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Effective Diffusion Coefficients of Point Defects in Impure Materials

L. K. Mansur

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EFFECTIVE DIFFUSION COEFFICIENTS OF POINT DEFECTS IN IMPURE MATERIALS

L. K. Mansur

ABSTRACT

Effective diffusion coefficients of vacancies and interstitials in a material containing impurities are derived in terms of impurity and point defect concentrations and reaction parameters. Irradiation and thermal conditions are considered. Several expressions presented earlier are reviewed. These are found to be limiting or approximate forms to a more general result. The regimes of importance of the point defect processes of thermal dissociation, trapping, recombination with bound point defects of the opposite type, and impurity-associated transport to sinks are evaluated in terms of the structure of the effective diffusion coefficients.

INTRODUCTION

When vacancies or interstitials diffuse in a material containing impurities, the point defect diffusion coefficients characteristic of the pure material are altered. The nature of the alterations is determined by the detailed reactions with the impurities. An effective diffusion coefficient may be calculated from the diffusion coefficient in the pure material and detailed knowledge of the point defect impurity reactions. The effective coefficient may be used for some purposes as if it were a simple coefficient characteristic of the material.

That is, under certain carefully defined conditions the real material with impurities behaves as if it were a simple material characterized by an effective diffusion coefficient whose form is obtained theoretically from knowledge of the real material.

The importance of the concept rests in part on this property. In certain experiments on the diffusion of point defects in impure materials, all that can be obtained are measures of effective diffusion coefficients. By knowledge of the theoretical form, however, it may be possible to unfold the more fundamental parameters. Effective diffusion coefficients are also useful in describing analytically the necessary relations between fundamental reaction parameters determining the several important physical regimes possible for the diffusion of point defects in impure materials.

The purpose of this paper is to obtain the effective diffusion coefficients of point defects in impure materials for mobile or immobile impurities with or without irradiation. Expressions derived in the literature are reviewed. It is shown that the present results under various approximations reduce to forms similar to those obtained earlier. The physical bases of the various terms appearing in the effective diffusion coefficients are described. The regimes where each process is dominant are described, and the necessary conditions on the fundamental reaction parameters are derived.

REVIEW

Effective diffusion coefficients of point defects in impure materials have been given in the literature in several forms over the past twenty years. We may conveniently classify these according to whether the impurity-point defect complexes are mobile or immobile, whether account is taken of the transport associated with association-dissociation reactions, and whether the treatment includes irradiation conditions or only thermal annealing. The treatments for thermal annealing apply only to vacancies since the thermal concentration of interstitials is usually negligible, while the treatments that cover irradiation conditions also include self-interstitials.

Effective Diffusion Coefficients for Thermal Conditions

Damask and Dienes [1] have treated vacancy annealing in the presence of immobile impurity-point defect complexes. Chemical rate equations are written describing the fates of vacancy and vacancy-impurity complexes. These equations use rate constants which are proportional to diffusion coefficients and the mean residence time of point defects bound at impurities. The result obtained in Ref. [1] can be written as

$$D_v^{ef} = D_v/(1 + \kappa_v \tau_v C^t) \quad , \tag{1}$$

where D_v^{ef} is the effective diffusion coefficient and D_v the vacancy diffusion coefficient in pure material. It is given by $D_v = D_v^0 \exp(-E_v^m/kT)$ where

D_v^0 is a constant, E_v^m is the vacancy migration energy,* k is Boltzmann's constant and T is the temperature. The capture coefficient $\kappa_v = 4\pi r_v' b^2 w_4$, when multiplied by the physical impurity concentration (per unit volume), C^t, describes the rate of capture of free vacancies per unit physical free vacancy concentration. Here b is a lattice dimension and w_4 is the jump frequency of a vacancy from an unbound to a bound site. The term w is a jump frequency where the nomenclature here agrees with the "five frequency model" for vacancy diffusion which has become conventional. In the absence of detailed measurements for a specific system we have previously taken $w_4 = D_v/b^2$ [2]. The radius r_v' describes the volume about the impurity in which a vacancy is captured. The mean time a vacancy is trapped before thermal release is given by $\tau_v = w_3^{-1}$ where w_3 is the jump frequency for dissociation of the vacancy-impurity complex. This frequency can be written as $w_3 = \nu_3 \exp[-(E_v^m + E_v^b)/kT]$ where E_v^m and E_v^b are the energies of vacancy migration and binding respectively [3]. The attempt frequency for dissociation, ν_3, in the absence of measured values for a specific system has been taken [2] as D_v^0/b^2, i.e., as in the pure matrix.

Where vacancy-impurity complexes are mobile with a diffusion coefficient D_v', a generalized form of eq. (1) has been given by Damask and Dienes [4] and Flynn [5] as

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*This energy E_v^m is that part of the free energy often referred to in thermodynamic terms as the enthalpy.

$$D_v^{ef} = \frac{D_v + D_v' \kappa_v \tau_v C^t}{1 + \kappa_v \tau_v C^t} \ . \tag{2}$$

It has been shown by Howard and Lidiard [6], however, that there is in general also transport by the association-dissociation reaction in addition to that by the migration of complexes described by D_v' above. We denote the overall impurity-associated diffusion coefficient as D_v^*. The further generalization of eq. (2) by Howard and Lidiard may then be written as

$$D_v^{ef} = \frac{D_v + D_v^* \kappa_v \tau_v C^t}{1 + \kappa_v \tau_v C^t} \ . \tag{3}$$

For fcc materials in which the impurity concentration gradient can be neglected and under several other assumptions, they show that $D_v^* = D_v' + D_v''$, where D_v'' is the diffusion coefficient describing transport by association-dissociation reactions.* In practice, as described by Howard and Lidiard, eq. (2) is often a good approximation to eq. (3). The equations (1)—(3) are only valid provided $C_v' \ll C^t$, i.e., the concentration of trapped vacancies is much less than the concentration of impurities. A form which applies to the case where $C_v' \ll C^t$ is not fulfilled is also given in Ref. [6] and we shall return to this point later.

Effective Diffusion Coefficients for Both Irradiation and Thermal Conditions

For point defect diffusion during irradiation with trapping at immobile traps, Schilling and Schroeder [8] have proposed that eq. (1)

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*The vacancy diffusivity D_v^* appearing in eq. (3) may be obtained under more general conditions in terms of the jump frequencies, w_j, which can be defined in relation to the impurity in the five frequency model for vacancy-impurity diffusion [7].

and its analog for interstitials obtained by replacing the subscript v with i also describe the effective diffusion coefficients in rate equations derived for pure materials, in place of the simple diffusivities. In this way they investigate the effects of point defect trapping on swelling.

Mansur and Yoo [2] have found that eq. (1) and its interstitial analog are limiting forms of a more general result that applies during irradiation for a material with immobile point defect-impurity complexes. They find that eq. (1) and its interstitial analog are valid where the concentrations of bound point defects are controlled by trapping-detrapping reactions and not by the recombination of bound defects with the opposite free defect. This applies for low impurity-point defect binding energies, for example. The more general forms are given as [2]

$$D_v^{ef} = D_v/[1 + \kappa_v\tau_v(C^t - C_v')/(1 + \tau_v C_i R_v)] \quad , \qquad (4)$$

$$D_i^{ef} = D_i/[1 + \kappa_i\tau_i(C^t - C_i')/(1 + \tau_i C_v R_i)] \quad , \qquad (5)$$

where κ_i and τ_i are the interstitial analogs to κ_v and τ_v defined following eq. (1). The quantities C_v and C_i are the physical free vacancy and interstitial concentrations. The recombination coefficients $R_v = 4\pi r_v D_i$ and $R_i = 4\pi r_i D_v$ describe recombination of free interstitials with bound vacancies and of free vacancies with bound interstitials respectively. The quantity $(C^t - C_v')$ or $(C^t - C_i')$ appears rather than C^t to account for the fact that a fraction of the impurities C_v'/C^t for vacancy trapping or C_i'/C^t for interstitial trapping, are already occupied and hence act as recombination centers.* These equations are not limited to conditions where $C_i', C_v' << C^t$.

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*The case where one type impurity may bind either vacancies or interstitials has also been treated [2,9].

MORE COMPREHENSIVE EFFECTIVE DIFFUSION COEFFICIENTS

Equations

In this section more general expressions are derived. It is then shown that in limiting cases these reduce to expressions similar to those above. Consider the least restrictive case where vacancies may be bound at solutes during irradiation and the vacancy-impurity complexes may be mobile. The equations describing the concentrations of free and bound vacancies and free interstitials may be written

<u>Free Vacancies</u>

$$G_v + \tau_v^{-1} C'_v - R C_i C_v - C_v \kappa_v (C^t - C'_v) - K_v C_v = \frac{\partial C_v}{\partial t} \qquad (6)$$

<u>Free Interstitials</u>

$$G_i - R C_i C_v - C_i R_v C'_v - K_i C_i = \frac{\partial C_i}{\partial t} \qquad (7)$$

<u>Bound Vacancies</u>

$$C_v \kappa_v (C^t - C'_v) - \tau_v^{-1} C'_v - C_i R_v C'_v - K^*_v C'_v = \frac{\partial C'_v}{\partial t} \quad . \qquad (8)$$

Except during the transient after initiation of irradiation or abrupt changes in temperature for example, the right hand sides of these equations may be replaced with zero. The terms G_v and G_i are the generation rates of vacancies and interstitials by both radiation and thermal processes and are described in detail in Ref. [9]. The symbol R is the coefficient of recombination for free vacancies and interstitials and is given by $4\pi r_0 (D_i + D_v)$ when r_0 is the corresponding radius of recombination and D_i and D_v are the interstitial and vacancy diffusion coefficients. The symbol

R_v for immobile vacancy traps is defined after eq. (5). In principle R_v should also contain the diffusivity of impurity-associated vacancies when this is non-zero. Since the interstitial diffusivity is normally many orders of magnitude larger than this, the definition of R_v containing only D_i is usually adequate.

The coefficients K_v and K_v^* are respectively the loss rates of vacancies to sinks per unit physical free vacancy concentration (K_v), and per unit bound vacancy concentration by pair migration and association-dissociation (K_v^*). These coefficients are comprised of contributions from each of j types of sinks. Thus, $K_v = \sum_j K_v^j = D_v \sum_j S_v^j$ and $K_v^* = \sum_j K_v^{*j} = D_v^* \sum_j S_v^j$ in terms of the diffusivities described earlier. The quantities S_v^j are the strengths of the sinks of type j for vacancies. For voids, $S_v^V = 4\pi \int r_V Z_v^V(r_v) n(r_v) dr_V$, where $Z_v^V(r_V)$ is the capture efficiency for vacancies of a void of radius r_V, and $n(r_V)dr_V$ is the number density of voids between radii r_V and $r_V + dr_V$ per unit volume. For dislocations $S_v^d = Z_v^d L$ where Z_v^d is the capture efficiency of a dislocation for vacancies and L is the dislocation density. We have assumed for the purposes of the present paper that the sinks strengths for impurity-associated vacancies equal those for free vacancies since departures from this have little relevance to the major points of this paper.

With the definition

$$D_v^{ef}(C_v + C_v') = D_v C_v + D_v^* C_v' \qquad (9)$$

we can now obtain the full expressions for the effective diffusion coefficient. The idea contained in eq. (9) is that the entire population of vacancies, free and bound, is assigned one diffusion coefficient,

D_v^{ef}, which is obtained as the weighted sum of simpler diffusion coefficients describing individual processes. Using eq. (8) we obtain

$$C_v' = \frac{C_v\kappa_v\tau_v(C^t - C_v')}{1 + R_v\tau_v C_i + \tau_v K_v^*} = \frac{C_v\kappa_v\tau_v C^t}{1 + C_v\kappa_v\tau_v + R_v\tau_v C_i + \tau_v K_v^*} \qquad (10)$$

and from eq. (9)

$$D_v^{ef} = \frac{D_v + D_v^*\left[\dfrac{\kappa_v\tau_v(C^t - C_v')}{1 + R_v\tau_v C_i + \tau_v K_v^*}\right]}{\left[1 + \dfrac{\kappa_v\tau_v(C^t - C_v')}{1 + R_v\tau_v C_i + \tau_v K_v^*}\right]} = \frac{D_v + D_v^*\left[\dfrac{\kappa_v\tau_v C^t}{1 + C_v\kappa_v\tau_v + R_v\tau_v C_i + \tau_v K_v^*}\right]}{\left[1 + \dfrac{\kappa_v\tau_v C^t}{1 + C_v\kappa_v\tau_v + R_v\tau_v C_i + \tau_v K_v^*}\right]} . \quad (11)$$

The effective interstitial diffusion coefficient may be obtained from eq. (11) by substituting the subscript i for v,

$$D_i^{ef} = \frac{D_i + D_i^*\left[\dfrac{\kappa_i\tau_i(C^t - C_t')}{1 + R_i\tau_i C_v + \tau_i K_i^*}\right]}{\left[1 + \dfrac{\kappa_i\tau_i(C^t - C_i')}{1 + R_i\tau_i C_v + \tau_i K_i^*}\right]} = \frac{D_i + D_i^*\left[\dfrac{\kappa_i\tau_i C^t}{1 + C_i\kappa_i\tau_i + R_i\tau_i C_v + \tau_i K_i^*}\right]}{\left[1 + \dfrac{\kappa_i\tau_i C^t}{1 + C_i\kappa_i\tau_i + R_i\tau_i C_v + \tau_i K_i^*}\right]} . \quad (12)$$

As discussed after eq. (8) for R_v, R_i for mobile interstitial-impurity complexes now contains the sum of free vacancy and bound interstitial diffusion coefficients in place of the free vacancy diffusion coefficient in the definition after eq. (5).

Where there are both free and bound vacancies and free and bound interstitials simultaneously at either the same or different types of impurities, then the additional reactions of bound vacancies with bound interstitials must be taken into account. The result then contains extra terms such that, for example, eq. (11) becomes

$$D_v^{ef} = \frac{D_v + D_v^* \left[\dfrac{\kappa_v \tau_v (C^t - C_v' - C_i')}{1 + R_v \tau_v C_i + R_{vi} \tau_v C_i' + \tau_v K_v^*}\right]}{\left[1 + \dfrac{\kappa_v \tau_v (C^t - C_v' - C_i')}{1 + R_v \tau_v C_i + R_{vi} \tau_v C_i + \tau_v K_v^*}\right]} \tag{13}$$

where one type of impurity binds either vacancies or interstitials. The symbol R_{vi} is the coefficient of recombination for a bound vacancy with a bound interstitial.

Limiting Forms

As special cases, eqs. (11) and (12) contain forms similar to eqs. (1) through (5) derived previously by several workers as described under REVIEW.

If transport by diffusion of complexes and by association-dissociation reactions is negligible, $D_v^* = D_i^* = 0$. Under these conditions and during irradiation eqs. (11) and (12) reduce precisely to eqs. (4) and (5) derived earlier by Mansur and Yoo [2]. This occurs by the vanishing of the terms in D*, and by the vanishing of the terms in K*.

For vacancy diffusion in the absence of irradiation, eq. (11) reduces to forms similar to eqs. (1)—(3) after making various approximations. Without irradiation $C_i \to C_i^e$, the thermal interstitial concentration, which can be ignored. Eq. (11) then becomes

$$D_v^{ef} = \frac{D_v + D_v^* \left[\dfrac{\kappa_v \tau_v (C^t - C_v')}{1 + \tau_v K_v^*}\right]}{\left[1 + \dfrac{\kappa_v \tau_v (C^t - C_v')}{1 + \tau_v K_v^*}\right]} \ . \tag{14}$$

If we now assume that $C'_v << C^t$ in eq. (14), we obtain a form similar though not identical to eq. (3), as obtained by Howard and Lidiard [6]. If we further set $D^*_v = D'_v$ in eq. (14), i.e., allow no transport by association-dissociation reactions, we obtain a form similar though not identical to eq. (2), as obtained by Damask and Dienes [4] and Flynn [5]. Finally, if we set $D^*_v = D'_v = 0$ in eq. (14), i.e., allow no vacancy transport by the movement of vacancy-impurity complexes, we obtain a form identical to eq. (1) as obtained by Damask and Dienes [1].*

In the previous paragraph the phrase "similar though not identical to" means that the special forms of eq. (14) obtained by these approximations contain the term $\tau_v K^*_v$ while eqs. (2) and (3) do not. This term describes impurity-associated migration of vacancies to sinks. Only if $\tau_v K^*_v << 1$ can this process be ignored. This would apply for short mean lifetimes for thermal release, τ_v, low sink strengths, S_v, or low impurity associated diffusion coefficients D^*_v. To estimate when this term might be important, suppose we take $\tau_v = \frac{b^2}{D_v} \exp (E^b_v/kT)$ in the approximation described following eq. (1). Then the above inequality becomes

$$b^2 S_v \left(\frac{D^*_v}{D_v}\right) \exp(E^b_v/kT) << 1 \quad . \tag{15}$$

For typical materials $b^2 S_v \sim 10^{-5}$ to 10^{-4}, so that if, for example, D^*_v is comparable to D_v, then above vacancy-impurity binding energies of $\sim$5 to 6 kT eqs. (2) and (3) are not good approximations to eq. (14).

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*Equation (14) also gives the effective diffusion coefficient for chemical interstitial in the presence of traps and sinks. For hydrogen diffusion, for example, the replacement of the subscript v with H in eq. (14) would give the effective hydrogen diffusion coefficient.

The reader may also note that when $C'_v \ll C^t$ is not fulfilled, and $D^*_v = D'_v$, the result given by Howard and Lidiard to cover this case, eq. (1.6) of Ref. [6], is not quite equivalent to eq. (14), even when the term $\tau_v K'_v$, which describes loss of bound vacancies to sinks in eq. (14), is omitted. Equation (1.6) of Ref. [6] can be written as

$$D_v^{ef} = \frac{C^t C_v D_v + D'_v C'_v (C^t - C'_v)}{C^t (C_v + C'_v) - C'^2_v} \quad . \tag{16}$$

By eq. (8), in the approximations described before eq. (16), we obtain without irradiation

$$C_v \kappa_v (C^t - C'_v) = \tau_v^{-1} C'_v \quad . \tag{17}$$

Using this result in eq. (14), again in the above approximations, we obtain

$$D_v^{ef} = \frac{C^t C_v D_v + D'_v C'_v (C^t - C'_v) - D_v C_v C'_v}{C^t (C_v + C'_v) - C'^2_v - C_v C'_v} \quad . \tag{18}$$

The last terms in the numerator and denominator of eq. (18), which is derived from eq. (14), do not appear in eq. (16) which is equivalent to eq. (1.6) of Ref. [6]. Eq. (18) is well approximated by eq. (16), however, when $C_v \ll C'_v$. Since for fcc metals [2]

$$\frac{C'_v}{C_v} = \frac{\tau_v \kappa_v (C^t - C'_v)}{(1 - 12\, C^t \Omega)} \approx \frac{12\, \Omega\, C^t \exp(E^b_v/kT)}{(1 - 12\, C^t\, \Omega)}$$

under thermal conditions, this occurs when $E^b_v > 5$ kT for the impurity concentration $\Omega C^t \sim 0.1\%$, for example. Also, when the condition $C_v \ll C'_v$ is not fulfilled, C_v, $C'_v \ll C^t$ under normal conditions and then the difference between eqs. (16) and (18) lies again only in negligible terms (i.e., those which do not contain C^t).

PHYSICAL REGIMES

The effective diffusivities for vacancies and interstitials in the presence of impurities with or without irradiation are given by eqs. (11) and (12) respectively. The physical significance of each term in these equations can be illustrated while also describing the range of parameters within which a particular physical process dominates. To be specific, consider eq. (11). The terms in the denominator of the term multiplying D_v^* and also appearing in the lower denominator describe the processes controlling the concentration of bound vacancies. These terms determine the contribution of the bound vacancies to the effective diffusivity and are written below

$$1 + \tau_v \kappa_v C_v + \tau_v R_v C_i + \tau_v K_v^* \quad . \tag{19}$$

There are thus four processes accounted for in determining the concentration of bound vacancies. The terms in (19), which are normalized to τ_v^{-1} in the form shown, can be identified with vacancy thermal release, trapping, recombination of bound vacancies with free interstitials, and impurity-associated transport to sinks respectively. Below we examine in turn the conditions under which the trapping, bound recombination, and impurity-associated transport terms may be important with respect to the thermal release term in determining the concentration of bound vacancies.

Trapping

The trapping term becomes important in limiting the number of bound vacancies when

$$\tau_v \kappa_v C_v \gtrsim 1 \quad . \tag{20}$$

Evaluating κ_v and τ_v as described following eq. (1), we reduce eq. (20) to

$$E_v^b \gtrsim -kT\ \ell n\ (4\pi\Omega C_v) \quad , \qquad (21)$$

where we have taken $r_v'b^2 \sim \Omega$, the atomic volume.* During irradiation the free vacancy concentration can be calculated [2], and the fractional free vacancy concentration, $C_v\Omega$, often lies in the range 10^{-7}–10^{-5}. Thus, the condition (21) becomes

$$E_v^b \gtrsim 10\ kT \qquad (22)$$

in order for the trapping rate to be *important* with respect to the thermal release rate in determining the bound vacancy concentration. The trapping rate is of course *non-negligible* at binding energies significantly below this and should be considered whenever $E_v^b \gtrsim 5\ kT$.

By a similar method it can be shown using eq. (12) that the trapping rate for interstitials is important to the same degree with respect to the thermal release rate of interstitials in determining the bound interstitial concentration whenever $\tau_i\kappa_i C_i \gtrsim 1$, i.e., whenever

$$E_i^b \gtrsim 10\ kT + E_v^m - E_i^m \quad . \qquad (23)$$

This type of asymmetry in the binding energies to give the same effects for vacancy binding and interstitial binding has been discussed in detail in Refs. [9] and [10]. Essentially it arises from the necessary relation between C_v and C_i during irradiation [eq. (25) below].

Bound Recombination

The condition for bound recombination to be important with respect to thermal release in determining the bound vacancy concentration is

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*Where $r'b^2 = n\Omega$, where n is the number of atomic volumes involved, this can be substituted into eq. (21) for Ω.

given by

$$\tau_v R_v C_i \gtrsim 1 \quad . \tag{24}$$

This also reduces to eq. (22), i.e.,

$$E_v^b \gtrsim 10\ kT \quad . \tag{22}$$

This is because

$$C_i S_i D_i = C_v S_v D_v \, . \tag{25}$$

by conservation of atoms.* Using eq. (25), the definitions of R_v and κ_v following eqs. (5) and (1) respectively, and recalling that $S_v \sim S_i$, we obtain the result that $\tau_v R_v C_i \sim \tau_v \kappa_v C_v$.

There is an important point to emphasize here. It has been shown previously [2,9] that vacancy traps in concentrations $\lesssim$ 0.1% significantly increase the fraction of point defects recombining and hence reduce swelling and creep rates even at binding energies significantly below that given by eq. (22). This is not paradoxical — the effect on the overall fraction of defects recombining can be significant when the concentration of bound defects is nevertheless controlled by the thermal release rate of bound vacancies and not by bound recombination.

Similarly, eq. (23) is the condition for the recombination of bound interstitials with free vacancies to be important with respect to the thermal release of bound interstitials in determining the bound interstitial population.

We also note that when $\tau_v \kappa_v C_v$, $\tau_v R_v C_i >> 1$, meaning that the concentration of bound vacancies is controlled by the trapping and bound

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*Where the thermal vacancy and interstitial concentrations C_v^e and C_i^e are non-negligible, eq. (25) becomes $(C_i - C_i^e) S_i D_i = (C_v - C_v^e) S_v D_v$.

recombination rates, we obtain the upper limit for the bound vacancy concentration as

$$C_v' = \frac{C^t}{2} \quad . \tag{26}$$

This follows directly from the rightmost relation in eq. (10) (neglecting the bound vacancy transport term which is discussed in detail in the next section) since then $C_v' = C_v \kappa_v \tau_v C^t / (1 + \tau_v \kappa_v C_v + \tau_v R_v C_i)$ and eq. (26) follows directly from the hypothesis given at the beginning of this paragraph.

Impurity-Associated Transport

For the impurity-associated transport of vacancies to be important with respect to the thermal release rate of bound vacancies in determining the concentration of bound vacancies, the condition

$$\tau_v K_v^* \gtrsim 1 \quad , \tag{27}$$

must be fulfilled. In the same vein as eq. (15) the condition (27) reduces to

$$b^2 S_v \left(\frac{D_v^*}{D_v}\right) \exp\,(E_v^b/kT) \gtrsim 1 \tag{28}$$

if $b^2 S_v \sim 10^{-5} - 10^{-4}$ then this condition becomes

$$E_v^b \gtrsim \left[10 + \ell n\left(\frac{D_v}{D_v^*}\right)\right] kT \quad . \tag{29}$$

If $D_v \sim D_v^*$, this gives a result similar to eq. (22) which defines the condition where trapping and bound recombination are important.

Note, however, from eq. (12) the condition where impurity-associated transport of interstitials to sinks is important with respect to thermal release of bound interstitials is given by

$$\tau_i K_i^* \gtrsim 1 \quad . \tag{30}$$

Following identical reasoning this reduces to

$$E_i^b \gtrsim \left[10 + \ell n\left(\frac{D_i}{D_i^*}\right)\right] kT \quad . \tag{31}$$

Comparing eqs. (31) and (29) we see that there is no asymmetry in the binding energies required for vacancies and interstitials in order for impurity-associated transport of point defects to be important with respect to thermal release of bound point defects in determining the bound point defect concentrations, in contrast to the result for bound recombination. In real systems, conditions (22), (23), (29), and (30) differ in the likelihood that they are fulfilled. Vacancy binding energies are often an order of magnitude lower than interstitial binding energies. When these conditions are far from being fulfilled the effective diffusion coefficients are essentially independent of the point defect concentrations.

SUMMARY AND DISCUSSION

Where impurity-point defect complexes are immobile, the impurities are characterized as traps and the effective point defect diffusion coefficient, or as it is sometimes called, delayed diffusion coefficient, is the free point defect diffusion coefficient reduced by a factor calculable from the trap characteristics. Where the complexes are mobile, the result is a weighted composite of free and impurity-associated diffusion coefficients. Under irradiation, both vacancies and interstitials diffuse simultaneously. Their recombination reactions make the four free and bound point defect concentrations interdependent. Effective diffusion coefficients for point defects in impure materials during irradiation thus contain additional features but reduce to the thermal forms in the absence of irradiation. The effective diffusion coefficients which have been set forth in the literature from time to time have been shown to be limiting or approximate forms of the effective diffusion coefficients given by eqs. (11) and (12).

The effective diffusion coefficient of point defects in a material containing impurities is a necessary and useful concept. It is a necessary concept because in terms of overall transport of point defects what is obtained is a composite measure of the effects of several point defect-impurity processes. Knowing that the measured diffusion coefficient is actually a composite entity and further, knowing its theoretical form allows interpretation and testing in terms of more fundamental parameters. It is easy to show, for example, that eqs. (6)—(8) describing the fates under irradiation (and thermal) conditions of free and bound vacancies in terms of free and impurity-associated diffusivities, trapping rate, thermal release rate, and bound recombination rates are indistinguishable from a set of two equations characteristic of a system with no impurities, provided the diffusion coefficients in the new equations are effective diffusion coefficients. Thus after substituting the definitions of R_v given following eq. (5) and R given following eq. (8) into eqs. (6) and (7) and taking for simplicity $r_0 = r_v = r$, we find

$$G_v - R^0 C_i (C_v + C_v') - K_v^{ef} (C_v + C_v') = 0 \quad , \tag{32}$$

$$G_i - R^0 C_i (C_v + C_v') - K_i C_i = 0 \quad , \tag{33}$$

where $R^0 = 4\pi r(D_i + D_v^{ef})$, $K_v^{ef} = D_v^{ef} S_v$ and D_v^{ef} is given by eq. (11). More generally, with vacancy and interstitial binding at impurities it can be shown that the equations become

$$G_v - R'(C_i + C_i')(C_v + C_v') - K_v^{ef}\ (C_v + C_v') = 0 \qquad (34)$$

$$G_i - R'(C_i + C_i')(C_v + C_v') - K_i^{ef}\ (C_i + C_i') = 0 \qquad (35)$$

where the new terms are $R' = 4\pi r(D_i^{ef} + D_v^{ef})$, $K_i^{ef} = D_i^{ef}\ S_i$ and D_i^{ef} is given by eq. (12). These equations are of course identical in form to the equations for point defects in a pure material [2,9] except that D_i^{ef}, D_v^{ef}, $(C_i + C_i')$ and $(C_v + C_v')$ appear rather than D_i, D_v, C_i, and C_v respectively.

As one application of these ideas, consider that the irradiation-induced swelling observed at one temperature has often been quantitatively fit with numerical values for vacancy migration energies characteristic of simple diffusion coefficients using simple rate equations and using the point defect concentrations computed from these in the expressions for void swelling. However, it is likely that these are in many cases actually effective coefficients and that the fit at a different temperature using the resulting simple exponential scaling would not be as good. The theoretical forms for the effective diffusion coefficients given by eqs. (11) and (12) show how the effective diffusion coefficients are actually expected to vary with temperature. How "fundamental" parameters other than the vacancy migration energy such as capture radii, binding energies and the several jump frequencies are related to observed changes is described by eqs. (11) and (12).

The effective diffusion coefficient is a useful concept because it is a composite of terms, each describing a physical process, constructed in precisely the correct way to permit evaluation of the relative importance of the processes for a given material. Utilizing the effective diffusion coefficients the relations (22), (23), (26), (29), and (31) have been obtained to elucidate the physical regimes.

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