The diffusivity of the vacancy in silicon: Is it fast or slow?

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A B S T R A C T

Vacancies in silicon are known to be highly mobile both at high temperatures (just below the melting point) and at cryogenic temperatures. Contrary to this, however, vacancy diffusivity near 800 °C — as deduced from the radiation-enhanced self-diffusion coefficient D_{sd} — was reported to be surprisingly low. An apparent explanation of this contradiction is that the defect concentrations (and accordingly D_{sd}) are reduced by an impurity-mediated recombination of vacancies and self-interstitials. This effect however is shown to be insufficient to account for such a low D_{sd}. A suggested solution to the puzzle is that self-interstitials (and vacancies as well) exist in two structural forms, a localized one and an extended one, of strongly differing diffusivities. A low diffusivity manifested in radiation-enhanced self-diffusion is likely to correspond to a low apparent diffusivity of self-interstitials (averaged over the two forms) rather than that of vacancies. The fast and slow forms of vacancies are concluded to be both of a high diffusivity at elevated temperatures while it is most likely that one of them (the extended one) becomes practically immobile at low temperatures.

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1. Introduction

Vacancies (V) and self-interstitials (I) in silicon are present in comparable equilibrium concentrations at the melting point [1,2]. Depending on the growth mode, the defects remaining after annihilation can be either V or I. Modern silicon crystals are normally grown in the vacancy mode. The remaining defects are vacancies, and they aggregate into voids (or, at a lower vacancy concentration, into the joint aggregates of vacancies and oxygen (oxide particles)). These aggregates, or "grown-in microdefects", are important to material quality. In order to simulate spatial patterns of microdefects in silicon crystals, it is necessary to know the properties of the vacancies and, in particular, the diffusivity D_V. This quantity is also important in many other fields. By analyzing several sources of data (metal diffusion [3–5], self-diffusion [6],

total vacancy amount in the voids [7], void size and density [2,8], the depth profile of vacancies in wafers after Rapid Thermal Annealing [9]) it was concluded [9] that D_V is remarkably high in a temperature range from 1100 °C (a typical temperature of void formation) to the melting point $T_m = 1412$ °C. In order of magnitude terms, D_V is between 10^{-5} and 10^{-4} cm²/s in this range. This result is in close agreement with the vacancy diffusivity at cryogenic temperatures reported by Watkins [10,11]. The diffusivity depends on the vacancy charge state. In intrinsic material (when the vacancy is most likely neutral) it is specified [11] as

$$D_V = (0.0012\,\text{cm}^2/s)\exp(-0.45\,\text{eV/kT}). \tag{1}$$

When applied to a high-T range (where the material — if not heavily doped — is intrinsic) this expression gives a high diffusivity — for instance $D_V(T_m) = 5.4 \times 10^{-5}$ cm²/s — and is quite consistent with values mentioned above.

On the other hand, the values of D_V in the middle-T range (around 800 °C) deduced from radiation-enhanced self-diffusivity by Bracht et al. [12] are three orders of

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magnitude lower than that expected by Eq. (1). The aim of the present work is to discuss this discrepancy and to seek a possible explanation.

2. Radiation-enhanced self-diffusivity limited by direct I–V recombination

Under proton irradiation [12], the point defects V and I are produced in pairs and lost by recombination and also by out-diffusion to the sample surfaces. Steady-state depth profiles of the two concentrations, C_V and C_I, are achieved after a short time [12] in thin (40 μm) samples and obey the equations

$$D_V d^2 C_V/dz^2 + G - \beta C_I C_V = 0, \tag{2}$$

$$D_I d^2 C_I/dz^2 + G - \beta C_I C_V = 0, \tag{3}$$

where G is the generation rate of I–V pairs that will separate into I and V, and β is the recombination coefficient equal to $4\pi r(D_I + D_V)$ for the diffusion-limited reaction. The capture radius r is assumed to be 0.5 nm. It is convenient to use, as variables, the diffusivity-concentration products, $S_V = D_V C_V$ and $S_I = D_I C_I$ since the measured self-diffusion coefficient D_{sd} is expressed through these quantities:

$$D_{sd} = (f_V S_V + f_I S_I)/\rho, \tag{4}$$

where ρ is the lattice site density (5×10^{22} cm^{-3}) and f_V and f_I are the correlation factors ($f_V = 0.5$ and f_I is slightly larger than 0.5). The Eqs. (2) and (3) then become

$$d^2 S_V/dz^2 + G - \alpha S_I S_V = 0, \tag{5}$$

$$d^2 S_I/dz^2 + G - \alpha S_I S_V = 0, \tag{6}$$

$$\alpha = 4\pi r(1/D_I + 1/D_V) \tag{7}$$

Subtracting Eq. (6) from (5) it follows that $dS_V/dz - dS_I/dz$ is a constant. This constant is equal to zero since both derivatives are zero at the half-depth—because both opposite sides of a sample act as sinks, and the defect profiles are symmetrical with respect to the half-depth. Therefore, $S_V - S_I$ is a constant. Now assuming, similar to Ref. [12], equilibrium values for the concentrations at the sample surfaces, one obtains

$$S_V(z) - S_I(z) = S_{Ve} - S_{Ie}, \tag{8}$$

where S_{Ve} is the equilibrium diffusivity-concentration product for V (also called the transport capacity, $D_V C_{Ve}$) and S_{Ie} is a similar product for I. The measured diffusivity D_{sd} exceeds the known equilibrium value of self-diffusivity, $(f_V S_{Ve} + f_I S_{Ie})/\rho$, by three orders of magnitude [12]. This means that $S_V + S_I$ is huge in comparison to either S_{Ve} or S_{Ie}—and hence, by Eq. (8), also in comparison to $S_V - S_I$. In other words, the two quantities, S_V and S_I, are practically identical and each far exceeds the equilibrium value at the surface, S_{Ve} or S_{Ie}. The problem of the depth profiles is thus simplified dramatically: one need to only calculate a single quantity $S(z) = S_V(z) = S_I(z)$ with a zero boundary condition. The resulting equation is

$$d^2 S/dz^2 + G - \alpha S^2 = 0, \tag{9}$$

and the expression (4) for D_{sd} is reduced to

$$D_{sd} = (f_V + f_I)S/\rho, \tag{10}$$

and thus $S(z)$ is directly expressed through the measured value of $D_{sd}(z)$.

The $S(z)$ function — obtained by solving Eq. (9) — is uniform throughout the major part of the sample depth with the exception of narrow near-surface regions. The most useful quantity is the bulk value of $S(z)$, denoted by S_0 and related to the production rate by Eq. (9): $\alpha S_0^2 = G$. Once S_0 is known, the kinetic coefficient α is expressed as G/S_0^2, and the effective diffusivity resulting from the combination of D_V and D_I is determined by Eq. (7):

$$D_{eff} = (1/D_V + 1/D_I)^{-1} = 4\pi r S_0^2/G. \tag{11}$$

By both high-T data [9] and low-T data [10] $D_V \ll D_I$ and thus D_{eff} can be assumed to be identical to D_V.

The self-diffusivity $D_{sd}(z)$ was reported [12] at $z \approx 360$ nm. The corresponding value of $S(z)$ should be converted into the required quantity S_0. For that, Eq. (9) is multiplied by dS/dz and integrated which gives:

$$(dS/dz)^2/2 + GS - \alpha S^3/3 = GS_0 - \alpha S_0^3/3 = (2/3)GS_0. \tag{12}$$

The integration constant (the right-hand part of this equation) is expressed using the values of dS/dz and S at the half-depth where $dS/dz = 0$ and $S = S_0$, taking into account the steady-state relation $\alpha S_0^2 = G$. At this point it is convenient to use a normalized quantity $Y = S(z)/S_0$. The derivative dY/dz (positive in the left half of the sample) is then expressed from Eq. (12), using again the relation $\alpha S_0^2 = G$:

$$dY/dz = [(4/3)(G/S_0)(1 - 1.5Y + 0.5Y^3)]^{1/2}. \tag{13}$$

Upon numerical integrating Eq. (13) one obtains the $z(Y)$ function by which Y is found in dependence of the combination $X = [(4/3)(Gz^2/S(z))]$. This dependence is shown in Fig. 1. Using the known values of z and $S(z)$, one calculates X (typically it is around 1) and then finds Y from the plot of Fig. 1—which gives $S_0 = S(z)/Y$. Typically Y
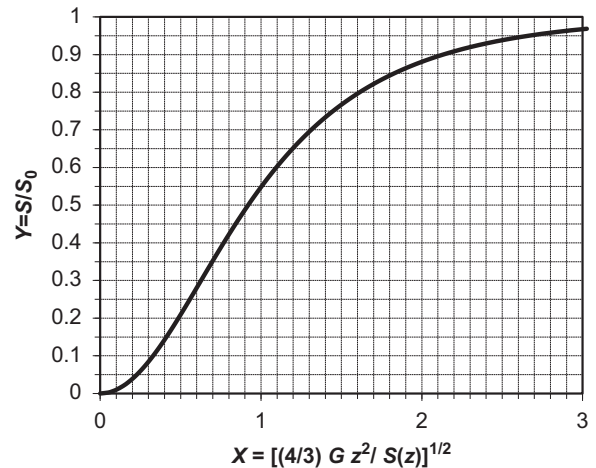

Fig. 1. The diffusivity–concentration product $S(z)$ in a sample under irradiation (the same for V and I) normalized by the bulk value S_0, in dependence of the combination $X = [(4/3)z^2 G/S(z)]^{1/2}$. The plot is used to deduce S_0 by a known $S(z)$ at a depth z.
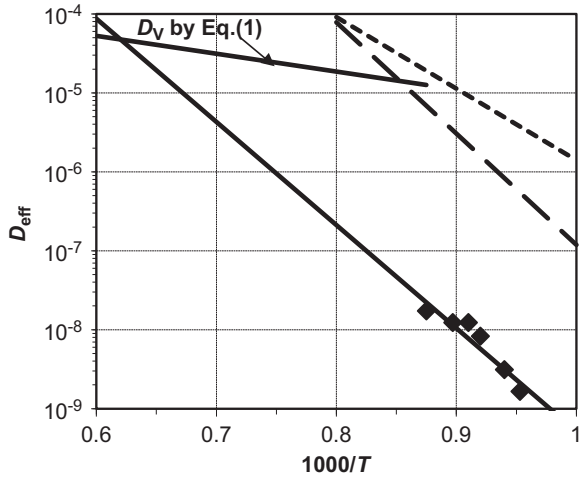
Fig. 2. Effective diffusivity D_{eff}, Eq. (11), deduced from data on $S(z)$ for several irradiation temperatures (symbols). The upper solid line shows the vacancy diffusivity by Watkins [11] extrapolated from low T, Eq. (1). The lower solid line is the best-fit Arrhenius dependence drawn through the points. The calculated D_{eff} for carbon-mediated I–V recombination is shown by the broken curve, and that for oxygen-mediated recombination by the dotted curve.

is around 0.7 meaning that the difference between the measured quantity $S(z)$ and the bulk value S_0 is not large. And yet this difference is important in order to get the temperature dependence of D_{eff} using Eq. (11) because the data for $S(z)$ are only available within the narrow temperature range 780–870 °C [12]. The resulting $D_{eff}(T)$ is shown in Fig. 2. The pair generation rate G is somewhat uncertain [12]; we have used the lower estimate, $G = 3 \times 10^{15}$ cm^{-3} s^{-1}. This produces a larger calculated D_{eff}. Yet even then, D_{eff} (identified at the moment as D_V) is three orders of magnitude lower than the vacancy diffusivity expected by Eq. (1). The latter is shown by the upper solid line in Fig. 2. The temperature dependence of D_{eff} is not regular and the activation energy E is not well defined. The best-fit line drawn through the points (Fig. 2) corresponds to $E = 2.6$ eV. $D_{eff}(T)$ is thus approximated as

$$D_{eff} = (6000\,\text{cm}^2/\text{s})\exp(-2.6/kT). \tag{14}$$

The large prefactor in Eq. (14) will be commented upon below. Remarkably, when extrapolated to the melting point, D_{eff} is quite high: about 10^{-4} cm^2/s.

3. An alternative interpretation: impurity-mediated I–V recombination

In the analysis above we followed an assumption [12] that I–V recombination occurs by a diffusion-limited direct reaction between I and V. It can, however, also be that the recombination of I and V — just as in the case of electrons and holes — is mediated by some impurity that can sequentially trap I and V defects, switching between two states. The concentrations C_V and C_I will be reduced by this additional recombination path, resulting in a reduced D_{sd}. The diffusion-limited trapping rate of self-interstitials is $4\pi r D_I C_I N_I$, where N_I is the trap concentration (whereas in the previous model, N_I was identical to C_V). The

capture radius, for the sake of simplicity, is assumed the same (0.5 nm) for all diffusion-limited reactions. This trapping rate should be equal to the generation rate G, or larger than G, if the backward reaction of releasing trapped I is significant. Hence, given the known values of $S = D_I C_I$ and of G, the trap concentration N_I should be larger than about 2×10^{15} cm^{-3}.

The only impurities present in such a high concentration in the float-zoned samples of Ref. [12] are oxygen and carbon. Their reported concentrations are between 10^{16} and 10^{17} cm^{-3}.

3.1. Carbon-mediated recombination

Carbon is initially present in its dominant equilibrium state—as substitutional C_s. Self-interstitials are trapped by C_s producing interstitial carbon C_i, and then C_i trap V, returning carbon to the initial state C_s. The steady-state balance equations for self-interstitials and for vacancies in the bulk reads

$$G = 4\pi r D_I(C_I N_s - N_i C_{Ie}/R_{is}) = 4\pi r D_V(C_V N_i - N_s C_{ve} R_{is}). \tag{15}$$

where N_i and N_s are the concentrations of interstitial and substitutional impurity states, and $R_{is} \ll 1$ is the equilibrium N_i/N_s ratio. The equilibrium concentration of self-interstitials is denoted as C_{Ie}, and that of vacancies as C_{Ve}. The net trapping rates include the backward reactions. For self-interstitials this reaction, $C_i \rightarrow C_s + I$, is essential due to a low R_{is}. For vacancies, the backward reaction $C_s \rightarrow C_i + V$ can be neglected since $C_V \gg C_{Ve}$ and $N_i \gg R_{is}N_s$. If the actual concentration N_i remains small in comparison to N_s then, by Eq. (15), the concentrations of I, C_s and C_i are, approximately, in an equilibrium ratio: $C_I N_s/N_i \approx C_{Ie}/R_{is}$. The balance equation for vacancies becomes

$$G = 4\pi r D_V R_{is} C_V C_I N_s/C_{Ie} = 4\pi r S_0^2 N_s R_{is}/S_{Ie}. \tag{16}$$

This equation is of precisely the same form as Eq. (11) for direct V–I recombination; the only difference is in the meaning of the effective diffusivity which is now not related at all to D_V but expressed rather through the self-interstitial transport capacity, $S_{Ie} = D_I C_{Ie}$:

$$D_{eff} = D_I C_{Ie}/(R_{is}N_s). \tag{17}$$

The $D_I C_{Ie}$ product is known by data on metal in-diffusion [3,4,9]:

$$S_{Ie} = D_I C_{Ie} = (6.7 \times 10^{26}\,\text{cm}^{-1}\text{s}^{-1})\exp(-5.15\,\text{eV}/kT). \tag{18}$$

This $S_{Ie}(T)$ function is shown in Fig. 3 (the curve marked I). The interstitial/substitutional ratio R_{is} was estimated using the reported carbon diffusivity and the carbon effect which shifts the surviving concentration of point defects in growing crystals in favor of interstitial defects [13]. At the melting point, R_{is} is about 2×10^{-4}. It decreases upon lowering T with an activation energy close to 2.2 eV. Using Eq. (17) with a tentative carbon concentration $N_s = 2 \times 10^{16}$ cm^{-3}, the predicted effective diffusivity is shown by the broken line in Fig. 2. It is too large to account for the actual values of D_{eff} (shown by the symbols). The carbon concentration is in fact most likely lower than the assumed value of 2×10^{16} cm^{-3}. In this case the predicted D_{eff} would be still higher. There is
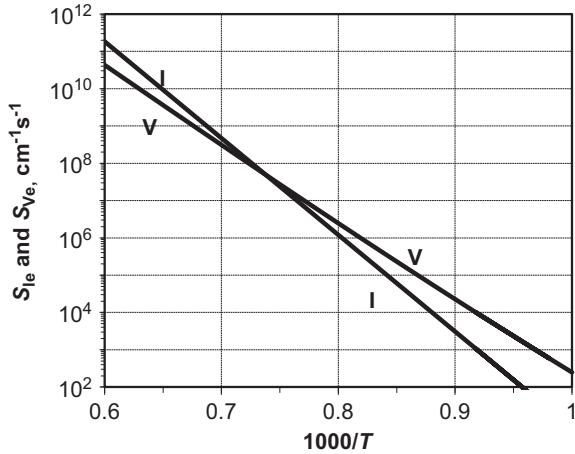
Fig. 3. Equilibrium diffusivity–concentration products $S_{Ie}(T)$ (for I) and $S_{Ve}(T)$ (for V) deduced [9] from various data and represented by Eqs. (18) and (21). For vacancies, a low-T branch of $S_{Ve}(T)$ [14] is taken into account.

another argument against carbon-mediated recombination: the C_i atoms are of a relatively high mobility, sufficiently high, in fact, for the complete out-diffusion loss of carbon during the course of proton irradiation.

3.2. Oxygen-mediated recombination

Oxygen is initially present in the interstitial state O_i. By trapping vacancies it becomes an off-center substitutional species O_s (also denoted VO—the well known radiation-induced A-center). The balance equations are identical to Eq. (15) only now the equilibrium ratio $R_{is} \gg 1$. It is accordingly more convenient to use the smaller version of the ratio $R_{si} = 1/R_{is}$. The backward reaction of releasing the trapped defects is now essential for vacancies (VO → $O_i + V$) due to a small R_{si}. For self-interstitials, the backward reaction $O_i → VO + I$ can be neglected. The V, VO and O_i species are approximately in an equilibrium ratio, $C_V N_i / N_s = C_{Ve}/R_{si}$ and the balance Eq. (16) is replaced with

$$G = 4\pi r D_I R_{si} C_V C_I N_i / C_{Ve} = 4\pi r S_0^2 N_i R_{si} / S_{Ve}. \quad (19)$$

This is again of the same form as before, except D_{eff} is now expressed through the vacancy transport capacity $S_{Ve} = D_V C_{Ve}$:

$$D_{eff} = D_V C_{Ve} / (R_{si} N_i). \quad (20)$$

The $D_V C_{Ve}$ product for the temperature range $T > 900\,°C$ can be deduced using several sources of data [9]. The activation energy for this range is about 4.3 eV. At $T < 900\,°C$ this product seems to have a smaller activation energy — about 3.6 eV [14] — implying that $D_V C_{Ve}$ is composed of two branches. The overall transport capacity due to vacancies is

$$S_{Ve} = D_V C_{Ve} = 4.8 \times 10^{23} \exp(-4.33\,eV/kT) + 2.3$$
$$\times 10^{20} \exp(-3.6\,eV/kT), \quad (21)$$

in units of $cm^{-1}s^{-1}$. This two-branch temperature dependence is shown in Fig. 3 (the curve marked V).

The ratio R_{si} for oxygen can be estimated [13] by vacancy binding into the VO and VO_2 species. It is roughly 4×10^{-7} at 1050 °C (the characteristic binding temperature) and decreases upon lowering T with an activation energy close to 1.8 eV. With $N_i = 5 \times 10^{16}\,cm^{-3}$ (the oxygen concentration), D_{eff} predicted by Eq. (20) is shown by the dotted line in Fig. 2. Here again it is too large to be consistent with the actual values of D_{eff}. In the temperature range of proton irradiation, the low-T branch of S_{Ve} by Shimizu et al. [14] is dominant in Eq. (21). If we choose not to trust this low-T branch and use only the extrapolated high-T branch for S_{Ve} then the calculated D_{eff} would be reduced only by a factor of about 3. This does not help much.

4. Discussion

The effective diffusivity D_{eff} of the intrinsic point defects under irradiation, as deduced from the measured enhanced self-diffusion coefficient, can be interpreted in different ways. If the defect concentrations are limited by direct I–V recombination then D_{eff} is identical to the smaller of the two diffusivities, D_V, and D_I, thought to be D_V. The value of D_{eff} found is however three order of magnitudes smaller than the expected value of D_V. If, on the other hand, the defect concentrations are limited by impurity-mediated recombination, then the expected values of D_{eff} due to the major impurities (oxygen and carbon) are now not related to D_V but here too again turn out to be much larger than the actual values of D_{eff}. An enhanced I–V recombination due to impurities cannot account for the very low value of D_{eff}.

One is thus forced to return to the concept proposed in Ref. [12], that D_{eff} is limited by direct I–V recombination and that the smallest of the two diffusivities, D_I and D_V, is indeed very low around 800 °C: about $10^{-8}\,cm^2/s$. This, though, presents a problem since both V and I are highly mobile at cryogenic temperatures [10] with small migration energies resulting in an extrapolated diffusivity larger than $10^{-5}\,cm^2/s$ at 800 °C.

This apparent contradiction can be resolved if either V or I (or both) can exist in different structural forms, of strongly differing mobility.

One possibility is that the two forms of a single defect (for instance of I) — a high-diffusivity form I_h and a low-diffusivity form I_l — coexist in an equilibrium ratio in which — at sufficiently high T — I_l dominates. In this case the apparent diffusivity D_I of I — averaged over the two forms — would be much smaller than the diffusivity D_{Ih} of the fast form. On the other hand, at cryogenic temperatures, the exchange between the two forms is of a negligible rate and the I_h species will freely migrate with their own high diffusivity D_{Ih}. The same concept may be true for vacancies: the fast form V_h migrates freely at cryogenic temperatures having a diffusivity specified by Eq. (1). At elevated T, however, the fast form V_h and the slow form V_l coexist in the equilibrium ratio which may result in a low averaged (apparent) diffusivity D_V.

Within this interpretation — of mutually equilibrated fast and slow forms at $T \geq 800\,°C$ — the apparent

diffusivity D (either D_V of V or D_I of I) is equal to

$$D = (D_h C_{he} + D_l C_{le})/(C_{he} + C_{le}) \qquad (22)$$

where the subscript indicating a particular defect, V or I, is temporarily omitted. The sum $D_h C_{he} + D_l C_{le}$ represents a contribution of the defect into the equilibrium self-diffusivity (transport capacity)—a quantity known experimentally and denoted as S_e (which is either S_{Ie} or S_{Ve}—specified by Eqs. (18) and (21)). Since the slow form dominates, the expression (22) is reduced to

$$D = S_e/C_{le} \qquad (23)$$

The effective diffusivity D_{eff} is the smaller of the two apparent values D_V and D_I. Although the diffusivity D_{Vh} of V_h is smaller than D_{Ih} of I_h, the relation between the apparent values D_V and D_I may be opposite.

Let us first assume that $D_I \ll D_V$, and accordingly $D_{eff} = D_I = S_{Ie}/C_{Ile}$. The two forms of I can be represented by the localized configuration and the extended atomic configuration of Seeger and Chik [15]. A huge prefactor in $S_{Ie}(T)$, Eq. (18) indicates an extended nature of the fast form I_h and accordingly a localized nature of the slow form I_l. One can expect that the prefactor in the equilibrium concentration C_{Ile} has a normal value—on the order of the lattice site density $\rho = 5 \times 10^{22}\,cm^{-3}$. The expected prefactor in $D_{eff} = D_I$ is thus of the order of $10^4\,cm^2/s$—surprisingly close to the prefactor in Eq. (14). This coincidence strongly supports the identification of the slower defect with I rather than with V. A low value of D_I results form a small fraction of highly mobile I_h (extended) species in the interstitial community $I_h + I_l$. The activation energy E_{Il} for C_{Ile} is estimated as 2.55 eV through the difference of the activation energy for S_{Ie} (5.15 eV) and for D_{eff} (2.6 eV). Another way to estimate E_{Il} is by the absolute value of $C_{Ile} = S_{Ie}/D_{eff} = 9 \times 10^{11}\,cm^{-3}$ at 870 °C (a representative temperature of proton irradiation) assuming that the prefactor in $C_{Ile}(T)$ is equal to ρ for the localized self-interstitial. This gives 2.45 eV—practically coincident with the above estimate. Therefore, the equilibrium concentration of I_l — the slow localized form of I — can be now specified:

$$C_{Ile} = (5 \times 10^{22}\,cm^{-3})\exp(-2.45\,eV/kT). \qquad (24)$$

Extrapolated to T_m this concentration is $2.4 \times 10^{15}\,cm^{-3}$. The total C_{Ie} may be still larger if the contribution of I_h is not negligible at T_m. The concentration $C_{Ie}(T_m) \geq 2.4 \times 10^{15}\,cm^{-3}$ is very large in comparison to the concentration difference $C_{Ve}(T_m) - C_{Ie}(T_m)$ which was determined by the total amount of vacancies in voids [9] and equals $\approx 1.6 \times 10^{14}\,cm^{-3}$. This means that the two equilibrium concentrations C_{Ve} and C_{Ie} are almost coincident at T_m. While this may look strange it is not impossible. A large $C_{Ie}(T_m)$ leads, with a known $S_{Ie}(T_m) \approx 2.5 \times 10^{11}\,cm^{-1}\,s^{-1}$, to a relatively low melting-point self-interstitial diffusivity $D_I = S_{Ie}/C_{Ie}$—about $10^{-4}\,cm^2/s$. The actual value of D_I seems to be much higher judging by microdefect patterns induced by a growth halt [16,17]. When crystal growth is halted for a short time, self-interstitials propagate from the halted interface into the crystal bulk by a distance corresponding to $D_I(T_m) \sim 10^{-3}\,cm^2/s$. On the other hand, there are data [18] indicating a much lower $D_I(T_m)$,

right on the order of $10^{-4}\,cm^2/s$. In short, the present identification of D_{eff} with D_I can be acceptable.

The alternative attribution of D_{eff} is to D_V, implying that D_V is low due to the dominance of the slow form V_l in the $V_l + V_h$ community. In this case the concentration of the slow form at 870 °C — expressed as S_{Ve}/D_{eff} — is higher than before since $S_{Ve} > S_{Ie}$ at this T. Recall that $S_{Ve}(T)$ is composed of two branches. If the appropriate low-T branch is used then $C_{Vle}(870\,°C) = 1.9 \times 10^{12}\,cm^{-3}$. Extrapolation to T_m by an equation similar to Eq. (24) leads to a very high — and hardly acceptable — concentration of $4 \times 10^{15}\,cm^{-3}$ for V_l. The total $C_{Ve}(T_m)$ can be even larger if the V_h contribution is not negligible.

Of the two possibilities for identifying the slower defect in the radiation-enhanced experiments — V or I — the identification with I is therefore preferable since it leads to a smaller, more acceptable, $C_{Ie}(T_m)$. Still more important, it is consistent with the large activation energy and the huge prefactor for $D_{eff}(T)$, Eq. (14). With this identification, one can specify the equilibrium concentration of the slow self-interstitial species using Eq. (24)—while nothing can be extracted about the vacancy properties. Still, the very existence of the two branches in $S_{Ve}(T)$ suggests that vacancies are also present in two distinct atomic configurations, V_h and V_l, and that the high-T branch (of a huge prefactor in $S_{Ve}(T)$) is controlled by the extended species. The low-T branch in $S_{Ve}(T)$ reported by Shimizu et al. [14] is then identified with a localized vacancy form. As was noted by Watkins [11], the prefactor in the low-T branch of $S_{Ve}(T)$ — which is $2.3 \times 10^{20}\,cm^{-1}\,s^{-1}$ — is close to the product of the prefactor in Eq. (1) and the lattice site density ρ (the expected prefactor in C_{Vle} for a localized vacancy). This is a reason for identifying the localized form of V with the fast (Watkins) species V_h. The concentration of V_h is thus found as S_{Ve}/D_{Vh} where S_{Ve} refers to the low-T branch and D_{Vh} is given by Eq. (1). The resulting expression is

$$C_{Vhe} = (2 \times 10^{23}\,cm^{-3})\exp(-3.15\,eV/kT). \qquad (25)$$

Extrapolation to T_m gives $7 \times 10^{13}\,cm^{-3}$. The value of the total $C_{Ve}(T_m)$ — of $V_h + V_l$ — based on the value of above-estimated $C_{Ie}(T_m)$ is close to $2.6 \times 10^{15}\,cm^{-3}$. This means that the V_l species (the extended form) dominates by far over V_h at T_m. This allows us to estimate — using the known value of $S_{Ve}(T_m) \approx 5 \times 10^{10}\,cm^{-1}\,s^{-1}$ — the diffusivity of V_l: $D_{Vl}(T_m) \approx 2 \times 10^{-5}\,cm^2/s$. This is somewhat smaller than $D_{Vh}(T_m) \approx 5 \times 10^{-5}\,cm^2/s$, and yet still quite high. The migration energy for V_l is not known. If it is essentially larger than 0.45 eV for V_f then the V_l species will become very slow indeed at lower T.

The scenario discussed above was based on the assumption of fast equilibration between the fast and slow forms in the temperature range of proton irradiation (around 800 °C) at least for self-interstitials. Another possibility is that the fast and slow species of either I or V (or both) do not exchange even at around 800 °C. In this case D_{eff} is simply the diffusivity of one of the slow species (it is not certain, of which one—V_l or I_l) provided that it is mostly the slow species — and not the partner fast species — that are produced by proton irradiation.

This version however cannot account for a huge prefactor in D_{eff}, Eq. (14) and therefore it is not considered probable.

5. Summary

The most likely interpretation of a very low radiation-enhanced self-diffusivity — corresponding to a very low effective diffusivity D_{eff} at around 800 °C — is as follows:

(1) Self-interstitials exist in two forms: I_h—an extended one of a high diffusivity and I_l—a localized one of a low diffusivity. The two forms are independent of each other at cryogenic temperatures, where I_h manifests itself by a fast migration. At elevated T, such as 800 °C, the two forms coexist in an equilibrium ratio, and the dominant form is I_l. This results in a low apparent (averaged) diffusivity D_I of the self-interstitial community and accounts for a low D_{eff} identified as D_I. In other words, the slow species are not the vacancies, as was assumed initially, but rather the self-interstitials due to the slow I_l component. Upon raising T, the apparent diffusivity D_I increases sharply — with an activation energy of about 2.6 eV — and becomes as high as 10^{-4} cm^2/s at the melting point, T_m.
(2) Vacancies are also likely to be present in two structural forms, an extended one and a localized one, only now it is the localized form that should be identified with the fast V_h species manifested in low-T radiation experiments. The V_h and V_l species are both highly mobile at elevated T, being responsible for two branches in the vacancy contribution into the transport capacity (equilibrium self-diffusivity): a low-T branch is controlled by V_h (the localized form) and the high-T branch by V_l (the extended form).
(3) Although the diffusivity of V_l was only estimated at T_m (where it is rather high, about 2×10^{-5} cm^2/s), it is thought that the migration energy for V_l is larger than that for V_h (which is 0.45 eV). In that case the V_l species will be practically immobile at T_{room}, contrary to V_h.

An interesting consequence of the co-existence of slow and fast vacancies is that the slow ones can be present, as a free species, in as-grown or annealed samples—contrary to fast ones that is trapped by oxygen within a short time even below T_{room} [10,11]. An ultrasonic softening reported in Czochralski samples [19] (as well as in Float-Zoned samples [20]) was attributed to free vacancies and not to the vacancies trapped by impurities, like VO (the A-center). The softening effect can be thus tentatively attributed to the extended vacancy species V_l.

Answering the question placed in the title: whether the diffusivity of vacancies is high or low, it can be said that one should first specify which of the two vacancy forms is meant. At elevated temperatures both are highly mobile but at low T there can be a strong difference in their diffusivities, one species (Watkins vacancy V_h) being highly mobile while the other is practically immobile.

An additional important question is whether the exchange between V_h and V_l is fast or slow at elevated temperatures. In case of a fast exchange, the vacancy community, $V_h + V_l$, can be treated in a conventional way, as just one species, although the diffusivity, expressed by Eq. (22), is not of an Arrhenius-type temperature dependence. If however the exchange is slow even at high T, then the vacancy behavior is more complicated: the two vacancy species should be considered separately. Regarding the self-interstitial community $I_h + I_l$, this can be treated (at least at $T > 800$ °C) as one species of an apparent diffusivity approximated by Eq. (14).

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