

Vacancy and self-interstitial concentration incorporated into growing silicon crystals

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The concentration of vacancies (for the growth rate V over the critical value V_c) and of self-interstitials (for $V < V_c$) incorporated into growing silicon crystals is obtained numerically by solving the axial diffusion problem for fast-recombining point defects. An analytical solution is obtained for the important near-critical case. A simple but quite precise interpolation expression is found. The critical growth rate V_c for the changeover from interstitial to vacancy incorporation is proportional to the near-interface temperature gradient G_0 even if the axial profile of the gradient, $G(z)$, is of considerable nonuniformity. The experimental critical ratio V/G_0 , together with the observed amount of vacancies in voids, provides a good estimate for the interstitial self-diffusional product at the melting point, $3 \times 10^{11} \text{ cm}^{-1} \text{ s}^{-1}$, in accord with reported data. © 1999 American Institute of Physics. [S0021-8979(99)01123-8]

I. INTRODUCTION

The dominant type of intrinsic point defects (vacancy or self-interstitial) incorporated into the silicon crystal during growth depends on the ratio V/G_0 (where V is the growth rate and G_0 is the near-interface axial temperature gradient).^{1,2}

The vacancy is dominant if this ratio (denoted by ξ) exceeds the threshold value of ξ_t ; it is manifested in the formation of voids (D defects).³⁻⁵ In Czochralski (CZ) crystals voids are formed only if ξ is not too close to ξ_t . Otherwise, at ξ slightly over ξ_t , oxide particles are produced instead of voids by the joint agglomeration of vacancies and oxygen atoms.² The void region of a crystal is thus surrounded by a narrow marginal band of particles, and this band is responsible for formation of the oxidation stacking fault (OSF) ring that is found after high-temperature oxidation of wafers.⁶

The self-interstitial is dominant at $\xi < \xi_t$, and is manifested in the formation of interstitial-type dislocation loops (A defects)⁷⁻⁹ if ξ is not too close to ξ_t . Otherwise, at ξ slightly below ξ_t , so called B defects are produced instead of A defects,¹⁰ presumably by a joint agglomeration of silicon and carbon interstitials.

The threshold (or critical) ratio ξ_t is an important silicon parameter. The experimental values for ξ_t differ somewhat.² The most recent value for ξ that correspond to formation of the OSF ring is $0.134 \text{ mm}^2/\text{min K}$.^{11,12} The critical value (ξ_t) is slightly lower than this. We shall adopt $\xi_t = 0.12 \text{ mm}^2/\text{min K}$.

The aim of this article is to analyze the dependence of the incorporated vacancy (interstitial) concentration on $\xi = V/G_0$ and to draw some conclusions on the point defect parameters. The calculations discussed here are for the one-

dimensional (axial) case. Strictly speaking, one should solve the diffusion problem for both axial and radial defect transport.¹² However the characteristic scale of axial diffusion¹ is normally much smaller than the crystal radius: for typical CZ crystals the axial scale is 1 cm while the radius is 7.5 cm or larger. Under such conditions the problem of defect incorporation into the growing crystal is reduced to one-dimensional (axial) diffusion. The advantage of this simplified approach is a straightforward (analytical, and thus useful) relation between the assumed point defect parameters and the value of both ξ_t and the incorporated defect concentration.

II. AXIAL DIFFUSION PROBLEM FOR VACANCIES AND INTERSTITIALS

The near-interface temperature profile $T(z)$ generally induces concentration profiles $C_i(z)$ and $C_v(z)$ (of interstitials and vacancies, respectively) and corresponding defect fluxes J_i and J_v from the interface into the crystal bulk. The interstitial flux is

$$J_i = -D_i dC_i/dz + VC_i - \alpha_i G C_i, \quad (1)$$

where the first term corresponds to Fickian diffusion, the second term to defect transportation by a moving crystal (convection term), and the third term to defect drift (also called thermal diffusion or thermomigration) caused by the gradient G . The drift velocity $\alpha_i G$ is generally assumed to be proportional to the gradient of the inverse temperature and to the diffusivity,¹³ so that

$$\alpha_i = D_i \epsilon_i / kT^2, \quad (2)$$

where the constant ϵ_i is the drift energy (the reduced heat of transport). The drift energy ϵ_i is a kinetic parameter of a not defined value or even a sign, but it is thought^{13,14} that the drift actually occurs in the uphill direction ($\epsilon_i > 0$).

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The vacancy flux J_v is given by a similar expression; the relevant coefficients are the vacancy diffusivity D_v and the drift coefficient α_v (the drift energy ϵ_v).

The incorporated (surviving) concentrations, located some distance from the interface, are generally dependent on the whole $T(z)$ profile. However within the relevant (rather narrow) near-interface region the $T(z)$ profile may often be linearized and can be described by only one parameter, the near-interface gradient G_0 . We will assume a linear dependence of the inverse temperature $1/T(z)$ on the axial distance z . Thus the gradient $G(z) = -dT/dz$ is equal to $G_0(T/T_m)^2$ where T_m is the melting temperature. Later (in Sec. VII) the effect of strong nonuniformity in $G(z)$ will be considered.

At the interface ($z=0$) each concentration is at its equilibrium value. In general, $C_i(0)$ and $C_v(0)$ may depend on V ; however, then the type of dominant defect would depend on V rather than on V/G_0 .

In fact, there are only two possible cases from which a V/G_0 type rule for the dominant defect type in a growing crystal may be derived from the diffusion equations described above. These two extreme cases are as follows.

- (A) The recombination rate of vacancies and interstitials is assumed to be very fast,¹ and then the recombination is strictly balanced by the backward reaction of pair generation. The two profiles $C_i(z)$ and $C_v(z)$ are then coupled by the mass action law

$$C_i(z)C_v(z) = C_{ie}(T)C_{ve}(T), \quad (3)$$

where C_{ie} and C_{ve} are the equilibrium concentrations. The resulting diffusion problem¹ contains only one growth parameter: $\xi = V/G_0$. Only one defect species is incorporated into the crystal—either interstitials (at $\xi < \xi_i$) or vacancies (at $\xi > \xi_i$) while the concentration of the other species decays fast on lowering T —according to Eq. (3). The effect responsible for the changeover (from interstitial to vacancy) is interstitial diffusion. It dominates at lower ξ but becomes less than the vacancy convection at larger ξ .

- (B) The recombination rate is assumed to be negligible,^{15,16} and then the two profiles $C_i(z)$ and $C_v(z)$ are decoupled; the diffusion problem for either profile includes only one growth parameter: $\xi = V/G_0$. Both vacancies and interstitials coexist in the crystal bulk in supersaturated concentrations; interstitials prevail at $\xi < \xi_i$ while vacancies prevail at $\xi > \xi_i$. The effect responsible for the changeover is the vacancy's uphill drift. It diminishes the bulk vacancy concentration at lower ξ but becomes negligible at larger ξ .

In both models the equilibrium concentration of vacancies at the melting point, C_{vm} , is larger than the interstitial equilibrium concentration, C_{im} . Only then will the changeover be from interstitial to vacancy with increasing pull rate. In model (B), however, the self-diffusional product for vacancy, $D_v C_{ve}$, must be assumed to be considerably larger than that for interstitial, $D_i C_{ie}$. This assumption strongly contradicts the modern view of the self-diffusion of silicon¹⁷ at temperatures close to T_m . There is general agreement that the major contribution to self-diffusion in silicon near the

melting point is that of self-interstitials, while the vacancy contribution is only about 10%. This argument is enough to rule out model (B).

Therefore we turn to the original model (A) which is essentially based on the inequality $D_v C_{ve} < D_i C_{ie}$ and on a fast recombination rate.¹ Recent molecular dynamic calculations¹⁸ show that a vacancy and an interstitial easily form a short-lived complex; the recombination rate is then limited only by diffusion of the two reacting species. This process is very fast, taking just a few microseconds.¹ The equilibrium relation, Eq. (3), between the two concentrations is thus strictly maintained.

The concentration of extra silicon atoms (with respect to the ideal lattice) is $C_i - C_v$, and it is reaction invariant (not changed by recombination). The flux of extra atoms, J , is constant along z for the steady-state case. This flux is composed of interstitial and vacancy contributions:

$$J = J_i(z) - J_v(z) = \text{const.} \quad (4)$$

Equation (4), together with Eq. (3), completely defines the actual value of J and the profiles of point defects. It can be written in the final form

$$J = -D_i dC_i/dz + D_v dC_v/dz + V(C_i - C_v) - G(\alpha_i C_i - \alpha_v C_v). \quad (5)$$

A positive total flux means survival of the interstitials (while vacancies decay fast). A negative flux means survival of the vacancies (interstitials decay fast). Zero flux corresponds to complete annihilation of both defects (that is, to the critical V/G_0 ratio).

Equation (5) provides an analytical expression for ξ_i if the diffusivities are considered to be constant within the relevant narrow temperature range of defect annihilation. Indeed, Eq. (5) can be satisfied at $J=0$ if both concentration profiles, $C_i(z)$ and $C_v(z)$, have the same dependence on z . According to Eq. (3), this common dependence is defined by the square root of the equilibrium product $C_{ie} C_{ve}$. Each equilibrium concentration is of an Arrhenius-type temperature dependence characterized by a defect formation energy (E_i for an interstitial, E_v for a vacancy). Therefore the concentration profile of either defect is proportional to $\exp(-E/kT)$ where E is the averaged formation energy,

$$E = (E_i + E_v)/2. \quad (6)$$

Since the profiles satisfy the equilibrium condition at the interface [$C_i(0) = C_{im}$, $C_v(0) = C_{vm}$], they are finally written in the form

$$C_i = C_{im} \exp(E/kT_m - E/kT),$$

$$C_v = C_{vm} \exp(E/kT_m - E/kT). \quad (7)$$

The assumed linear dependence of $1/T(z)$ means that the profiles, Eqs. (7), have an exponential dependence on the axial distance z , proportional to $\exp(-EG_0 z/kT_m^2)$. The diffusion and drift terms in Eq. (5) are then proportional to G_0 while the convection term is proportional to V , and the equation is satisfied at some particular (critical) V/G_0 ratio,

$$V/G_0 = \xi_t = [D_{im}C_{im}(E - \epsilon_i) - D_{vm}C_{vm}(E - \epsilon_v)] / [(C_{vm} - C_{im})kT_m^2]. \quad (8)$$

Here, D_{im} and D_{vm} are the diffusivities at T_m (in the above analysis the temperature dependence of D_i and D_v was neglected in the near-interface annihilation region).

In further numerical calculations we neglect the drift contributions assuming that both ϵ_i and ϵ_v are much lower than E . There is experimental evidence showing that the interstitial drift, if any, is not strong (see the Appendix). The vacancy term in the numerator of Eq. (8) is only a small correction since $D_{vm}C_{vm} \ll D_{im}C_{im}$, and for this reason the precise value of vacancy drift is of little importance. The expression for the critical ratio is then reduced to that¹ given originally,

$$\xi_t = (E/kT_m^2)(D_{im}C_{im} - D_{vm}C_{vm}) / (C_{vm} - C_{im}). \quad (9)$$

If taken into account, the temperature dependence of D_i and D_v results only in a small shift in ξ_t (less than by 1%, as is found by numerical computation in Sec. III). Accordingly expression (9) is quite precise.

With the critical ratio being known ($\xi_t = 0.12 \text{ mm}^2/\text{min K} = 2 \times 10^{-5} \text{ cm}^2/\text{s K}$), expression (9) provides a valuable relation between the point defect parameters. This is particularly so if the self-diffusional product $D_{im}C_{im}$ is specified; then the concentration difference, $C_{vm} - C_{im}$, is found from expression (9). To do so, the averaged formation energy E should be specified; the number adopted (see below) is $E = 4.4 \text{ eV}$. The $C_{vm} - C_{im}$ difference is a scale for incorporated (surviving) vacancy concentration, C_{vs} . In most cases, the incorporated vacancies are almost completely consumed by voids.² The amount of vacancies in voids is thus identical to C_{vs} . The experimental dependence of C_{vs} on V/G_0 was obtained by measuring the density and size of the voids¹⁹ of many crystals. It is best described by a computed curve (discussed in Sec. III) if the $D_{im}C_{im}$ product is taken to be as

$$D_{im}C_{im} \approx 3 \times 10^{11} \text{ cm}^{-1} \text{ s}^{-1}. \quad (10)$$

On the other hand, the D_iC_{ie} product was deduced from diffusion profiles of some impurities (e.g., gold, platinum, and zinc).^{20–22} Extrapolation of these data to T_m gives¹⁷ about $2.310^{11} \text{ cm}^{-1} \text{ s}^{-1}$ which is pretty close to Eq. (10). Another approach is to judge $D_{im}C_{im}$ directly by the self-diffusion coefficient (measured quite close to the melting point^{17,23–25}) assuming the prevailing contribution is that of self-interstitials. The reported self-diffusivity is somewhat scattered, and the value of Eq. (10) is within the scatter.

Finally we note that the value, Eq. (10), of the interstitial self-diffusional product is consistent with the *entire* set of experimental data (critical V/G_0 , void density and size, impurity diffusion, and self-diffusivity).

The self-diffusional value obtained here is well within but at the high end of reported self-diffusional values from other types of experiments. We note that if the general expression, Eq. (8), for ξ_t were used instead of expression (9), together with drift energies comparable to the formation energies, then the required $D_{im}C_{im}$ product (to ensure a proper vacancy scale $C_{vm} - C_{im}$) would be higher still, and hard to

reconcile with the self-diffusivity reported.¹⁷ This is yet another argument in favor of a relatively small drift energy of interstitials.

To calculate the dependence of the incorporated defect concentration on V/G_0 we must now specify more point defect parameters.

The vacancy diffusivity D_{vm} (at T_m) and the migration energy E_{vd} (the quantity that defines the Arrhenius-type temperature dependence of D_v) were deduced² from the observed density, size, and formation temperature of voids: $D_{vm} = 2 \times 10^{-5} \text{ cm}^2/\text{s}$ and $E_{vd} = 0.35 \text{ eV}$. Similar estimates within a refined theory of void formation²⁶ indicate a somewhat higher value, $D_{vm} = 4 \times 10^{-5} \text{ cm}^2/\text{s}$; the latter is adopted in this article. The value of D_{vm} may be not quite accurate. However, the vacancy diffusion provides only a minor contribution to the total flux J , and one need not be too strict about the vacancy diffusivity when considering defect incorporation.

The self-interstitial diffusivity D_{im} is a crucial parameter, and we prefer to use a set of D_{im} within a reasonable range estimated¹ to be around $3 \times 10^{-4} \text{ cm}^2/\text{s}$, and to check the sensitivity of the results to the assumed D_{im} . Since D_{im} is considerably higher than D_{vm} , the migration energy of self-interstitials is likely to be very small (and less than E_{vd}). We tentatively adopt $E_{id} = 0.2 \text{ eV}$. Larger values, like $E_{id} = 1 \text{ eV}$ assumed in Ref. 12, would be inconsistent with the observations of extremely high interstitial diffusivity even below room temperature²⁷ (although this argument may be doubtful since it attributes this high diffusivity to radiation-induced recombination enhancement). At any rate, the computed curves for the incorporated concentration (including the critical value computed for the V/G_0 ratio) turn out to be only slightly sensitive to the assumed migration energy within a range of $E_{id} < 1 \text{ eV}$.

The D_iC_{ie} product (deduced from profiles of fast-diffusing impurities¹⁷) is characterized by the activation energy of 4.8–5 eV; this value gives the sum of E_i and E_{id} . The migration energy E_{id} was adopted as 0.2 eV, and it leaves 4.6–4.8 eV for the interstitial formation energy E_i .

The vacancy formation energy E_v was found^{2,25} to be similarly high, over 4.4 eV, to account for the observed nucleation temperature of voids (around 1100 °C). The first-principle and molecular dynamic values for both E_v and E_i are considerably lower: close to 4 eV or somewhat less.¹⁸ The value of 4 eV is consistent with the energy per dangling bond (close to 1 eV) deduced from the surface energy of a (111) silicon facet.²⁸

The point defect incorporation problem contains only the average value of the two formation energies, $E = (E_i + E_v)/2$. The probable range for this energy is quite narrow, from 4 to 4.8 eV, and we will adopt an intermediate value, $E = 4.4 \text{ eV}$.

III. NUMERICAL SOLUTION FOR INCORPORATED DEFECT CONCENTRATION

To compute the defect axial profiles at arbitrary V/G_0 and to take into account the temperature dependence of the

TABLE I. Point defect parameters (deduced from the critical V/G_0 ratio and the vacancy amount in voids) in dependence on the assumed interstitial diffusivity.

D_{im} (cm^2/s)	C_{vm}/C_{im}	C_{im} (cm^{-3})	C_{vm} (cm^{-3})	A
2×10^{-4}	1.139	1.5×10^{15}	1.7×10^{15}	0.104
3×10^{-4}	1.227	1×10^{15}	1.23×10^{15}	0.141
5×10^{-4}	1.401	6×10^{14}	8.4×10^{14}	0.209

diffusivities, it is convenient to introduce a new variable, $Y = (C_i/C_v)^{1/2}$. The defect concentrations are then expressed as $C_i = K(T)Y$ and $C_v = K(T)/Y$ where

$$K(T) = (C_{ie}C_{ve})^{1/2}. \quad (11)$$

The $K(T)$ function is proportional to $\exp(-x)$ where $x = E/kT - E/kT_m$, and the variable x is convenient to use instead of the distance z .

The total flux J equals VC_s where C_s is the incorporated concentration difference. If $J > 0$, then C_s is identical to the incorporated interstitial concentration, C_{is} . If $J < 0$, then $C_s = -C_{vs}$ where C_{vs} is the incorporated vacancy concentration.

Equation (5) is thus transformed to

$$(D_i Y + D_v/Y) d(\log Y)/dx = (kT^2 V/GE)(Y - 1/Y - C_s/K) + D_i Y - D_v/Y. \quad (12)$$

Here the drift terms are omitted; to take them into account one should add $(D_v \epsilon_v/Y - D_i \epsilon_i Y)/E$ to the right-hand part of Eq. (12).

At any specified V/G_0 the value of C_s is found by the condition that integration of Eq. (12) from some distant arbitrary point (for instance, $x=6$) back to the interface ($x=0$) results in the satisfied boundary condition $Y(0) = (C_{im}/C_{vm})^{1/2}$. The computed dependence of C_s on V/G_0 yields the critical V/G_0 ratio, that which corresponds to $C_s=0$.

The computations were made for several selected values of D_{im} (Table I). At every D_{im} the C_{vm}/C_{im} ratio is found by adjusting the computed value of the critical V/G_0 to the experimental value of $0.12 \text{ mm}^2/\text{min K}$ adopted above. This concentration ratio (Table I) is almost identical to that found from analytical expression (9) at specified D_{im} and ξ_t . Since the product $D_{im}C_{im}$ is specified by Eq. (10), both C_{im} and C_{vm} are found too (Table I).

The computed incorporated concentration is presented in Fig. 1 as a function of the reduced growth rate, V/V_t . The critical growth rate (for the defect changeover) is $V_t = \xi_t G_0$, and thus V/V_t is proportional to V/G_0 . The variable V/V_t is more convenient to use since in practice in crystal growth the gradient G_0 may be not measured or simulated while V_t is easily determined by growing a crystal at a ramped rate.

The incorporated concentration of both interstitials (at $V/V_t < 1$) and vacancies (at $V/V_t > 1$) does not depend much on the adopted value of D_{im} , and for this reason only two curves, one for the lowest and one for the highest assumed D_{im} , are shown in Fig. 1. The circles in Fig. 1 represent the

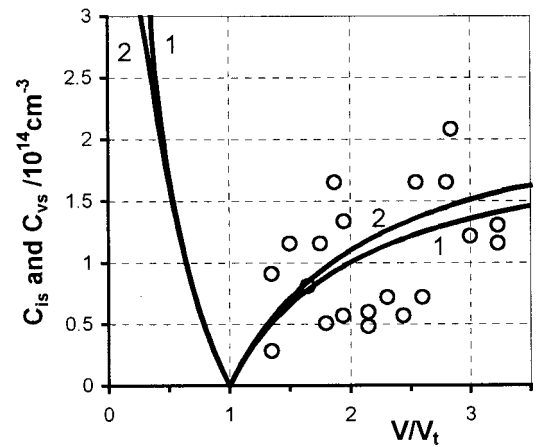


FIG. 1. Incorporated concentration of self-interstitials (at $V/V_t < 1$) and of vacancies (at $V/V_t > 1$). Curves 1 and 2 are computed assuming $D_{im} = 2 \times 10^{-4}$ and $5 \times 10^{-4} \text{ cm}^2/\text{s}$, respectively. The circles represent the reported concentration of vacancies (Ref. 18) deduced from the density and size of the voids.

amount of vacancies in voids reported in Ref. 19. Although the points are scattered, the computed vacancy concentration is in overall accord with the experiment, due to the value adopted, Eq. (10), for the $D_{im}C_{im}$ product. Any shift in this product would cause a proportional shift in the computed curves in Fig. 1. Therefore these data prove to be suitable to use for estimation of the $D_{im}C_{im}$ product but not helpful in the selection of the best value for the interstitial diffusivity D_{im} .

The nucleation rate of voids (and of oxide particles too) depends not mostly² on the absolute value of the incorporated (surviving) vacancy concentration C_{vs} but on the normalized concentration $S_v = C_{vs}/C_{vm}$. The incorporated interstitial concentration will be normalized in a similar way by its own equilibrium concentration: $S_i = C_{is}/C_{im}$. The quantities S_i and S_v are the incorporated fractions of defects initially present at T_m .

The dependence of S_i and S_v on V/V_t is remarkably sensitive to the assumed interstitial diffusivity (Fig. 2). For a

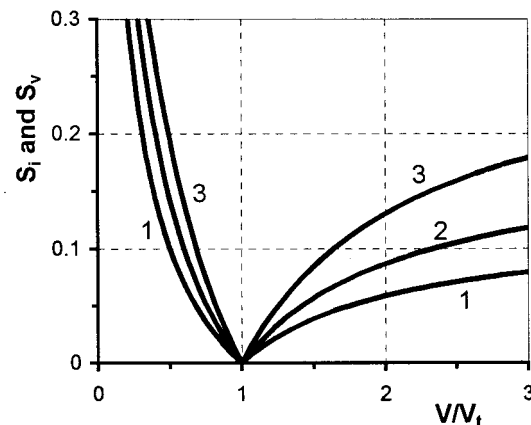


FIG. 2. Incorporated fraction of self-interstitials, $S_i = C_{is}/C_{im}$ (at $V/V_t < 1$) and that of vacancies, $S_v = C_{vs}/C_{vm}$ (at $V/V_t > 1$). Curves 1, 2, and 3 correspond to assumed interstitial diffusivity of $D_{im} = 2, 3$, and $5 \times 10^{-4} \text{ cm}^2/\text{s}$.

typical vacancy growth mode the V/V_t ratio is about 2. The corresponding value of S_v varies from 0.06 (at $D_{im}=2 \times 10^{-4} \text{ cm}^2/\text{s}$) to 0.13 (at $D_{im}=5 \times 10^{-4} \text{ cm}^2/\text{s}$).

IV. INCORPORATED CONCENTRATIONS AT V CLOSE TO V_t

The case of V close to the critical growth rate V_t is especially important since the incorporated concentration is diminished, and a drastic change in the type of defect agglomerates produced occurs.^{2,29} A crystal free of voids and dislocation loops is grown in some window of V .

The simplified diffusion equation (neglecting the temperature dependence of the diffusivities) results in a quite precise analytical expression (9) for ξ_t . It would therefore be worth trying this approach to get an analytical expression for the small incorporated concentration too. At $V=V_t$ the concentration profiles are denoted by $C_{it}(z)$ and $C_{vt}(z)$; they are given by Eqs. (7); the dependence on T is reduced to an exponential dependence on z due to the assumed linear profile of the inverse temperature:

$$C_{it}=C_{im} \exp(-z/L), \quad C_{vt}=C_{vm} \exp(-z/L), \quad (13)$$

where L is the characteristic annihilation length,

$$L=kT_m^2/EG_0. \quad (14)$$

Typically (at $G_0=50 \text{ K/cm}$) the annihilation length is about 1 cm.

At small nonzero flux J the concentrations will deviate slightly from Eqs. (13) and be

$$C_i=C_{it}+U_i, \quad C_v=C_{vt}+U_v. \quad (15)$$

The small deviations, U_i and U_v , are related according to Eq. (3); neglecting higher order terms one obtains $U_i/U_v=-C_{it}/C_{vt}$. This ratio does not depend on z . Accordingly, Eq. (5) is reduced to a linear equation for the deviation difference $U=U_i-U_v$:

$$J=-DdU/dz+V_tU+(V-V_t)(C_{it}-C_{vt}), \quad (16)$$

with the effective diffusivity $D=(D_{im}C_{im}+D_{vm}C_{vm})/(C_{im}+C_{vm})$.

Equation (16) is valid only within a limited (although large) distance z ; at very large z the small deviations, U_i and U_v , become greater than the decreasing basic concentrations, C_{it} , and C_{vt} . A general solution of Eq. (16) includes an exponentially increasing term $\exp(V_t z/D)$ which is considerable at large z but can be neglected in the near-interface region. The solution of Eq. (16) is then reduced to the sum of two particular solutions, one for the term J and the other for the term $(V-V_t)(C_{it}-C_{vt})$:

$$U=J/V_t-(V-V_t)(C_{it}-C_{vt})/(V_t+D/L). \quad (17)$$

The boundary condition ($U=0$ at $z=0$) defines the flux J and thus the incorporated concentration of vacancies ($C_{vs}=-J/V$ at $V>V_t$) or interstitials ($C_{is}=J/V$ at $V<V_t$). The final expression (linear in a small deviation $V-V_t$) is

$$C_{vs}(\text{or } -C_{is})=(C_{vm}-C_{im})(V/V_t-1)/(1+A), \quad (18)$$

where the constant A is

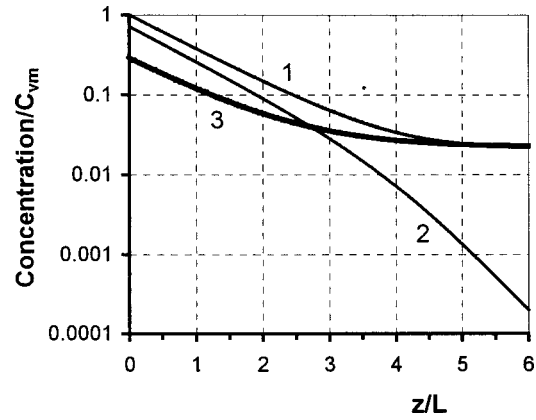


FIG. 3. Computed axial profiles of vacancies (curve 1) and of interstitials (curve 2) for $V/V_t=1.1$ (a near-critical growth mode); the assumed interstitial diffusivity is $D_{im}=5 \times 10^{-4} \text{ cm}^2/\text{s}$. Curve 3 represents the difference between the two concentrations, C_v-C_i , both that computed numerically and that following from the analytical solution, Eq. (17).

$$A=D/LV_t=[(1+s)(c-1)]/[(1-s)(c+1)]. \quad (19)$$

Here $c=C_{vm}/C_{im}>1$ is the concentration ratio while $s=D_{vm}C_{vm}/D_{im}C_{im}<1$ is the self-diffusion ratio. The values of A (in dependence of the assumed D_{im}) are listed in Table I.

Expression (18) is in good agreement with the numerical results for the incorporated concentrations at V close to V_t . More than that, the whole axial profile of the concentration difference C_i-C_v as defined by analytical expression (17) is very close to that obtained by numerical computations described in Sec. III. As an illustration, the computed vacancy and interstitial profiles at $V/V_t=1.1$ (a near-critical vacancy mode) are shown in Fig. 3. Curve 3 is the analytical solution for the C_v-C_i profile; it is indistinguishable from the profile found numerically.

The drift terms were omitted in Eq. (16). If they were taken into account, they would only result in replacing the second term, V_tU , with $(V_t-\alpha G)U$. Here $\alpha=(\alpha_i C_{im}+\alpha_v C_{vm})/(C_{im}+C_{vm})$ is the averaged drift coefficient. Accordingly, formula (18) for the incorporated concentration remains valid if expression (19) is modified by replacing V_t with $V_t-\alpha G$:

$$A=[(1+s)(c-1)]/[(1-s)(c+1)-2(c\epsilon_i-s\epsilon_v)/E]. \quad (20)$$

This general expression is applicable only if the critical growth rate, V_t , is larger than the uphill drift velocity of either defect. Otherwise, point defects would simply not penetrate into the crystal bulk. This condition is satisfied if the drift energies of the two point defects are not too large. In particular, the condition $V_t>\alpha_i G$ is reduced, according to Eq. (8), to an inequality $c\epsilon_i-s\epsilon_v<(1-s)E$ which shows that the denominator in Eq. (20) is larger than $(1-s)(c-1)$.

V. ANALYTICAL EXPRESSION FOR THE INCORPORATED DEFECT CONCENTRATION

At large V/V_t the initial concentration difference is frozen in, and the surviving vacancy concentration C_{vs} approaches $C_{vm} - C_{im}$. The two precise expressions for C_{vs} (within the limit of high V and V close to V_t) can be now combined to get an interpolation formula that is correct for both cases. It is achieved, for instance, if the first term in the denominator of Eq. (18) is changed from 1 to V/V_t . The resulting expression is

$$C_{vs} = (C_{vm} - C_{im})(V - V_t)/(V + AV_t). \quad (21)$$

This expression nicely describes the computed vacancy concentration in the whole range of $V > V_t$. It is also very applicable to the interstitial case at $0.3 < V/V_t < 1$ [then C_{vs} in Eq. (21) should be replaced with $-C_{is}$]. If it were plotted in Fig. 2, the interpolation curves, Eq. (21), for various D_{im} would be indistinguishable from the computed curves.

Therefore analytical expression Eq. (21), provides a simple and accurate solution to the defect incorporation problem. This useful expression is considered an important result of this article.

Even in the general case of non-negligible drift energies, of the order of 1 eV, say, expression (21) [with the coefficient A now defined by Eq. (20)] was found to represent the numerical results for C_{vs} and C_{is} in the same range of V/V_t well.

VI. INCORPORATED RADIAL PROFILES OF POINT DEFECTS

The gradient G_0 is normally nonuniform along the interface; it increases appreciably in the radial direction.^{11,30} The critical growth rate $V_t = \xi_t G_0(r)$ follows this variation. Therefore some radial defect profile is incorporated into a growing crystal. This profile is described by expression (21). In particular, a crystal may be grown in a vacancy mode: $V > V_t(r)$ for the whole interface, in which case a decreasing radial concentration profile of vacancies is incorporated. If $V < V_t(r)$ for the whole interface, the crystal is grown in a fully interstitial mode. An increasing radial profile of the interstitials is incorporated.

At intermediate V a mixed growth mode with a vacancy core surrounded by a coaxial interstitial ring is realized. The mixed mode is remarkable for the formation of a narrow particle band at the edge of the vacancy core,^{2,29} and this band gives rise to an OSF ring.

The incorporated radial defect profiles evolve upon subsequent cooling due to diffusion. For the vacancy mode the radial redistribution is of minor importance because of the relatively low diffusivity of vacancies. On the contrary, interstitials can diffuse by several centimeters during the cooling period. Therefore the interstitial concentration may be strongly diminished by outdiffusion to the crystal surface and to the inner vacancy core (the vacancy core shrinks accordingly). An initially incorporated concentration C_{is} is on the order of 10^{14} cm^{-3} (Fig. 1) for a representative interstitial

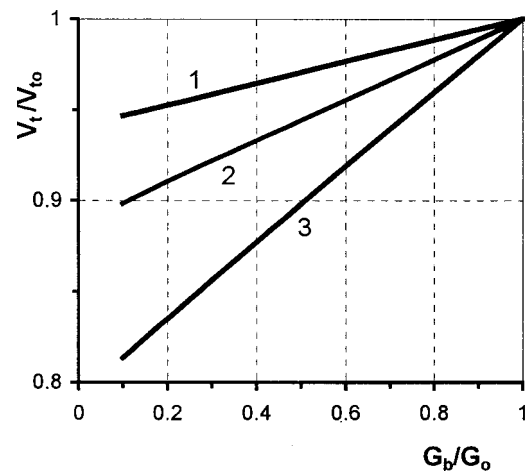


FIG. 4. Shift in the critical growth rate caused by the difference between the near-interface gradient G_0 and the bulk gradient G_b . The transient from G_0 to G_b is described by the scale parameter p , and curves 1, 2, and 3 correspond to $p = 0.5$, 1, and 2 (slow, intermediate, and fast transients). The computed curves are for $D_{im} = 3 \times 10^{-4} \text{ cm}^2/\text{s}$.

growth mode (V is about $V_t/2$). The final amount of interstitials agglomerated into loops may be much lower,^{1,8} for instance, below 10^{13} cm^{-3} .

VII. EFFECT OF AXIAL NONUNIFORMITY IN THE TEMPERATURE GRADIENT ON THE CRITICAL GROWTH RATE

Up to now the near-interface temperature profile was assumed to be linear in coordinates $1/T$ and z . If so, the temperature gradient G is equal to $G_0(T/T_m)^2$ and is practically constant within the relevant range of defect annihilation. This range is kT_m^2/E in temperature (about 50 K) or $L = kT_m^2/EG_0$ in distance (about 1 cm). Equation (12) contains the gradient G that can be of arbitrary dependence on T (or on z). Sometimes $G(z)$ is a remarkably decreasing function within the several first centimeters from the interface¹¹ so that the near-interface gradient G_0 is considerably higher than the bulk gradient G_b . This kind of axial nonuniformity in $G(z)$ may be described qualitatively by an exponential dependence of G on the variable $x = E/kT - E/kT_m$:

$$G = (G_0 - G_b)\exp(-px) + G_b. \quad (22)$$

Here the parameter p shows the relative scale of nonuniformity in G . Small p means that the scale of nonuniformity is large (G is quite uniform and close to G_0 within the annihilation range). Large p means strong nonuniformity within the annihilation distance.

Equation (12) was numerically solved using the function, Eq. (22), for several values of the scale parameter (p) and of the nonuniformity ratio (G_b/G_0). The critical growth rate for the reference case of a uniform gradient will now be denoted by V_{t0} (equal to $\xi_t G_0$). The actual critical rate V_t is now dependent on the nonuniformity parameters p and G_b/G_0 . The computed relative critical growth rate, V_t/V_{t0} , is shown in Fig. 4 in dependence on G_b/G_0 for three representative values of the scale parameter. This dependence is practically linear which means that V_t is proportional to the effective gradient of G_0 and G_b combined:

$$V_t = \xi_t [G_0 - \gamma(G_0 - G_b)]. \quad (23)$$

The factor γ deduced from the plots of Fig. 4 is almost proportional to the scale parameter p :

$$\gamma = 0.11p, \quad (24)$$

so that the correction term in Eq. (23) is proportional to the product $p(G_0 - G_b)$. This product is convenient to express by Eq. (22) through the derivative of the gradient $G(z)$:

$$p(G_0 - G_b)E/kT_m^2 = -(dG/dz)/G, \quad \text{at } z=0. \quad (25)$$

The reported value¹¹ of G and dG/dz corresponds to a correction of only 2%; the critical growth rate is almost entirely controlled by the near-interface gradient G_0 , in spite of a pronounced variation in $G(z)$.

This conclusion is generally true if the scale of the $G(z)$ profile is comparable to the annihilation distance L or less ($p < 1$). The correction term in Eq. (23) is then less than 10% at any G_b/G_0 .

Even if V_t is appreciably shifted by strong nonuniformity in $G(z)$, for instance, at $p=2$ and $G_b/G_0=0.5$ (Fig. 4), the computed dependence of the incorporated concentration on V/V_t does not deviate much from that shown in Fig. 2. Accordingly, expression (21) is applicable even for a non-uniform $G(z)$ profile.

VIII. SUMMARY

The main points developed here may be summarized as follows.

- (1) Steady-state crystal growth results in the incorporation of point defects (either self-interstitials or vacancies) a short distance from the crystal/melt interface. Both the type and the concentration of incorporated defects depend on the V/G_0 ratio of the growth rate to the near-interface axial temperature gradient.
- (2) The defect incorporation problem was solved—and reduced to a simple analytical expression—in a simplified approach of only axial defect transport in the vicinity of the interface. Such an approach is correct if the axial gradient G_0 is large enough: then the scale of axial near-interface defect profiles is small in comparison to the crystal's radius.
- (3) Vacancies are incorporated if the growth rate V is over the critical rate $V_t = \xi_t G_0$ and the incorporated concentration C_{vs} is an increasing function of V/V_t . By comparison, the theoretical and experimental dependence of C_{vs} on V/V_t , the product of the diffusivity and the equilibrium concentration for interstitials, that is obtained is $310^{11} \text{ cm}^{-1} \text{ s}^{-1}$ (at the melting point). This value is in accord with the self-diffusion data.
- (4) The incorporated interstitial concentration (at $V < V_t$) is a decreasing function of V/V_t .
- (5) The concentration scale for incorporated defects (of vacancies at V well over V_t , and of interstitials at V well below V_t) is 10^{14} cm^{-3} .

- (6) The axial gradient G may decrease fast upon moving away from the interface, and yet the critical growth rate V_t for the defect changeover is almost entirely controlled by the near-interface value, G_0 .

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APPENDIX: AN ESTIMATE FOR THE SELF-INTERSTITIAL DRIFT VELOCITY IN SILICON

In one of the early works on microdefect formation in float-zone silicon³¹ the microdefect patterns induced by an abrupt change in the growth rate were studied. A transition from the growth rate V_1 (slightly below V_t) to the lower growth rate V_2 introduced a boundary between interstitial-poor and interstitial-rich regions. The opposite change—from V_2 to V_1 —also introduced a boundary between interstitial-rich and interstitial-poor regions. If the interstitials were to drift (presumably in the uphill direction, back to the interface), then either boundary would shift from the initial position (where V was changed) towards the interface during the cooling period. The interstitial-rich region is manifested as a region of A defects (loops). No resolvable shift of the A region towards the interface was found.³¹ The drift velocity V_{dr} can be then estimated to be less than 0.2 mm/min (at $G_0=30 \text{ K/mm}$). Accordingly, the drift coefficient $\alpha_i = V_{dr}/G_0$ is less than $10^{-6} \text{ cm}^2/\text{s/K}$, and the drift energy ϵ_i is of the order of 1 eV, or less, according to expression (2). **Therefore ϵ_i is essentially lower than the average formation energy ($E=4.4 \text{ eV}$).**

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