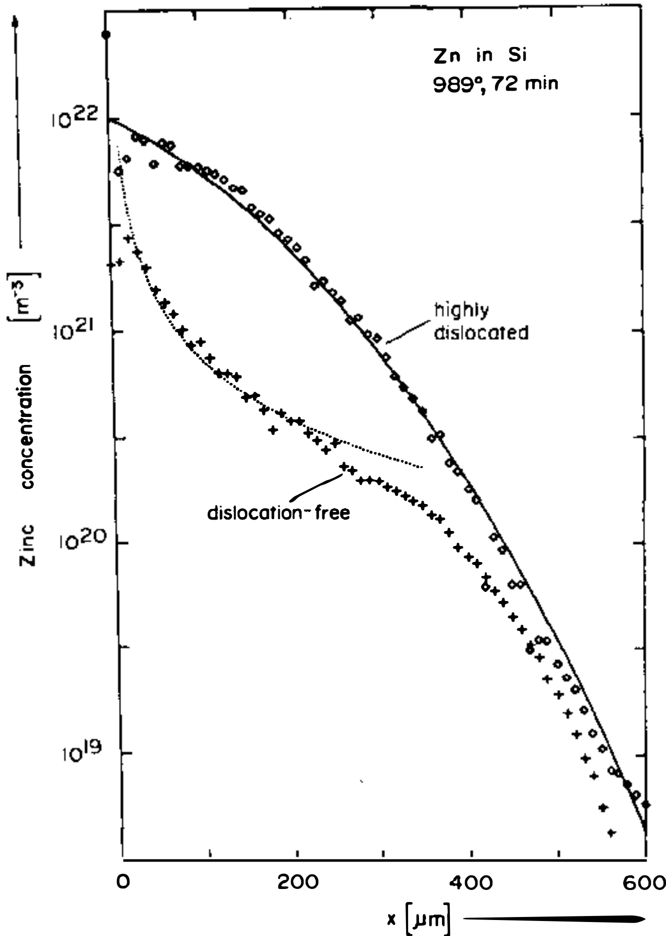

Figure 11 Concentration profiles of zinc in silicon. Solid line: erfc-profile for constant diffusivity; dotted line: kick-out type profile (71).

small but noticeable vacancy contribution, which is consistent with the conclusion from dopant diffusion experiments that both vacancies and self-interstitials are present under thermal equilibrium conditions. At 700°C the Au concentration profiles are characterized by a constant diffusivity (5), which indicates that at this temperature the kick-out mechanism for Au is kinetically hampered whereas the Frank-Turnbull mechanism still operates. This appears to be the case for the incorporation of substitutional nickel in silicon also (19, 61).

The diffusion of substitutional carbon in silicon (see Figure 1) is an example of a case in which diffusion is accomplished by a fast-diffusing self-interstitial carbon complex with $D_i C_i^{eq} < D_I C_I^{eq}$ so that a normal constant effective diffusivity described by Equation 9 is observed (59, 73). Contrary to the case of Au, Pt, Zn, and S, for carbon D_i has been measured independently (74).

Diffusion in Germanium

A key experiment concerning diffusion mechanisms in germanium was performed by Stolwijk et al (75), who investigated the diffusion of copper in germanium. Copper diffuses in germanium via a substitutional-interstitial mechanism (1). Analogous to the case of gold in silicon, its diffusion behavior may be used to check diffusion profiles for any indication of a self-interstitial contribution via the kick-out mechanism. No such contribution has been found. A concentration profile of copper in a germanium wafer is shown in Figure 12. The dashed U-shaped profile, which is typical for the kick-out mechanism, does not fit the experimental data, whereas the data may be well described by the constant diffusivity $D_{eff}^{(V)}$ following from Equation 11. The agreement between $D_V C_V^{eq}$ determined from Cu diffusion profiles with corresponding tracer measurement of self-diffusion in germanium is excellent (75). This shows that self-diffusion in germanium is carried by vacancies.

Diffusion in III–V Compounds

GENERAL REMARKS Substitutional-interstitial diffusion mechanisms play a much larger role in III–V compounds than in silicon or germanium since some of the most important dopants, such as Zn or Be, diffuse via this type of mechanism (10, 22). Extensive investigations have been performed, especially for GaAs and InP, which are the most important base materials for optoelectronic applications and fast integrated circuits. In spite of all this research the quantitative and detailed understanding of diffusion processes has not reached the level of our knowledge of silicon. The reasons are manifold: Since donor or acceptor dopants at high concentrations are usually involved, charge state and concentration profile–induced electric field effects must be considered (64, 65). Comparison of effective diffusion coefficients with self-diffusion coefficients to obtain more detailed information on the diffusion mechanism is difficult due to a lack of reliable self-diffusion data (21) and a possible strong dependence of self-diffusion on the doping level. Obviously the presence of two sublattices also complicates the situation. This is, for example, the case when a climb of dislocations that involves point defects from both sublattices is considered (10). In the analysis of substitutional-interstitial mechanisms, most investigators (e.g.

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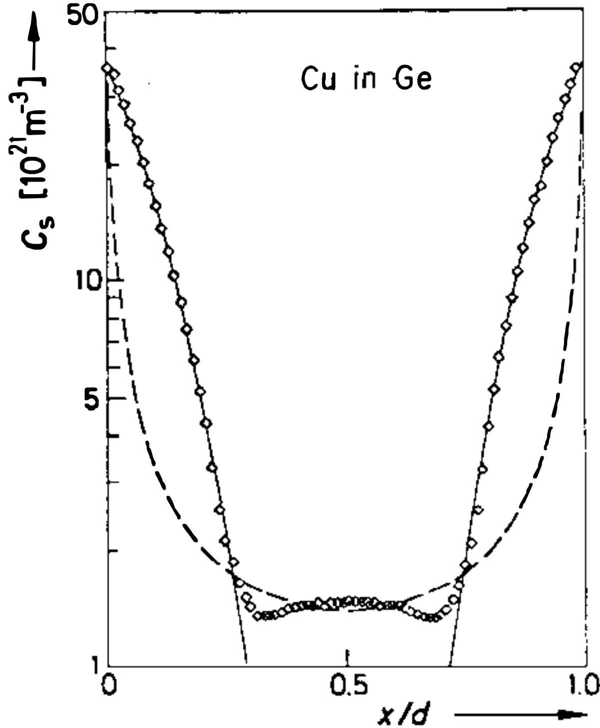

Figure 12 Concentration profiles of Cu into a dislocation-free germanium wafer after diffusion for 15 minutes at 878°C (75). The solid line holds for the Frank-Turnbull and the dashed line for the kick-out mechanism.

60, 76–80) completely neglected the role of self-interstitials, which add an additional mechanism of diffusion behavior not accessible when only vacancies are considered. Because of the strong doping dependence of the effective diffusion coefficients, the diffusion behavior may change from being intrinsic point defect limited to being interstitial diffusion limited within a given concentration profile. This leads to complex profile shapes similar to those shown in Figure 11 for the diffusion of zinc in silicon. Additional complications arise due to p-n junction formation (65) and the dependence of effective diffusion coefficients on the pressure of the more volatile group V elements (22, 65). In the following section I only deal with a very limited number of technologically relevant diffusion systems, such as Cr in GaAs and Zn in GaAs and InP, although many experimental investigations have recently been performed for other systems such as Cd,

Mg, Mn, Be, Si, and Ag in GaAs, InP, and other binary and ternary group III–V semiconductors (24, 25, 71, 77–89).

CHROMIUM IN GaAs Chromium acts as a deep acceptor when substitutionally dissolved on gallium sites and is extensively used for fabricating semi-insulating GaAs (90). As long as spatially uniform doping conditions are considered, no charge state effects must be taken into account, and the substitutional-interstitial diffusion mechanism of Cr may be described in terms of the Frank-Turnbull mechanism (Equation 6) and/or the kick-out mechanism (Equation 7). In-diffusion profiles are fairly complex, with a profile shape near the surface resembling a kick-out profile (76) and a deeper part characterized by a larger and constant diffusion coefficient (76, 91). Out-diffusion profiles may be characterized by a constant diffusivity that is much slower (91–95).

Tentatively, the diffusion behavior may be rationalized by assuming the coexistence of both gallium vacancies and self-interstitials, and that D_{eff} of substitutional chromium is given by Equation 15. Contrary to the case of gold in silicon, here C_i^{eq} and C_s^{eq} depend on the chromium vapor pressure. Let us assume that for the gallium sublattice $D_I C_I^{eq}$ is larger than or in the same order of magnitude as $D_V C_V^{eq}$ and slower than $D_i C_i^{eq}$. Then during in-diffusion near the surface, $D_{eff}^{(I,V)}$ is lower than $D_{eff}^{(i)}$ so that a kick-out profile results. Because of the $(C_s^{eq}/C_s)^2$ term, $D_{eff}^{(I,V)}$ increases with depth and finally the in-diffusion of Cr_s will be limited by the in-diffusion of Cr_i, which leads to a constant diffusivity (96)

$$D_{eff}^{(i)} \simeq (D_i C_i^{eq}/C_s^{eq}) C_I/C_I^{eq}. \qquad 22.$$

Equation 22 contains the effect of a supersaturation of self-interstitials that have diffused into the interior. In addition, there is an increase of Cr_s due to the action of dislocations. Contrary to the case of gold in silicon, the chromium plateau concentration away from the surface does not reach C_s^{eq}, but stays far below this value (76, 91). The most likely reason for this behavior lies in the dislocation-climb-induced generation of a nonequilibrium concentration of intrinsic point defects in the arsenic sublattice, which finally limits the attainable C_s concentration by dislocation-climb processes. This complication also makes it difficult to distinguish the Frank-Turnbull from the kick-out mechanism by the time dependence of the concentration in the bulk, which appears to favor the Frank-Turnbull mechanism (91). For the out-diffusion profiles, the prevailing chromium vapor pressure is much lower so that now $D_{eff}^{(i)}$ controls the out-diffusion process since it is likely to be lower than the $D_{eff}^{(I,V)}$, which increases with decreasing chromium vapor pressure.

ZINC IN GaAs AND InP Zinc diffusion in GaAs is probably the most inves-

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tigated diffusion process in III–V compounds (10, 22, 23, 62, 63, 71, 97–100). Zinc acts as a single shallow acceptor in most III–V compounds and can be used for doping purposes. As first suggested by Longini (22), zinc diffuses via a substitutional-interstitial mechanism. The strong doping dependence of D_{eff} is explained in terms of appropriately charged Zn interstitials in Equation 16 or 17. Isoconcentration diffusion experiments (zinc diffusion in sufficiently highly zinc-doped material) have shown that in Equation 16 or 17 $j = 1$ is fulfilled, which leads to $|m|+j = 2$ in Equation 19.

For normal in-diffusion experiments, complicated diffusion profiles have been obtained for high surface concentrations that partly show kink and tail features, as indicated in Figure 13 for some early profiles of radioactive zinc (98). Zinc diffusion is extremely fast at high zinc concentrations, due to a large increase in the concentration of highly mobile positively charged Zn interstitials when the Zn concentration is increased. Comparison of $D_{eff}C_s^{eq}$ with self-diffusion, $D^{SD} = D_V C_V^{eq}$ (and/or $D_I C_I^{eq}$), in undoped GaAs shows that in general $D_{eff}C_s^{eq}$ is much larger. Based on our earlier discussion on substitutional-interstitial mechanisms the observation that $D_{eff}C_s \gg D^{SD}$ may have two explanations: (1) The first explanation

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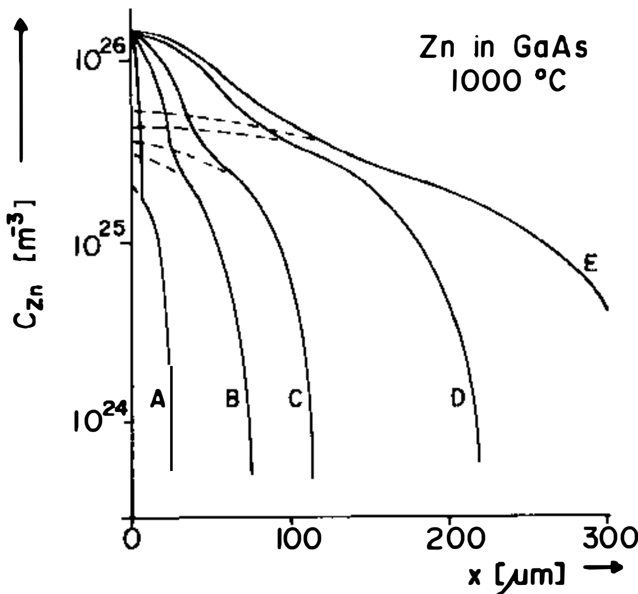

Figure 13 Set of radiotracer profiles for zinc in GaAs at 1000°C for the following diffusion times; (*A*) 10 min, (*B*) 30 min, (*C*) 90 min, (*D*) 9 h, (*E*) 30 h (98).

assumes that self-diffusion does not depend on the Fermi level. Then such a result may be obtained only in highly dislocated material, since then $D_i C_i^{eq} \gg D^{SD}$ is fulfilled; nevertheless $D_{eff} = D_{eff}^{(i)}$ holds
point defect concentration is held close to its equilibrium value due to dislocation climb processes. Since the in-diffusion of zinc is almost independent of the initial dislocation content (71, 97), this explanation requires that the in-diffusion of zinc created such a high supersaturation of I_{Ga} or undersaturation of V_{Ga} that interstitial-type dislocation loops are formed that dominate the generation and/or absorption of intrinsic point defects and make the in-diffusion process almost independent of the original dislocation content (71). This interpretation is in line with various observations of dislocation formation during in-diffusion of Zn in GaAs (97, 101). (2) The second explanation assumes that self-diffusion is carried by charged point defects and is therefore strongly dependent on the Fermi level. Therefore, to determine the diffusion mechanism via the effective diffusion coefficient, $D_{eff} C_s^{eq}$ must be compared with the self-diffusion coefficient at the doping level of C_s^{eq}. This quantity is generally not known, but may be much larger than $D(n_i)$ provided that positively charged point defects play a role.

It is likely that for high concentration diffusion both nonequilibrium as well as charged point defects must be taken into account. The best quantitative attempt at this was the early work of Winteler (97), who was the first to investigate the role of charged gallium vacancies and self-interstitials in the diffusion of zinc in GaAs.

Zinc diffusion in InP is governed by a concentration dependence similar to zinc diffusion in GaAs and many other III–V compounds (10, 22). An effective diffusion coefficient proportional to the square of the substitutional zinc concentration C_s describes the concentration profiles reasonably well. Recently it has been found that a solid zinc source leads to profiles characterized by a constant effective diffusivity (102) for about the same surface concentration. It is likely that due to the solid source the intrinsic point defect concentration is decreased so that the intrinsic point defect diffusion governs D_{eff}. The two possible cases leading to a constant D_{eff} have been discussed above and are related either to V_{In}^{-} or to I_{In}^{3+}.

The diffusion of zinc into n-type InP leads to abrupt diffusion fronts that are steeper than described by the usual C_s^2 dependence (103, 104). The reason for this abrupt profile is simple. The usual C_s^2 concentration dependence is due to

$$D_{eff}^{(i)} \propto p^2, \qquad 23.$$

where p is given by C_s. Equation 23 still holds, but beyond the p-n junction

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p is dominated by the electron concentration n coming from the n-type background dopant,

$$p \approx n_i^2/n, \qquad 24.$$

which leads to a drastic decrease of $D_{\text{eff}}^{(i)}$ near the p-n junction (104). Zinc diffusion into lightly-doped n-type InP gives rise to a second diffusion front (105) which may be characterized by a constant diffusivity and attributed either to a second independent diffusion process (106) or more likely to electric field effects (65).

BERYLLIUM IN GaAs Beryllium, because of its comparatively high solubility but much lower vapor pressure than zinc, is presently the main acceptor dopant in III–V compounds for integrated circuit applications (90). Beryllium diffusion in GaAs depends on its concentration and on the arsenic vapor pressure similar to zinc diffusion (24, 25). It has therefore been concluded that it diffuses by a substitutional-interstitial mechanism; both the Frank-Turnbull and the kick-out mechanism have been considered (24, 25). Widely varying beryllium diffusion coefficients have been reported for comparable beryllium concentrations and temperatures (24, 25, 107). The reason for this apparent difference lies in the different supply conditions for the beryllium. If there is an external source of beryllium as, e.g. during liquid phase epitaxy growth of beryllium-doped GaAs (107a), C_i in Equation 18 is much larger than in the case when the beryllium interstitials are supplied from substitutionally incorporated beryllium, as in the case of annealing of beryllium-doped GaAs grown by molecular beam epitaxy (25). A similar drastic reduction in the effective diffusivity was observed for zinc in GaAs after the external source of zinc had been removed (10, 108). Based on the effect of beryllium and zinc on the disordering of GaAs/GaAlAs quantum well structures, it has been concluded that both beryllium and zinc diffuse by the kick-out mechanism (109).

Finally, the dependence of D_{eff} on the vapor pressure of the more volatile group V component has often been used to obtain more information on diffusion mechanisms in III–V compounds (10, 23). As yet it has not been sufficiently recognized that for a D_{eff} dominated by the diffusion of charged point defects, the pressure dependence generally is different from that of $D_{\text{eff}}^{(i)}$. For example, in the case of a constant $D_{\text{eff}}^{(V)}$ or $D_{\text{eff}}^{(I)}$, no dependence on the vapor pressure is expected.

SUMMARY

Fast diffusion in semiconductors spans a wide range of mechanisms and areas of applications. The present article has dealt with the possible role

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of interstitial molecules, such as oxygen and hydrogen in silicon. In both cases the presence of such molecules is likely but has not yet been proven experimentally. The Frank-Turnbull and the kick-out mechanism are the two substitutional-interstitial diffusion mechanisms that govern the movement of many predominantly substitutionally dissolved fast-diffusing elements in silicon, germanium, the III–V compounds, and probably also in the II–VI compounds. Depending on the values of the parameters involved, specific concentration profiles may result that allow one to distinguish between these mechanisms and also to draw conclusions on the defects—vacancies, or self-interstitials—governing self-diffusion. In the case of silicon, the elements Au, Pt, Zn, and S diffuse via the kick-out mechanism and self-interstitials dominate self-diffusion. Copper in germanium diffuses via the Frank-Turnbull mechanism and self-diffusion is governed by vacancies. The profiles in III–V compounds, especially for fast diffusing dopants, are more complex and presently do not allow a quantitative understanding of the prevailing diffusion mechanisms, although it is likely that both types of substitutional-interstitial mechanisms and the coexistence of both vacancies and self-interstitials on both sublattices must be taken into account.

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