REVIEW

K. Maser

Darken's equation and other diffusion relations in the light of atomistic kinetic concepts

Abstract The atomistic kinetic approach of the DOCC sites concept (meaning, very simplified, that the dopant migration in solids progresses via sites which are suitable for occupation by dopant corpuscles summarized as dopant-occupiable sites, i.e. DOCC sites) is here used as a basis on which several diffusion models are thoroughly analysed. Since it is able to cover all effects determining dopant migrations, so that it may be valid in general, it proves other statements on dopant transport to be incorrectly formulated. Following this conception, Darken's equation leads to a link between the Fickian diffusion coefficient of an ideal solution and the activity coefficient of the non-ideal solution, which has up to now been ignored. Contrasting with Darken's hypothesis, Einstein's relation between the Fickian diffusion coefficient and the mobility of dopant particles proves true even in cases of non-ideal solutions. The supposed vacancy wind effect and the diffusion of dopant-defect pairs as molecule-like joined complexes are shown to be physically unrealistic. Orlowski's dopant flux formula proves false. Roth's and Plummer's model on oxidation-enhanced diffusion in silicon is shown to involve incorrectnesses.

Introduction

Darken's equation (eq. (12) in [1]) formulates the diffusivity of atoms of each component in a binary metallic system as a function of independent mobility and activity coefficients. In contrast, the model which will here be explained points out a strong link between these terms. Since the connection between these parameters has not yet been taken into numerical accounts, the values that have been calculated in this way ought eventually to be corrected.

Although diffusion processes have been known for more than a century, and play an indispensable role in modern semiconductor technology, several problems remain to be solved [2–28]. Even in many cases of liquid systems the distributions of solutes are more complicated [29–32] than Fick's inferences from his H_2O-NaCl solution experiment [33], that diffusivities would be constants. Therefore, also Einstein's diffusion model [34, 35] cannot be accepted as a generally valid statement, because it is limited to Fick's result. From this point of view, the diffusivity–mobility relation, which was derived by Einstein in cases of liquid systems [34, 36], is worth analysing for its use in solid-state diffusion statements, because it adheres to the presuppositions of Darken's equation.

Scrutinizing models on dopant transport in solids, which differ each from another, first requires the definition of the basis on which they may critically be discussed. For this purpose the DOCC sites concept is believed to be the proper frame [25, 37, 38], because it takes into account the local inhomogeneous distribution of sites, via which dopant corpuscles move, summarized as dopant-occupiable sites, i.e. DOCC sites. Unlike several phenomenological thermodynamic approaches, which in some cases involve even intuitive assumptions (pp. 196, 434 of [21]), the DOCC sites concept is free from hypotheses. Its atomistic-kinetic approach describes the dopant transport process by the same mathematical formula as for the simple vacancy mechanism [39, 40]. However, it extends the latter and takes into account all punctiform sites, which are suitable for occupation by dopant particles. DOCC sites may act not only as vacancies and interstices but also as entities which are suitable for the residence of dopant particles (e.g. corpuscles together with dopants may form pairs and complexes) [41–48]. Accordingly, the dopant flux is determined by the DOCC sites concentration and by the dopant jump rate (i.e. the probability of dopant particles to jump from their starting positions in the adjacent

K. Maser
Technische Universität Berlin, Institüt für Mikroelektronik und Festkörperelektronik, Jebensstrasse 1, D-10623 Berlin, Germany

DOCC sites during a given time interval). The functional dependencies of these two parameters on position are crucial criteria for either Fickian diffusion (strictly speaking, the constancy of diffusivities) or non-Fickian dopant transport phenomena (involving dopant up-hill migration and varying diffusion coefficients [42]). From this point of view, the DOCC sites concept may be valid in general, whereas several other statements are limited to special conditions or they are inexactly formulated. Bardeen's atomistic kinetic diffusion model [43], which considers in another theoretical way the result of Darken's thermodynamical statement [1], is shown below to be based on an incorrectly expressed dopant flux formula.

Other models and predications are also worth discussing. The oxidation-enhanced diffusion of dopants in silicon [47] is inconsistently formulated. The vacancy wind effect [49–51] appears as sheer hypothesis. The diffusion of dopant-defect pairs believed to proceed as joined complexes [48, 50, 52–56] is explained in such way that the dopant particles may elementarily jump [57]. Orlowski's dopant flux formula proves false, because the gradient terms of vacancies and interstices involve wrong signs [58–60].

Selected models of dopant transport processes

Darken's diffusion statement and Manning's dopant flux formula

Firstly, a remark to the use of symbols in the current paper. In order to avoid misunderstandings, which could be caused by the use of symbols differing from each other but meaning one and the same physical parameter, the notation is preferentially retained for each article being discussed. For instance, the dopant jump distance is designated by λ in Bardeen's diffusion model, but by α in the DOCC sites concept. However, Darken's symbols are preferentially used in this section to describe the diffusion process in terms of the original paper.

Darken's equation (eq. (12) in [1]), which formulates the diffusivity (D_i) of the ith constituent in a binary metallic system as a function of mobility (M_i), atom fraction (N_i) and activity coefficient (γ_i)

$$D_i = kTM_i\left(1 + N_i\frac{\partial \ln \gamma_i}{\partial N_i}\right) \tag{1}$$

presupposes the following conditions:

1. The sum (S) of the solvent concentration (C_1) and the solute concentration (C_2) is a constant: $S = C_1 + C_2 = \text{const.}$
2. The volume of the system is independent of the local concentrations C_1 and C_2.
3. Resulting from the assumptions (1) and (2), the vacancy concentration is also independent of position and local composition, which was taken into Darken's consideration.

4. Interactions between the two components, which may change the migration of one of them, are neglected, so that the non-Fickian dopant transport phenomena are excluded from the consideration.
5. Following points (1)–(4), the dopant flux (J_2) is limited to Fick's Law: $J_2 = -D_2(\partial C_2/\partial x)$.

According to the thermodynamic understanding of transport processes, the force effecting the migration of neutral solute particles in a solvent is equal to the negative gradient of the potential energy of these entities (i.e. Gibbs's chemical potential, usually called the partial free energy). This means that for μ_C, the chemical potential per solute atom, the average force (F_2) acting on each of these migrants amounts to $F_2 = -\partial\mu_C/\partial x$. Accordingly, the average migration velocity of a solute atom is equated formally to the product of this force (F_2) and the mobility (M_2) of the migrant. Hence the flux density (J_2) in atoms of component 2 per unit time across a unit plane normal to the direction of diffusion is described by the formula $J_2 = -C_2M_2(\partial\mu_C/\partial x)$. Using Fick's Law [see point (5) above], one obtains the expressions

$$D_2\left(\frac{\partial C_2}{\partial x}\right) = C_2M_2\left(\frac{\partial \mu_C}{\partial x}\right) \tag{2a}$$

$$D_2 = C_2M_2\left(\frac{\partial \mu_C}{\partial C_2}\right) \tag{2b}$$

Using again the approximations that the specific volume of the system as well as the sum ($C_1 + C_2$) are independent of position and of composition, the atom fraction $N_2 = C_2/(C_1 + C_2)$ leads to

$$D_2 = M_2\left(\frac{\partial \mu_C}{\partial \ln N_2}\right) \tag{3}$$

From the definition of activity (a_2), namely, $\mu_C = kT \ln a_2$, it follows (eq. (11) in [1]) that

$$D_2 = kTM_2\left(\frac{\partial \ln a_2}{\partial \ln N_2}\right) \tag{4}$$

and from the definition of the activity coefficient, $\gamma_2 = a_2/N_2$

$$D_2 = kTM_2\left[1 + N_2\frac{\partial \ln \gamma_2}{\partial N_2}\right] \tag{5}$$

Equation (5) is identical with Darken's formula (eq. (12) in [1]). Since the diffusion of component 1 is described by a similar expression denoted by the corresponding subscript, the constancy of the sum ($C_1 + C_2$) leads to the effective diffusion coefficient (p. 194 in [1])

$$D_2^{\text{eff}} = \left(N_1D_2^* + N_2D_1^*\right)\left[1 + N_2\frac{\partial \ln \gamma_2}{\partial N_2}\right] \tag{6}$$

of constituent 2 in the binary alloy. Therein, the parameters D_1^* and D_2^* are individual diffusivities, which are assumed to be given by tracer measurements. In such investigations the diffusion of a tracer (i.e. a radioactive isotope of the dopant component, which is added to the

diffusion system) is believed to be determined both by the chemical potential of an ideal solution as well as by the constancy of mobility. Since the latter is assumed to have the same value as in the case of the non-radioactive isotope, Darken's formula has frequently been used in order to estimate the chemical potential of a non-ideal solution as function of concentration.

Darken's inference (p. 194 in [1]), that the Einstein relation ($D_i = kTM_i$) would be applicable only to ideal solutions, is worth discussing. The DOCC sites concept points out that the diffusion coefficient (D) of the Fickian dopant flux component is directly proportional to the mobility (M) of the drift term, even in the cases when these two parameters are functions of position, concentration, etc. Accordingly, deviations from the kT value can only exist for the D^{eff}/M ratio and only in that case when the non-Fickian dopant flux portions additionally flow to the Fickian and the drift component within in the total dopant flux $J^{\text{tot}} = -D^{\text{eff}}(\partial C/\partial x)$. Since Einstein himself limited his diffusion model [34] to the local symmetry of probability functions of dopant jumps in order to obtain Fick's constancy of dopant diffusivities [33], statements other than the former are required to be taken into considerations in order to involve inhomogeneous host materials, asymmetric probability functions of dopant jumps, variable diffusion coefficients and non-Fickian phenomena.

Following Darken's intention, the dopant flux (J) would only be induced by the dopant gradient ($\partial C/\partial x$), whereas Manning's dopant flux formula (eqs. (38, 42) in [16]) points out a non-Fickian dopant flux component

$$J^{\text{vac grad}} = +DC\frac{\partial \ln C_v}{\partial x} \qquad (7)$$

which is only caused by the vacancy gradient. Therein the symbols mean: C = dopant concentration, C_v = vacancy concentration and D = Fickian diffusion coefficient [i.e. the coefficient of that dopant flux portion which is only driven by the dopant gradient ($\partial C/\partial x$)]. In order to scrutinize these two contrasting assertions, the current paper aims both to elucidate the basic statements for Darken's equation and for Fick's and Einstein's constancy of diffusivities, as well as to understand the activity coefficient in the case of solid-state diffusion when the sites suitable for occupation by mobile dopant particles obey position-dependent distribution functions. In other words: the discussion on several dopant transport models here presented purposes to clarify whether or not a link does exist between the Fickian variable diffusion coefficient (as explained above) of the tracer species, which is up to now simply believed to be a constant corresponding to an ideal solution, and the activity coefficient of the non-ideal solution.

Bardeen's deduction of Darken's equation

In order to corroborate Darken's result of a thermodynamic continuum statement by means of a deduction from another physical viewpoint, Bardeen [43] considered an atomistic kinetic approach of dopant transport processes in solids. This model is based on following conditions:

1. The transport process of each component in a binary metallic system is mediated by vacancies.
2. The vacancies and the metal atoms are inhomogeneously distributed.
3. As a result of the concentration gradient in a non-ideal solution, Gibbs free energy of atoms changes with position, so that the potential barriers over which diffusion takes place will not be symmetric.

Avoiding misinterpretations, formulae in this section are written in Bardeen's symbols, referring to following parameters:

N_A, N_B, N_V = concentrations of constituents A and B and of vacancies in the binary alloy

λ = lattice constant = distance between adjacent crystallographic planes = jump distance of atoms

k_f, k_b = forward and backward jump coefficients, respectively, for atoms of a constituent to jump from their starting plane into vacancies of the adjacent plane, so that k_f and k_b are proportional to the corresponding frequency of jumps

x = position coordinate

This means that N_A and N_V are the concentrations of A atoms and of vacancies on plane 1 (position x), with gradients $\partial N_A/\partial x$ and $\partial N_V/\partial x$ leading to the corresponding concentrations $[N_A + \lambda(\partial N_A/\partial x)]$ and $[N_V + \lambda(\partial N_V/\partial x)]$ on plane 2 positioned at $(x + \lambda)$. Accordingly, the flux of A atoms flowing from plane 1 to plane 2 (forward direction) is (eq. (23) in [43])

$$i_{Af} = k_f \lambda N_A \left[N_V + \lambda\left(\frac{\partial N_V}{\partial x}\right)\right] \qquad (8)$$

and from plane 2 to plane 1 (backward direction) (eq. (24) in [43]):

$$i_{Ab} = k_b \lambda N_V \left[N_A + \lambda\left(\frac{\partial N_A}{\partial x}\right)\right] \qquad (9)$$

The net flux (i_A) of A atoms is the difference ($i_{Af} - i_{Ab}$), which amounts to

$$i_A^M = \lambda^2\left(k_f N_A N_V' - k_b N_A' N_V\right) + \lambda(k_f - k_b)N_A N_V \qquad (10)$$

where

$$N_A = N_A(x), \quad N_A' = \frac{\partial N_A}{\partial x}, \quad \text{etc.}$$

However, Bardeen's diffusion model has inconsequently been developed. Contrasting with Eq. (10), the difference ($i_{Af} - i_{Ab}$) is formulated as (eq. (25) in [43])

$$i_A^B = \lambda^2 k_A\left(N_A N_V' - N_A' N_V\right) + \lambda(k_f - k_b)N_A N_V \qquad (11)$$

The comparison of coefficients of the first term on the right-side hand of the latter two relations leads to the

equality $k_A = k_f = k_b$, so that the second term expressing the asymmetry of the jump rates vanishes. From this inconsistent result, being in contrast to the presupposition of asymmetric jumps, Bardeen has deduced two inferences:

1. The mechanism of diffusion via vacancies leads to Darken's phenomenological equations if vacancies are in local thermal equilibrium.

2. No gradient of vacancies is to be expected in the case of diffusion of a radioactive tracer.

It must be remarked that Bardeen's conclusion is imperfectly expressed. Determining the activity coefficient of a non-ideal solid-state solution in dependence on the solute concentration may assume Fickian diffusion (meaning $D = \text{const.}$) of the ideal solution, but Bardeen's doctrine, that this decisive presupposition would always automatically be satisfied in the case of tracer diffusion, proves false. As Masters's and Fairfield's [44] experiments of iso-concentration diffusion (giving the surface concentration of the tracer equal to that of the previously performed prediffusion) point out, the concentration profiles of the radioactive As-76 isotope in the As-prediffused silicon crystal differ markedly from those without prediffusion. Deducing from these measurements, it is not certain, whether or not each diffusion process would have abolished the gradient of vacancies and provided their thermal equilibrium value for the subsequent tracer diffusion. It is to be assumed that entities altering the migration of the tracer may remain from the processes before tracer diffusion and that other ones may be created by the latter, so that Darken's and Bardeen's criteria are not satisfied.

Fick's view and Einstein's model of diffusion

The dependence of the dopant flux on the dopant gradient was first formulated by Fick [33], guided by solute distributions in aqueous NaCl solutions. On the patterns of Ohm's law for electric current flow and Fourier's equation for heat conductivity, Fick assumed that the solute concentration would act in a similar way as the voltage and the temperature. Following this, the negative gradient of the chemical potential of dopant particles is the force which drives these entities to migrate through a continuous solvent. Fick's law and the constancy of diffusivities were first theoretically founded by Einstein [34] with the help of a model involving the decisive condition of symmetric probability functions of dopant jump distances.

The mathematical treatment of Einstein's model is based on the following details. Denoting $C(x,t)$ as the dopant concentration C at position (x) and time (t), then its amount will be altered to $C(x,t+\tau)$ by the jumps of the dopant particles which have reached the reference position (x) from their starting points $(x+X)$ during the time interval $(t, t+\tau)$, where X means the jump distances of the dopant particles. Provided that their probability distribution (P) is only a function of X, but is independent of position, concentration, etc., the concentration $C(x,t+\tau)$ at position (x) and time $(t+\tau)$ is given by the integral

$$C(x,t+\tau) = \int_{-\infty}^{+\infty} C(x+X,t)P(X)\mathrm{d}X \tag{12}$$

Representing $C(x+X)$ as Taylor series

$$C(x+X) = C(x) + X\frac{\partial C}{\partial x} + \frac{X^2}{2}\frac{\partial^2 C}{\partial x^2} + \cdots \tag{13}$$

then Eq. (12) can be rewritten as the sum of integrals

$$C(x,t+\tau) = C\int_{-\infty}^{+\infty} P(X)\mathrm{d}X + \frac{\partial C}{\partial x}\int_{-\infty}^{+\infty} XP(X)\mathrm{d}X$$
$$+ \frac{1}{2}\frac{\partial^2 C}{\partial x^2}\int_{-\infty}^{+\infty} X^2 P(X)\mathrm{d}X + \cdots \tag{14}$$

with $C = C(x,t)$. The standardizing condition

$$\int_{-\infty}^{+\infty} P(X)\mathrm{d}X = 1 \tag{15}$$

as well as Einstein's decisive symmetry demand

$$P(+X) = P(-X) \tag{16}$$

simplify the integrals of Eq. (14), so that $C(x,t+\tau)$ becomes

$$C(x,t+\tau) = C(x,t) + \frac{\langle x^2 \rangle}{2}\frac{\partial^2 C(x,t)}{\partial x^2} \tag{17}$$

with

$$\langle x^2 \rangle = \int_{-\infty}^{+\infty} X^2 P(X)\mathrm{d}X \tag{18}$$

Since $C(x,t+\tau)$ can, for small τ time intervals, be expressed by

$$C(x,t+\tau) = C(x,t) + \tau\frac{\partial C(x,t)}{\partial t} \tag{19}$$

then Eq. (17) leads to the expression

$$\frac{\partial C(x,t)}{\partial t} = \frac{\langle x^2 \rangle}{2\tau}\frac{\partial^2 C(x,t)}{\partial x^2} \tag{20}$$

Following Einstein, the diffusion coefficient D can be interpreted as a limiting value

$$D = \lim_{\tau\,\text{small}} \frac{\langle x^2 \rangle}{2\tau} \tag{21}$$

the amount of which is constant for sufficient small τ intervals. Accordingly, D is identical with Fick's diffusion constant [35].

Noteworthy is that Einstein himself [34] interpreted the diffusivities as constants, although several investi-

gations pointing to concentration-dependent diffusion coefficients of gaseous and liquid systems were already known in his time [29–32]. The constancy of diffusivities is inevitably connected with symmetric probability functions of dopant jump distances, for which Einstein excluded any interactions of these particles with each other. Each asymmetric $P(X)$ function alters the D value as well as giving rise to an additional concentration term on the right-hand side of Eq. (17). Following Einstein, but exceeding his model, the asymmetric $P(X)$ function of jump distances (X) gives the mean value

$$\langle x \rangle = \int\limits_{-\infty}^{+\infty} X P(X) \mathrm{d}X \qquad (22)$$

which may be understood as the linear displacement of dopant migrations. Accordingly, Eq. (17) can be extended to

$$C(x, t + \tau) = C(x, t) + \langle x \rangle \frac{\partial C(x,t)}{\partial x} + \frac{\langle x^2 \rangle}{2} \frac{\partial^2 C(x,t)}{\partial x^2} \qquad (23)$$

Comparison with Eq. (19) leads to the relation

$$\frac{\partial C(x,t)}{\partial t} = \frac{\langle x \rangle}{\tau} \frac{\partial C(x,t)}{\partial x} + \frac{\langle x^2 \rangle}{2\tau} \frac{\partial^2 C(x,t)}{\partial x^2} \qquad (24)$$

This link between the differential quotients $\partial C / \partial t$, $\partial C / \partial x$ and $\partial^2 C / \partial x^2$ may enable us to view non-Fickian dopant transport phenomena in their true aspects. Since the continuity relates $\partial C / \partial t$ to the divergence of the dopant flux (J), $\partial C / \partial t = -\partial J / \partial x$, the first term on the right-hand side of Eq. (24) points to a non-Fickian dopant flux, which is not only caused by the dopant gradient $\partial C / \partial x$. Accordingly, the quotients $\langle x \rangle / \tau$ and $\langle x^2 \rangle / 2\tau$ are variables, which may depend on position, concentration, etc. In other words: each varying diffusion coefficient $D = \langle x^2 \rangle / 2\tau$ in Eq. (24) is inevitably connected with dopant flux portions not obeying Fick's law. This result agrees with explanations of atomistic kinetic dopant transport models (see following section). Notable is that the quotient $\langle x \rangle / \tau$ of Eq. (24) has the opposite sign to the $\langle v_{\mathrm{F}} \rangle$ term of Peterson's formula (eq. (2.17) in [35]), where $\langle v_{\mathrm{F}} \rangle$ designates the mean atom drift velocity from the driving force caused by an electrical field, thermal or chemical potential gradient. From the viewpoint of thermodynamics, the random walk of dopant particles (being the presupposition for Einstein's symmetry demand of dopant jump distances) is not satisfied when inhomogeneously distributed species interactions are involved. The interactions are prone to destroy randomicity and so are identified as correlation effects (chap. 2 in [51]).

Asymmetric probability functions of dopant jumps are fundamentally included in models of dopant transport in solids because host materials may non-uniformly be changed by several effects. The mismatch of solute atoms in solvent crystals leads to their deformations, depending on the kind and concentration of the solute. In several fabrication steps of modern semiconductor technology, the silicon host crystal is further inhomogeneously altered by oxidation and nitridation, which are also performed on outer surfaces. Besides the deformation of the adjacent crystal region by the coverage layer, these operations abolish the thermal equilibrium of vacancies and self-interstitials, which decisively influence dopant transport processes in solids.

In order to avoid any deviations of vacancy and self-interstitial concentrations from their thermal equilibrium values, unusual experimental conditions are sometimes needed. For example, Ghoshtagore's [45, 46] investigations of donor and acceptor diffusion in silicon refer to a special combination of details, namely, embedded epitaxy zones acting as doping sources, inert gas ambient during diffusion processes, and low-level concentrations (meaning intrinsic conditions). The resulting dopant profiles obey Fick's law and give diffusivities independent of position in the total measured diffusion zone of 3–4 orders of magnitude for dopant cocentrations. These values are the lowest ones for Fickian diffusion which have ever been obtained, so they are interpreted to be the intrinsic diffusivities at thermal equilibrium. Their dependence on temperature satisfies the Arrhenius equation in the total investigated interval of 1150–1400°C, from which the formation energy of mono-vacancies mediating the dopant transport is inferred to amount to 2.35 eV.

Summarizing these effects, both the concentration of the sites mediating the dopant migration in solids as well as the dopant jump rate (i.e. the probability of dopant particles jumping into these sites during a given time interval) are to be put as position-dependent parameters into the basic statement in order to develop models of dopant transport processes in solids, which may be valid in general. From this viewpoint (see next section), Einstein's symmetry of dopant jump distances and Fick's constancy of diffusivities are to be understood as special cases, when diffusion processes proceed in regions where the entities mediating dopant transport processes are uniformly distributed. Accordingly, the Fickian diffusion coefficient is directly proportional to the concentration of these entities [6].

The DOCC sites concept

The DOCC sites concept is an atomistic kinetic description of dopant transport processes in solids, whose main feature involves the inhomogeneous distributions of entities mediating and/or influencing the dopant flux. The mobile dopant species interact with the DOCC sites in order to provide migrations of these particles. Unlike phenomenological thermodynamic statements assuming a continuous course of solid-state diffusion [21, 49, 50, 51], the atomistic kinetic approaches consider dopant migration in solids to proceed by discrete jumps of dopant particles via distinct sites [9–16]. Putting this into concrete terms, each dopant migration in solids requires simultaneously to satisfy the following two conditions:

1. Sites suitable for occupation by particles of the mobile dopant species (meaning DOCC sites) must exist.
2. Particles of the mobile dopant species must have sufficient energy to occupy DOCC sites.

Expressing condition (2) by a quantitative parameter, the dopant jump rate is the probability of a dopant particle jumping from its starting position in the adjacent DOCC site during a given time interval. Following this, both the DOCC sites concentration and the dopant jump rate, which completely determine the dopant flux, should be inserted as position-dependent functions in the basic statement in order to develop an universally applicable dopant transport model. Since this mathematical feature is in principle able to take into account the influences of all entities and effects on dopant migrations, the DOCC sites concept may be valid in general.

Since dopant movements in solids are determined by several interactions between particles of the mobile dopant species and entities of host materials, numerous transport models have been developed. Early papers on the simple occupation of vacancies and interstices by dopants [2–7] have decisively been corrected by Johnson's inference from activation energies that solute atoms would tend to trap "holes" (vacancies are meant by Johnson) to form solute-hole molecules [8]. Accordingly, the dopant-vacancy interactions are to be understood as inversions and reorientations. Inversion means the dopant jumps into the adjacent vacancy, so that these two entities change their sites each for the other, whereas the vacancy moves around the fixed dopant during the reorientation stage.

Many models of acceptor and donor diffusion in silicon have adopted Johnson's insight to formulate the fluxes of these elements in terms of Fickian diffusion of corresponding dopant-vacancy pairs [21, 52–56]. Mobile pairs obeying Fick's law have also been presupposed in cases of interstitial diffusion, where they are assumed to move as joined silicon-interstitial/dopant-interstitial combinations [48]. However, the diffusion of pairs in the form of mobile molecule-like complexes as formulated in several investigations (p. 434 in [21, 24]) may merely be an intuitive assumption or an abstraction, because places lodging such complexes are unknown [23]. Fair (personal communication, 1995) has explained the As diffusion in Si crystals via pairs in such a way that the dopant particles would always perform their jumps in elementary form, because the pairs would dissociate. He states: "The pair does not jump as a paired molecule. Thus, I agree that everything is reduced to migration of elementary particles". Whether or not the dopant flux is carried by atoms, ions or pairs, both the DOCC sites concentration and the dopant jump rate always refer to the dopant particle species actually performing the dopant jumps.

Whatever the mobile particles which carry the dopant flux may be, DOCC sites always act as such entities from which and to which these mobilants may jump, even though they form pairs, etc., in their residence places. By this generalization the simple DOCC sites mechanism can be mathematically formulated as the simple vacancy mechanism, which has already been developed in great detail [39, 40]. However, only the meanings of some symbols are changed. The coupled DOCC sites mechanism taking into account kick-out reactions [27] will not be explained in this section.

The simple DOCC sites mechanism (one-dimensional model, all quantities are written as scalars) is illustrated in Fig. 1. Squares and circles symbolize DOCC sites and mobile dopant particles, respectively. Simplifying the problem, only one species of dopant particle and only one type of DOCC site are considered, which are in the lattice planes of a cubic crystal. The temporal change ($\partial C/\partial t$) of the dopant concentration C on a lattice plane (position x) is determined by four flux components, which start from or arrive at this plane, respectively. Each dopant flux component is carried by the dopant particles, which have sufficient energy to jump from their starting plane into the DOCC sites on the adjacent finishing plane.

For example, $J(1)$ is the flux portion moving from x to $x + \alpha$, where α is the lattice constant. This means that if $C(x)$ is the total dopant concentration on the lattice plane x and $\beta(x + \alpha)$ the DOCC sites concentration on the adjacent plane $(x + \alpha)$, then only the relative fraction $\Gamma(+,x)$ of all dopants determined by the product $C(x)\beta(x + \alpha)$ can jump from x to $(x + \alpha)$ during a given time interval. Accordingly, $\Gamma(+,x)$ means the corresponding jump rate in the positive direction for these dopant particles starting from x. Similar product statements have already been proposed by other authors [2–7, 9, 10, 20, 41], but they are limited by several conditions. Designating K the dopant DOCC site neighbourhood constant, the amounts of the four dopant flux components at the lattice plane x obey the relations

$$J(1) = \alpha K C(x)\beta(x + \alpha)\Gamma(+,x) \tag{25}$$
$$J(2) = \alpha K C(x - \alpha)\beta(x)\Gamma(+,x - \alpha) \tag{26}$$
$$J(3) = \alpha K C(x + \alpha)\beta(x)\Gamma(-,x + \alpha) \tag{27}$$
$$J(4) = \alpha K C(x)\beta(x - \alpha)\Gamma(-,x) \tag{28}$$

The jump rates of dopant ions (charge q) resulting from the influence of the electric field (E) are estimated at
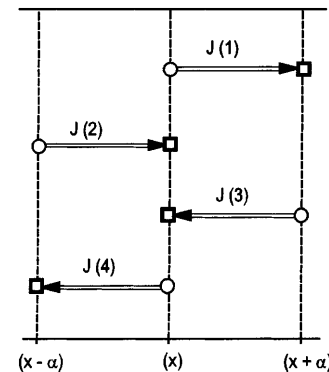

Fig. 1 The simple DOCC sites mechanism

$$\Gamma(\pm) = \omega \exp(\pm\,\Delta W/kT), \tag{29}$$

$$\Delta W = (\alpha/2)\,qE \tag{30}$$

Here ω is the isotropical dopant jump rate. The mathematical treatment is analogous to that of the simple vacancy mechanism developed in [39, 40]. The one-dimensional version gives the temporal change $[\partial C(x,t)/\partial t]$ as the sum of the four components

$$\alpha\frac{\partial C(x,t)}{\partial t} = +J(2) + J(3) - J(1) - J(4) \tag{31a}$$

as well as the continuity equation $\partial C/\partial t = -\partial J_{\mathrm{N}}/\partial x$, where $J_{\mathrm{N}}(x,t)$ means the (resulting) net dopant flux. The approximations of the parameters β, ω, C and E, which may be functions of position x and time t, by Taylor series including second-order terms, lead to the net (total) dopant particle flux density

$$\begin{aligned} J_{\mathrm{N}} = \alpha^2 K\,[&-\beta\omega C' - \beta\omega' C \\ &+ \beta'\omega C + \beta\omega C\,(qE/kT)] \end{aligned} \tag{31b}$$

The derivatives β', ω' and C' correspond to $\partial\beta/\partial x$, $\partial\omega/\partial x$ and $\partial C/\partial x$. Unlike other authors, the term "diffusion"in this paper always refers to the Fickian dopant flux component $J_{\mathrm{F}} = -\alpha^2 K\,\beta\,\omega\,(\partial C/\partial x)$. Therefore, each position-dependent diffusion coefficient of the first term (driven by C') of the right-side hand of Eq. (31b)

$$D_{\mathrm{F}}(x) = \alpha^2 K\beta(x)\omega(x) \tag{32}$$

requires necessarily to take into account the non-Fickian dopant flux portions caused by the gradients $\partial\beta/\partial x$ and $\partial\omega/\partial x$. Although the local variation of D_{F} contrasts with Fick's formulation and with Einstein's corresponding explanation, D_{F} is usually designated as the Fickian diffusion coefficient. Fick's well-known diffusion constant implicitly assumes β and ω being independent of position.

Using Eq. (32) as well as the relations $E = -\partial\Phi/\partial x$ and $\Phi = (kT/q)\ln\Psi$, Eq. (31b) gives the expression

$$J_{\mathrm{N}} = -D_{\mathrm{F}}\frac{\partial C}{\partial x}\left[1 + \frac{\partial\ln\left(\frac{\Psi\omega}{\beta}\right)/\partial x}{\partial\ln\,C/\partial x}\right] \tag{33}$$

which can be simplified to

$$J_{\mathrm{N}} = -D_{\mathrm{F}}\frac{\partial C}{\partial x}\left[1 + \frac{\partial\ln(\Psi\omega/\beta)}{\partial\ln\,C}\right] \tag{34}$$

Expressing the net (total) dopant flux (J_{N}) in an analogous way to the Fickian component, $J_{\mathrm{F}} = -D_{\mathrm{F}}(\partial C/\partial x)$, by the product

$$J_{\mathrm{N}} = -D_{\mathrm{N}}(\partial C/\partial x) \tag{35}$$

then Eq. (34) leads to the effective (total) diffusion coefficient

$$D_{\mathrm{N}} = D_{\mathrm{F}}\left[1 + \frac{\partial\ln(\Psi\omega/\beta)}{\partial\ln\,C}\right] \tag{36}$$

Replacing in Eq. (1) the quotient $(N_i/\partial N_i)$ referring to the atom fraction (N_i) of the ith species by the expression $(1/\partial\ln C_i)$ of its concentration (C_i), the comparison of coefficients of Eq. (36) with Darken's formula

$$D_i = kTM_i\left[1 + \frac{\partial\ln\gamma_i}{\partial\ln C_i}\right] \tag{37}$$

gives the activity coefficient (γ) as a function

$$\gamma = \frac{\Psi\omega}{\beta} \tag{38}$$

of the electric potential (expressed by Ψ), the dopant jump rate (ω) and the DOCC sites concentration (β). Following this statement, the chemical potential (μ_{C}) of a constituent obeys the relation

$$\mu_{\mathrm{C}} = \mu_{\mathrm{C0}} + kT\ln[(\Psi\omega/\beta)C] \tag{39}$$

where the reference potential μ_{C0} is independent of position. Consequently, each position-dependent activity coefficient $\gamma = (\Psi\omega/\beta)$ necessarily requires us to take into account the local diffusion coefficients D_{F} and D_{N}.

Darken's assumption (p. 194 in [1]), that Einstein's relation $D = kTM$ would be applicable only to ideal solutions, is physically incorrect. Equation (31b) gives the drift dopant flux (J_{Drift}) being driven only by the force (qE) as

$$J_{\mathrm{Drift}} = \alpha^2 K\beta\omega C\,(qE/kT) \tag{40}$$

where the parameters β, ω, C and E may be functions of position in general. Inserting Eq. (32) into Eq. (31b) as well as using the drift velocity (v) obeying the relations

$$v = J_{\mathrm{Drift}}\,/\,C \tag{41}$$

$$v = MqE \tag{42}$$

one may obtain an expression $D_{\mathrm{F}} = kTM$; however, the mobility M here depends on the position corresponding to $D_{\mathrm{F}}(x)$. The DOCC sites concept shows that Einstein's link between M and D_{F} is true even in that case when the demand on symmetrical distribution of dopant jump distances (being the basis of Einstein's deduction [34] for $D = $ const.!) is not satisfied because of the position dependence of β and ω [39, 40, 42]. Accordingly, D_{F} may also be a function of the position-dependent dopant concentration, so that Darken's limitation turns out to be incorrect.

Equations (32) and (38) permit us to develop the dependence

$$\gamma = \frac{1}{\alpha^2 K}\frac{\Psi D_{\mathrm{F}}}{\beta^2} \tag{43}$$

of the activity coefficient (γ) on the Fickian diffusion coefficient (D_{F}), which has hitherto been disregarded in some phenomenological thermodynamic statements on dopant transport processes in solids (e.g. [21]).

Putting the latter results into Eq. (37), we obtain the effective diffusivity D_{N} (as D denoted by Darken) as

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$$D_{\text{N}} = D_{\text{F}} \left\{ 1 + \frac{\partial}{\partial \ln C} \left[\ln \left(\frac{1}{\alpha^2 K} \frac{\Psi D_F}{\beta^2} \right) \right] \right\}$$

and therefore, because $\alpha^2 K$ is a constant of the host material

$$D_{\text{N}} = D_{\text{F}} \left[1 + \frac{\partial \ln \left(\Psi D_{\text{F}} / \beta^2 \right)}{\partial \ln C} \right] \tag{44}$$

Equation (44) is quite different from Darken's formula, so that the fundamentals of these two relations should be discussed. The atomistic kinetic approach of the DOCC sites concept is based on the principles that the dopant flux in solids is only carried by the dopant species, for which occupiable sites exist, *and* that these mobile dopant particles must have sufficient energy to jump into the sites suitable for occupation. Since the two corresponding parameters "DOCC sites concentration" and "dopant jump rate" are taken into account as position-dependent variables, they permit us to involve all effects influencing dopant migrations. From this point of view, the DOCC sites concept may be valid in general for dopant transport processes in solids. This concept shows the Fickian diffusion coefficient to be determined by the product of the DOCC sites concentration times the dopant jump rate. Consequently, Fick's diffusion constant requires that these two parameters are independent of position. Since this condition is not always satisfied in solid-state diffusion processes, additional aspects have to be considered. The basic relation [Eq. (31b)] demonstrates that the position dependence of the variable Fickian diffusion coefficient is unavoidably connected with the non-Fickian dopant flux portions caused by the gradients of the two main parameters. Furthermore, the activity coefficient is shown to be determined by the quotient of the dopant jump rate divided by the DOCC sites concentration. Since these connections have been disregarded in Darken's formula, it cannot generally be accepted. Determining the activity coefficient of a non-ideal solution by comparison of its effective diffusion coefficient (D_{N}) with the Fickian diffusion coefficient (D_{F}) of an ideal solution on the basis of Darken's formula, as predicated in tracer investigations, proves false. Equation (44) shows that such measurements yield the DOCC-sites concentration, but not directly the activity coefficient.

Since D_{F} is due to the product β times ω [see Eq. (32)], methods are unknown up to now which could determine separately each of these two parameters. The DOCC sites concept is thought to be a suitable basis to discuss other models. The generalized dopant flux relation [Eq. (31b)] leads to the following inferences:

1. The so-called vacancy wind effect, which is supposed to drive a dopant flux component proportional to the vacancy flux (J_{V}) [16, 21 (sect. 11.7.1)], proves incorrect. The vacancy gradient ($C'_{\text{V}} = \beta'$ in the case of a pure vacancy mechanism) of Eq. (31b) does not inevitably mean a vacancy flux, because the gradient C'_{V} could be induced by several effects. Of course, vacancies must satisfy their own continuity equation, taking into account the interactions of these entities together with dopants and self-interstitials. The influence of the vacancy gradient on the dopant flux is independent of the way by which the former is caused. The sole presupposition for this connection is the existence of the vacancy gradient, unconcerned whether or not vacancies may flow. From this point of view, the vacancy wind effect is inferred to be sheer hypothesis.

2. Orlowski's dopant flux terms [57–59] involving the gradients C'_{I} and C'_{V} of interstices and vacancies have wrong signs. Equation (31b) has the opposite sign for the β' term (meaning C'_{I} and C'_{V} in Orlowski's formula) compared to that for the Fickian C' component, but the signs of these components are equal to each other in the originals. The plus sign of the β' term in Eq. (31b) is physically plausible. Provided that only this gradient could exist and the other ones vanish, the dopant particles would preferentially flow in that direction, in which they can increasingly occupy sites. Accordingly, the dopant migration would proceed to the maximum in the β profile, where a dopant accumulation would develop, to which these particles would tend to move. This behaviour contrasts with Fickian diffusion, where the dopants move downhill in their own concentration profile.

3. Gossmann's and Poate's statement [22] of acceptor and donor diffusion in silicon for integrated circuit technology is limited to the Fickian dopant flux component. Although the vacancies and self-interstitials, via which the dopant migration proceeds, deviate from their thermal equilibrium values, the non-Fickian C'_{I} and C'_{V} dopant flux portions are ignored, so that the process simulation of the authors is found to be inconsistent.

4. Equations (38) and (39) exceed fundamentally the assumptions of recent thermodynamic considerations [21, 60] that the activity and the chemical potential of dopant particles would only be functions of their concentration (C). Following this, the dopant migration is believed to obey Fick's Law, where the thermodynamic factor (designated there as Φ) of the diffusion coefficient ($D = MkT\Phi$, Eq. (5.9) in [60]) is assumed to describe also the "negative diffusion" (dopant uphill migration). It must critically be emphasized that this factor Φ obscures the vacancy gradient term in the sum for the dopant flux in Manning's formula [16] and in Eq. (31b), which is responsible for the dopant uphill migration. Any formulations of the dopant flux in terms of Fick's law disregard the non-Fickian dopant flux portions, which are caused by the gradients β' and ω'. Accordingly, product statements of the effective diffusion coefficient and the (total) dopant flux, as formulated in terms of Fick's law and the Φ factor, are not suitable to explain the physical background of non-Fickian dopant transport phenomena.

Roth's and Plummer's OED model

The thermal oxidation of silicon causes a supersaturation of self-interstitials and an undersaturation of vacancies, so that the diffusion of some dopants is enhanced and that of others is retarded [48]. Since the prediction of dopant profiles in silicon plays an important role in modern microelectronic device technology, several models considering the influence of non-equilibrium process-induced point defects on dopant migrations have been developed. One of them is the model for the oxidation-enhanced diffusion (OED) of boron and phosphorus in heavily doped silicon regions, which has been proposed by Roth and Plummer [47]. The following analysis of this model, based on the DOCC sites concept, exhibits some details on the interactions between dopant particles and entities mediating dopant migrations, which may be helpful to elucidate the fundamentals in this matter. To avoid misinterpretations to other designations, some symbols have been changed in this section. The Roth–Plummer model is based on the following three assumptions:

Firstly, dopant ions (boron and phosphorus) and silicon atoms (self-interstitials) are asssumed to migrate via interstices (interstitial sites), so that these entities interact with each other.

Secondly, regardless of the missing minus sign (eq. (9) in [47]), the self-interstitial flux J_I is believed to obey the relation

$$J_I = -D_I C_I^* \frac{\partial}{\partial x}\left(\frac{C_I}{C_I^*}\right) \tag{45}$$

where C_I, C_I^* and D_I denote the self-interstitial concentration, the equilibrium value of C_I and the self-interstitial diffusivity respectively. Neglecting recombination effects, the self-interstitial continuity (eq. (10) in [47])

$$\frac{\partial C_I}{\partial t} = D_I\left[\frac{\partial C_I^*}{\partial x}\frac{\partial}{\partial x}\left(\frac{C_I}{C_I^*}\right) + C_I^*\frac{\partial^2}{\partial x^2}\left(\frac{C_I}{C_I^*}\right)\right] \tag{46}$$

is deduced from Eq. (45), so that D_I is treated as a constant.

Thirdly, the phosphorus concentration C_P is provided to satisfy the continuity equation (eq. (11) in [47])

$$\frac{\partial C_P}{\partial t} = \frac{\partial}{\partial x}\left[D_I C_P \frac{C_I}{C_I^*}\frac{\partial}{\partial x}\ln\left(C_P\frac{C_I}{C_I^*}\frac{n}{n_i}\right)\right] \tag{47}$$

where n and n_i mean the electron concentration and the intrinsic carrier concentration.

In order to examine thoroughly the model [47], the following connections should be considered.

The flux J_I of the self-interstitials can be described by the corresponding mathematical formalism of the DOCC sites concept, similar to the dopant flux. In the case that H means the concentration of interstices (interstitial sites) being suitable for occupation by self-interstitial atoms, the condition of $\omega_I = \text{const.}$, for the self-interstitial jump rate leads from Eq. (31) to the relation

$$J_I = \alpha^2 K \omega_I\left[-HC_I' + H'C_I\right] \tag{48}$$

where J_I denotes the total self-interstitial flux. Therefore, the Fickian component, $J_{I\,Fick} = -D_I C_I'$, which is driven solely by the self-interstitial gradient $\left(C_I' = \partial C_I/\partial x\right)$, is connected with the self-interstitial diffusivity

$$D_I = \alpha^2 K \omega_I H \tag{49}$$

Inserting Eq. (49) into Eq. (48), one obtains the total self-interstitial flux

$$J_I = -D_I H \frac{\partial}{\partial x}\left(\frac{C_I}{H}\right) \tag{50}$$

Comparision of the coefficients with Eq. (45) does yield the equality $C_I^* = H$, but the meaning of D_I is quite different. In order to obtain Eq. (46) from Eq. (45), D_I must be constant. However, according to Eq. (49), D_I increases linearly with H. Since the model [47] ignores this detail, its results may not be consistent.

In the case of low donor concentration, the internal electric field E is given by

$$E = -\left(\frac{kT}{q_0}\right)\left(\frac{n'}{n}\right) \tag{51}$$

wherein q_0 means the absolute amount of an elementary charge, so that the charge of an electron is $q_e = -q_0$. Assuming, furthermore, that each donor is ionized and its term has the charge $q = +q_0$, the dopant flux density can be expressed as

$$J = -D\left[C' + C\frac{\omega'}{\omega} + C\frac{n'}{n} - C\frac{\beta'}{\beta}\right] \tag{52}$$

which is equivalent to the expression

$$J = -D\,C\frac{\partial}{\partial x}\ln\left(\frac{C}{\beta}\frac{\omega}{\omega_0}\frac{n}{n_i}\right) \tag{53}$$

Therein, ω_0 denotes an arbitrary finite constant reference jump rate in order to provide a dimensionless argument in the ln function. The value of ω_0 is not critical, and it cancels out because of the differentiation. Accordingly, the phosphorus ion flux density obeys the relationship

$$J_P = -D_P C_P \frac{\partial}{\partial x}\ln\left(\frac{C_P}{C_P^*}\frac{\omega_P}{\omega_0}\frac{n}{n_i}\right) \tag{54}$$

where C_P^* means the concentration of sites (i.e. interstices in the Roth–Plummer model) suitable for occupation by phosphorus ions, and ω_P is the jump rate of phosphorus ions to occupy these suitable sites. Furthermore, C_P denotes the phosphorus ion concentration, and the diffusion coefficient D_P refers only to the Fickian component, $J_{P\,Fick} = -D_P C_P'$. The latter is that portion of the total flux [Eq. (54)] which is driven solely by the gradient $C_P' = \partial C_P/\partial x$. Equation (54) leads to the phosphorus ion continuity

$$\frac{\partial C_P}{\partial t} = \frac{\partial}{\partial x}\left[D_P C_P \frac{\partial}{\partial x}\ln\left(\frac{C_P}{C_P^*}\frac{\omega_P}{\omega_0}\frac{n}{n_i}\right)\right] \tag{55}$$

Comparison of the pre-ln coefficient of Eq. (47) with that of Eq. (55) gives the dependence of the phosphorus diffusion coefficient (D_P) on the self-interstitial parameters C_I, C_I^* and D_I of Eqs. (45) and (46) as

$$D_P = D_I C_I / C_I^* \qquad (56)$$

The connection with the DOCC sites concept formulating D_P as the product $D_P = \alpha^2 K C_P^* \omega_P$ leads to the following two inferences:

1. The phosphorus jump rate ω_P would be equal to the self-interstitial jump rate ω_I because of the relation $D_I = \alpha^2 K C_I^* \omega_I$ [see Eq. (49) with $H = C_I^*$]. However, the equality $\omega_P = \omega_I$ is physically doubtful.

2. The concentration C_P^* of sites being suitable for occupation by phosphorus ions is equal to the concentration C_I of sites being occupied by self-interstitial atoms

$$C_P^* = C_I \qquad (57)$$

Accordingly, self-interstitials may be considered to act as DOCC-sites mediating the dopant flux. This hypothesis agrees with Hu's predication [48] for the case of phosporus diffusion, that the diffusing entity is a complex of a phosphorus atom and a self-interstitial as a pair, which could alternatively be viewed as a phosphorus interstitialcy.

However, the arguments of the ln functions of Eqs. (47) and (55) exhibit a contradiction to Eq. (57). Regardless of the jump rate ω_P, which is ignored in [47], the concentration C_P^* would rise as the quotient C_I^*/C_I, which runs inversely to the $C_P^* = C_I$ identity of Eq. (57). Consequently, further investigations seem to be needed in order to solve this conflict and to develop consistent models of dopant transport in silicon crystals.

Inferences from process-induced defects and effects instead of thermodynamic phenomenological assumptions

Since the Fickian diffusion as a consequence of the dopant concentration gradient irreversibly progresses, numerous theoretical attempts have been made to interpret also the mass flows of multicomponent systems from the viewpoint of the irreversible processes of thermodynamics. The first treatment in this matter was due to Onsager [61, 62], who expressed the simultaneous fluxes of three substances in the same solution by the phenomenological relations

$$J_1 = L_{11}X_1 + L_{12}X_2 + L_{13}X_3$$
$$J_2 = L_{21}X_1 + L_{22}X_2 + L_{23}X_3 \qquad (58)$$
$$J_3 = L_{31}X_1 + L_{32}X_2 + L_{33}X_3$$

The coefficients L_{ij}, etc. (in Onsager's terminology designated as conductances) obey the reciprocal relations

$$L_{12} = L_{21}; \quad L_{13} = L_{31}; \quad L_{23} = L_{32} \qquad (59)$$

The symbol J_1 means the flux density of the substance 1 relative to the solution, and the forces X_1, X_2 etc., are given by the negative gradients of appropriate chemical potentials. Accordingly, the cross-over term $L_{12}X_2$ refers to that flux component of substance 1 which is due to the potential gradient of substance 2 induced by the corresponding concentration gradient of the latter.

Noteworthy is that Onsager himself formulated the phenomenological relations on the pattern of the linear superposition of fluxes and forces (see also [63]), so that his framework extends the results of Helmholtz [64] referring to the superimposition of electrical and chemical potential gradients in electrolytes as well as the explanations of Boltzmann [65] on thermoelectric phenomena.

Although in 1888 Nernst [66] had emphasized that, even in the case of hydrodiffusion, Fick's linear law on the diffusant flux density had been found to be not valid in general, nevertheless, Onsager's linear superposition of Fickian flux components is in some cases up to the present time still assumed to govern mass transport processes in solid-state solutions.

Condensing these results: the discontinuous process of mass transport in a solid material, which proceeds by discrete jumps of mobile particles via suitable sites, is inadequately described by a relation which is taken from continuous phenomena (e.g. conduction of heat), so that the interactions between solutes and solvents are ignored. The main discrepancies between the phenomenological relations and other statements will be discussed in the following.

Inferred from the Kirkendall effect, the vacancy mechanism is favoured to govern mass flows in solids [67]. Accordingly, an atom can jump to a neighbouring site if it is vacant. Diffusion in a binary metal alloy can then be expressed by using different diffusion coefficients for the two metals, where the lattice is a reference frame. The principles of the irreversible thermodynamics of an alloy with vacant sites are therefore assumed to be applicable to mass flow phenomena, if the vacancies are treated as one of the constituents of the alloy [67].

Following this, vacancies are considered to be the third constituent in the binary metal system of Eq. (58). Taking the lattice as a reference frame, as explained by Bardeen and Herring [67], must be distinguished from the barycentric system presupposed in several thermodynamic phenomenological models. The decisive condition of the latter, that the total number of lattice sites would be conserved, gives the balance of flows. Therefore, the sum over all flows of atoms in one direction is balanced by an equal flow of vacancies in the opposite direction. In contrast to these ideal conditions, both the constancy of the lattice sites as well as the constancy of the vacancies were in 1948 critically estimated to be doubtful hypotheses in some cases of solid-state diffusion [72].

Whenever vacancies are occupied by dopant particles, the host material will in consequence of these interactions be manifoldly changed compared to its pure state.

The difference in atom volumes between solvent and solute particles (so-called mismatch) may give rise to strains in the lattice planes, so that even distant undoped crystal regions may be deformed. The occupation of vacancies by dopants also modifies the balance between the former and self-interstitials (i.e. host atoms at interstices), so that these reactions may proceed far from the corresponding equilibrium values of pure crystals and may be able to alter other crystal regions. Accordingly, the phosphorus diffusion from an embedded phosporus-doped silicon zone, acting as the diffusant source, into the bulk of the matrix crystal was found to be enhanced by an outer phosphorus diffusion zone. Since these two zones were isolated from each other by an undoped silicon epitaxy layer which showed no irregularities, the authors interpreted the effect by excess vacancies, which are due to the dissociation of phosporus-vacancy pairs (so-called E-centres) developing at the surface of the outer diffusion zone [68]. Crystal regions may furthermore be changed by dopant-interstitials being analogously located with self-interstitials at interstices. Last, but not least, the creation, annihilation and distribution of vacancies depend on their nearest-neighbour particles.

Summarizing the foregoing influences of dopants on host crystals, two main effects should be distinguished from each other: the lattice spacing and the sum over all the sites (meaning vacant and occupied) on a lattice plane may vary with the dopants. In other words: since the reference volume, to which the concentration amounts are related, is given by the distance between lattice planes, its expansion may depend on the dopant concentration itself. Accordingly, lattice planes, which are located in crystal regions disturbed by position-dependent dopant concentration profiles, may migrate with respect to an undisturbed crystal zone.

This connection between the consequences of processes appears reasonable: those process-induced effects, which are responsible for crystal deformations, for changes of the lattice spacings and for migrations of lattice planes, may also alter the total number of sites (i.e. the sum over particles and vacancies) per unit volume. Thence the conservation of sites per unit volume, which is assumed in several process calculations to be a prerequisite (expressed by the vanishing sum over the fluxes of all entities, i.e. particles and vacancies, crossing a lattice plane), may be only an approximate description, when the crystal region is modified by the actual process. Therefore, the subsequent progress of a diffusion process may be influenced by the crystal changes, which have been caused by the process itself during the preceding course until the actual instant.

The foregoing details point out several problems in the evaluation of dopant transport processes in solids, which are more complicated than defining the mean-volume frame of reference or the number-fixed coordinate system as discussed elsewhere (p. 355 in [69]).

Both the linear dependencies of flux components on driving forces (phenomenological equations) and the conservation of sites are the decisive relations of the classical theory, which are additionally applied to the thermodynamic framework of irreversible processes in order to calculate mass fluxes in solids. Since the principles of irreversible thermodynamics themselves do not favour any transport mechanism, only the supplementary relations of isothermal mass migrations in solids are here the subject of discussion (p. 4 of [70]).

Of course, non-Fickian dopant transport phenomena in solids, having already been observed in some cases, cannot adequately be formulated on the basis of linear relations expressed analogicously to Fick's law. The main problem, which remains to be solved, is the same as for the DOCC sites concept, namely developing functional dependencies on position of both the concentration of dopant-occupiable sites (designated as accessible sites in Philibert's terminology (p. 93 in [69]) as well as the jump rate of dopant particles to occupy these sites, when at distinct process times only local dopant concentration profiles deviating from standard solution functions are known.

Involving the effect of concentration-dependent lattice spacings in a dopant flux relation requires us to develop a new model. Accordingly, extension of the DOCC sites concept to a more comprehensive statement may be useful, since it has hitherto been limited to constant distances between lattice planes. The ranges of validity of dopant transport models and of other supplements, which are added to the thermodynamics, are only experimentally provable (p. 31 in [70]).

The discrepancy between the kinetic approaches and the classical thermodynamic phenomenological statements will in the following be explained on the basis of the relations formulated by De Groot and Mazur [70]. The authors intentionally limited their explanations to diluted mass systems, since even in 1984 they thought that non-linear dependencies of fluxes on concentration gradients had been insufficiently investigated (p. 4 in [70]). Thence the mean volume velocity and the barycentric velocity are neglected, and the volume of the doped region is assumed to be independent of the dopant concentration, so that the diffusion coefficient is considered to be practically uniform. As a result of these simplifications, the dopant flux in a crystal is expressed by the same formula as in the case of fluid media (pp. 34, 35 and 254–257 in [70]).

However, several investigations on dopant transport processes in solids via vacancies point out that the linear dependence of the flux on the driving concentration gradient is only satisfied when both the concentration of the vacancies as well as the dopant jump rate are locally uniformly distributed [71]. The position-dependent vacancy distribution acts twofold on the dopant migration: firstly, the Fickian diffusion coefficient, which is the multiplication factor to the negative gradient of the dopant concentration, proportionally increases with increasing vacancy concentration; and secondly, the vacancy concentration gradient gives rise to a non-Fickian dopant flux portion. In other words: mass fluxes in

solids, which are mediated by locally inhomogeneously distributed dopant-occupiable sites, may obey rather non-linear functional dependencies on concentrations and gradients of all entities other than Fick's linear law. Since, in 1948, non-linearities in dopant flux relations were discussed as being responsible for the Kirkendall effect [72, 73], the thermodynamic phenomenological statements resting on linear flux relations may give only approximate formulae to estimate dopant distributions in solids. From this point of view, Darken's equation is also questionable (pp. 211, 233 in [69]).

Point defects, via which the dopant migration takes place, may have a drastic effect on it, when their actual concentrations deviate from the equilibrium amounts of the pure material (pp. 7, 119 in [51]). Inferring from several investigations on acceptor and donor diffusion in silicon, Orlowski [74] has repudiated the classical equations, which are usually applied to determine the L-coefficients of the phenomenological flux relations. Quotation: "The problem is, of course, to determine the matrix elements L_{ij}. Their specific functional form cannot be simply found from the Onsager reciprocal relation, the Gibbs-Duhem relation, or the conservation of lattice sites, because these relations are devoid of the intrinsic features of the codiffusion dynamics" (p. 401 in [74]). Orlowski's statement involves "dynamic effects giving rise to redistribution of the interstitials by the impurity diffusion itself" (p. 399 in [74]). Corresponding coupled dopant and point-defect dynamics occur by interactions between phosphorus atoms (or ions) and silicon interstitials, which are assumed to be responsible for the experimentally proved phosphorus uphill migration in the vicinity of locally damaged silicon regions (p. 732 in [75]).

The flow direction of that non-Fickian dopant flux component, which is induced by the concentration gradient of occupiable sites, to the position of maximal concentration has also been proved in the case of hydrogen profiling in wet thermally grown silicon dioxide layers on silicon substrates. Using the N-15 nuclear reaction analysis (NRA) method to measure H concentration distributions, a considerable H accumulation (increasing with increasing N-15 ion irradiation dose) has been found to take place in the dioxide-silicon transition zone, where the maximal concentration of appropriate trap sites is located. Since the analyzing N-15 ion beam itself causes the changes of the H profile actually being measured, the investigations undoubtedly point out, that this non-Fickian H-flux component induced by the gradient of occupiable sites must satisfy two conditions in order to build up the H peak in the transition zone: firstly, flow uphill of the H peak to its maximum position near the maximum position of trap sites, secondly, exceed the Fickian H-flux portion moving downhill in the H concentration profile. Remarkably, during the NRA measurement the entire dioxide-silicon system becomes impoverished in H by out-diffusion from the bulk dioxide through the surface into the ambient vacuum, although the H peak is simultaneously built up in the transition zone [76].

In addition, other authors, e.g. Lebon (p. 145 in [77]), have thought the classical thermodynamics of irreversible processes to be in principle unable adequately to describe processes taking place far from equilibrium, in particular high frequency and short wavelength phenomena. We infer from this predicament that solid-state transport processes cannot be described sufficiently within the classical thermodynamic-phenomenological framework, when the gradients of host atoms, vacancies, dopant particles, dopant- and self-interstitials foil the equilibrium between these entities. Consequently, in all cases of isothermal dopant migrations in solids, the basic relations of the transport mechanism and the parameters involved therein must be found as supplements to thermodynamic frameworks by theoretical and experimental investigations (p. 1559 in [77]).

From the details discussed above, realistic isothermal dopant transport models, which involve the defects and effects of such technological important processes as implantation, annealing, oxidation, etc., remain to be developed as a basis for calculations of dopant distributions. The kinetic theories are in principle the most favourable ones for the physical understanding, because they give a complete account of the transport mechanism and lead to numerical amounts for the coefficients appearing in the phenomenological relations (p. 236 in [78], p. 3 in [79]). Since the set of phenomenological relations is an extra-thermodynamic hypothesis and it is quite conceivable that in some particular cases the relationships between fluxes and forces may not be linear, the domain of validity of a dopant transport model is only provable by experiment (p. 45 in [80]).

Using the terminology of thermodynamics, mass transport phenomena progressing in crystals via inhomogeneously distributed occupiable sites should be distinguished from Markoffian transition processes between particular states of a system (p. 680 in [81]), so that Pauli's master equation is also not applicable to particle fluxes in solids (p. 298 in [82]). Pauli's formula, which describes the transition of a physical system from one state to another by the change in the probability of the initial state with respect to time, is connected with two decisive presuppositions [83]:

1. The change in the probability of a particular state with respect to time is assumed to occur analogously to radioactive decay.

2. The transition coefficients (meaning the transition probabilities per unit time) of these changes between two groups of states are predicted to be independent of the transition directions (symmetry theorem), from which the master equation is inferred to govern irreversible processes in general, whether or not the systems are in equilibria (sect. 15.1, sect. A12 in [81]).

Following on from this, critical remarks must be made to applications of Pauli's theoretical results to dopant transport processes in solids. Appreciating the Kirkendall effect, Seitz [84] in 1948 asserted that the vacancy mechanism of dopant migrations in metals was

to be strongly preferred over the direct interchange or interstitial mechanisms (p. 1516 in [84]). Accordingly, "... a given atom can move from one site to another only when a vacant lattice site appears among its neighbors and the given atom jumps into this neighboring position" (p. 1515 in [84]). Generalizing Seitz's explanation: whenever a dopant corpuscle moves in a crystal by jumping from a lattice plane (starting position) to an adjacent site (finishing position) of the neighbouring plane, this finishing site must be suitable (meaning occupiable) with respect to this jumping dopant corpuscle and its actual energy. Thence the number of dopant particles which leave a distinct lattice plane during a given time interval is also determined by the number of occupiable sites which are located on the adjacent planes. Consequently, this situation is quite different from the radioactive decay of isotope particles occurring independently of their adjacent entities, so that Pauli's equation is not applicable to mass transport processes.

Extending Seitz's dopant transport model, which is based on uniform vacancy currents throughout doped crystal regions, to a more comprehensive concept also involving position-dependent profiles of dopant-occupiable sites, one has to expect non-linear mass flow terms, whereas De Groot's and Mazur's basic relations are limited to linear effects even in the case of anisotropic crystals (pp. 34, 35 in [70]). From investigations on non-equilibrium effects associated with mass flows in solids, Oldham and Blackburn [86] have summarized the consequences when dopant corpuscles occupy vacancies as follows: the vacancy concentration must vary continuously with position, or porosities must form or dimensional changes in the solid material must occur (p. 151 in [85]). From this point of view, the dopant jump rate (i.e. the probability of a dopant particle occupying a suitable site on the adjacent lattice plane during a given time interval) may also depend on the jump direction, when lattice planes are differently deformed, whereas this parameter is independent of the transition direction in Pauli's relation. In addition, the number of occupiable sites may also vary with position.

Last, but not least, both the concentration of dopant-occupiable sites as well as the dopant jump rate are to be understood as effective parameters, which compress the whole mathematical description of the irreversible isothermal dopant transport process to a short formula explaining clearly both Fickian diffusion as well as non-Fickian phenomena. The Fickian diffusion constant characterizes that special case when the host material is only inessentially changed by dopant particles and other influences. The decisive criterion for the validity of models on mass fluxes in solids is the description of non-linear dependences of fluxes on forces (non-Fickian dopant flux components). For this purpose, the DOCC sites concept may be a useful model. However, determining its two parameters, the concentration of occupiable sites as well as the jump rate, as functions of position, dopant concentration, etc., is a task which remains to be accomplished.

Conclusion

The models which are here more thoroughly analysed only incompletely reflect the multiplicity of contrasting statements in the literature. Although in 1968 DeHoff [12] suggested a reformation of Fick's first law for solid-state diffusion and replaced this traditional description by an atomistic approach, even recent comprehensive publications have confined their explanations to phenomenological thermodynamic formulations based on several Fickian flux components and on intuitive assumptions (pp. 196, 434 in [21]). Therefore discussion on a generally acceptable model of dopant transport processes in solids has been valid up to now. The DOCC sites concept here used as a basis for the scrutiny of dopant transport models is an atomistic approach, which improves DeHoff's one by the consideration of the position dependence of two parameters determining dopant migrations. From this point of view, it could be a reasonable task for thermodynamic estimations to formulate the dopant jump rate as a function of position-dependent distributions of both (dopants and DOCC sites) in order to develop a unified model of dopant transport processes in solids. Finally, it would be an important step forward to deduce the dopant flux relation of the atomistic model from the principles of thermodynamics in order to verify the phenomenological assumptions on interactions between entities.

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