



Intrinsic Point Defects and Impurities in Silicon Crystal Growth

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The incorporation of intrinsic point defects into a growing crystal is affected by the presence of impurities that can react with vacancies and self-interstitials. The critical value of the ratio of the growth rate, V , to the axial temperature gradient, G , (V/G ratio) that separates the interstitial growth mode from the vacancy growth mode, is shifted by impurities, and this effect can be described by simple analytical expressions. Some impurities, such as oxygen, nitrogen, and hydrogen, trap vacancies and cause a downward shift in the critical V/G ratio (and also a fast increase in the fraction of trapped vacancies, on lowering T). Other impurities, like carbon, trap self-interstitials, and cause an upward shift in the critical V/G ratio (and also an increase in the fraction of impurity interstitials, on lowering T). The impurities affect both the incorporation and agglomeration stages of microdefect production.

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The structural properties of as-grown silicon are controlled by the type and concentration of intrinsic point defects incorporated into the growing crystal.¹⁻³ An incorporation model¹ that is now commonly accepted, assumes a fast recombination of intrinsic point defects in the vicinity of the crystal/melt interface. The annihilation stage is effectively complete when the temperature is below the melting point by about 100°C. Since then, only one kind of defect, either vacancy or self-interstitial, is present in a supersaturated concentration while the competing defects rapidly disappear. In a simple approximation of a one-dimensional diffusion field,¹ there is some universal critical value of the ratio of the growth rate, V , to the axial temperature gradient, G (V/G) that separates the vacancy growth mode (at higher V/G) from the interstitial growth mode (at lower V/G). Due to a radial and axial nonuniformity in G and V , the same crystal may contain both vacancy-type and interstitial-type regions separated by a well-defined boundary.²⁻⁴

The surviving intrinsic defects will agglomerate, upon the subsequent lowering of T , into various structural microdefects. For standard vacancy growth mode (at V/G well above the critical value), the basic microdefects are now recognized as voids⁵⁻⁷ while for standard interstitial growth mode (at V/G well below the critical value), the basic microdefects were found to be interstitial-type dislocation loops.⁸⁻¹⁰ The microdefect kind is drastically changed when V/G is close to the critical value, in other words, at a reduced concentration of incorporated point defects. At low vacancy concentration, oxide particles are formed instead of voids by joint agglomeration of vacancies and oxygen;² this effect is responsible for the formation of oxidation-induced stacking faults in a ring-like distribution.¹¹⁻¹³ At low self-interstitial concentration, so-called B-defects (globular interstitial aggregates) are formed instead of loops.^{4,9,14}

The critical V/G ratio is of fundamental importance in the growth of dislocation-free silicon crystals of controlled microdefect properties. The reported numbers for the critical ratio scatter considerably, in the range from 0.12 to 0.2 mm²/min K.^{1,13,15} One of the reasons for such a scatter is an uncertainty in the measured or calculated value of G , in the vicinity of the crystal/melt interface. However, there are also fundamental reasons for a scattered critical V/G ratio: (i) the effect of impurities on the incorporation of intrinsic point defects into the growing crystal, and (ii) the effect of the interface shape on the diffusion field of point defects in the vicinity of the interface.¹⁶

This paper is devoted to the impurity effect on the critical V/G

ratio and to the related effect of trapping vacancies or self-interstitials by impurities, upon lowering the temperature.

Critical V/G Ratio for Pure Crystals and Flat Interface

The diffusion of point defects in the vicinity of the crystal/melt interface can be treated, approximately, as a one-dimensional problem, since the characteristic length of defect annihilation¹ is considerably smaller than the crystal diameter (this length is about 2 cm in modern Czochralski crystals, for $G \approx 30$ K/cm). In this approximation, the crystal/melt interface is flat; the critical growth rate V_t , for the change-over from interstitial to vacancy incorporation, depends, strictly speaking, on the entire axial temperature profile $T(z)$. However, the most important feature of the $T(z)$ profile is the near-interface value of G (defined as $-dT/dz$). The V_t is dependent mostly on G . Particularly, for a linear axial profile of the inverse temperature and for temperature-independent diffusivities of the point defects, there is a precise analytical solution for the critical ratio (denoted by ξ_t), through the point defect parameters¹⁷

$$\xi_t = V_t/G$$

$$= (1/kT_m^2)[(E - \varepsilon_i)D_iC_{im} - (E - \varepsilon_v)D_vC_{vm}]/[C_{vm} - C_{im}] \quad [1]$$

where $E = (E_i + E_v)/2$ is the defect formation energy averaged over the two species, $\varepsilon_i, \varepsilon_v$ are the drift energies that characterize the defect drift along the temperature gradient, D_i and D_v are the diffusivities, and C_{im}, C_{vm} are the equilibrium concentrations at the melting point (T_m). The subscripts i and v refer to interstitial and vacancy, respectively. The critical growth rate, V_t corresponds to the zero total flux of the excess silicon, which is the difference of the interstitial and vacancy fluxes

$$J = J_i - J_v$$

$$= [-D_i \nabla C_i + D_v \nabla C_v] + [V(C_i - C_v)]$$

$$+ [-D_i C_i \nabla(\varepsilon_i/kT) + D_v C_v \nabla(\varepsilon_v/kT)] \quad [2]$$

where the three bracketed terms correspond to Fickian diffusion, convection, and thermal drift, respectively. The two concentration profiles, $C_i(z)$ and $C_v(z)$, are related by the condition of fast recombination: the product of the two is equal to the product of the equilibrium concentrations, $C_{ie}(T)C_{ve}(T)$. Equation 2 can be integrated to find the flux, J , in dependence of the growth rate V .¹⁷ The V_t

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Table I. Point defect parameters. The top line of numbers is after Ref. 17, the bottom row is for smaller formation energies.

C_{vm} (cm^{-3})	C_{im} (cm^{-3})	D_{im} (cm^2/s)	D_{vm} (cm^2/s)	E_{id} (eV)	E_{vd} (eV)	E (eV)	ε_i (eV)	ε_v (eV)
1×10^{15}	7.7×10^{14}	4×10^{-4}	5×10^{-5}	0.35	0.35	4.6	0	0
1×10^{15}	7.7×10^{14}	4×10^{-4}	5×10^{-5}	0.95	0.35	4	0	3

corresponds to zero flux. At $V < V_t$, the function $J(V)$ is positive which corresponds to interstitial incorporation. Otherwise, $J(V) < 0$ which corresponds to vacancy incorporation.

Impurity Effect on ξ_t through the Equilibrium Concentrations of Intrinsic Point Defects

The critical ratio, ξ_t , is sensitive to the equilibrium defect concentrations, mostly through the denominator of Eq. 1 since the two concentrations, C_{vm} and C_{im} , are nearly equal.¹⁷ Therefore, even relatively small shifts in the concentrations (denoted by δC_{im} and δC_{vm}) will cause an appreciable shift in ξ_t . This shift is approximated taking into account only a change in the denominator of Eq. 1

$$\xi_t = \xi_{to} / [1 + (\delta C_{vm} - \delta C_{im}) / (C_{vm} - C_{im})] \quad [3]$$

where ξ_{to} refers to the nondoped crystal. Generally, the equilibrium concentrations may be shifted due to

1. A shift in the Fermi level by a charged dopant that is present in the concentration not much lower than the intrinsic electron concentration. The equilibrium concentration of negatively charged defects (vacancies) will change in proportion to the electron concentration. This mechanism can explain well¹⁸ the reported effect of boron impurity¹⁹ which is to increase ξ_t . The boron acceptors reduce the electron concentration; δC_{vm} is negative and proportional to the boron concentration. The donor dopants are expected to reduce the critical ratio ξ_t by this mechanism.

2. A lattice strain induced by impurity atoms, if the impurity atom size is different from that of a host atom.²⁰ The impurity-induced lattice stress is a superposition of local stress fields around the impurity atoms and some constant pressure; only the latter stress component affects the equilibrium concentrations.²¹ The strain effect on C_{vm} or C_{im} turns out to be negligible at the conventional doping level, below $10^{19} cm^{-3}$.

Impurity Effect on ξ_t Through Vacancy Trapping

There are some other impurities (oxygen, nitrogen, hydrogen, carbon) which also exhibit an effect on ξ_t .^{14,16,22,23} These impurities are either neutral or of low concentration, and the mechanism of the impurity effect is through chemical reactions of impurity species with the intrinsic point defects. The two basic reactions are

1. Vacancy trapping and releasing by a major impurity state. Particularly, this applies to interstitial impurities with a small substitutional component; in this case the trapped (or bound) vacancies are identical to the substitutional impurity atoms.

2. Self-interstitial trapping and releasing by a major impurity state. Particularly, this applies to substitutional impurities with a small interstitial component; in this case, the trapped (or bound) self-interstitials are identical to interstitial impurity atoms, and trapping occurs by the kick-out reaction.

In this section we consider an impurity that traps vacancies. If the trapping and releasing reaction is fast, the free vacancies of the concentration C_v and the trapped vacancies of the concentration C_v^* coexist in the equilibrium ratio

$$C_v^* / C_v = (C_{vm}^* / C_{vm}) \exp(E_b / kT - E_b / kT_m) \quad [4]$$

where C_{vm}^* is the concentration of trapped vacancies at T_m , in equilibrium with the major impurity state, and E_b is the energy gain on

formation of one trapped vacancy. For simple atomic traps, like oxygen, E_b is identical to the binding energy of a vacancy to an impurity atom, and C_{vm}^* is just proportional to the total impurity concentration, C . The situation is a bit more complicated for nitrogen (see below) but Eq. 4 still holds. It should be noted that the total impurity concentration, C , is assumed to be much higher than the incorporated vacancy concentration (which is typically less than $10^{14} cm^{-3}$), to neglect a small loss of the major impurity state for formation of trapped vacancies.

Within the incorporation model,^{1,17} the concentrations of free vacancies and of self-interstitials at the crystal/melt interface are of equilibrium values (C_{vm} and C_{im} , respectively), due to fast consumption/generation reactions at the interface. In the presence of vacancy traps, the free vacancies, in the same concentration C_{vm} , coexist with the trapped vacancies; and the total concentration of the vacancy species is increased. Due to the fixed proportion (Eq. 4) between the free and trapped vacancies, both vacancy species are equally spent on the recombination with self-interstitials. Therefore, the vacancy convection flux in Eq. 2 should be modified by replacing C_v with the total concentration of the vacancy species, $C_v + C_v^*$. Since the denominator in Eq. 1 comes from the convection term, a shift in the critical V/G ratio due to the presence of trapped vacancies can be qualitatively described by replacing C_{vm} with the total concentration of the vacancy species at T_m which is $C_{vm} + C_{vm}^*$, in the denominator of the Eq. 1

$$\xi_t = \xi_{to} / [1 + C_{vm}^* / (C_{vm} - C_{im})] \quad [5]$$

This shift (due to the presence of trapped vacancies) is very similar to that caused by a shift in the free vacancy concentration (Eq. 3).

The formula (Eq. 5) would be precise at $E_b = 0$ and with temperature-independent diffusivities, since then the flux (Eq. 2) is modified just by multiplying C_v by a constant factor, $1 + C_v^* / C_v$, and by simultaneously dividing D_v by the same factor. With nonzero E_b and the temperature-dependent diffusivities, one should find the critical ratio by numerical integration of the modified flux equation (Eq. 2), in order to find the function $J(V)$ and the growth rate V_t of zero flux. The integration (quite similar to that described in Ref. 17) was performed using the point defect parameters specified by Table I. The parameter set includes the melting point values for the equilibrium concentrations (C_{vm}, C_{im}) and for the diffusivities (D_{im}, D_{vm}), and the energies of migration (E_{id}, E_{vd}), formation (E), and drift ($\varepsilon_i, \varepsilon_v$). The measured temperature dependence of the concentration difference, $C_{ve} - C_{ie}$, indicates²⁴ that the formation energy of a self-interstitial, E_i , and that of a vacancy, E_v , are almost the same. It is thus adopted that $E = E_i = E_v$.

The two parameter sets were actually used; the top line of numbers in Table I corresponds to the set specified in Ref. 18 under the assumption of a low migration energy of self-interstitials (here this energy is taken to be the same as the vacancy migration energy). Since the sum of the formation and migration energies for self-interstitial, $E_i + E_{id}$, is known to be 4.95 eV,²⁵ this assumption implies a rather high formation energy, $E_i = 4.6$ eV. The quantum calculations²⁶ suggest a remarkably lower formation energies, about 4 eV for the vacancy. The interstitial migration energy (with $E_i = E_v$) is then 0.95 eV. These values are used in the second param-

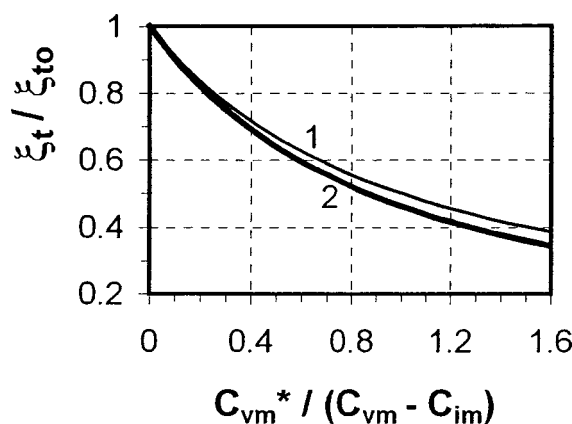


Figure 1. Relative shift in the critical V/G ratio caused by vacancy trapping impurity, in dependence of the normalized concentration of trapped vacancies at T_m . Curve 1: analytical expression (Eq. 5), curve 2: numerical computation at $E_b = 2$ eV, for either of the two parameter sets.

eter set, shown in the bottom row of numbers in Table I. A high vacancy drift energy is now introduced. This is done for the following formal reasons: (i) to keep the same critical ratio ξ_{to} for the two sets, and (ii) to demonstrate that the drift, even as strong as that, is not essential for the impurity-induced shift in the critical V/G ratio. The second parameter set is quite close to that of Ref. 27. By the results of this paper, the second parameter set seems preferable.

The dependence of the shifted ratio, ξ_t/ξ_{to} , on the impurity parameter $C_{vm}^*/(C_{vm} - C_{im})$, was computed for several values of binding energy E_b . The computed curves for the two parameter sets are almost identical, and they deviate only slightly from the simple formula (Eq. 5). An example is shown in Fig. 1, for $E_b = 2$ eV (this value is representative for the particular impurities discussed below). The qualitative analytical expression (Eq. 5) contains just one intrinsic point defect parameter, the concentration difference $C_{vm} - C_{im}$, whereas the transport equation (Eq. 2) includes many parameters. And yet, Eq. 5 well describes the impurity-induced shift which is quite insensitive to all the parameters except $C_{vm} - C_{im}$.

An impurity that traps vacancies causes a reduction in ξ_t , and thus an expansion of the vacancy region at the expense of the interstitial region, when the two regions coexist in one crystal.

Another important consequence of vacancy trapping is to reduce the fraction of free vacancies in the incorporated vacancy community, on lowering T , according to Eq. 4. Below some characteristic "binding temperature" T_b , the bound (trapped) vacancies will prevail over the free vacancies. An example of computed axial profiles of self-interstitials (curve labeled I), free vacancies (curve labeled V) and trapped vacancies (curve labeled V^*) is shown in Fig. 2, for particular values of V/V_t and $C_{vm}^*/(C_{vm} - C_{im})$. In the interstitial growth mode (Fig. 2a) both free and bound vacancies disappear by recombination with self-interstitials, and some self-interstitial concentration is incorporated. In the vacancy growth mode (Fig. 2b) the survived vacancy population consists of the two species, V and V^* , of some constant total concentration, but the ratio of the two species changes gradually in favor of trapped vacancies. The binding temperature corresponds to the intersection point of curves V and V^* .

When T_b is less than the void nucleation temperature T_n , vacancy trapping does not affect void formation and their properties very much. On the other hand, if T_b becomes greater than T_n , then void formation will be either strongly modified or completely suppressed, due to a lack of free vacancies. This effect is discussed further in the section below devoted to the nitrogen impurity.

Vacancy trapping by oxygen.—The oxygen impurity in silicon is well known to exist in the interstitial state. The substitutional (off-center) state of oxygen, or the vacancy/oxygen complex VO (known

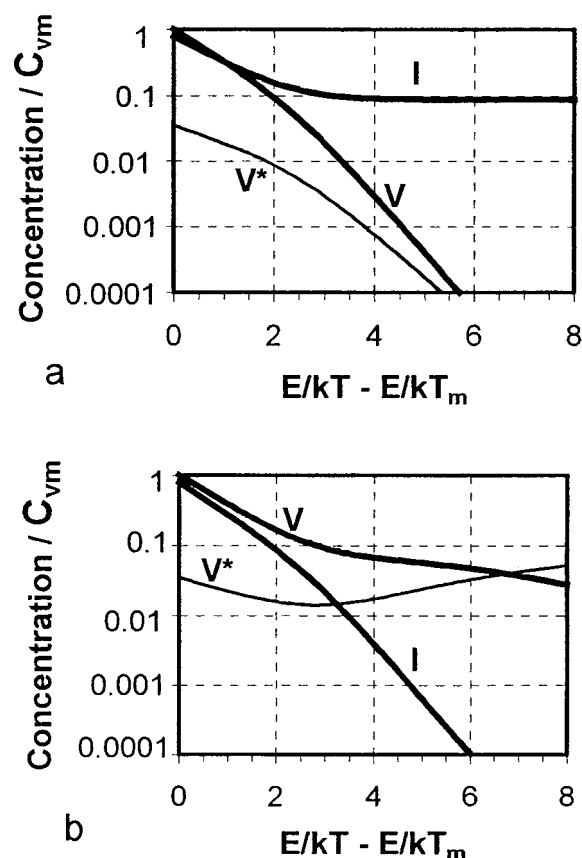


Figure 2. Axial concentration profiles of free vacancies (V), trapped vacancies (V^*), and self-interstitials (I) at $C_{vm}^*/(C_{vm} - C_{im}) = 0.15$ and $E_b = 2$ eV, for the second parameter set. (a, top) Interstitial mode, $V/V_t = 0.7$; (b, bottom) vacancy growth mode, $V/V_t = 1.5$.

also as A-center) is produced in irradiation experiments.²⁸ By annealing the irradiated samples, the A-centers disappear at $T > 350^\circ\text{C}$, presumably by attaching more oxygen atoms and not by dissociation. The binding energy of a vacancy to an oxygen atom may be large enough for the VO species to be present in appreciable amount even at high T , in equilibrium with free vacancies. Evidence of high temperature vacancy trapping by oxygen comes from the fact that, in the course of crystal growth, some vacancies escape consumption by voids; these "residual vacancies" control subsequent oxygen precipitation, giving rise to a complicated banded pattern.^{3,29} This effect is accounted for if the free vacancies become bound (trapped) by oxygen, below some characteristic binding temperature T_b (estimated to be around 1050°C); otherwise the vacancies would be completely consumed by the voids. A vacancy, due to its four dangling bonds, can absorb either one or two oxygen atoms, giving rise to VO and VO_2 species. We assume that the reactions of transformation of V into VO (by vacancy diffusion) and of VO into VO_2 (by oxygen diffusion) are fast enough to support the equilibrium ratio between the species concentrations C_v , C_1 , and C_2 (of V , VO, and VO_2 , respectively). It is also assumed that the free energy change, upon attachment of the first and the second oxygen atom to a vacancy, is the same. A qualitative argument in favor of such a simplification is that an oxygen atom in the A-center is close to the two of the silicon neighbors²⁸ leaving the two other silicon neighbors in the same state as that in the free vacancy. With this assumption, the mass-action law for the above reactions reads

$$C_1/C_v = C_2/C_1 = AC \exp(E_b/kT) \quad [6]$$

where C is the oxygen concentration; the prefactor A includes a change in the vibrational entropy due to the dangling bonds, on attaching an oxygen atom to a vacancy. The binding temperature may be defined by the condition $C_1/C_v = C_2/C_1 = 1$. Below T_b , this concentration ratio becomes high, and then $C_2 \gg C_1 \gg C_v$, which means that the prevailing vacancy state is VO_2 . At temperatures greater than T_b , this ratio becomes small, and $C_2 \ll C_1 \ll C_v$. This means that free vacancies prevail with some small fraction of VO species and a much smaller fraction of VO_2 .

The VO species (trapped vacancies) that are present at T_m will shift the critical V/G ratio according to Eq. 5; the concentration C_{vm}^* is equal to $R_s C$ where R_s is the equilibrium fraction of substitutional oxygen (VO). The general expression (Eq. 5) is then presented in the form

$$\xi_t = \xi_{t0}/(1 + C/C_o) \quad [7]$$

where the constant $C_o = (C_{vm} - C_{im})/R_s$. The oxygen-induced shift in ξ_t was indeed found;^{16,22} the dependence of ξ_t on the oxygen content, C , can be described by Eq. 7 with $C_o = 4 \times 10^{18} \text{ cm}^{-3}$; the corresponding value of R_s is 5×10^{-5} . With specified value of R_s , both E_b and T_b can be estimated. In order to do so, we note that the equilibrium concentration, C_{2e} , of a VO_2 species (that has no dangling bonds), can be written neglecting a vibrational entropy of this defect. In the equilibrium state ($C_v = C_{ve}$), a VO_2 species can be created without participation of a vacancy, by taking two oxygen atoms from the solid solution and removing a silicon atom to the sample surface. Then, the mass action law relates the atomic fractions of VO_2 and of oxygen

$$(C_{2e}/\rho) = (C/\rho)^2 \exp(-E_2/kT) \quad [8]$$

where ρ is on the order of the lattice site density ($5 \times 10^{22} \text{ cm}^{-3}$) and E_2 is the energy increment by the considered reaction. The relations (Eq. 6) specify the concentrations of VO and VO_2 species in equilibrium with a vacancy solution

$$(C_1/C_v)^2 = C_2/C_v = (C_{2e}/C_{ve}) \quad [9]$$

The concentration C_2 differs from the equilibrium value C_{2e} by including the vacancy supersaturation factor, C_v/C_{ve} . By comparing Eq. 9 and 4, the binding energy is expressed as $E_b = (E_v - E_2)/2$. At the melting point, the C_1/C_v ratio is identical to $R_s C/C_{vm}$, and Eq. 8 and 9 provide a relation between E_2 and R_s ; the resulting value of the VO_2 formation energy is $E_2 = 0.3 \text{ eV}$. Accordingly, the binding energy of a vacancy to an oxygen atom is $E_b = 1.85 \text{ eV}$ (at $E_v = 4 \text{ eV}$). Each equilibrium concentration, C_{2e} (of VO_2) and C_{1e} (of VO) is now specified as a function of T , by Eq. 8 and 9. These concentrations are plotted in Fig. 3, at $C = 8 \times 10^{17} \text{ cm}^{-3}$. The binding temperature is close to 1070°C . The actual concentrations C_v , C_1 , and C_2 are in the same ratio as the equilibrium concentrations C_{ve} , C_{1e} , and C_{2e} .

The curves in Fig. 3 are based solely on the high temperature oxygen effect on ξ_t . They should be considered only as a rough description of the actual relation between the V, VO, and VO_2 species, based on the assumptions made. And yet, the resulting value of the binding temperature is in a reasonable agreement with a rough estimate of T_b based on the residual vacancy consideration.²⁹ If E_v were assumed to be 4.6 eV , a too high value of T_b (about 1100°C) would be obtained. This is an argument in favor of a lower formation energy ($E_v = 4 \text{ eV}$) which is adopted from now on.

In conclusion, the equilibrium concentration of VO species (substitutional oxygen, or A-center) is relatively low, about $4 \times 10^{13} \text{ cm}^{-3}$ at T_m . It is, however, enough for an appreciable shift (about 20%) in the critical V/G ratio. The critical ratio in Czochralski (CZ) silicon is always shifted downward, with respect to the "genuine" critical ratio for impurity-free silicon. On lowering T , the

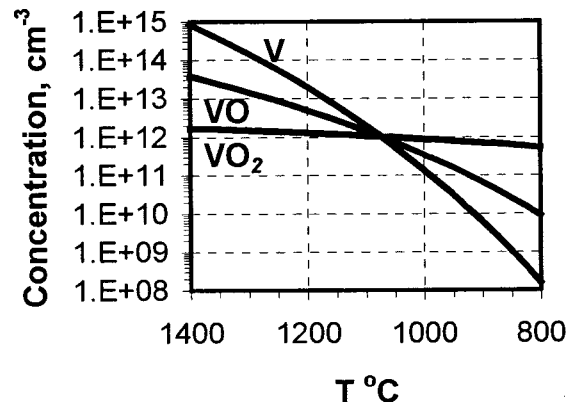


Figure 3. Equilibrium concentrations of vacancy species V, VO, and VO_2 , at the oxygen concentration $C = 8 \times 10^{17} \text{ cm}^{-3}$.

fraction of trapped vacancies increases, and approaches 50% at about 1060°C . Since the voids are formed at a higher temperature (at about 1100°C), the vacancy trapping by oxygen is of a minor importance for the void formation.

Vacancy trapping by nitrogen.—The nitrogen impurity is thought to be present in the di-interstitial (molecular) state, N_2 , at room temperature.³⁰ Though it dissociates on raising T , producing atomic interstitials, N_1 , the first-principle calculations^{31,32} suggest that the di-interstitial state prevails even at T_m . The authors of Ref. 32 calculated the energies of various nitrogen/vacancy species: substitutional nitrogen (VN, a complex of a vacancy and one interstitial nitrogen atom), substitutional molecule (VN_2), and also the V_2N_2 complex, all produced from the basic molecular state, N_2 . The species concentrations, in equilibrium with the solid solution of nitrogen molecules, can be expressed by a mass-action law using the reported energies. A change in the vibrational entropy upon formation of these species will be neglected, and the resulting numbers should be considered as rough estimates. The square brackets will be used to denote the atomic fraction of the species (the ratio of the concentration to the site density ρ).

For atomic nitrogen interstitials

$$[N_1] = [N_2]^{1/2} \exp(-2.15 \text{ eV}/kT) \quad [10]$$

Formation of substitutional nitrogen, VN, for the equilibrium case ($C_v = C_{ve}$), can be performed without assisting vacancies (by removal of a silicon atom to the crystal surface), and the mass-action law reads quite similarly to Eq. 10 with the formation energy of 1.74 eV .³² When, however, this species is produced by trapping a vacancy, the concentration of VN is proportional to C_v , and therefore, includes the supersaturation factor C_v/C_{ve}

$$[VN] = (C_v/C_{ve})[N_2]^{1/2} \exp(-1.74 \text{ eV}/kT) \quad [11]$$

The concentrations of the other vacancy/nitrogen species are expressed similarly

$$[VN_2] = (C_v/C_{ve})[N_2] \exp(-2.33 \text{ eV}/kT) \quad [12]$$

$$[V_2N_2] = (C_v/C_{ve})^2[N_2] \exp(-1.26 \text{ eV}/kT) \quad [13]$$

Assuming for the total nitrogen concentration, C , a typical value of 10^{15} cm^{-3} , the calculated concentrations at T_m (when $C_v/C_{ve} = 1$) are all much lower than the concentration of the molecular form. The latter is thus close to $C/2 = 5 \times 10^{14} \text{ cm}^{-3}$. The concentrations of the other species, as defined by Eq. 10-13, are as follows (in units of cm^{-3}): atomic interstitials N_1 : 1.9×10^{12} ; sub-

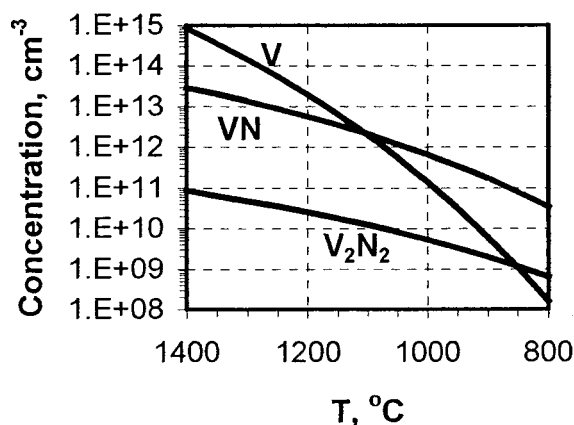


Figure 4. Equilibrium concentrations of vacancy species V, VN, and V_2N_2 in nitrogen doped silicon, at the nitrogen concentration $C = 10^{15} \text{ cm}^{-3}$. The VN_2 species is of too low concentration to show in the figure.

stitutional species VN: 3.1×10^{13} ; VN_2 : 5.5×10^7 ; and V_2N_2 : 8.6×10^{10} . The formation energy is the lowest for the V_2N_2 . It induced the authors of Ref. 31, 32 to suggest that V_2N_2 is the prevailing vacancy/nitrogen species. However, due to the difference in the prefactors in Eq. 11 and 13, the actually prevailing species (at T_m) is VN, the substitutional nitrogen atom. The concentration ratio C_v^*/C_v is specified by Eq. 11 and reduced to the general form of Eq. 4: the energy gain $E_b = E_v - 1.74 \text{ eV} = 2.36 \text{ eV}$. Equation 5, with Eq. 11 for the concentration of the trapped vacancies, is presented in the form

$$\xi_t = \xi_{t0} / [1 + (C/C_0)^{1/2}] \quad [14]$$

where the constant $C_0 = 5.6 \times 10^{16} \text{ cm}^{-3}$. The difference from the previous case of oxygen is only in the dependence of the concentration of trapped vacancies, C_{vm}^* , on the total impurity concentration: C_{vm}^* is now proportional to $C^{1/2}$, due to the dominance of molecular interstitial state. The expected downward shift in ξ_t is about 12%, which is consistent with the observed effect of nitrogen to expand the vacancy region in Czochralski crystals grown at a ramped rate.²²

The equilibrium concentrations of the vacancy species, at $C = 10^{15} \text{ cm}^{-3}$, are plotted in Fig. 4. The binding temperature is close to 1115°C, if the contribution of the V_2N_2 species is neglected. For the actual case of supersaturated vacancy solution, the relative contribution of the V_2N_2 species is increased due to the square dependence on the supersaturation, according to Eq. 13. To include this effect, one should find the nonequilibrium concentrations of all the vacancy species using Eq. 11-13 and specifying the total incorporated concentration of vacancies, which is typically about 10^{14} cm^{-3} .¹⁷ The relative contribution of V_2N_2 species, though enhanced, turns out to be still small at T_b : about 8%. Therefore, the dominant type of trapped vacancies at T_b is still the substitutional nitrogen, VN.

According to the above estimates, the nitrogen impurity is a powerful trap for vacancies, in comparison to oxygen. The void formation in nitrogen-doped CZ silicon occurs under condition of well-pronounced trapping of vacancies by nitrogen. The trapping kinetics is either by dissociation of N_2 and subsequent reaction of N_1 with vacancies, or by reaction of V directly with N_2 , to produce VN and N_1 . The interstitial nitrogen atoms produced by the latter reaction will trap vacancies, contributing to the overall rate of VN formation. We assume that, by one or both of these paths, the equilibrium between the free and bound vacancies is maintained (a quantitative proof of this assumption requires a separate study). In this case, the free vacancy loss to voids is accompanied by a release of

trapped vacancies, to support the equilibrium C_v/C_v^* ratio, and finally, almost all vacancy species are consumed in the formation of voids. A reduction in the free vacancy fraction is equivalent to a reduced effective mobility of the vacancy population (of which only a fraction is mobile). The density of produced voids is inversely proportional to this effective mobility, to the power of 1.5.² At reduced vacancy mobility (and thus at reduced vacancy flux to the voids), a larger density of voids will be produced before the vacancy loss to the voids becomes fast enough to suppress further void nucleation. Accordingly, the void density in nitrogen-doped silicon should increase, at the same growth parameters. A reduced concentration of free vacancies results in a lower nucleation temperature of voids and, therefore, in a further reduction in the effective vacancy mobility. This effect contributes into the increased void density. Both an increase in the void density and a downward shift in the void nucleation temperature, due to nitrogen doping, were indeed reported.³³⁻³⁵ Whether these effects can be described quantitatively by the vacancy trapping alone, needs further investigation.

On the other hand, nitrogen is well known to completely suppress void formation in float-zoned (FZ) silicon.^{36,37} It can be explained by the difference in the void formation temperature between CZ and FZ crystals. In CZ crystals the void formation is thought to be assisted by oxygen, which is either adsorbed at the void surface³⁸ or involved in nucleation of the primary oxide particles which are then transformed into voids, by cavitation.³⁹ As pointed out above, the nucleation temperature, in the absence of nitrogen, is close to the vacancy binding temperature by nitrogen. The free vacancy concentration, though somewhat reduced by formation of VN, is still sufficient for the production of voids: in increased density, due to a reduced effective vacancy mobility. In nitrogen-free FZ silicon, T_n is expected, due to the lack of oxygen, to be substantially lower than that in CZ silicon (although this is not yet proven experimentally). This value of T_n is well below the nitrogen-controlled binding temperature (which is around 1115°C). Under such conditions, provided the concentration of nitrogen is sufficient to trap all the vacancies, the free vacancy concentration is so reduced upon lowering T as to completely prevent void formation. The vacancy species, VN, will be completely preserved in the crystal.

This conclusion is supported by the results obtained by the Pt-diffusion technique used to count grown-in vacancy species in both CZ and FZ samples.^{40,41} The counted vacancy species are not necessarily only free vacancies but also other species like VO_2 or VN (these are counted by replacing oxygen or nitrogen by a Pt atom). It was found that the Pt concentration is very low both in CZ samples and in FZ samples nondoped with nitrogen,^{40,41} which shows that the initially incorporated vacancies, in a concentration of about 10^{14} cm^{-3} , are almost completely consumed by the voids. The FZ samples studied in Ref. 40 were nitrogen-doped, unlike those reported in Ref. 41 (private communication by Pichler and Quast). The Pt concentration in nitrogen-doped FZ samples was up to 10^{14} cm^{-3} , which proves that the incorporated vacancies are preserved from agglomeration, most likely as VN species. The presence of these grown-in point defects may account for a strong increase in the resistivity, due to formation of deep centers, observed in nitrogen-doped FZ crystals after a very short annealing at 900 or 1000°C.⁴² A plausible mechanism of this effect is a reconstruction of initially inactive VN species into deep centers. The deep nitrogen-related centers (presumably substitutional nitrogen atoms) were also found in implanted samples.⁴³

In conclusion, the nitrogen effect in FZ crystals is to expand the vacancy region but to shrink the void-containing portion of this region.

Vacancy trapping by hydrogen.—Hydrogen was the first impurity reported to affect formation of grown-in microdefects.¹⁴ It was found that the critical growth rate, for disappearance of swirl defects (loops), was strongly reduced, by a factor of 2, in the presence of hydrogen, roughly, in concentration of 10^{15} cm^{-3} . The concentration of vacancy-hydrogen complexes can be estimated from Eq. 5 at

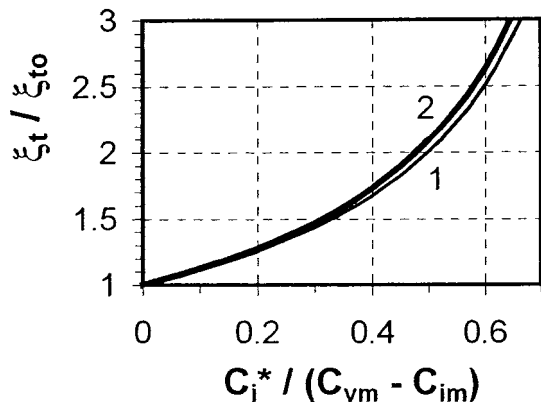


Figure 5. Relative shift in the critical V/G ratio caused by interstitial trapping impurity, in dependence of the normalized concentration of impurity interstitials at T_m . Curve 1: analytical expression (Eq. 16), curve 2: numerical computation at $E_k = 2$ eV, for either of the two parameter sets.

$\xi_t / \xi_{to} = 0.5$; it is as high as $2 \times 10^{14} \text{ cm}^{-3}$ (at T_m). No further details of vacancy trapping by hydrogen can be given, due to the lack of information on the vacancy-hydrogen complexes.

Impurity Effect on ξ_t Through Self-Interstitial Trapping

The effect of predominantly substitutional impurity with a minor interstitial component is quite symmetric to the above case of vacancy trapping. Now the self-interstitials are trapped by the major impurity species, to create, by the kick-out reaction, a minor interstitial impurity state. Again, we assume that the self-interstitials (of concentration C_i) and the impurity interstitials (of concentration C_i^*) coexist in the equilibrium ratio

$$C_i^* / C_i = (C_{im}^* / C_{im}) \exp(E_k / kT - E_k / kT) \quad [15]$$

where E_k is the energy gain by the kick-out reaction, and C_{im}^* is the concentration of impurity interstitials, in equilibrium with the major substitutional component, at T_m . In other words, $C_{im}^* = R_i C$ where R_i is a small fraction of interstitial impurity state at T_m , and C is the total impurity concentration.

At the melting point, the self-interstitials are present in the equilibrium concentration C_{vm} along with the trapped (impurity) interstitials, in concentration C_{vm}^* . Both interstitial species are consumed upon recombination with vacancies. The interstitial convection flux is now modified by replacing C_i with the total interstitial concentration $C_i + C_i^*$. A shift in the critical ratio is qualitatively described by replacing C_{im} with $C_{im} + C_{im}^*$ in the denominator of the Eq. 1

$$\xi_t = \xi_{to} / [1 - C_{im}^* / (C_{vm} - C_{im})] \quad [16]$$

In the precise formulation, the modified flux equation 2 is integrated, to get the $J(V)$ function and define the critical growth rate V_t of zero flux. The computed dependence of the shifted critical ratio on the impurity parameter $C_{im}^* / (C_{vm} - C_{im})$ is compared (Fig. 5) to that defined by the qualitative formula, Eq. 16. Like in the case of vacancy trapping, a shift in the critical V/G ratio is insensitive to a particular parameter set; it is well described by the analytical expression, Eq. 16.

The impurity that traps self-interstitials induces an increase in ξ_t , and thus an expansion of the interstitial region at the expense of the vacancy region, when the two regions coexist in same crystal.

On lowering T , interstitial trapping results in a gradual replacement of self-interstitials by impurity interstitials, according to Eq. 15. Below some characteristic kick-out temperature, T_k , the impurity interstitials will prevail over the self-interstitials. An example of computed axial profiles is shown in Fig. 6, for particular values of

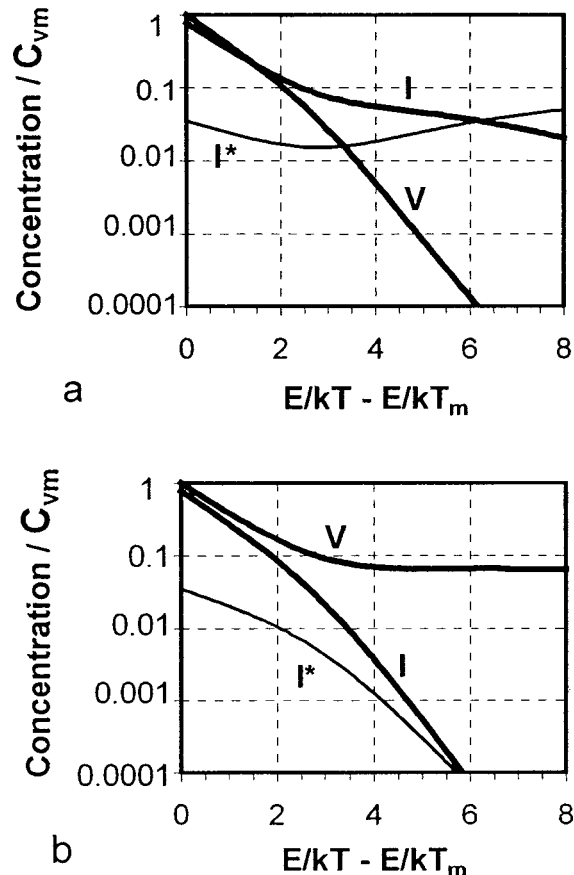


Figure 6. Axial concentration profiles of self-interstitials (I), impurity interstitials (I^*), and vacancies (V) at $C_{im}^* / (C_{vm} - C_{im}) = 0.15$ and $E_k = 2$ eV, for the second parameter set. (a, top) Interstitial mode, $V/V_t = 0.7$; (b, bottom) vacancy growth mode, $V/V_t = 1.5$.

V/V_t and $C_{im}^* / (C_{vm} - C_{im})$. The profile of self-interstitials is labeled I, that of impurity interstitials I^* , and that of vacancies V. In the interstitial growth mode (Fig. 6a), the interstitial species are incorporated in some constant concentration, but the ratio of the two species is gradually changing, in favor of impurity interstitials. The T_k corresponds to the intersection point of the curves I and I^* . For the vacancy growth mode (Fig. 6b), both kinds of interstitials decay, due to recombination with vacancies, and some vacancy concentration is incorporated.

Interstitial trapping by carbon.—Carbon impurity was reported²³ to cause a change from vacancy growth mode to interstitial growth mode, at a doping level of $1.7 \times 10^{17} \text{ cm}^{-3}$. The V_t was intermediate between 3 and 4 mm/min in nondoped crystal, and increased to over 4 mm/min in carbon-doped crystal. This effect allows only for a rough estimate of the carbon-induced shift in ξ_t by about 20%. Equation 16 for a shift is reduced to the form similar to Eq. 7, only now the addition sign in the denominator is replaced by the subtraction sign

$$\xi_t = \xi_{to} / (1 - C/C_o) \quad [17]$$

where the characteristic constant $C_o = (C_{vm} - C_{im}) / R_i$. The estimated shift corresponds to $C_o \approx 10^{18} \text{ cm}^{-3}$, and the interstitial carbon fraction at T_m is estimated as $R_i = 3 \times 10^{-4}$.

This important carbon parameter, in conjunction with some other reported data on carbon,⁴⁴ makes it possible for a comprehensive description of carbon behavior in a wide temperature range. First, we make use of the effective diffusivity of carbon, $D(T)$, and the

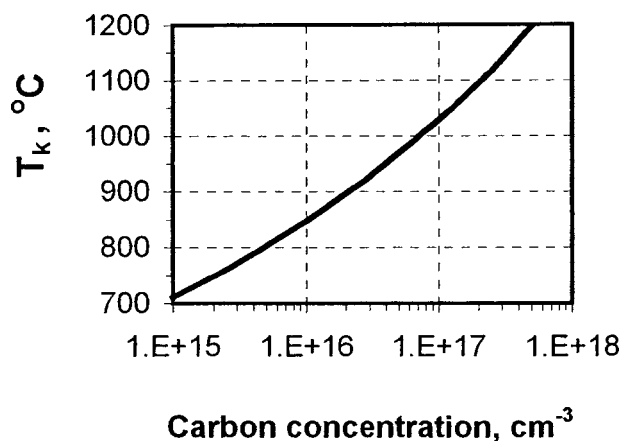


Figure 7. The kick-out temperature, T_k , for carbon impurity in silicon (below T_k , the carbon interstitials prevail over the self-interstitials).

solubility, $C_{se}(T)$, measured in a range of high T (the references are cited in the review of Ref. 44). The product DC_{se} turns out to be very small in comparison to the self-diffusivity product, $D_i C_{ie}$, which means that the carbon in-diffusion is limited by the supply of interstitial carbon, and not by out-diffusion of kicked-out self-interstitials. In such a case, the effective diffusivity is reduced to the diffusivity of the carbon interstitials, D_i^* , multiplied by the equilibrium fraction of these mobile species: $D = D_i^* (C_i^*/C) = R_i D_i^*$. The $D(T)$ dependence is characterized by an activation energy of 3.1 eV; the diffusivity extrapolated to the melting point is 1.1×10^{-9} cm²/s. Since the value of R_i at T_m was just estimated, we get an estimate for the carbon interstitial diffusivity at T_m : $D_i^* = 3.5 \times 10^{-6}$ cm²/s. The interstitial carbon diffusivity is known⁴⁴ at very low T , and thus $D_i^*(T)$ can be approximated by an Arrhenius plot in the whole range from low T up to T_m

$$D_i^* = 4.4 \times 10^{-4} \exp(-0.7 \text{ eV}/kT) \text{ cm}^2/\text{s} \quad [18]$$

The resulting migration energy, 0.7 eV, is slightly less than the value of 0.88 eV deduced from only low temperature data.⁴⁴ With known $D(T)$, we can now write down the equilibrium fraction of interstitial carbon, $R_i(T)$

$$R_i(T) = 4.8 \times 10^3 \exp(-2.4 \text{ eV}/kT) \quad [19]$$

We are interested in the ratio of self- and carbon-interstitials, C_i^*/C_i . This ratio is expressed through R_i , from the mass-action law for the kick-out reaction

$$C_i C_i^* = K(T) = C_{ie}/R_i$$

and hence

$$C_i^*/C_i = R_i(T)C/C_{ie}(T) \quad [20]$$

The last of these expressions is just a form of Eq. 15, and the kick-out energy, E_k for carbon is now specified: $E_k = E_i - 2.4 \text{ eV} = 1.6 \text{ eV}$. The kick-out temperature T_k is defined by the Eq. 20 at $C_i^*/C_i = 1$. The dependence of T_k on the carbon concentration, C , is shown in Fig. 7.

It was found⁴⁵ that the nucleation temperature T_n of interstitial microdefects in FZ crystals strongly increased with increasing the carbon content. To understand this effect, it is important to know the ratio of self- and carbon-interstitials at the microdefect formation stage. Since the reported nucleation temperature⁴⁵ turns out to be well above T_k , the carbon interstitials are minor species, and their concentration C_i^* is defined by Eq. 20 to be proportional to the carbon content, C (and to the total concentration of interstitial species that is close to C_i). The strong carbon effect on T_n can be

understood if the critical interstitial clusters are made not of the prevailing species (self-interstitials) but of minor species, carbon interstitials.

In modern CZ crystals the carbon content is low, about 3×10^{15} cm⁻³. The kick-out temperature, 770°C, is well below the nucleation temperature reported to be over 900°C.¹⁵ Yet the fraction of carbon interstitials at T_n is still appreciable, 10% at 930°C. It is likely that the interstitial agglomeration in CZ crystals is also controlled by the carbon impurity.

The carbon-containing globular clusters may be identified with the so-called B-defects which are present along with the interstitial-type loops (A-defects) and also form a separate B-band at the edge of an interstitial region.^{3,4} A possible interpretation is that the B-defects are the precursors of the A-defects, and that the $B \rightarrow A$ conversion occurs if the B-defects are large enough for that.

Conclusions

Vacancy trapping by impurities can affect both the stage of incorporation of intrinsic point defects into the growing crystal and the lower-temperature stage of vacancy agglomeration into voids.

1. At the incorporation stage, the critical V/G ratio (that separates interstitial and vacancy growth modes) is shifted downward in favor of vacancy incorporation. This effect is due to an increased total equilibrium concentration of the vacancy species (free and trapped vacancies) at the melting point. A shift in the critical V/G ratio is well described by a simple analytical expression. The shift is appreciable (more than 10%) if the equilibrium concentration of trapped vacancies is higher than about 2×10^{13} cm⁻³. Since oxygen (at a concentration of about 8×10^{17} cm⁻³), nitrogen and hydrogen (at a concentration of about 10^{15} cm⁻³) induce an appreciable downward shift in the critical V/G , it is concluded that these impurities trap vacancies even at high T (near the melting point), and the equilibrium concentration of trapped vacancies is larger than the value indicated above. (i) For oxygen, the trapped vacancies are thought to be substitutional oxygen atoms (known as A-centers from the low temperature irradiation experiments). (ii) For nitrogen, there are several species that can be considered as trapped vacancies. However, rough estimates indicate that the prevailing trapped vacancy is just substitutional nitrogen atom: a complex VN of a vacancy and an interstitial nitrogen atom.

2. At the melting point, the free vacancies greatly exceed the trapped species in concentration, for the impurities considered here. However, on lowering the temperature, the fraction of trapped vacancies increases rapidly, and these species become dominant below some binding temperature, T_b . An enhanced trapping at low T will affect the void formation in the vacancy growth mode. If the void nucleation temperature, T_n , is greater than T_b , then vacancy trapping is not important for the void production. In the opposite case, when T_b is well over the temperature at which the voids would be formed without trapping, the free vacancies will already be strongly trapped before the void production can start. Here, void formation is completely suppressed, and the grown-in crystal will contain the trapped vacancies (point defects) instead of voids. For the intermediate case (a moderate trapping at T_n) the void properties will be modified in an essential way: the nucleation temperature T_n decreases, due to a decreased concentration of free vacancies, and the effective mobility of the vacancy population is reduced which results in a higher void density. All three of these possibilities seem to occur commonly.

1. For oxygen, T_b is roughly estimated to be about 1060°C. Voids in Czochralski (CZ) silicon are known to form at a higher T (at T_n typically close to 1100°C). Vacancy trapping by oxygen is thus not very important in void production. The trapping of vacancies by oxygen is nonetheless a very important effect in CZ silicon growth; due to this effect, some vacancies escape consumption by voids. These residual vacancies control subsequent oxygen precipitation, giving rise to a complicated banded pattern and the so-called anomalous oxygen precipitation.²⁹

2. For nitrogen, the estimated binding temperature is relatively high, around 1115°C. In CZ silicon, it corresponds to the intermediate trapping case and therefore to a decreased void formation temperature and to an increased void density.

3. For nitrogen in FZ silicon the void production temperature (in material not doped with nitrogen) is expected to be considerably lower than that in CZ crystal, due to the effect of oxygen on void production. This case corresponds to a strong vacancy trapping and suppression of the void formation (provided the amount of nitrogen is enough to trap all the vacancies). In this case, the as-grown material is expected to contain the VN species instead of voids.

The available data on the above impurities are qualitatively consistent with this general concept of vacancy trapping. The list of impurities that trap vacancies is likely to include more examples. For instance, the donor dopants may trap the vacancies due to Coulomb attraction. There are some indications for this effect^{23,46} but quantitative data are still lacking.

Some impurities can trap self-interstitials, which results in similar effects. Particularly, for a substitutional impurity with a minor interstitial component, the trapped interstitial is identical to the interstitial impurity atom. The presence of trapped (impurity) interstitials, along with self-interstitials, can affect both the incorporation and agglomeration stages of microdefect formation. At the incorporation stage, the critical V/G ratio is shifted upward, in favor of interstitial incorporation. On lowering T , the self-interstitials are gradually replaced by impurity interstitials; the latter species are dominant below some characteristic T_k . An upward shift in the critical V/G was reported for the carbon impurity, and T_k was estimated in dependence of the carbon content. The interstitial agglomeration occurs at a temperature higher than T_k , and yet it is affected by the presence of carbon, presumably due to the involvement of mobile carbon interstitials in formation of critical interstitial clusters.

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